Further Development of a Novel Fluoride Releasing Acrylic Orthodontic Adhesive

Hadi Mohammad Ismail

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School of Dental Sciences

Newcastle University

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Abstract

White spot lesions (WSL) are a common complication with fixed orthodontic treatment. Fluoride incorporation into orthodontic adhesives is an effective way to prevent WSL. New fluoride releasing adhesives are being developed for this purpose. Four experimental groups were prepared by mixing different ratios of powder (polymethylmethacrylate and sodium fluoride; 10:0, 9:1, 8:2 and 7:3 wt) with liquids (60% methylmethacrylate and 40% 2-hydroxyethylmethacrylate). Therefore, this work aimed to further develop the fluoridated acrylic resin materials for possible use as an orthodontic adhesive.

Acetone was added at 0%, 10%, 20%, 30% and 40wt% to reduce the materials' viscosity. Addition of acetone up to 20% did not have detrimental effects on setting characteristics. The materials continued to release fluoride over 160 days.

Different photo-initiators were investigated and the 1% camphorquinone and 1% 2-Dimethylamino ethyl methacrylate group was chosen for further development based on achieving the highest degree of conversion (DoC) at 40s of light curing.

To improve bonding characteristics 4-methacryloyloxyethyl trimellitate anhydride (4-META) was added as an adhesion promoting monomer at 0% and 5wt%. The experimental materials were compared with a resin-based orthodontic adhesive (Transbond^{TM}XT) and a glass ionomer cement (Ketac^{TM} Cem) as commercial comparator. DoC, fluoride release and recharging, water sorption and solubility were measured. Shear bond strength (SBS) was measured for the 9:1 group at two time points after 30 minutes and 30 days of insertion in phosphate buffered saline. All experimental materials had significantly higher DoC than Transbond^{TM}XT. All experimental materials had comparable or higher fluoride release compared to Ketac^{TM} Cem. All of the developed materials showed similar recharge behaviour to the Ketac^{TM} Cem specimens. The solubility of the materials increased with increasing NaF concentrations. SBS of the experimental materials were significantly decreased at 30 days water storage compared to 30 minutes and were lower than Transbond^{TM}XT. Addition of 4-META and NaF did not influence the SBS of the material.

In summary, the developed light-cured fluoridated material showed good fluoride release and high recharge ability, which may prevent WSL. The developed material shows good DoC, in a reasonable timeframe, which would indicate stability. However, as a result of high water sorption and as a consequence of fluoride release, the SBS of the materials decreased after being in water.

In conclusion, this material shows potential as a fluoride releasing orthodontic adhesive, which could help to reduce decay during fixed appliance treatment. Further work is required to

improve the stability and bond strength of the material, which could involve investigation of different monomer combinations or different fluoride sources.

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Chapter 1: **Introduction**

There is significant demand for orthodontic treatment in the UK with 44% of 12 year old children wanting treatment and 37% deemed in need of orthodontic treatment according to the Child Dental Health Survey 2013 (Steele *et al.*, 2015). Orthodontic treatment is most commonly undertaken using fixed appliances (Chestnutt *et al.*, 2006). Bonding systems are used to secure orthodontic brackets to teeth during fixed orthodontic treatment.

White spot lesions (WSL) are one of the common complications of fixed orthodontic treatment. Studies have reported development of enamel demineralization only one month after appliance placement (O'Reilly and Featherstone, 1987; Gorton and Featherstone, 2003) and it has been reported that 73% of orthodontic patients develop WSL (Richter *et al.*, 2011; Arruda *et al.*, 2012). Fluoride is known to be effective in reducing WSL and one of the ways of delivering fluoride is through its incorporation into orthodontic adhesives. Clinical and laboratory studies have shown the contribution of fluoride releasing orthodontic adhesives towards reduction of WSL (Corry *et al.*, 2003; Gorton and Featherstone, 2003; Lodaya *et al.*, 2011). In addition to WSL, enamel may be lost during debonding and adhesive removal ranging from 4.57 µm to 55.6 µm in depth (Fitzpatrick and Way, 1977; Pus and Way, 1980; Hosein *et al.*, 2004; Al Shamsi *et al.*, 2007; Ryf *et al.*, 2012; Janiszewska-Olszowska *et al.*, 2015). Ideally, adhesive failure should occur between the adhesive and enamel on debonding, with little or no adhesive remaining on the tooth surface after debonding. Cohesive failure within the adhesive layer will result in the need to remove adhesive from the tooth, which could result in enamel damage. Cohesive failure within the tooth structure, can result from fracture of enamel during debonding (Joseph and Rossouw, 1990; Meng *et al.*, 1998; Rix *et al.*, 2001b; Chen-Sheng *et al.*, 2008).

Currently, composite resins are the most widely used bonding agents in fixed orthodontic treatment. This is due to them having a high bond strength and proven clinical success for the bonding of brackets. These adhesives are mostly based on the monomers bisphenol A diglycidyl methacrylate (BisGMA) and urethane dimethacrylate (UDMA) which are cross-linked (Graber TM, 2005) and hydrophobic. Therefore, the polymer network is highly cross-linked which contributes to greater strength and lower water absorption, slowing down the transportation of water and ions into the polymer (Asmussen and Peutzfeldt, 2002; Cohen *et al.*, 2003). Therefore, even with the addition of a soluble fluoride salt, fluoride release from the material may be poor (Cacciafesta *et al.*, 2007). Problems during debonding have also been reported, including enamel loss during debonding and adhesive removal and in some case enamel fracture (Ireland *et al.*, 2005; Kim *et al.*, 2014)

To make bracket debonding easier and safer, some manufacturers have developed a methyl methacrylate (MMA) based orthodontic adhesive. This is available as a commercial product (Super-Bond, MCP Bond®). MMA produces a linear polymer with low density chains (Ferracane *et al.*, 1998; Ferracane, 2006) which results in a softer, more flexible and potentially weaker material (Gorelick *et al*., 1978). Therefore, less enamel loss and fracture is seen after debonding a MMA based orthodontic adhesive in comparison to a conventional composite resin (Brown and Way, 1978; Su *et al.*, 2010; Kim *et al.*, 2014). A new fluoride releasing MMA based orthodontic adhesive resin has been developed at Newcastle University (Su *et al.*, 2010). The original proposed material was chemically cured and composed of a monomer mixture of 2-hydroxy ethylmethacrylate/MMA, with polymethylmethacrylate and sodium fluoride as a filler and source of fluoride, respectively. It has been shown to release fluoride at levels comparable to a GIC. It has also been shown to have comparable bond strength and less adhesive remaining on the tooth surface after debonding compared to a conventional composite resin see appendix 1.

Previous work developing the fluoride releasing acrylic resins has concentrated on optimising fluoride release. However, the developed material still had a number of shortcomings. It was very viscous, set very slowly by chemically activation and its bond strength decreased after immersion in water for 30 days (Su *et al.*, 2010). For these materials to be appropriate for use as an orthodontic adhesive it is important that they have adequate handling characteristics to enable accurate dispensing, optimum bracket placement and set within a reasonable time to allow early activation of the appliance. The handling characteristics of orthodontic adhesives have been linked to several factors such as ease of application, viscosity and setting kinetics of the adhesive (Papakonstantinou *et al.*, 2013). In addition, the bond strength of developed materials should be adequate to retain brackets throughout treatment and should be easily removed after finishing of treatment.

Therefore, this project was aimed to optimize the handling characteristics of the materials as well as the bond strength of the materials for uses as an orthodontic adhesive. The developed materials are designed to combine beneficial properties of GIC and composite resin based orthodontic adhesives. Certain properties of these developed materials were also compared with commercial GIC cement and resin based composite orthodontic adhesive.

Chapter 2: **Literature review**

In this chapter some common complications during fixed orthodontic treatment, in particular white spot lesions and enamel loss will be discussed. All types of orthodontic adhesives will be considered, in particular fluoride releasing orthodontic adhesives. A description of the ideal properties of orthodontic adhesives will be presented, including test approaches and limitations. Finally, the chemical composition of resin based orthodontic adhesives, will then be discussed.

2.1 Introduction to some common complications during fixed orthodontic treatment

There is huge demand for orthodontic treatment. According to the 2013 Children's Dental Health Survey, 37% of UK children at age 15 were judged to need orthodontic treatment (Steele *et al.*, 2015). Most orthodontic treatment is carried out for children aged 10-14 and cost GBP 258 million according to the National Health Service in England and Wales between April 2011 and March 2012 (NHS Dental Statistics for England, 2012).

There are two types of orthodontic appliances that are used for treating malocclusions - removable appliances and fixed appliances. Fixed type orthodontic treatment provides a better treatment outcome in terms of improving malocclusions (Richmond *et al.*, 1992) and it can be used to provide all types of tooth movement. Therefore, fixed type orthodontic treatments are most commonly used (Chestnutt *et al.*, 2006). The success of fixed orthodontic treatment is partially dependant on the attachment of the appliances to the tooth surface. For this reason orthodontic adhesives are used. However, there are several common complications which occur during fixed orthodontic treatment, such as enamel demineralization around brackets, enamel loss during debonding and adhesive removal. These complications will compromise one of the primary aims of treatment, which is improving aesthetics and should be considered during treatment. These complications and possible solutions will be discussed in the sections below.

2.1.1 *White spot lesion formation (WSL)*

Enamel demineralization adjacent to brackets is one of the most undesirable and common complications of fixed orthodontic therapy (Chang *et al*., 1997), despite multiple advances in orthodontic materials and techniques in recent years. This is due to the orthodontic appliance impairing the efficacy of oral hygiene in orthodontic patients. Studies have reported the development of enamel demineralization from only one month after appliance placement (O'Reilly and Featherstone, 1987; Gorton and Featherstone, 2003) appearing as a white chalky tissue around the brackets, known as white spot lesions (WSL) (see Figure 2.1). Clinical studies have reported a high incidence of WSL affecting about 73% of orthodontic patients (Richter *et al.*, 2011). Different approaches have been used to prevent enamel demineralization and WSL formation.

Figure 2.1 Orthodontic white spot lesions on enamel surfaces. This picture is taken from web. http://texomaorthodontist.com/2012/09/11/white-spot-lesions/.

Mechanical removal of the bacterial biofilm is effective in reducing WSL formation. It has been found that frequent prophylaxis, such as every three months, including scaling, irrigation of sub-gingival pockets with chlorhexidine and fluoride application are effective in reducing demineralization (Zimmer and Rottwinkel, 2004). However, this is costly as it takes additional chairside time in the clinic.

Application of fluoride is another way to prevent WSL formation. Fluoride is an effective anticariogenic agent in reducing enamel demineralization. The mechanisms of action of fluoride in reducing WSL formations are as follows: firstly, it prevents demineralisation through formation of less soluble fluor-hydroxyapatite crystals. Secondly, fluoride enhances remineralisation of an already demineralized enamel surface through enhancing precipitation of calcium phosphates, and formation of fluor-hydroxyapatite crystals on the enamel surface, which has a lower solubility than the original hydroxyapatite crystals (HAP) (Wiltshire and Janse van Rensburg, 1995; Cate, 1999). Thirdly, fluoride has an antibacterial effect. It has been shown that fluoride releasing adhesives may decrease the amount of the *Streptococcus mutans*, the most cariogenic bacteria, in the biofilm (Seppa *et al.*, 1993; Loyola-Rodriguez and Garcia-Godoy, 1996; Pandit *et al.*, 2011). The importance of fluoride application is recognised in the Public Health England document, "Delivering Better Oral Health", which assigns patients undergoing orthodontic treatment to a "high risk" category and advises patients to brush twice daily with fluoridated toothpaste, typically those continuing 1,350-1,500 ppm fluoride, to use a fluoride mouth rinse daily (0.05% sodium fluoride (NaF)) at a different time to brushing and changing dietary habits such as reducing sugary food and drink consumption. It also suggests a number of fluoride based interventions dentists can undertake to reduce demineralization

including topical fluoride application two or more times a year (2.2% NaF) and prescription of a high fluoride toothpaste (2800 ppm / 5000 ppm) for patients with active disease. (Public Health England, 2014).

Different methods have been used for the delivery of fluoride to the teeth of orthodontic patients. These include topical fluorides such as mouthrinse, gel, varnish and toothpaste, all of which have been shown to be effective in reducing WSL formation (Demito *et al.*, 2004; Øgaard *et al.*, 2006; Benson *et al.*, 2013). However, most of these regimes depend on patient cooperation and it is the responsibility of patients to maintain these regimes to prevent WSL formation (Maxfield *et al.*, 2012). It has been shown that less than 15% of patients comply with fluoride rinsing daily (Geiger *et al.*, 1992). According to a study in Norway only 23% of adolescent orthodontic patients comply fully (Hadler-Olsen *et al.*, 2012). Most orthodontic patients are of teenage and may be unlikely to follow oral hygiene instructions, especially during the first 5 months of treatment. However, it has been shown to improve after this time (Thikriat *et al.*, 2011).

In addition to topical fluoride application, fluoride-releasing materials such as bonding materials, sealants and elastomers have been used and it was found they are effective in reducing enamel demineralization (Wiltshire, 1999; Mattick *et al.*, 2001; Benson *et al.*, 2005; O'Reilly *et al.*, 2013). Fluoride releasing adhesives are effective in preventing or reducing demineralization because they provide a fluoride reservoir that does not depend on patient cooperation and is localized in the area most susceptible to white spot lesions.

Investigation of the efficacy of fluoride releasing orthodontic adhesives in reducing demineralization around brackets has been done either *in vitro* in laboratory experiments or in *in vivo* clinical studies of patients and volunteers. In laboratory studies, brackets have been attached to human and bovine teeth using the materials under test. The samples were then exposed to an artificial acid challenge. In some studies optical techniques were used to investigate enamel surfaces around brackets pre- and post-acid exposure, to study the differences made by the material. Photos or stereomicroscope images or QLF (Quantitative light induced fluorescence) images of the teeth have been used for this purpose (Corry *et al.*, 2003; Paschos *et al.*, 2015). Other studies investigated mechanical properties such as hardness of the enamel surfaces around brackets were tested before and after acid exposure (Kohda *et al.*, 2011; Lodaya *et al.*, 2011; Melo *et al.*, 2014; Raji *et al.*, 2014). These studies have found effectiveness of fluoride releasing adhesives in reducing enamel demineralization compared to non-fluoride releasing adhesive. These laboratory studies are easy, cheap, sensitive to enamel changes and can be done in a short time. However, these studies are typically done in artificial conditions that are not representative of what is happening in the mouth and disregard the

effects of complex bacterial biofilms and their by-products that are produced in the mouth. In addition, they are mostly undertaken for a short period of time, with no standardized protocol for laboratory tests for this purpose (Benson, 2010).

To overcome these shortcomings clinical studies have been undertaken, using visual inspection (Chapman *et al.*, 2010; Eser *et al.*, 2011) or QLF to detect WSL formation (Robertson *et al.*, 2011). Patient's teeth have been examined before, during and after orthodontic treatment for changes on the enamel surface. Where teeth are scheduled for extraction, a mechanical property such as micro-hardness has been measured (Gorton and Featherstone, 2003; Pascotto *et al.*, 2004). They found the micro-hardness of the enamel surface of non-fluoride releasing adhesives was lower than that of the fluoride releasing adhesives. These studies truly represent the effects of fluoride releasing orthodontic adhesives in real life and are more reliable in terms of actual performance of the material (Benson, 2010). However, in order to undertake such studies there are ethical issues to consider, where permanent but preventable damage might occur to the teeth without intervention. Additionally, all clinical studies must be approved by an ethics committee and this can be a lengthy process.

In both clinical and laboratory studies it appears that fluoride releasing orthodontic adhesives contribute towards reduction of enamel demineralization around brackets (Corry *et al.*, 2003; Gorton and Featherstone, 2003; Pascotto *et al.*, 2004; Eissaa *et al.*, 2013). Low, sustained levels of free fluoride release for a long period of time are helpful in remineralisation (Arends and Christoffersen, 1990). Nevertheless, there is no clear evidence confirming the amount of fluoride release that would be sufficient for prevention of enamel demineralization, because of individual patient variations in factors such as oral hygiene, oral flora and diet. Various levels have been suggested, including daily fluoride release of about 0.63 to 1.3 μg/cm² is effective for prevention of enamel demineralisation (McNeill *et al.*, 2001) and free fluoride concentrations of 1ppm or 50 mmol/L in the liquid phase (Arends and van der Zee, 1990). However, these are based on *in vitro* studies and there is no evidence based clinical study to confirm the critical level of fluoride required to prevent enamel demineralization. For an orthodontic adhesive to be effective in preventing demineralization, it should provide sustained slow release of fluoride for a long period of time, because completion of orthodontic treatment usually takes 2-3 years. The ability to release fluoride, the quantity and rate of fluoride released and the duration of fluoride release is different for each fluoridated orthodontic adhesives(Grobler *et al.*, 1998; Vermeersch *et al.*, 1998; Karantakis *et al.*, 2000; Duraisamy *et al.*, 2012a). These differences may come from the differences in the nature and composition of each material. Fluoride releasing orthodontic adhesives will be discussed later in section 2.2.

In addition to fluoride application, amorphous calcium phosphate (ACP), is an essential mineral phase formed in mineralized tissues and the first commercial product as artificial hydroxyapatite, has been used to reduce WSL formation. It has been shown that using casein phosphopeptide-ACP (CPP–ACP) paste is effective in reducing enamel demineralization, when applied directly to the enamel surface in a fluoride tray for a minimum of 3 to 5 minutes each day at night after brushing (Robertson *et al.*, 2011). In an *in vitro* study a CPP–ACP paste was found to be effective in reducing demineralization when the paste was applied to a dried enamel surface (Behnan *et al.*, 2010). There is another version of CPP–ACP which is fluoride containing, which is also effective in reducing enamel demineralization. There are some controversy on the effect of CPP–ACP treatment prior to bonding on the shear bond strength (SBS) of brackets to teeth. It has been shown that non fluoride containing CPP–ACP application may decrease the bond strength of the bonded bracket when applied to tooth surface before bonding with BisGMA/TEGMA based orthodontic adhesive (Transbond XT) (Çehreli *et al.*, 2012). It also decreased SBS of enamel to other resin based adhesives (Shadman *et al.*, 2015). In contrast, it has been shown that non-fluoride CPP–ACP treatment of enamel does not appear to decrease the micro-SBS of etch-and-rinse and self-etching adhesives (Adebayo *et al.*, 2007; Park *et al.*, 2013). In addition, when ACP was incorporated into a commercial resin cement which is composed of UDMA and other Di-methacrylate monomers (Agies-ortho), it was found that it is less effective than fluoride varnish in reducing demineralization however, it is more effective than using CPP–ACP paste (Behnan *et al.*, 2010).

In addition to the above mentioned methods for preventing WSL formation, application of a protective barrier on enamel has been used, termed sealants. The sealants, which are made of filled and unfilled resins, are applied to the surface of enamel around brackets in order to make a physical barrier to prevent demineralization. Studies have shown their effectiveness in reducing WSL formation and it has been shown to be as effective as fluoride varnish in *in vitro* studies (Behnan *et al.*, 2010; Knösel *et al.*, 2012). Others have added fluoride to these sealants to act as an additional preventive factor. However, the addition of fluoride has been shown to add no extra benefit (Leizer *et al.*, 2010). There are issues regarding durability of sealants which require reapplication of the sealant every 3 months, this will become a costly procedure (Knösel *et al.*, 2015). In addition to the possible demineralization caused by acid etching, as sealants are applied after acid etching

2.1.2 *Enamel loss*

Enamel loss may occur during bonding, debonding and adhesive removal. For all composite based adhesives, acid etching is used to produce a porous surface to enhance bonding. This aids

penetration of resin tags to the etched enamel prisms and the formation of micro-interlocking between enamel and adhesive. Consequently a strong bond is obtained, however, this strong adhesive bond may lead to complications such as enamel loss in the area of the enamel during bracket debonding (Lin *et al.*, 2011).

Orthodontic adhesives require not only sufficient bond strength to retain brackets from masticatory and orthodontic forces during service, they should also allow easy removal of brackets upon completion of treatment (a process termed debonding). During debonding, pliers are used to detach brackets, which may lead to pain (Mangnall *et al.*, 2013) enamel cracking and fracture (Meng *et al.*, 1998; Rix *et al.*, 2001b; Chen-Sheng *et al.*, 2008). After debonding, adhesive remnants remain on the enamel surface, which need to be removed using rotatory instruments and this will lead to enamel loss, ranging from 4.57µm to 55.6 µmin depth (Fitzpatrick and Way, 1977; Pus and Way, 1980; Hosein *et al.*, 2004; Al Shamsi *et al.*, 2007; Ryf *et al.*, 2012; Janiszewska-Olszowska *et al.*, 2015). Attempts have been made to reduce pain and enamel damage during debonding, for instance, by using ultrasonic instrumentation (Boyer *et al.*, 1995), electrochemical heating (Jost-Brinkmann *et al.*, 1997) or laser irradiation (Ma *et al.*, 1997; Oztoprak *et al.*, 2010). However, these methods have the disadvantages of being time-consuming procedures and being of high cost. Another way to overcome these problems, is through developing orthodontic adhesives with easy removal, this is either through using unfilled linear acrylic resins or via inclusion of thermo-degradable additives into orthodontic adhesives (Kameda *et al.*, 2014; Kim *et al.*, 2014). This will be discussed in further detail in section 2.3.1.

2.1.3 *Bond failure*

Another complication is bond failure during treatment, which slows treatment progression and is costly in terms of time, material and patient inconvenience (Mandall *et al.*, 2003). Once the bracket has failed, the remnant adhesive residue should be removed, which in addition to being time consuming, can also lead to removal of up to 50 µm of enamel surface (Al Shamsi *et al.*, 2007). Therefore, orthodontic adhesives should have an optimal bond strength to retain brackets throughout treatment. There is no clear evidence on the optimal bond strength for this purpose but most studies refer to 6-8 MPa as an adequate bond strength for orthodontics (Reynolds, 1975). This is explored in more detail in a later section 2.3.1.

2.2 Orthodontic adhesives

In orthodontics, bonding systems are used to secure orthodontic brackets to teeth. Traditional orthodontic bonding systems consist of three agents:

- Enamel conditioner (acid etchant); an acid which is used to produce micro-porosities on the enamel surface to allow mechanical retention of resin tags.
- Primer solution; an unfilled resin composed of monomers with solvents added that is painted onto the enamel surface after acid etching to enhance penetration of resin tags into the etched enamel surface and to improve the effectiveness of the final bond. In some new systems, conditioning and priming are combined in to 1 solution known as a self-etching primer. This either comes as a one step or two step self-etching primer, in which acidic monomers are used to produce etching as well as adhesion.
- Orthodontic adhesive; which is applied after primer application. Some orthodontic adhesives can be applied without using acid etching and primer applications such as glass ionomer cements (GICs) and resin modified glass ionomer cements (RMGIC).

Orthodontic adhesives can be classified into conventional resin based, MMA-based orthodontic adhesives and fluoride releasing orthodontic adhesives such as GIC, RMGIC and compomers:

2.2.1 *Conventional resin based adhesives*

Direct bonding of attachments revolutionized the placement of orthodontic appliances. The adhesion mechanism of composite resins is micromechanical, between an etched enamel surface and composite resin with the aid of a suitable primer/bonding agent (Mickenautsch *et al.*, 2012). Currently, composite resins are the most widely used bonding agents in fixed orthodontic treatment. This is due to quickly achieving a clinically acceptable bond strength through light curing and ease of application. The majority of these are based on the monomers bisphenol A diglycidyl methacrylate (BisGMA) and urethane Di-methacrylate (UDMA) which are cross-linked (Graber TM, 2005). As both of these monomers are di-functional and hydrophobic, the polymer network is highly cross-linked which contributes to greater strength, lower water absorption and less polymerization shrinkage. This slows down transportation of water and ions in the polymer (Asmussen and Peutzfeldt, 2002; Cohen *et al.*, 2003). There are issues of enamel loss during debonding and adhesive removal and problems of WSL during fixed orthodontic treatment as discussed in section 2.1. Therefore, to prevent WSL formation fluoride is added to the conventional orthodontic adhesives. This modified group are known as fluoride releasing composite resin orthodontic adhesives.

Attempts have been made to integrate fluoride into conventional resin based adhesives in different forms such as the addition of water soluble salts like (NaF,SnF_2) and ion leachable glass (Wiegand *et al.*, 2007). Laboratory studies have revealed a poor fluoride release in terms of quantity and duration of fluoride release (Ghani *et al.*, 1994; Cacciafesta *et al.*, 2007). Fluoride release from composite resins containing fluoride is characterized by short-term

release at very low levels (Chan *et al.*, 1990; Naoum *et al.*, 2011), that they are unlikely to have any therapeutic effect (Fox, 1990). This could be due to the chemical composition of composite resins which are mostly based on crosslinking polymers like BisGMA and UDMA which are hydrophobic and once polymerized produce a rigid polymer and with low water sorption ability and consequently low fluoride releasing ability. Fluoride releasing composite resins release less fluoride compared to glass ionomer cements (GICs) and resin modified glass ionomer cement (RMGIC) (Weidlich *et al.*, 2000; dos Santos *et al.*, 2013). In addition, they have a higher bond failure rate (Trimpeneers and Dermaut, 1996) and a lower bond strength compared to conventional composite resins after 48 hours of bonding (Chan *et al.*, 1990).

Based upon the polymerization activation mechanism, different types of conventional resin based orthodontic adhesives are present, including chemically cured, light cured and dual cured composites (Eliades *et al.*, 2000). Generally there is no superiority of chemical over light cured orthodontic adhesives in terms of bond strength, failure rate and setting characteristics of the material. No difference has been shown in DoC, monomer leaching and cytotoxicity between two commercial chemically cured and light cured adhesives based on BisGMA and TEGMA. A chemically cured, no-mix adhesive (Rely-bond; Reliance, Ithaca, Ill) and a visible light-cured adhesive (Reliance) were used (Gioka *et al.*, 2005). Light cure systems have advantages over chemical cured in terms of handling of the materials. The light cure adhesive can be easy to use and the working time can be extended when necessary. Consequently, with light cure systems there is sufficient time for precise bracket placement, in addition to having time for removal of excess material before light curing of the material. Therefore, currently, light curing orthodontic adhesives are most commonly used (Yoshida *et al.*, 2012). Another advantage of light cure adhesive resins over chemically cured is a reduced chance of air entrapment and oxygen inhibition. As they supplied as a single tube they do not need any mixing while, chemically cured orthodontic adhesives come either as two paste or liquid and powder which need to be mixed before use. An increase in the number of porosities has been shown after mixing the two pastes of a chemically activated material in comparison to each of the pastes alone (Fano *et al.*, 1995).

2.2.2 *Methylmethacrylate based orthodontic adhesives (MMA-based orthodontic adhesives)*

There are attempts to use less crosslinked monomers like methylmethacrylate (MMA) for orthodontic adhesive use to make bracket debonding easier and safer. This is available as a commercial product (Super-Bond, MCP Bond®). This product has also been described as 4-META-based adhesives or 4-META/MMA-TBB available as powder of

polymethylmethacrylate (PMMA) and Tri-n-butylborane (TBB) as activator with liquid methylmethacrylate (MMA) and 4-methacryloyloxyethy trimellitate anhydride at 5% (4-META). It has been shown that this adhesive results in a strong bond to enamel (Mogi, 1982) and metals (Takeyama *et al.*, 1978; Mogi, 1982). The 4-META containing adhesives provide significantly higher bond strength than the conventional orthodontic adhesives (Clark *et al.*, 2003; Rikuta *et al.*, 2008). Some *in vitro* studies have reported enamel fracture during debonding (Toledano *et al.*, 2003). Therefore, several attempts have been made to modify 4-META/MMA-TBB, so as to make the material easier and safer at debonding without loss of adequate bond strength in addition to making the materials release fluoride (Kawabata *et al.*, 2006; Kawabata *et al.*, 2007). For this purpose a degradable additive (α-tricalcium phosphate) and fluoride compounds such as calcium fluoride (CaF_2) and Sodium fluoride (NaF) have been incorporated into the material (Kawabata *et al.*, 2006; Kawabata *et al.*, 2007; Iijima *et al.*, 2013). The addition of these additives results in more residual resin remaining after debonding compared to the original 4-META/MMA-TBB resin. Thus the possibility of enamel fracture decreased by addition of additives (Kawabata *et al.*, 2006; Kawabata *et al.*, 2007). In addition, they provide fluoride release after NaF addition (Iijima *et al.*, 2013). This might be due to presence of 4-META which increased water uptake characteristics of polymers of MMA due to formation of hydrogen bonds at polar sites with water molecules and this may promote fluoride release of the material (Unemori *et al.*, 2003). Details about 4-META will be discussed in section 2.4.1.

MMA-based resins have potential for use as an orthodontic adhesive. Su *et al.*, (2010) developed a new experimental fluoride releasing acrylic resin for using as an orthodontic adhesive. The material was based on MMA and 2-Hydroxyethylmethacrylate (HEMA) as a liquid and NaF and PMMA were used as powder as a filler and as a source of fluoride. HEMA is hydrophilic and it is an excellent adhesion promoting monomer and it readily absorbs water in polymer form (Arima *et al.*, 1995; Van Landuyt *et al.*, 2007). Therefore, HEMA was used to promote rapid diffusion of water and accelerate fluoride release. Water molecules bonding via hydrogen bonding to the polar sites of HEMA contribute to water diffusion through polymer matrices (Yiu *et al.*, 2006). NaF was used as a source fluoride which easily dissolves in water into Na^+ and F^- ions. Therefore the material can release large amount of fluoride (Su *et al.*, 2010). One of the disadvantages of using NaF is once it leaches out it leaves a porosity in the material consequently affecting the mechanical properties of the material (Arends *et al.*, 1995). However, this could contribute towards making the material easier to remove during debonding which as demonstrated by the lower ARI (adhesive remnant index) found by Su *et al.* (2010) when compared to a commercial BisGMA/TEGMA based material (Transbond XT) (Su *et al.*,

2010). Another reason might be due to polymer matrix of the material which was composed of a copolymer of HEMA and MMA which are linear, flexible and porous (Tay *et al.*, 2002a). Details about HEMA and MMA can be found in section2.4.1.

Further to the fluoride releasing ability of the material, it has comparable bond strength to commercial orthodontic adhesives (Su *et al.*, 2010). The bond strength of the material was decreased after being in water for 30 days. This could be due to HEMA, which was plasticized by water, however, the material needed HEMA to maintain the fluoride release of the material. The developed material was chemically cured with a long setting time (3-4) minutes that potentially makes it clinically difficult to use. In addition to problems of mixing the powder and liquid together before use increased the chance of oxygen incorporation into the material. Zahroon *et al.* (2014) further developed this material to be cured by light activation and for potential use as a fissure sealant. Camphorquinone (CQ) and 2-dimethylaminoethyl Methacrylate (DMAEMA) were used for this purpose. However, the material still needed 120 seconds of light curing to obtain a DoC of 56%. To optimise the fluoride release, four experimental groups were developed based on different NaF concentrations, namely 0%, 10%, 20% and 30% NaF (Zahroon, 2014; Al-Sammarraie, 2015). The experimental materials demonstrated higher fluoride release than commercial GIC based fissure sealants and interestingly also showed considerable recharge potential (Zahroon, 2014).

2.2.3 *Glass ionomer cement (GIC)*

Glass ionomer cements (GICs) are composed of fluoride containing aluminosilicate glass and polyalkenoic acid, which sets by an acid base reaction occurring between the liquid and powder. During setting, fluoride is released from the glass (Wiegand *et al.*, 2007). GICs contain hydrogel phases which aid remineralisation of enamel and dentin through supporting movement of calcium, strontium and other ions particularly fluoride ions. These hydrogel phases are believed to be responsible for the fluoride uptake and re-release from topical fluoride gels, fluoridated mouth rinses and dentifrices (Ewoldsen and Demke, 2001).

The highest levels of fluoride are released during the first 24-48 hours (Creanor *et al.*, 1994; Chatzistavrou *et al.*, 2010). This is likely to be due to the burst of fluoride released from the glass particles when reacting with the polyalkenoic acid during the setting reaction (Wiegand *et al.*, 2007). During the first 24 hours, the amount of fluoride released from GICs ranges between about 40 to 100 µg/cm² (Xu and Burgess, 2003). Daily fluoride release declines rapidly over the first week (Vermeersch *et al.*, 2001) and is then followed by a slow fluoride release for a longer period over 3 months (Vermeersch *et al.*, 2001). GICs, in addition to long-term fluoride release, can also absorb fluoride from external sources, such as topical fluoride gels

(Ashcraft *et al.*, 1997), fluoridated toothpastes and mouth rinses; therefore, they act as a rechargeable slow release fluoride device (Hatibovic-Kofman and Koch, 1991; Lin *et al.*, 2008). The amount of fluoride release after re-fluoridation exposing to 0.05% NaF has been shown to be higher than the release from within the materials without recharging (Cildir and Sandalli, 2005). Therefore, in most studies GICs are taken as the gold standard for fluoride release and recharge to compare with other commercial or experimental materials.

Several clinical studies confirm the local anticariogenic effect of GICs on the enamel around brackets owing to fluoride release (Hallgren *et al.*, 1990; Marcusson *et al.*, 1997; Twetman *et al.*, 1997; Gorton and Featherstone, 2003; Pascotto *et al.*, 2004; Shungin *et al.*, 2010). This is based on taking optical photographs before and after treatment. Bonding with a GIC leads to an increase in the fluoride content on the outer surface of enamel at 2 µm depth to 33% compared to 8% of deeper surfaces at 100 µm from dentine enamel junction (Chatzistavrou *et al.*, 2010).

GICs are most commonly used for band cementation because of their anticariogenic and adhesive properties, fluoride release and recharge behaviour, (Millett *et al.*, 2007) as well as due to their capacity to bond even in the presence of moisture (Ewoldsen and Demke, 2001). However, GICs are not routinely used for bonding orthodontic brackets due to the increased risk of debonding during treatment compared to conventional composite resin (Miller *et al.*, 1996; Norevall *et al.*, 1996). They show a significantly higher failure rate (50.89%) compared to composite resin (7.96%) (Miguel *et al.*, 1995). Therefore, it is not generally recommended to use GICs for bonding (Chu et al.,1989) owing to too low shear bond strength for example 5.3 MPa (Ashcraft *et al.*, 1997). However, bonding with GIC provides easier debonding and clean-up time in addition to reduction of WSLs around orthodontic brackets (Norevall *et al.*, 1996).

2.2.4 *Resin modified glass ionomer cement (RMGIC)*

Resin modified glass ionomer cements (RMGIC) have a similar composition to that of GICs with added 10% to 20% resin monomers. The hydrophilic monomer HEMA is generally used for this purpose. Either light or chemical activation are used to polymerize the monomers. RMGICs are superior to GICs in their physical properties and stability (Ewoldsen and Demke, 2001). Mechanisms of adhesion of RMGICs are micromechanical and chemical bonding, the latter contributing to the prolonged adhesion of RMGIC (Mitra *et al.*, 2009).

The highest amount of fluoride is released by RMGICs during the first 24 hours, which ranges between about 17 to 60 µg/cm² (Xu and Burgess, 2003; Duraisamy *et al.*, 2012a), it then declines rapidly over the first week (Vermeersch *et al.*, 2001) until it reaches 3 to7 µg/cm² at

the 3rd week. Both GICs and RMGICs demonstrate an increase in fluoride release after exposure to 2% sodium fluoride *ex vivo* (Coonar *et al.*, 2001). RMGICs prevent demineralization around orthodontic brackets in comparison to the non-fluoride releasing materials (conventional orthodontic adhesive) (Wilson and Donly, 2001). Corry et al., (2003) suggested that RMGICs supplemented with fluoride exposure inhibit WSLs *in vitro*. In addition, the fluoride availability from RMGICs is controlled by pH, with increased release at low pH (Forsten, 1995). It has been shown that fluoride release rate of GIC and RMGICs increase with decreasing pH from neutral (pH 7) to acidic (pH 4) (Carey *et al.*, 2003; Moreau and Xu, 2010).

RMGICs have a lower shear bond strength of a bracket to enamel (15-18 MPa) compared to conventional resin adhesives (22-25 MPa) (Bishara *et al.*, 1999; Owens and Miller, 2000; Sfondrini *et al.*, 2001; Manuel *et al.*, 2003; Ali and Maroli, 2012). This is related to a higher failure rate reported for RMGICs compared to composite resin (Gaworski *et al.*, 1999). However, the weaker chemical bonding between the adhesive and the enamel contribute to an easier clean up clinically after debonding (Summers *et al.*, 2004). RMGICs further aid preservation of the integrity of the enamel surface, because they can be used without etching (Fricker, 1996), however, it appears that using RMGICs without etching reduces the bond strength significantly (Manuel *et al.*, 2003; Godoy-Bezerra *et al.*, 2006).

2.2.5 ***Polyacid modified resins (Compomers)***

Compomers are composed of aluminosilicate glass, the ion-leachable glass fillers used in GICs but in smaller sizes, in a matrix of carboxyl modified resin monomers and light activated conventional resin monomers such as BisGMA and UDMA. Initial setting is performed by light-activated polymerization which is followed by an acid-base reaction that arises from sorption of water (Wiegand *et al.*, 2007).

Compomer fluoride release levels are significantly lower than those of GICs (Grobler et al., 1998). The highest amount of fluoride released by compomers is during the first 24 hours, which ranges between about 3 to 28 µg/cm² (Xu and Burgess, 2003; Duraisamy *et al.*, 2012a). It then declines rapidly over the first week until it reaches 1- 4 µg/cm² at day 21 (Xu and Burgess, 2003). The pattern of fluoride release from both materials is characterized by an initial rapid release followed by a rapid reduction in the rate of release (Itota *et al.*, 2004b). In addition, compomers are capable of taking up fluoride from dentifrice solutions and later releasing it to the demineralising solution, maintaining a relatively constant release for a month and at a higher level than that seen between days 5 and 7 (Vieira *et al.*, 1999). It has been confirmed that bonding brackets with compomers results in less decalcification around brackets than with

conventional composite resin (Chung *et al.*, 1998; Millett *et al.*, 2000). In addition, fluoride release from compomers like RMGICs is pH-controlled, and fluoride release may be increased by the effect of hydrolytic enzymes and under acidic conditions (Geurtsen *et al.*, 1999).

Compomers have a lower shear bond strength of the bracket to enamel compared to conventional resin adhesives (Haydar *et al.*, 1999; Duraisamy *et al.*, 2012b). In a clinical trial comparing a conventional orthodontic adhesive to a compomer, a higher bond failure rate was found for the compomer compared to the conventional orthodontic resin adhesive (Mavropoulos *et al.*, 2003). However, bonding with compomers results in less adhesive remnant than conventional orthodontic adhesives after debonding (Vicente *et al.*, 2006).

2.3 Properties of ideal orthodontic adhesives

In orthodontics, bonding systems are used to secure orthodontic brackets to teeth. The ideal orthodontic adhesives should (Mandall *et al.*, 2003):

1- Provide sufficient bond strength to keep orthodontic brackets in place throughout the treatment.
2- Be easily removed after completion of treatment without damaging the tooth surface.
3- Provide easy handling for clinical use.
4- Prevent enamel decalcification and caries around the brackets.
5- Be inexpensive.

In this section, each property of orthodontic adhesive and its testing procedure and limitations will be discussed in detail:

2.3.1 *Bond strength*

Bond strength testing is a common means of evaluating the clinical performance of an orthodontic adhesive. It is an important factor that determines success and efficacy of orthodontic treatment. Orthodontic adhesives should provide sufficient bond strength to retain brackets throughout treatment. However, too high a bond strength might lead to fracture of enamel during debonding (Rix *et al.*, 2001b). Insufficient bond strength leads to bond failure of brackets during treatment time, consequently retarding treatment (Mandall *et al.*, 2003).

There is no clear evidence in the literature as to what the magnitude of the bond strength of an orthodontic adhesive is to be considered adequate for clinical use. Most studies have cited the study by Reynolds (Reynolds, 1975) who proposed 6-8MPa as adequate bond strength for orthodontic purpose (Al Shamsi *et al.*, 2006). However, this assumption may not be entirely accurate for the following reasons: firstly, it was based only on tensile bond strength and did not account for the complex forces and fatigue developed during mastication and chewing, in addition to the stresses arising during activation of the arch wire. Secondly, it fails to include

the environmental factors which exist in the mouth, such as extreme pH change, temperature change and oral microflora and by-products. In addition, the potential for bond strength reduction due to the aging of adhesive was disregarded (Brantley and Eliades, 2000).

Generally, there are three types of orthodontic bond strength testing study:

- *In vitro* studies, are the most commonly reported studies. In these experiments, the study design can be easily controlled and each variable can be accounted for. Both bovine and human enamel are used for this purpose. However, *in vitro* tests disregard the effects of complex forces developed during mastication and biting in addition to the effect of acid formation and microbial by-products and temperature changes that occur in the mouth. Therefore, care should be taken when comparing the results of the *in vitro* test with that of *in vivo*. However, *in vitro* tests may give an indication about the clinical performance of the orthodontic adhesive.

  During treatment and debonding, orthodontic brackets are exposed to a combination of loads in all directions. Therefore, different modes of applying force have been used for testing orthodontic bond strength such as torsion, tensile and shear/peel loading (Katona, 1997; Rix *et al.*, 2001b; Katona and Long, 2006; Chen-Sheng *et al.*, 2008; Lin *et al.*, 2011). In tensile testing the force is applied perpendicular to the adhesive layer, whilst in shear testing the force is applied in the plane of the adhesive and in torsion the force is applied in torque. These different test setups produce markedly different results for the same adhesive (Fox *et al.*, 1994; Katona and Long, 2006).

- *In vivo* studies have been done either through using a removable appliance holding brackets bonded to enamel slabs and inserting into patient's mouth or through debonding of the brackets at the end of treatment and measuring bond strength using a special device. Whilst these tests do not simulate the actual force that a bonded bracket is subjected to in a clinical situation, they are most appropriate for studying the clinical behaviour of the bond strength. Bond strengths measured *in vivo* are significantly lower than those measured from *in vitro* testing (Pickett *et al.*, 2001; Murray and Hobson, 2003; Hajrassie and Khier, 2007). In addition to the above type of studies some clinical studies have been done in which bracket survival is taken as an indicator of bond strength (Gaworski *et al.*, 1999; Ireland *et al.*, 2003; Reis *et al.*, 2008). However, in these cases a full control of the test environment is not possible due to individual variations in diet, eating and oral hygiene practices which might affect the outcome.
- *Ex vivo* studies in which finite element analysis of the bracket, enamel and adhesive are used (Katona, 1997; Chen-Sheng *et al.*, 2008; Lin *et al.*, 2011). In these studies,

mathematical models are constructed to simulate the different types of force applied during orthodontic debonding. This can be considered as an *in vitro* measurements.

There is no standard protocol for measuring bond strength *in vitro*. There are some confounding factors that affect bond strength such as type of the teeth used, storage media and time of storing before boding, storage media of the bonded specimens, curing time and cross head speed of the debonding forces (Finnema *et al.*, 2010) as well as bracket base design (Sharma-Sayal *et al.*, 2003). Therefore, care should be taken when comparing the results of different studies. In order to understand each of these factors I am going to discuss them in detail.

Factors that affect Bond strength testing:

2.3.1.1 Types of Bond strength testing

During treatment and debonding, orthodontic brackets are exposed to a combination of loads in all directions. Therefore, different modes of applying force have been used for testing orthodontic bond strength such as torsion, tensile and shear/peel loading (Katona, 1997; Rix *et al.*, 2001b; Katona and Long, 2006; Chen-Sheng *et al.*, 2008; Lin *et al.*, 2011). In tensile testing the force is applied perpendicular to the adhesive layer, whilst in shear testing the force is applied in the plane of the adhesive and in torsion the force is applied in torque. These different test setups produce markedly different results for the same adhesive (Fox *et al.*, 1994; Katona and Long, 2006).

The most commonly used method is shear bond strength (SBS). However, it is more technique sensitive than tensile bond strength (Thomas *et al.*, 1999). Many methods have used to apply SBS such as wire loops and steel blades or rods (Rognvald and Peter, 2001; Lamper *et al.*, 2012; Shooter *et al.*, 2012; Vinagre *et al.*, 2014). The wire loop method has been compared against the blade method for SBS debonding in sample of bovine teeth and using composite resin based orthodontic adhesive (Transbond XT). It was found that the SBS result using blade was higher and more variable (24.8 MPa, coefficient of variation 29.91%) than using wire loop (17.12 MPa, coefficient of variation 18.44%) (Mojtahedzadeh *et al.*, 2006). The same finding was confirmed in a resin–dentin microshear bond strength (μSBS) of two adhesive system in which μSBS was higher and more variable using a blade compared to a wire loop (Muñoz *et al.*, 2014). However, other work on resin-dentin SBS has shown the opposite in which wire loop gave a higher SBS than blade (Sinhoreti *et al.*, 2001). There are some factors which might contribute to the variability of the results of SBS related to using a blade. Firstly, the blade produces puncture loading, because it contacts the bonded interface in a smaller point area than the orthodontic-wire loop does (Muñoz *et al.*, 2014). Secondly, the design of the blade affects the force outcome, a wider blade tip may have a larger contact area with the adhesive in comparison

to a narrow blade tip. Thirdly, the blade is likely to blunt with time and between samples, leading to inconsistent load application. Finally, the position of the force application, whether on adhesive, bracket or on both adhesive and bracket, is another variable factor that is difficult to control due to irregular tooth surface and adhesive thickness. However, using a wire loop may have a problem of wire dislodgment. In addition, the wire loop is not rigid compared to a blade therefore some of the energy might be absorbed during upward movement of the crosshead of the debonding system (Mojtahedzadeh *et al.*, 2006). Frictional resistance of the wire loop is another confounding factor might affect the SBS result. Friction of the wire loop might be overcome by using a high gauge wire to completely fill all the area under the tie wing between the tie wing and the base of the bracket (Littlewood and Redhead, 1998).

The direction of force application has been shown to influence SBS results (Fox *et al.*, 1994). In SBS testing using a wire loop the ideal direction of pull is parallel to the loading interface (Littlewood and Redhead, 1998). Deviation of the debonding force by a 15° angle will lead to a significant difference in comparison to 0° angle. A 15° angle towards the enamel surface increases SBS and 15° angle away from enamel decreases the SBS value (Klocke and Kahl-Nieke, 2006). The direction of force should be carefully controlled in order to reduce variability.

Crosshead speed of the debonding force during SBS testing is another confounding factor that should be taken into account especially when comparing the results of different studies using different crosshead speeds. Crosshead speeds ranging from 0.5 -5 mm/min have been used in the literature. However, in the clinical scenario the brackets are subjected to forces at higher maximum impact velocity where the viscoelastic property of the orthodontic adhesive is immaterial. In order to mimic that condition a study was conducted using 200 mm/minute in comparison to 1mm/minute and it was found that SBS decreases significantly with increasing debonding force. This could be due to to the induction of a stiff body response and the elimination of the viscoelastic properties of the adhesive (Eliades *et al.*, 2004). Despite that, some studies have shown no significant difference at low crosshead speeds of 0.1, 0.5, 1, 2 and 5 mm/minute (Klocke and Kahl-Nieke, 2005; Shooter *et al.*, 2012). Other studies have shown a significant difference between 0.5 and 5 mm/minute (Bishara *et al.*, 2005). These discrepancies might be attributed to the type of debonding apparatus, where in the former a sharp debonding blade and wire loop were used while in the latter a flattened steel rod was used for debonding. According to a systematic review and meta-analysis done on *in vitro* tests, it was concluded that crosshead speed affects SBS in which each each millimetre per minute of greater crosshead speed increased SBS by 1.3 MPa (Finnema *et al.*, 2010). However, the author does not have any explanation of the discrepancies between those studies which show that bond

strength increases with increasing crosshead speed compared to others which show no difference.

2.3.1.2 Tooth Selection

Human and animal teeth have been used *in vitro* for bond strength testing. Human teeth such as premolars, upper central incisors, lower incisor and molars have been used for bond strength testing (Lamper *et al.*, 2012; Arici and Bulut, 2014; Vinagre *et al.*, 2014). Maxillary central incisors are ideal teeth for orthodontic bond strength testing due to their flat surface and consequently relatively consistent adhesive thickness during bonding. However, incisors are mostly extracted due to periodontal conditions which are more common in elderly patients. Aging might have an effect on mechanical properties of human enamel such as hardness and elastic modulus, which increase in older enamel (Park *et al.*, 2008) in addition to increasing mineral content and toughness in older enamel (Zheng *et al.*, 2013). Those teeth are likely to be exposed to prolonged fluoride exposure, and have a higher fluoride content in the outermost surface (Weatherell *et al.*, 1972) which might affect bond strength and care should be taken. The shape of molars and premolars is highly variable (Oesterle *et al.*, 1998). This may create an uneven adhesive layer thickness between the teeth and the bracket and the bracket base may not closely fit to the tooth. Despite this, sound premolars are mostly extracted for orthodontic purpose and therefore commonly used. However, collecting a sufficient amount of healthy teeth requires time and time in storage after extraction may influence results. In addition to this it has been shown that SBS is different in different tooth types in *in vitro* studies. However, different studies report conflicting results. For example, one study showed canines (upper 12·3 MPa, lower 12·1 MPa) and premolars (upper 11·9 MPa, lower 10·9 MPa) to have higher shear bond strength in comparison to the central incisors (upper 6·9 MPa, lower 9·0 MPa) (Rognvald and Peter, 2001). However, Hobson *et al.* (2001) showed no significant difference between upper central incisors, canines and premolars. Therefore, orthodontic bond strength measurements should be made using the same tooth type in order to minimize avoidable variations.

Bovine teeth are not identical to human teeth in either chemistry or micro-structure (Yassen *et al.*, 2011), however, they have been suggested as a useful substitute to human teeth in orthodontic bonding tests (Oesterle *et al.*, 1998) for the following reasons. Firstly, it is difficult to obtain sufficient human teeth in terms of quantity and quality as most are extracted due to extensive carious lesions. In addition, it is difficult to control the age of the extracted human teeth, in contrast to bovine teeth which can be extracted at a specific age. Human teeth are small and irregular shaped in comparison to large and flat surface of bovine teeth. Finally concerns

about infection hazards and ethical issues are more complex with human teeth compared to bovine teeth. However, bond strength test results on bovine teeth should be compared with caution to those using human teeth. One study, which only used 10 samples per group, showed no significant differences in SBS values using bovine and human teeth and a light cured composite resin (Fowler *et al.*, 1992). However, SBS measured using bovine teeth are typically lower than those measured using human teeth by 44% (Oesterle *et al.*, 1998). Other studies have shown significant differences in SBS on bovine and human teeth (Rüttermann *et al.*, 2013) which could be due to the differences in crystal configuration and more lattice defects in bovine enamel compared to human enamel (Fonseca *et al.*, 2008; Tanaka *et al.*, 2008). Both permanent and primary bovine teeth have been used for bond strength testing and no significant difference seen between them (Oesterle *et al.*, 1998). The number of samples used in studies are different from one study to another generally they are between 15-30 samples per group (Evans *et al.*, 2002; Swanson *et al.*, 2004; Klocke and Kahl-Nieke, 2005; Su *et al.*, 2010; Parrish *et al.*, 2011; Yoshida *et al.*, 2012; Vinagre *et al.*, 2014) see Table 2.1.

Table 2.1 The type of teeth and the number of samples used in some previous studies.

References	Number of samples per group	Type of teeth used
(Parrish *et al.*, 2011)	22	Flattened bovine incisor
(Vinagre *et al.*, 2014)	15	Human premolar
(Swanson *et al.*, 2004)	20	Human molar
(Evans *et al.*, 2002)	15	Bovine incisor
(Yoshida *et al.*, 2012)	8	Bovine incisor
(Klocke and Kahl-Nieke, 2005)	30	Bovine incisor
(Su *et al.*, 2010)	18	Human premolar

While many studies have used both bovine and human enamel with an intact surface, some studies have used a ground enamel surface to obtain a flat substrate (Arnold *et al.*, 2002). This was to overcome the roughness variability of the substrate (Gibb and Katona, 2006). The procedure of grinding of the outermost enamel surface is inappropriate if attempting to replicate clinical conditions. In addition to that, extra variability may arise in the roughness as well as in the thickness of the remaining enamel after grinding as this is difficult to control. In terms of the impact of grinding the tooth surface on bond strength, this is controversial in the literature. Some studies show increasing bond strength on ground surfaces compared to the intact enamel surface (Hadad *et al.*, 2006), while others report no difference in the tensile bond strengths

(Perdigao and Geraldeli, 2003). It has previously been suggested that the roughness of bovine teeth does not correlate to the tensile and shear bond strength (Jung *et al.*, 1999; Barkmeier *et al.*, 2009; Sabatoski *et al.*, 2010). However, there is an old study hypothesised that the topography of the adherent surface (bovine enamel and dentine) can affect bonding of a resin based adhesive system (Eick *et al.*, 1972). In general using the intact enamel surface better replicates the clinical situation.

Most studies have measured bond strength 24 hours after a bracket has been bonded, which is different to the clinical scenario where load would be applied shortly after bracket placement, as most clinicians activate orthodontic appliance within 10-15 minutes of the appliance placement. Bond strength values tend to increase with time, with SBS and tensile bond strength shown to be significantly higher at 24 hours compared to 30 minutes after bracket bonding using a range of filled and unfilled BisGMA, UDMA and TEGMA based commercially available orthodontic adhesives (including Concise™ Self-curing, Transbond™ XT Light-curing and Heliosit® Orthodontic Light-curing) (Bishara *et al.*, 1999; Yamamoto *et al.*, 2006; Su *et al.*, 2010; Yoshida *et al.*, 2012; Vinagre *et al.*, 2014). This is most likely due to the increasing degree of conversion (DoC) of the orthodontic adhesive with time. In addition in some *in vitro* studies bond strengths were measured after long period of time (a month) in order to know the long term bond strength of the material. It has been shown that storing teeth for a month in distilled water resulted in in increasing SBS of brackets bonded to human premolars using Transbond XT (Su *et al.*, 2010).

2.3.1.3 Bonding procedure

Bonding in orthodontics is achieved firstly by etching the enamel surface to dissolve enamel rods and produce a porous surface to enhance mechanical retention of adhesive resin prior to primer application. There are two techniques of etching either a conventional technique or using self-etching primers. Several studies have compared self-etching primers with conventional etching in terms of SBS. Some studies reported no superiority of one over another (Tamer *et al.*, 2003; Chalgren *et al.*, 2007). However, others showed decreased SBS with self-etching primers compared to conventional etching (Bishara *et al.*, 2001; Goracci *et al.*, 2013). Self-etching primers may produce smaller and fewer tags in comparison to phosphoric acid, consequently producing less irreversible damage to the tooth surface (Fjeld and Øgaard, 2006). The length of resin tags in enamel surface is not believed to be associated with the tensile bond strength (Shinchi *et al.*, 2000). Surprisingly, it has been shown using conventional etching leads to less enamel decalcification than using self-etching primer (Ghiz *et al.*, 2009).

In conventional etching several factors might influence SBS and tensile bond strength, such as type of etchant, duration of etching and concentration of etchant (Olsen *et al.*, 1996; Shinchi *et al.*, 2000; Gardner and Hobson, 2001; Chang *et al.*, 2005; Chalgren *et al.*, 2007). Phosphoric acid is generally used for acid etching. No difference was found in SBS either using phosphoric acid in gel form or in liquid form (Chalgren *et al.*, 2007). Duration of acid etching should be considered during bracket bonding to enamel. No differences in SBS were reported when the enamel was etched for 10, 20 and 30 second of etching with 37% phosphoric acid, while SBS significantly decreased when the etching time was decreased to 5 seconds (Olsen *et al.*, 1996). 30 seconds of acid etching has been recommended for cleaning and producing a proper etch (Gardner and Hobson, 2001). Regarding concentration of etchant, no differences were seen in the tensile bond strength when between 3% to 65% phosphoric acid was used for 30 seconds (Shinchi *et al.*, 2000). However, higher acid concentrations might lead to longer resin tags, which could have a potential adverse effect on the enamel substrate (Shinchi *et al.*, 2000).

Primer, typically an unfilled resin, is applied on the etched enamel surface prior to application of the adhesive and bracket. This is to enhance penetration of resin tags into the porous enamel surface to improve effectiveness of the final bond. There are several *in vitro* studies showing no significant difference in orthodontic SBS between using a primer or without using it (Chalgren *et al.*, 2007). A randomized clinical trial has shown no significant difference in the failure rate between using primer (11.1%) and without primer (15.8%) for a period of 12 months using pre-coated brackets (Nandhra *et al.*, 2015). However, this study was criticized as other factors that relate to performance of the material, such as type of bracket used, debonding process and duration of the study should be considered prior to omitting one step from bonding procedure (Eliades, 2014). In addition, the advantages of primers in sealing the enamel surface to prevent leakage and enamel demineralization should also be considered (Ghiz *et al.*, 2009).

The amount of adhesive used and amount of the force applied during positioning of the brackets are confounding factors which may influence the bond strength. In an attempt to standardize the amount and thickness of the orthodontic adhesive, attempts have been made to establish a standard protocol. For instance, a protocol was used in which standardized amount of adhesive with standardized amount of force for distinct time was used, aiming to achieve an equal thickness for all the samples (Korbmacher *et al.*, 2006; Chen-Sheng *et al.*, 2008; Lamper *et al.*, 2012). However, this may simulate the clinical scenario only in the case of using pre-coated brackets. Therefore, it has been proposed that it is generally acceptable if a skilled orthodontist prepares samples for *in vitro* testing (Rahiotis *et al.*, 2013).

2.3.1.4 Storage media

Extracted teeth used for bond strength testing are generally kept first in disinfecting solutions and then stored in storage media such as water, an aqueous solution of chloramine T, ethanol, formalin, thymol and artificial saliva (Rolland *et al.*, 2007; Gittner *et al.*, 2010). The purpose is to prevent the teeth from desiccating. Even though enamel has a high inorganic content (95%) and low organic component, it may be affected by drying out and desiccation (Jaffer *et al.*, 2009).

Pre-test storage media, a solution in which extracted teeth were stored prior to bonding, may have an effect on the SBS and tensile bond strength (Jaffer *et al.*, 2009; Gittner *et al.*, 2010). It has been shown that storing ground bovine teeth for 7 months at 4°C, prior to bonding to pre-coated brackets using Transbond XT, in each of water, isotonic saline, Chloramine T at 1% and 10% and 10% formalin solution resulted in no significant difference in SBS while most liquid storage media gave significantly higher SBS than storing the teeth in dry (air) or within 70% ethanol (Jaffer *et al.*, 2009). In another study on human teeth bonded with ceramic brackets using Transbond XT, it was shown that storing teeth in 96% ethanol leads to lower SBS than storing in 0.1% thymol. However, in this study they mentioned that the ethanol group were stored for an unknown period (Gittner *et al.*, 2010). However, in another study on μSBS of composite resin to enamel it was shown that storing teeth in 0.1% thymol resulted in lower μSBS than storing in distilled water (Tosun *et al.*, 2007).

In addition to the type of storage, the duration of pre-test storage varies in the literature from 24 hours to 5 years. No significant difference in μSBS of composite resin to enamel was shown at 2 hours and 2 months time of storing teeth in distilled water, 0.1% thymol and 10% formalin solution (Tosun *et al.*, 2007). In addition, no differences were found in dentin micro tensile bond strength of the freshly extracted teeth compared to those that were stored for 2 years immersed in 0.5% chloramine solution or dry condition (Mobarak *et al.*, 2010). In addition, it was suggested that storage of human molar teeth for up to 5 years in distilled water does not affect enamel SBS (Williams and Svare, 1985). However, more recently it has been shown that minerals leach out of the enamel surface (Secilmis *et al.*, 2013). Therefore, it is recommended to use extracted teeth within 6 months to obtain some standardization.

2.3.1.5 Lighting Conditions

In photo-activated orthodontic adhesives the light intensity and exposure time affects bond strength. It has been shown that SBS increases with increasing light intensity from 500 to 3000 mW/cm^2 for 4s from 2 MPa to 17 MPa in a sample of bovine teeth bonded to metallic brackets using Transbond XT (Staudt *et al.*, 2006). However, it has been shown that increasing the

exposure time has a greater impact on SBS than increasing light intensity in a study using a halogen light at 200 and 400 mW/cm^2 for 3,5 and 10 seconds of light curing in a range of filled BisGMA, UDMA and TEGMA based commercially available light curing orthodontic adhesives like (Beauty Ortho bond, Transbond^{TM} XT Light-curing and Orthophia LC) (Yoshida *et al.*, 2012). There are several studies which have shown the effect of exposure time on increasing SBS (Serdar *et al.*, 2004; Swanson *et al.*, 2004; Usumez *et al.*, 2004; Staudt *et al.*, 2005; Lamper *et al.*, 2012). It has been shown that increasing light exposure time from 6s to 10s leads to a significant increase of the SBS from 8.6 MPa to 11.6 MPa of a commercial adhesive (Transbond XT) using an LED light with 1600 mW/cm^2 intensity (Gomes *et al.*, 2014). However, whilst SBS will increase with increasing exposure time a threshold is reached above which it might not offer any extra benefit. For example, some studies have shown no significant difference between 20 s and 40 s of exposure time (Serdar *et al.*, 2004). In addition, the impact of the type of the adhesive system used should not be discounted. For example it has been shown that increasing the exposure time from 20 s to 40 s using a halogen LCU leads to an increase in SBS of the brackets with the two component self-etching primers like (Transbond plus and Clearfil SE bond) whilst no difference was observed with the single component etching primers like (iBond and Ideal1) and conventional three step Transbond XT (Lamper *et al.*, 2012). Another factor that should be considered is the type of light curing unit used. For example a study has shown an increase in bond strength with increasing exposure time for the same material with a halogen LCU but not with an LED LCU. In most of the studies 40 seconds of light curing has been used as a control group, as this was considered practical in terms of orthodontic bonding (Oesterle *et al.*, 1995; Evans *et al.*, 2002; Usumez *et al.*, 2004; Mavropoulos *et al.*, 2008). Different types of LCUs have been used to polymerize light cured orthodontic adhesives. There is no clear clinical evidence in superiority of one type of light over others in terms of bond failure (Fleming *et al.*, 2013).

The efficacy of the light cured orthodontic adhesive depends on the amount of energy absorbed by the light cured composite resin. Radiant exposure (J/cm^2) which is the product of light intensity (mW/cm^2) and exposure time (seconds) affects the bond strength, with SBS increasing with increasing radiant exposure (Mavropoulos *et al.*, 2008). This is based on the idea of the total amount of energy that is delivered to the orthodontic adhesive. It has been shown that increasing the radiant exposure from 6000 mJ/cm^2 to 18000mJ/cm^2 using a halogen light with 3000 mW/cm^2 with 2 and 6 second respectively, leads to an increase in SBS from 8 MPa to 15 MPa (Erion and Banu, 2011). The exposure reciprocity law is based on the concept that comparable material properties can be achieved as long as the radiant exposure is kept constant irrespective of the light intensity and exposure time, no matter how the radiant exposure is

obtained by different combinations of light intensity and exposure time (Leprince *et al.*, 2013). The concept of reciprocity law is controversial and will be discussed in section 2.61 B. The concept of the reciprocity law does not seem to hold for orthodontic adhesives (Mavropoulos *et al.*, 2008) and this is likely to be because a thin layer of adhesive is used, unlike a conventional restoration and secondly, the light activation occurs primarily indirectly through the tooth surface.

Another factor that can influence degree of cure and bond strength is the distance between the light curing tip and the bracket base. It has been shown that an orthodontic adhesive achieved higher SBS at 0 mm distance using an LED LCU compared to 3 and 6 mm distance (Cacciafesta *et al.*, 2005). This was due to decreasing intensity of the exposure light with increasing the distance between the light curing tip and the bracket base (Price *et al.*, 2004). The angle of the light curing tip is another factor that should be considered during bond strength testing, however, it has been shown that curing an orthodontic adhesive (Transbond XT) for 40 seconds using 0°, 45° and 90° angles at 3 mm distance shows no difference in SBS results (Yusoff *et al.*, 2008)

2.3.1.6 Assessment of bond failure

Adhesive remnant index (ARI) has been used to score the residual adhesive after debonding on the enamel surface. This is to evaluate the site of adhesive failure between enamel, adhesive and bracket base. It was first introduced by Artun and Bergland in 1984. This index system used four scores as follows: score (0) no adhesive left on the tooth; score (1) less than half of the adhesive left on the tooth; score (2) more than half of the adhesive left on the tooth; and score (3) all adhesive left on the tooth with a distinct impression of the bracket mesh (Artun and Bergland, 1984). This index has been modified to account for the amount of adhesive remnant more quantitatively resulting in a modified ARI which was based on 5 scores: score (5) no adhesive; score (4) less than 10% of the adhesive retained; score (3) between 10% and 90% of the adhesive left; score (2) more than 90% and; score (1) all adhesive remain on the tooth surface with imprints of the bracket base (Bishara *et al.*, 2000). Both of the scores are measured subjectively either under light microscopy with 10X and 20X magnification or with the naked eye. A study has shown a difference scoring with 20X compared to 10X and 0X magnification (Montasser and Drummond, 2009). It was found that at higher magnifications, there is a tendency for lower scores to decrease and for higher scores to increase compared with lower magnifications. (Montasser and Drummond, 2009). Several attempts have been made to develop a quantitative method for measuring ARI scoring such as SEM scanning, finite element analysis and three dimensional profilometry (Kim *et al.*, 2007; Chen-Sheng *et al.*, 2008; Cehreli

et al., 2012). However, it has been shown that qualitative visual scoring using the ARI (using stereomicroscope under 20X) is capable of generating similar results compared to those assessed by quantitative image analysis techniques such as SEM images and elemental mapping (Cehreli *et al.*, 2012). Therefore, a qualitative method using visual inspection is commonly used to investigate ARI, despite subjectivity of the method. However, care should be taken when comparing results of different studies based on different magnifications and different methods in regard to ARI scoring.

It has been shown that the percentage of ARI increased with increasing SBS (Osorio *et al.*, 1998), as well as factors such as bracket base design and adhesive properties, which might contribute to the residual adhesive (O'Brien *et al.*, 1988).

2.3.2 *Easy removal and less adhesive remnant during debonding*

Whilst the orthodontic adhesive should provide sufficient bond strength to retain brackets during treatment it is important that the adhesive is easily removed at completion of orthodontic treatment. Ideally, little or no adhesive should be retained on the tooth surface after debonding. During debonding bond failure occurs either at bracket/adhesive and/or enamel/adhesive interface. The latter is more favourable since it contributes to minimise the time required and enamel loss after debonding (Fox *et al.*, 1994). Therefore, to reduce the amount of adhesive remnant, it is important to consider increasing bond strength between adhesive and bracket (within sufficient bond strength scope).

Different techniques have been used to remove the residual adhesive on the enamel surface after debonding, including a slow speed bur, high speed bur, aluminium oxide disc and ultrasonic scaler. Studies have been done to determine the effect of these techniques on human teeth (Ireland *et al.*, 2005; Cehreli *et al.*, 2008; Cochrane *et al.*, 2012). It has been found that removal of residual adhesive can lead to enamel loss ranging from 4.57µm to 55.6 µm (Fitzpatrick and Way, 1977; Hosein *et al.*, 2004; Al Shamsi *et al.*, 2007; Ryf *et al.*, 2012).

In an attempt to decrease enamel loss researchers have attempted to develop new orthodontic adhesives with the potential of easy removal, this is either through the use of unfilled linear acrylic resin (Su *et al.*, 2010) or via inclusion of thermo-degradable additives into orthodontic adhesives (Tsuruoka *et al.*, 2007; Ryu *et al.*, 2011; Saito *et al.*, 2015). Su *et al.* (2010) developed a new orthodontic adhesive which was made of copolymer of HEMA and MMA with polymer powders of PMMA and NaF salt as filler. The developed material demonstrated a lower ARI in comparison to a commercial composite resin based orthodontic adhesive, in addition to having a lower hardness than the comparator. This was particularly apparent after water storage for 30 days due to the presence of HEMA resulting in water absorption, softening and therefore

easy removal (Su *et al.*, 2010). Polymers of MMA-based resins are linear or only lightly cross-linked, which results in a softer, more flexible and potentially weaker material (Gorelick *et al*., 1978). At the end of orthodontic treatment on average less enamel loss has been shown to occur during adhesive removal of an unfilled polymethylmethacrylate adhesive than removal of highly filled composite adhesive (Brown and Way, 1978; Su *et al.*, 2010). Additionally, less enamel fracture was seen after debonding an MMA-based resin (Super-Bond and experimental MMA-based resin) in comparison to a conventional BisGMA/TEGMA based composite resin (Kim *et al.*, 2014).

Another method of developing easily de-bonded adhesives is through inclusion of thermo-degradable materials into an experimental resin, such as heat-expandable microcapsules. (Tsuruoka *et al.*, 2007; Ryu *et al.*, 2011; Saito *et al.*, 2015). This is based on the notion of lowering the glass transition temperature. Debonding of the adhesive can then be encouraged by application of a high temperature of up to 160 C° for up to 20 seconds. However, care should be taken as there are inherent risks of using high temperature such as burning of dental tissues and pulp damage. There is also increased risk of bond failure during consumption of hot drinks and foods by the patients.

2.3.3 *Handling characteristics of orthodontic adhesives*

Further important properties of orthodontic adhesives are their handling properties, which are mainly dependent on the rheological properties of orthodontic adhesives. These are determined by the components of the material such as filler amount, size and shape, monomer blend, and degree of cross-linking (Papakonstantinou *et al.*, 2013). It is essential for an orthodontic adhesive to have a low viscosity so as to penetrate into the pores of the enamel surface and form resin tags after being etched. However, using an adhesive resin without fillers, may lead to poorer bond strength and inferior handling properties compared to filled resin (Lee *et al.*, 2006; Faltermeier *et al.*, 2007). To overcome this problem first a primer is used, which is unfilled resin, then a more viscous adhesive resin used to secure the bracket. The viscosity of the adhesive must also be optimised, to allow easy positioning of the brackets. However, there is no clear evidence in the literature regarding the optimal viscosity of orthodontic adhesives.

In addition to viscosity, the primer and adhesive must be capable of achieving an adequate DoC in a reasonable length of time beneath the bracket base. In order to evaluate the handling characteristics, both the rheological characteristics and polymerization reaction should be considered.

2.3.3.1 Rheological properties of orthodontic adhesives

Orthodontic adhesives should have optimum viscosity during application that allows controlled positioning of brackets on the teeth surface without the bracket moving before curing. Low viscosity monomers have been used to lower the viscosity of resin based orthodontic adhesives, such as 2-Hydroxyethylmethacrylate (HEMA), methylmethacrylate (MMA), triethylene glycol Di-methacrylate (TEGMA) and HEMA-Phosphate. TEGMA, HEMA and 3-hydroxypropyl methacrylate (HPMA) were used as diluents to investigate their effect on the viscosity of urethane Di-methacrylate (UDMA) formulations using a Bohlin rheometer at 23C°, 37C° and 60C°. It was found that viscosity decreased substantially as the diluent concentration increases in the experimental UDMA/diluent formulations (Silikas and Watts, 1999). TEGMA has been used widely in conventional orthodontic adhesives to reduce viscosity of the BisGMA and UDMA. A study using a steady shear sweep test (shear ramp parameter) to measure the viscosity of different filled and unfilled UDMA based resins in comparison to BisGMA based resin. It demonstrated that both filled and unfilled UDMA as well as unfilled BisGMA are Newtonian in behaviour in contrast to filled BisGMA which was non-Newtonian (viscosity increase with increasing shear rate). They also found that the viscosity of both filled and unfilled UDMA based resin decreased with increasing TEGMA concentrations (Papakonstantinou *et al.*, 2013). In addition to using low viscous monomers, solvents are used to lower resin viscosity. Water, ethanol and acetone are the most commonly used solvents in dental adhesives (Van Landuyt *et al.*, 2007).

In general, the viscosity of composites is affected by the type and ratio of the resin matrix components, the size and shape of the inorganic filler and the filler content. (Lee *et al.*, 2003; Beun *et al.*, 2009). A study has been undertaken to investigate the rheological properties of flowable, conventional hybrid and condensable composite resins. The advanced rheometric expansion system was used to measure the shear strain, according to the material condition to measure the viscosity of different types of composite. It was found that the composite resins have psuedoplastic non-Newtonian nature. It was also demonstrated that the lower viscosity of flowable composite, compared to conventional composite, is related to a lower proportion of filler particles (Lee *et al.*, 2003). Another study was conducted to investigate the effects of monomer and filler concentration on the rheological properties related to handling characteristics of composites. A 60:40 BisGMA: TEGMA blend was mixed with silane-treated barium glass, fumed silicate or round silica. It was found that resin matrices were Newtonian fluids and all experimental composites exhibited pseudoplasticity. The viscosity exponentially increased as the percentage of the filler volume was increased, but decreased with increasing

temperature. For identical filler volumes, as the filler size decreased, viscosity increased (Lee *et al.*, 2006).

The viscosity and rheological behavior can be measured using a number of conventional techniques, including rotational rheometer, oscillatory rheometry and capillary rheometry. Different rheometrical techniques have been used to measure viscosity of the resin based adhesives such as steady shear sweep test, advanced rheometric expansion system and vertical oscillation rheometer (Lee *et al.*, 2007; Papakonstantinou *et al.*, 2013). However, the problems in using of these viscometers for the determination of the viscosity of orthodontic adhesives are complexity, adhesive evaporation, in addition to the paste nature of the orthodontic adhesives that make it difficult to measure its viscosity. Therefore, alternative test methodologies are required.

A simple method, a syringe and a device to produce force, has been used to measure relative viscosity of the calcium phosphate bone cement (Fatimi *et al.*, 2012) "When the material is extruded at a constant rate the shear stress is related to the pressure required to depress the barrel of the syringe, whereas the shear rate is a function of the flow rate. Thus, a material of low viscosity requires only a low pressure to produce a high flow rate, whereas a more viscous material may require a high pressure to produce a relatively small rate of flow" (McCabe and Walls, 2009). Therefore viscosity can be obtained using equation 1.1 below (see figure 2.2)

Equation 2.1 Viscosity= kp/Q (p=pressure, k=constant, Q= plunger speed)

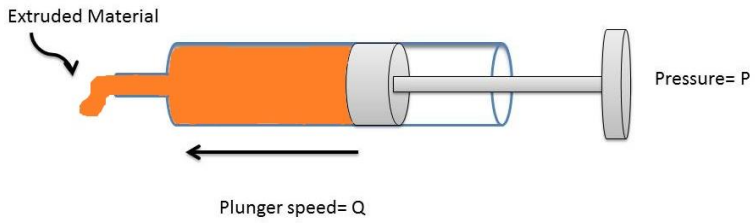


Figure 2.2 The rheological properties of Fluids and pastes can be represented by extrusion of materials from a syringe (McCabe and Walls, 2009)

The microcapillary rheometer has been shown to be a reliable and reproducible method for quantitative rheological measurement of Newtonian and non-Newtonian rheological behaviors (Allahham *et al.*, 2004). A capillary rheometer can be used to obtain the force that is required to extrude the material from a syringe catheter device, known as injectability (Ratier *et al.*, 2004). Injectability is defined as the ability of calcium phosphate bone cement to move through a syringe–catheter device (Ratier *et al.*, 2004). Injectability has been used to measure extrusion behaviour of pastes like calcium phosphate bone cement.

For this purpose, a simple syringe with or without a needle has been used to quantitatively measure extrusion (injectability). Different methods have been used for measuring injectability, including using a mechanical test machine to apply a constant force, with the load rate determined by the materials viscosity (Wang, 2006). However, whilst this method may work for materials of similar viscosity it is less useful for measuring a wide range of viscosities as for viscous materials a high load is required to extrude the material, while for less viscous materials a high load may lead to rapid extrusion of the material.

Another method proposed is using mechanical test machine to measure the maximum applied force at a steady given load rate or to monitor the force applied during whole extrusion (Allahham *et al.*, 2004; Bohner and Baroud, 2005; Fatimi *et al.*, 2012). Controlling the compression rate is useful as the rate of compression is stable with the only difference being the materials viscosity which determines the amount of force required to extrude the material for a given displacement.

Both injectability methods have been used for a wide range of materials from very viscous pastes (such as calcium phosphate bone cement) to liquids (Bercier *et al.*, 2010; Fatimi *et al.*, 2012; Montufar *et al.*, 2013). However, this method has not been applied to measure the viscosity of orthodontic adhesives. Currently most commercial orthodontic adhesives are delivered in a sealed dark syringe, to allow easy application. Therefore, the adhesives must be extruded from the syringe or capsule (injected) for use. Therefore, it is more practical to measure injectability of the adhesives since it is more clinically relevant rather than just measuring viscosity.

The injectability is defined as the ability of cement to move through a syringe–catheter device (Ratier *et al.*, 2004). Injectability is measured by weighing the residual mass of the material retained into the syringes after loading with a constant force (Alves *et al.*, 2008). Injectability has been used to measure extrusion behaviour of pastes like calcium phosphate bone cement.

Injectability does not measure viscosity directly however, injectability is related to viscosity of the material. A material with the lowest injectability coefficient has the highest viscosity (Ginebra *et al.*, 2001). When a force is used to extrude a syringe filled with a paste from, the injectability coefficient is determined as the percentage by weight of that part of the amount of a paste that could be extruded from a syringe with respect to the total mass of the cement introduced in the syringe (Khairoun *et al.*, 1998; Ginebra *et al.*, 2001).

2.3.3.2 Setting characteristics of orthodontic adhesives

During polymerization carbon double bonds of methacrylate monomers are converted to a polymer network of single carbon bonds so the ratio of conversion of monomer to polymer is

called degree of conversion (DoC). DoC attained during polymerization is an important determinant of the physical and mechanical properties of dental resins (Ferracane and Greener, 1986; Calheiros *et al.*, 2008) in particular solubility and degradation. A linear relationship has been demonstrated between Knoop micro-hardness and DoC of a commercial di-methacrylate based (Tetric EvoCeram) composite resin (Price *et al.*, 2011). Generally, DoC of dental resins are of the order of 43- 75% (Lovell *et al.*, 1999; Moraes *et al.*, 2008; Nithya *et al.*, 2009). The DoC for adequate clinical performance has not yet been established. Low DoC contributes to high permeability of the adhesive, low mechanical strength, more water sorption and results in leaching of monomers, polymerization initiators and inhibitors, hence biocompatibility of the material is compromised (Santerre *et al.*, 2001; Van Landuyt *et al.*, 2007).

Type of brackets and polymerization activation methods have influence on DoC of orthodontic adhesives. Eliades et al (2000) examined DoC of light cured, chemically cured and dual cured orthodontic adhesives. With a ceramic bracket, the dual-cured adhesive showed the highest DoC followed by the light-cured and the chemically-cured adhesives showing the lowest DoC, whilst with the metallic bracket, the DoC of a light-cured adhesive was comparable with that of the chemically-cured adhesive (Eliades *et al.*, 2000). In addition to the type of bracket and polymerization activation method, other factors interact to control the extent of polymerization such as resin composition (Kedjarune *et al.*, 1999), photoinitiator concentration, light intensity (Soh *et al.*, 2003) and exposure time (Cadenaro *et al.*, 2005; Moraes *et al.*, 2008; Ceballos *et al.*, 2009; Eliades, 2010; Ferreira *et al.*, 2011). They will be discussed further in section 2.5 as intrinsic and extrinsic factors that control photo-polymerization.

Different techniques have been used to determine the DoC of adhesive resins such as FTIR (Fourier transform infrared spectroscopy), Raman spectroscopy, EPR (electron paramagnetic resonance), NMR (nuclear magnetic resonance), DSC (differential scanning calorimetry) and DTA (differential thermal analysis). The most widely used technique is FTIR (Moraes *et al.*, 2008).

FTIR has been used to investigate DoC in dental adhesive resins within various applications such as sealants, orthodontic adhesives and restoratives as well as for monitoring the extent and rate of acid base reaction of GICs. FTIR use is based on the notion that when infrared radiation (IR) light passes through a polymer sample the molecules are excited to vibration of chemical bonds at frequencies characteristic of the chemical bonds present. The excited molecules absorb the radiation then real time IR spectra are produced in relation to wavenumbers obtained (Wendl *et al.*, 2004; Rahiotis *et al.*, 2013). Most studies are performed at mid IR region of 4000- 400 cm^{-1}. FTIR spectra have been taken as a single scan to monitor DoC of copolymer resin of MMA and HEMA (Zahroon, 2014), in order to obtain real time spectra of the material following

light exposure. However, in most studies co-addition scans are taken and the number of scans taken varies amongst studies. Some take 12 co-addition scans (Conde *et al.*, 2009), 16 co-addition scans (Calheiros *et al.*, 2008) , 32 co-addition scans (Loguercio *et al.*, 2011; Rastelli *et al.*, 2012) and 64 co-addition scans (Fróes-Salgado *et al.*, 2009). The reason behind taking co-addition scans is to increase the signal to noise ratio.

The setting reaction of an orthodontic adhesive can be monitored by quantifying the carbon-carbon double bond (C=C) conversion. The DoC of a material is generally calculated by comparing the intensity of the carbon double bond in the aliphatic band, which is around 1638cm^{-1}, relative to a band of a bond which is not affected by polymerization, which is called the internal reference peak. In most Di-methacrylate resins the aromatic band of the carbon-carbon single bond, which is around 1608cm^{-1}, is taken as the internal reference, as carbon single bonds are not affected by the polymerization reaction (Chung *et al.*, 2002; Calheiros *et al.*, 2008). However, in cases where there is no aromatic monomer, the carbonyl group of C=O at 1715cm^{-1} has been taken as an internal standard (Pianelli *et al.*, 1999; Kashi *et al.*, 2007; Guo *et al.*, 2009) or the N-H reference band at 3380cm^{-1} can also be used (Rahiotis *et al.*, 2013). In order to obtain the percentage of DoC the following equations (Equation 2.2 and Equation 2.3) are used:

Equation 2.2……..% DoC =100(1- %C=C)

Equation 2.3… $(\%C = C) = \frac{[Abs\ (1638\ cm^{-1})/(\text{Abs (Internal Reference peak)}]\text{polymer}}{[Abs\ (1638\ cm^{-1})/(Abs\ (Internal\ reference\ peak)]monomer}$

In which, Abs is absorbance intensity.

One of the limitations of the attenuated total reflectance-FTIR technique (ATR-FTIR) is that it is a surface analytical technique with a mean of 2-4 µm depth. This means the middle zone of minimum conversion in the adhesive sample cannot be analysed (Rahiotis *et al.*, 2013). Therefore, care should be taken to obtain intimate contact of the sample with the diamond crystal of ATR-FTIR stage of FTIR. In addition, to intimate contact, the intensity of the FTIR spectrum is affected by contact pressure (Friedrich and Weidler, 2010), therefore requiring constant pressure between samples tested. However, one of the reasons for taking an internal reference peak is to counter the effect of differences in pressure.

In addition to FTIR, DSC has been used to monitor heat produced during polymerization as the polymerization reaction is an exothermic reaction. DSC is commonly used to study heat flow of dental adhesive resins because it is easy to use and a small amount of material can be tested (Gao *et al.*, 2012). Another advantage of DSC is that it follows the polymerization reaction in real time through monitoring heat release during polymerization. Consequently DoC can be

obtained based on the assumption that the heat produced during the reaction is proportional to the percentage of the monomers that contribute in the polymerization process (Cadenaro *et al.*, 2005; Emami and Soderholm, 2005). Based on this if the only thermal event is a polymerization reaction, then the reaction rate is proportional to the heat flow (Ma and Gao, 2006). DoC can be obtained from calculating theoretical heat release of carbon-carbon double bonds which is 56 kJ/mol over time using the following equation (Schneider *et al.*, 2008; Schneider *et al.*, 2012).

DoC= (Heat release of the material/ Theoretical heat release) X 100.

In addition to obtaining the DoC of the test material against reaction time, polymerization rate as a function of irradiation time can be obtained from the DSC. Once a monomer sample undergoes an isothermal reaction in a DSC, the DSC apparatus monitors heat release over time. Polymerization rate can be calculated from enthalpy of the sample, molecular weight and mass of the sample (Cook, 1992).

Photo-calorimetry is a valuable technique and it gives reliable results if used correctly. However, it is very sensitive to some experimental variables and variation in sample preparation such as thickness of the sample (Maffezzoli *et al.*, 1995), test conditions and temperature (Jakubiak *et al.*, 2001). Therefore, small aluminium crucibles are used in constant temperature throughout the experiment. In addition, photo-DSC is very sensitive to the type and intensity of the LCU used. Different types of LCU have been used with DSC for monitoring photo polymerization of dental adhesive resins such as LED LCU (Gao *et al.*, 2012), halogen lights and plasma arc lights (Emami and Soderholm, 2005), giving light intensities ranging from 1 mW/cm² to 1000 mW/cm² (Lovell *et al.*, 1999; Emami and Soderholm, 2005; Gatti *et al.*, 2007). Therefore it is difficult to compare heat flow from different studies due to the different light sources and different intensities used. Moreover, time of polymerization varies from 10 seconds to 10 minutes. Furthermore, photo-DSC is sensitive to the polymerization conditions, therefore some researchers use nitrogen gas to provide a purged environment (Lovell *et al.*, 1999; Schneider *et al.*, 2012) whilst in other cases polymerisation is undertaken in air with the samples covered with a transparent matrix (Zahroon, 2014). In both cases the intention is to prevent the surface of the examined material from, suffering oxygen inhibition as oxygen inhibition affects the polymerization reaction and may therefore reduce the overall value of heat release.

2.3.4 *Fluoride release*

Several studies have been undertaken to measure fluoride release of orthodontic adhesives. However, there is no standard protocol for fluoride releasing studies. There are variations in the size and shape of the samples among studies. Some studies used disc shaped samples immersed

in storage media (Xu and Burgess, 2003; Dionysopoulos *et al.*, 2013; Zahroon, 2014) while others used brackets bonded with the test material on human teeth (Wheeler *et al.*, 2002). A study has been done to compare fluoride release from disc shapes and bracketed teeth with two fluoride containing orthodontic adhesives, RMGIC and compomer. The study found significant differences in fluoride release between disc shapes and bracketed teeth (Rix *et al.*, 2001b). In addition to variations in the shape of the specimen, different storage media like distilled water, saliva and lactic acid were used. Storage media has an effect on the amount of fluoride release. It appears that saliva decreases fluoride release in comparison to distilled water (Yoda *et al.*, 2006; Madhyastha *et al.*, 2013). In addition to storage media, temperature has effect on fluoride release, with fluoride release from GIC increasing with higher temperatures from 4°C to 37C° (Yan *et al.*, 2007; Madhyastha *et al.*, 2013). Therefore, care should be taken when comparing results of different studies.

Different methods have been used to measure the amount of fluoride release by materials, including ion selective electrode (ISE) and ion chromatography (IC). ISE has been used widely to measure the total fluoride ions (free and complex fluoride ions) at concentrations 0.5 to 0.1 ppm. With ISE acetic buffer solutions (TISAB) are used to release free fluoride ions from complex fluoride ions (McCabe *et al.*, 2002; Itota *et al.*, 2004a; Itota *et al.*, 2004b). This increases the amount of real fluoride ions released by the test material and it is known that only free fluoride ions are effective in enhancing remineralisation (Arends and Christoffersen, 1990). The advantage of ISE is that it is easy to use. IC is another method for measuring fluoride ions, which measures free fluoride ions at concentrations up to 0.001 ppm (McCabe *et al.*, 2002). This method has advantages over ISE in measuring lower levels of fluoride ions up to 0.001 ppm (McCabe *et al.*, 2002; Itota *et al.*, 2004a; Itota *et al.*, 2004b) and in measuring only free ions. However, it is more complicated than ISE.

In addition to the fluoride releasing ability of orthodontic adhesives, fluoride recharging is another interesting property of fluoride releasing orthodontic adhesives. Fluoride releasing orthodontic adhesives can take up fluoride from the oral environment to replace the fluoride that has been lost. Orthodontic adhesives vary in their capacity to absorb and re-release fluoride. There are several ways of delivering fluoride into the oral environment such as using dentifrices, mouthwashes and fluoride gels. Topical fluoride agents can be used to restore the fluoride release capability of orthodontic adhesives, and it has been shown that those materials which have higher recharge capability are those which have higher initial fluoride release (Xu and Burgess, 2003). Recharging is essential to maintain continuous increased levels of fluoride. This is why for clinical use the fluoride recharging ability will become an important factor in choosing materials (Mousavinasab and Meyers, 2009). Different factors influence fluoride

release and recharge characteristics of the fluoride releasing adhesives such as the matrices, filler type and fluoride content, setting mechanism and environmental conditions. (Wiegand *et al.*, 2007; Dionysopoulos *et al.*, 2013). The amount of glass ionomer matrix of the glass filler affects the fluoride releasing and recharging abilities of the adhesives like RMGIC and compomer (Itota *et al.*, 2004b) .

Fluoride releasing adhesives, when re-exposed to a fluoridated mouth rinse after their fluoride content is exhausted, provide sustained fluoride release when compared to those prior to exhaustion (Benson *et al.*, 2005). In some fluoride releasing materials such as GIC and RMGIC the amount of fluoride release after re-fluoridation is higher than the release from within the materials (Cildir and Sandalli, 2005). However, this re-charging potential appears to diminish over time and with repeated exposure to supplemental fluoride (Coonar *et al.*, 2001). The pattern of fluoride release after exposure to supplemental fluoride is a burst-effect (Attar and Turgut, 2003; Cohen *et al.*, 2003). It means a high amount of fluoride is released in the first day then the fluoride release returns to the pre-exposure level after 2 to 3 days (Young *et al.*, 1996).

There are some suggestions regarding the mechanism of fluoride recharging. Firstly, it has been suggested that recharging behaviour of adhesives is caused by surface effects not chemical recharging (Gao and Smales, 2001) because fluoride uptake and rerelease is probably due to the processes of surface retention and matrix diffusion of fluoride (Cohen *et al.*, 2003; Preston *et al.*, 2003). Secondly, it has been suggested that recharging is due to the replacement of intrinsic fluoride and fluoride diffusion into porosities within the material (Xu and Burgess, 2003).

There is no standard recharging protocol. Different studies have been done *in vitro* to measure the fluoride recharging ability of orthodontic adhesives. The test material is exposed to an external fluoride source after its own fluoride content is exhausted to study fluoride uptake of the material and this can be compared to fresh samples (Lim *et al.*, 2011). Fluoride solutions have been used at different concentrations from 200 ppm to 1000 ppm (Coonar *et al.*, 2001; Lim *et al.*, 2011), with fluoride rinsing with 1000 ppm NaF found to be effective for recharging orthodontic adhesives (Ahn *et al.*, 2011). Therefore, care should be taken when comparing results of different fluoride recharging studies.

The amount of fluoride released into water appears to be related to the contribution of the two mechanisms. The first one is an immediate reaction which involves rapid dissolution from the outer surface into solution. The second mechanism is long-term diffusion of ions through the bulk cement (Verbeeck *et al.*, 1998; Lee *et al.*, 2000; Wiegand *et al.*, 2007).

The fluoride release of fluoridated resin based orthodontic adhesives is regulated by the water absorption capacity of the materials. The mechanism of fluoride release comes from either acid

base reaction of the materials such as in case of GIC, RMGIC and compomer (Verbeeck *et al.*, 1998; Lee *et al.*, 2000), or in fluoride releasing composite resin depends on dissolution of the additive fluoride sources like soluble salts of NaF, CaF_2 and SnF_2 or ion leachable glasses that are added to the material. Therefore, for fluoride release to occur, water must be absorbed into the material before diffusion of fluoride to its surroundings. This is describes as diffusion/dissolution mechanism (Verbeeck *et al.*, 1998). To understand fluoride release and recharging ability of orthodontic materials it is crucial to study water sorption of the materials. Water absorption has been measured by monitoring weight changes before insertion of disc shaped samples of a material into water and after being in water for a specific time. By knowing the amount of weight changes and volume of the disc shaped samples, water absorption can be calculated using Equation 2.4 (Cefaly *et al.*, 2003; Marghalani, 2012). Water sorption is highly influenced by the porosity of the material in which high porosity leads to high water sorption in GICs (McCabe *et al.*, 2009). It will also be affected by the amount of soluble fraction within the material. The kinetics of water sorption depend on two processes, water diffusion and diffusion of soluble fraction out of the sample (see Figure 2.3)(Van Noort, 2013).

In addition to water absorption, water solubility is important in order to understand how soluble the material is after being in a solution. For this purpose disc shaped samples are stored in water for specific time, desiccated to remove all water and weighed (Van Noort, 2013). The weight change that occurs may be due to leaching out of monomers, initiators and other components of the material and may therefore impact on the biocompatibility of the material. Solubility measurement is an important indicator of how well the material can withstand the oral environment without degradation. Degradation of the material leads to bond failure which consequently lengthens treatment time. Water solubility can be measured using Equation 2.5 (Cefaly *et al.*, 2003; Marghalani, 2012).

Equation 2.4…….Water absorption ($\mu g/cm^2$) = (W1-W0) /V

Equation 2.5 Water solubility ($\mu g/cm^2$) = (W0-W2) /V

In which: W0= weight of the samples before water insertion, W1=weight of the samples after water insertion, W2= weight of the samples after desiccation and V=volume of the material.

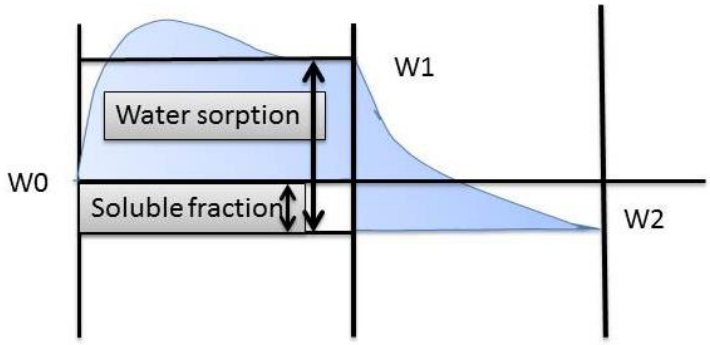


Figure 2.3 Schematic presentation of the kinetics of water sorption and the dissolution of the soluble fraction from (Van Noort, 2013).

Water sorption and solubility are in the range of 30-50 µg/cm² for most polymer resins, higher than this is likely to affect performance of the material (Van Noort, 2013). Sorption and solubility have been measured for orthodontic cements for banding and bonding after being stored in different solutions like distilled water, artificial saliva, and ethanol and mouthrinse solution in order to understand how orthodontic adhesives behave in these solutions (Toledano *et al.*, 2006). In general, resin based orthodontic adhesives are less soluble in comparison to glass ionomer cements.

2.4 Composition of resin based orthodontic adhesive

2.4.1 *Monomers*

2.4.1.1 Di-methacrylate

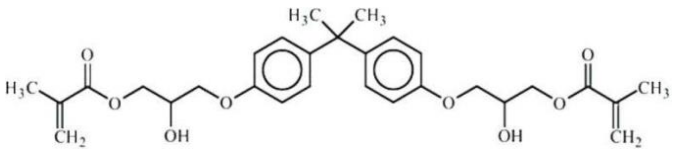
Conventional orthodontic adhesives consist of two principal components, an organic matrix and an inorganic filler. The organic matrix is formed by free radical polymerization of Di-methacrylates such as BisGMA (bisphenol A diglycidyl methacrylate), UDMA (urethane Di-methacrylate) and TEGMA (triethylene glycol Di-methacrylate). BisGMA, TEGMA and UDMA are the most commonly used cross-linking agents in dental adhesives. This crosslinking contributes to greater strength, lower water absorption and less polymerization shrinkage.

BisGMA, also called Bowens-resin, has a high molecular weight. It is the most commonly used base monomer in dental composites. It is a very viscous monomer that makes it difficult to incorporate reinforcing fillers into the matrix and results in a low conversion rate (Lovell *et al.*, 1999). Therefore, TEGMA, a low viscosity diluent monomer, is often added to optimize the viscosity and increase the final conversion of the matrix phase (Lovell *et al.*, 1999; Sideridou *et al.*, 2002) (see figure 2.4). TEGMA has low molecular weight therefore resulting in high

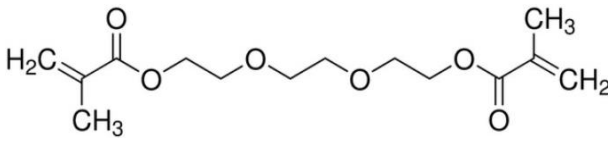
polymerization shrinkage as well as lower mechanical properties. Polymerization shrinkage can be decreased by increasing the percentage of BisGMA in BisGMA/TEGMA mixture (Atai *et al.*, 2005). It has been shown that the percentage of 40:60 of BisGMA/TEGMA is the optimal concentration to optimize viscosity, decrease residual monomers and increase DoC (Davidenko *et al.*, 2005). BisGMA and TEGMA exhibit 5.2% and 12.5% volumetric shrinkage respectively that is reduced to 2% and 6% respectively in the resin composites due to inclusion of inorganic fillers (Labella *et al.*, 1999).

UDMA has been used to act as a substitute to BisGMA as UDMA has a flexible ester group compared to rigid benzoic groups of BisGMA (see Figure 2.4). This offers better materials handling properties (Papakonstantinou *et al.*, 2013). Differential scanning calorimetry (DSC) shows homo-polymerization of UDMA reach a higher DoC (43%) compared to BisGMA (7%) (Dickens *et al.*, 2003). Another study has shown in a mixture of BisGMA/TEGMA together DoC increased with increasing UDMA% up to 50% (Atai *et al.*, 2005). However, a UDMA-based resin matrix provides poorer mechanical properties such as hardness and flexural strength compared to a BisGMA based resin matrix (Zhang *et al.*, 2013). In adhesives, UDMA is often used alone or in combination with TEGMA and /or BisGMA. It has been shown in a mixture of BisGMA/UDMA/TEGMA that substitution of BisGMA or TEGMA by UDMA resulted in an increase in tensile and flexural strength, and that substitution of BisGMA by TEGMA increased tensile, but reduced flexural strength (Asmussen and Peutzfeldt, 1998). TEGMA has been used as diluent to decrease the viscosity of UDMA and also can increase conversion rate of resulted polymer (Sideridou *et al.*, 2002). In addition to TEGMA, other low molecular weight monomers have been used as diluents with UDMA including, 2-Hydroxyethylmethacrylate (HEMA) and 3-hydroxypropyl methacrylate (HPMA) (Silikas and Watts, 1999).

A.



B.



C.

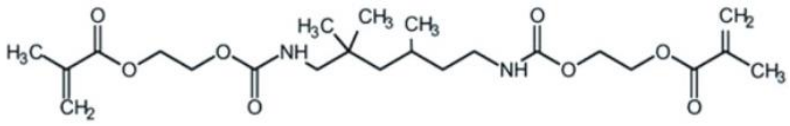


Figure 2.4 Molecular structure of A- BisGMA, B- TEGMA and C- UDMA

2.4.1.2 Methylmethacrylate (MMA)

Methylmethacrylate (MMA) is one of the oldest monomers used in dentistry. It has a low molecular weight and can be used as a solvent or diluent for other monomers (Neumann *et al.*, 2005) (Figure 2.5). It is a mono-functional monomer and it is less reactive than di-functional monomers. Therefore, MMA reaches its maximum shrinkage-strain rate, after a prolonged time in comparison with the di-functional monomers (Atai *et al.*, 2005). PMMA can be produced using free radical polymerization of MMA. The free radical polymerization of acrylates and methacrylate is a chain polymerization across the carbon-carbon double bond of the monomer. MMA-based resins are uncommonly used for permanent restorations due to their lower strength, high coefficient of thermal expansion and high residual monomer. Polymers of MMA are used as an orthodontic adhesive and denture base or liners. However, different factors within the oral environment such as saliva, forces of mastication and dietary changes may have physical and mechanical detrimental effects on acrylic resins (Bettencourt *et al.*, 2010). MMA-based resins have a potential for using as orthodontic adhesives (Newman *et al.*, 1968; Su *et al.*, 2010).

The most common commercial MMA-based orthodontic adhesives are based on mixtures of 4-META/MMA/TBB and it is available as a commercial product as Super-Bond, whose polymerization is initiated by tri-n-butylborane (TBB). 4-META significantly affects water uptake and solubility characteristics of polymers of MMA. 4-META is shown to increase water sorption of the PMMA, however, it does not affect solubility of the PMMA (Unemori *et al.*, 2003). MMA-based orthodontic adhesives have an advantage over conventional BisGMA/TEGMA based orthodontic adhesives like Transbond XT in that they lead to less enamel fracture than Transbond XT (Kim *et al.*, 2014) as it is more flexible and therefore easier to debond from the tooth surface.

2.4.1.3 HEMA (2-Hydroxyethylmethacrylate)

HEMA is a low molecular weight hydrophilic methacrylate monomer that is commonly used in dental adhesives (Figure 2.5). HEMA is widely used in the biomedical fields in the construction of hydrogels (Kulygin and Silverstein, 2007) and contact lenses as well as in dentistry. HEMA is prepared in a single step by the addition of CH_2OH group to the MMA side group (Montheard *et al.*, 1992). HEMA is a mono-functional monomer and after polymerization it forms weaker, linear polymers, unlike multifunctional monomers that are capable of crosslinking. Polymers of HEMA are flexible and porous (Tay *et al.*, 2002a). However, crosslinking agents can be used to improve mechanical properties of the polymers of HEMA (Arima *et al.*, 1995). HEMA can be used to control the rheological behaviour of viscous Di-

methacrylate monomers such as BisGMA and UDMA (Silikas and Watts, 1999; Atai *et al.*, 2005; Kodkeaw *et al.*, 2010) and it can be used as a solvent (Ely *et al.*, 2012). Its hydrophilicity makes this material an excellent adhesion promoting monomer and it readily absorbs water in polymer form (Arima *et al.*, 1995; Van Landuyt *et al.*, 2007).

A copolymer of MMA and HEMA at 60:40 ratio has been used to develop fluoride releasing materials for using as orthodontic adhesives, fissure sealants and a denture liner (Su *et al.*, 2010; Zahroon, 2014; Al-Sammarraie, 2015). The reason for choosing HEMA was mostly due to the hydrophilicity of the material which makes the material readily absorb water, to enhance water diffusion and fluoride release of the material. It was reported that HEMA added to base monomers like bisphenol A glycerolate diacrylate, glycerol 1,3- diglycerolate diacrylate and diurethane Di-methacrylate leads to more water sorption than TEGMA for the same composition (Kodkeaw *et al.*, 2010). Water molecules bonding via hydrogen bonding to the polar sites of HEMA contribute to water diffusion through polymer matrices (Yiu *et al.*, 2006). HEMA is prone to hydrolysis faster by basic solutions than by acidic solutions. However, acid hydrolysis of HEMA increases with increasing temperature and acid concentration (Kazantsev *et al.*, 2003).

HEMA has been used in primers of dentine bonding agents to increase bond strength (Eick *et al.*, 1993; Nakaoki *et al.*, 2000) through improving the infiltration of the resin into the wet dentin surface. It has been suggested that the bond strength to enamel significantly increased with the introduction of small quantities of HEMA to the dentine bonding adhesives (between 10% and 19%); however, with greater quantities (36%) bond strength decreases due to water attraction and osmosis through the polymerized adhesive layer (Torkabadi *et al.*, 2008). HEMA may decrease the vapour pressure of water and it is relatively unvolatile (Pashley *et al.*, 1998). HEMA may also contribute to less acetone loss and decrease the evaporation rate of acetone (Yiu *et al.*, 2005; Nihi *et al.*, 2009) due to the hydrophilicity of HEMA, as the more hydrophilic the monomer in an adhesive system the more solvent is retained (Malacarne-Zanon *et al.*, 2009).

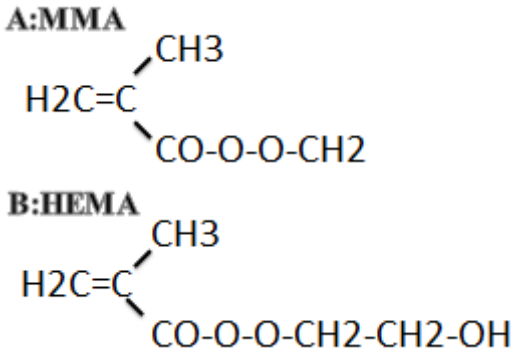


Figure 2.5 Molecular structure of A MMA and B HEMA.

2.4.1.4 4-META (4-methacryloyloxyethy trimellitate anhydride)

4-META presents in nature as a white crystalline structure. It can be prepared by the reduction of 2-hydroxyethyl methacrylate and trimellitic anhydride chloride in the presence of pyridine to remove hydrogen chloride (Chang *et al.*, 2002). 4-META has hydrophilic aromatic group and hydrophobic methacrylate group (Figure 2.6).

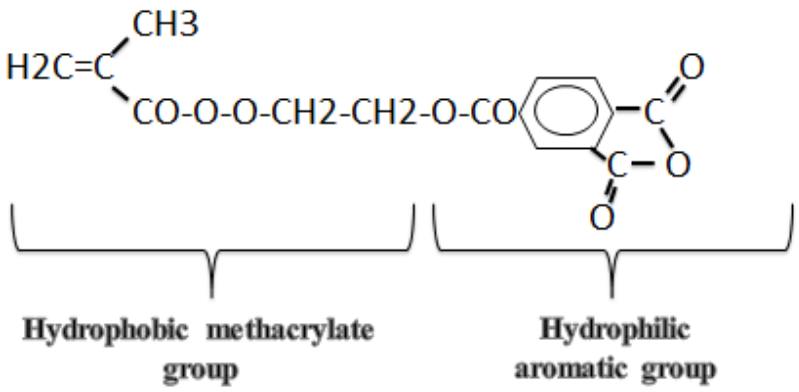


Figure 2.6 Molecular structure of the 4-META monomer.

4-META is used as an adhesion promoting monomer, it increases the bond strength of acrylic resin with enamel (Takeyama *et al.*, 1978) through promoting the infiltration of monomers into dental hard tissue and after polymerization there is excellent adhesion obtained with the enamel (Nakabayashi *et al.*, 1982; Hotta *et al.*, 1992). 4-META monomer is able to adhere to hydroxyapatite and form an ionic bond with calcium in hydroxyapatite (Yoshida *et al.*, 2004). 4-META has been used to improve bond strength of brackets to amalgam, gold alloy, metal alloys and porcelain in conjunction with conventional orthodontic resins (Ohno *et al.*, 1992; Björn *et al.*, 1995; Büyükyilmaz *et al.*, 1995; Zachrisson *et al.*, 1996; Minami *et al.*, 2013). Furthermore adding 1-5% 4-META by volume has been shown to enhance the bond strength of the acrylic resin to the dental alloy (Takeyama *et al.*, 1978; Khasawneh *et al.*, 2003; Shimizu and Takahashi, 2012), because the molecule forms both hydrophilic and hydrophobic bonds when added to the acrylic resin. However, it has been shown that the tensile bond strength of a monomer matrix of TEGMA containing 2 or 5% 4-META leads to decreasing bond strength to bovine dentine in comparison to groups without 4-META (Nikaido *et al.*, 1990). However, no evidence was found in literature on the effect of 4-META on HEMA.

4-META is commonly used together with MMA in the form of 4-META/MMA-TBB adhesives and it is available as a commercial product as (Super-Bond, MCP Bond®), whose polymerization is initiated by tri-n-butylborane (TBB). 4-META containing adhesives provide significantly higher bond strength than the conventional orthodontic adhesives (Clark *et al.*,

2003). Water absorption of MMA based adhesive increases with an increasing 4-META concentration up to 5%wt (Unemori *et al.*, 2003).

4-META is commonly used in solvated self-etching primers or one step bonding agents as an acidic monomer (Tay *et al.*, 2002b; Carvalho *et al.*, 2005). Care should be taken to select the appropriate type of solvent used as using alcohol based solvents like ethanol leads to esterification of the compound however, with acetone esterification does not occure (Fujita *et al.*, 2007).

2.4.2 *Fillers*

Fillers are another component of resin based orthodontic adhesives. Fillers commonly used include quartz, fused silica and many types of glass including aluminosilicates and borosilicates, some containing barium oxide (McCabe and Walls, 2009). All monomers used in resin based adhesives including BisGMA, UDMA and TEGMA, HEMA and MMA, undergo shrinkage during polymerization. Fillers are used to decrease the volumetric shrinkage of resin based adhesives that occurs during polymerization (Labella *et al.*, 1999).

In addition to lowering shrinkage, fillers have other advantages, including increasing bond strength and increasing the strength of the material. Orthodontic adhesives with higher filler content offer higher bond strength than lower filled or unfilled resins (Faltermeier *et al.*, 2007). There is correlation between mechanical properties of composite (hardness and diametral tensile strength) and the volume fraction of filler content (Chung and Greener, 1990). Fillers are not only added to the adhesive, they are included in some of primers as well in order to enhance bond strength. Addition of 10% silica nano-filler into mixture of Bis-GMA, TEGMA and UDMA has been shown to increase the cohesive strength of the adhesive (Conde *et al.*, 2009).

PMMA powder has been used as a filler. Most MMA-based orthodontic adhesives have used PMMA as an organic filler and they are available as a liquid mixture of MMA and PMMA as powder. They are available as commercial products, for example Super-Bond and MCP Bond®. Beads of PMMA also have been used as fillers of experimental composite resins. Addition of 2% by wt spherical PMMA filler, with 30 µm diameter to the composite resin has been shown to enhance certain properties of composite resin, including compressive strength and prevention of crack propagation without altering water sorption capacity of the material (Kondo *et al.*, 2010). However, these authors do not describe the exact composition of the composite resin. In addition it was reported an increase in flexural strength and hardness after addition of PMMA powder to ethylene glycol Di-methacrylate (EGDM) (Atsuta and Turner, 1983; Bajpai *et al.*, 1993).

Fillers have the additional advantage in providing a potential source of fluoride. Some fillers have fluoride releasing ability such as fluoroaluminosilicate glasses (FAG) which has been used in RMGIC and compomers. In resin based adhesives, fluoride can be incorporated into either the polymer matrix as a fluoride releasing monomer (Ling *et al.*, 2009; Xu *et al.*, 2012) or in the form of fillers. Fluoride releasing components have included fluoroaluminosilicate glasses (FAG), stannous fluoride (SnF_2), organic amine fluorides (CAFH) and ytterbium fluoride (YbF_2). Organic salts of fluoride such as sodium fluoride (NaF), potassium fluoride (KF), calcium fluoride (CaF_2) and stannous fluoride (SnF_2) have been incorporated as fluoride releasing fillers into the polymer matrix (Patel *et al.*, 1998; Nakabo *et al.*, 2002; Anusavice *et al.*, 2005; Kodkeaw *et al.*, 2010).

NaF is water soluble salt that dissolves easily into Na^+ and F^- ions. It has been used in water fluoridation and has been incorporated into dental adhesive resins as a source of fluoride. NaF has been used with a monomer mixture of MMA/HEMA as a source of fluoride in the development of fluoride releasing orthodontic adhesive, fissure sealant and denture base linear (Su *et al.*, 2010; Zahroon, 2014; Al-Sammarraie, 2015). The material has a fluoride release at amounts comparable to GIC. In addition, NaF has been added to flowable composite resins and has been shown to have preventive effect as a result of releasing fluoride ions (Tiveron *et al.*, 2015). However, in this work the composition of the monomer mixture is not discussed and this will have a significant impact on fluoride release. In addition NaF has been added to a BisGMA/TEGMA mixture showing fluoride releasing ability (Nakabo *et al.*, 2002). However, after the NaF was treated with γ-methacryloxypropyltrimethoxysilane this resulted in slow release of fluoride from the BisGMA/TEGMA mixture (Nakabo *et al.*, 2002). NaF has been added into a matrix of diurethane Di-methacrylate (DU-DMA)/HEMA, BisGMA/HEMA for using as a denture coating material. The material had released over the four weeks of the study (Kodkeaw *et al.*, 2010). NaF has been added to commercial MMA-based acrylic orthodontic adhesives 4-META/MMA-TBB (Super-Bond/F3) and it has been shown that the material can release fluoride for up to 6 months (Iijima *et al.*, 2013).

Potassium fluoride (KF) is another fluoride salt that has been used in dental adhesives. It was reported that in polymer systems comprised of poly(ethyl methacrylate) powder (PEM), with tetrahydrofurfuryl methacrylate (THFM), and *n*-butyl methacrylate (nBM), the water uptake in the KF containing samples is much less than corresponding NaF samples (Patel *et al.*, 1998).

In addition to NaF and KF, CaF_2 has been used in dental adhesives. CaF_2 has a lower water solubility 0.016 g/L at 18 in comparison to NaF which is 42 g/L at 20°C. Therefore it was reported that CaF_2 released less fluoride ions in comparison to NaF in the first four weeks in a matrix of DU-DMA/HEMA, BisGMA/HEMA used as a denture coating material (Kodkeaw *et*

al., 2010). However, CaF_2 has the ability to release at a low sustained level for as long as 4 months at 0.10 g/cm^2·h, in a polymer resin of UDMA/TEGMA at ratio 70:30 (Anusavice *et al.*, 2005). Water soluble salts like NaF, KF, CaF_2 and SnF_2 provide high levels of fluoride release. However, one of the disadvantages of using them is that once the fluoride has leached out it leaves porosity in the resin and this will affect the mechanical properties of the material (Arends *et al.*, 1995).

2.4.3 ***Solvents***

Solvents are used to lower resin viscosity. The most commonly used solvents in resin based materials are acetone, ethanol and water. In addition to these, some monomers of low molecular weight have been used as solvents such as HEMA, MMA, MAA methacrylic acid, 3-hydroxypropyl methacrylate (HPMA) and TEGMA (Silikas and Watts, 1999; Atai *et al.*, 2005; Van Landuyt *et al.*, 2007; Kodkeaw *et al.*, 2010). The primary aim of solvents in resin based adhesives is to lower resin viscosity. They facilitate infiltration of viscous monomers into demineralized dentine and enamel. In addition, solvents act as a carrier to help easy movement of monomer blends and initiators into tooth structure. Solvents have been used to facilitate dissolution of the initiator system into the monomer mixture. Acetone has been used in order to decrease the viscosity of BisGMA/TEGMA at 8% to allow dissolving of the initiator in the monomer mixture (Lovell *et al.*, 1999). Therefore solvents have been added to almost all commercial bonding agents (primers) up to 80% (Reis *et al.*, 2003).

One of the important characteristics of a solvent is vapour pressure which should be considered when incorporating solvents into dental adhesives. Vapour pressure is a physical property that determines the time at which a solvent would need to evaporate at a given temperature (Ekambaram *et al.*, 2015). It has been shown that acetone based adhesives evaporate at a higher rate and have a higher solvent evaporation capacity than ethanol, water and ethanol/water-based materials, with mass loss ranging from 2.15 to 21.80% (Abate *et al.*, 2000; Nihi *et al.*, 2009). Therefore acetone-based adhesives may have a shorter useful life than ethanol- and water-based adhesives (Perdigao *et al.*, 1999). The high volatility of acetone is related to poor hydrogen capacity to monomers in the adhesive resin (Yiu *et al.*, 2005), with the hydrogen bonding capacity of acetone 30% of ethanol (δh: 7J/cm^3 vs 19.4J/cm^3) (Ekambaram *et al.*, 2015).

Addition of solvents has impact on bond strength of dental adhesive systems to dentine not enamel. It has been shown the solvent type (acetone or ethanol) had no influence on enamel bond strength, but had a great influence on dentin bonding, which should be taken into account when choosing the adhesive system (Lopes *et al.*, 2006). In addition it was suggested that the presence of organic solvents does not influence micro tensile bond strength (micro-TBS) to

enamel. However, micro-TBS to dentin was significantly affected by the absence of solvents in the adhesive system (Reis *et al.*, 2003).

Organic solvents have an effect on the DoC of adhesive resins. This is dependent on the amount of solvent used. At low solvent concentrations the DoC increases. It has been shown that using solvents like ethanol and acetone up to 2.5 to 5Mol respectively, leads to an increase in DoC for a BisGMA/TEGMA mixture (Holmes *et al.*, 2007). In another study using ethanol up to 30wt% for a range of monomer mixtures including HEMA/BisGMA, TEGMA/BisGMA resulted in increasing DoC (Cadenaro *et al.*, 2008; Cadenaro *et al.*, 2009). This is potentially due to increased diffusion of free radicals and growth of polymer chains after solvent addition. However at higher solvent concentrations, the rate and extent of polymerization decreases (Holmes *et al.*, 2007; Cadenaro *et al.*, 2008). One of the reasons proposed is absorption of the heat generated during the polymeric exothermic reaction by the solvent (Lee *et al.*, 2004). Another reason is that with increasing solvent concentration, the possibility of physical separation of free radicals, photo-activation constituents and growing polymer chains from each other happens and this may lead to decreased monomer conversion (Holmes *et al.*, 2007). However, in all cases this will depend on the photo-polymerization time, as with increasing polymerization time the DoC increases (Cadenaro *et al.*, 2009). The amount of the solvent up to which DoC increases depends on type of solvent used which was found to be 5M for acetone in comparison to 2.5M for ethanol in a monomer mixture of BisGMA/TEGMA (Holmes *et al.*, 2007).

2.4.4 ***Initiator system***

In composite resins, polymerization of monomers occurs due to free radical polymerization. For this reaction to occur, small amounts of initiators are required which will be consumed during the polymerization reaction. A variety of methods can be used to produce free radicals such as thermal, photochemical and chemical methods. The polymerization of composite resins can be activated by chemicals or by light.

2.4.4.1 Chemical initiators

A chemical initiator commonly used in chemical initiator systems is benzoyl peroxide (BPO). To provoke the decomposition of BPO, an aromatic tertiary amine is used such as *N*,*N*-dimethyl-*p*-toluidine (DMPT), 4-(*N*,*N*-dimethylamino)phenethylalchohol (DMPOH), 4-(*N*,*N*-dimethylamino)phenylacetic acid (DMAPAA), EDAB or *N*,*N*-dihydroxyethyl-*p*-toluidine (DHPT) (Achilias and Sideridou, 2004; Sideridou *et al.*, 2006). The role of the tertiary amine is to react with the BPO (reduction-oxidation) and yield free radicals. DMPT has been shown to demonstrate higher activity with BPO than DHPT, however it is more temperature sensitive

(Mathew *et al.*, 1997). BPO in a Di-methacrylate mixture is sensitive to temperature and therefore should be stored in a refrigerator to prevent radical formation (Kwon *et al.*, 2012)

Another chemical initiator is tri-n-butyl borane (TBB), which does not need a tertiary amine. It has been shown using high performance liquid chromatography (HPLC) that post-polymerization, at 24 hours, 1 week, of PMMA/MMA resins with TBB initiator contain less residual monomer compared to a PMMA/MMA resin initiated with CQ (Hirabayashi and Imai, 2002). TBB has been shown to be an option for a dual cure system as a chemically accelerated initiator component (Hirabayashi, 2003).

Composite resins with chemical initiators are supplied in various formats: as two paste, powder and liquid or paste and liquid, in which one of the paste or powder contains an initiator like BPO and the other paste or liquid contains a tertiary amine. These need to be mixed together either manually or mechanically (McCabe and Walls, 2009). However, this increases the chance of oxygen integration during mixing in addition to the chance of increasing voids in the resultant polymer (Fano *et al.*, 1995). This will affect the mechanical and physical properties of the resultant polymer.

2.4.4.2 Photo-initiators

One of the important factors that affects polymerization and the mechanical and physical properties of light curing composite resins is the chemical composition of the photo-initiator system. Two components are present in most commercial photo-activated dental resins. First the photo initiator which can absorb light directly, secondly a co-initiator or activator that does not absorb light but interacts with the activated photo-initiator to generate a reactive free radical and initiate polymerization. However, some photo-initiators do not need co-initiator as discussed below.

In light cured dental adhesive resins different photo-initiator systems have been used with composite resins including camphorquinone (CQ), phenylpropanedione (PPD) and phosphine oxide.

A Camphorquinone (CQ)

CQ combined with different tertiary amines, which act as an electron donors are widely used photo-initiator system in dental resins and composites (Sun and Chae, 2000; Jakubiak *et al.*, 2003; Leprince *et al.*, 2013) (Figure 2.7). The absorption range of CQ is about 360-470 nm with a peak absorbance wavelength at around 470nm (Figure 2.12 and Figure 2.13) (Schroeder *et al.*, 2008; Arikawa *et al.*, 2009). The emission spectra of most conventional LED light curing units (LCU) matches with the absorption spectrum of CQ.

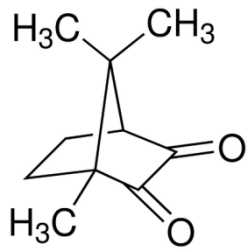


Figure 2.7 Chemical structure of CQ

The type and quantity of co-initiator used with the photo-initiator affects the quality of the resulting polymerization. Several amines have been used with CQ as co-initiators such as 2-dimethylaminoethyl Methacrylate (DMAEMA), EDAB, N,N-cyanoethylmethylaniline (CEMA), NN-dimethyl p-toluidine (DMPT), N,N-diethanol p-toluidine (DEPT) or N,N-dimethyl-p-aminobenzoic acid ethylester (DABE) (Yoshida and Greener, 1993; Teshima *et al.*, 2003; Emami and Soderholm, 2005; Furuse *et al.*, 2011). A study employing Fourier transform infrared (FTIR) to measure DoC of BisGMA/TEGMA experimental resins and CQ with different co-initiators, showed that experimental resins with DMAEMA co-initiator provide higher DoC compared to resins containing other co-initiators including CEMA, DMPT, DEPT or DABE (Furuse *et al.*, 2011) because DMAEMA interacts strongly with monomers which have a methacrylate functional group capable of copolymerization with the matrix monomer (see Figure 2.8). Others investigators demonstrated higher DoC of CQ with DMAEMA co-initiator over DMPT co-initiator (Yoshida and Greener, 1993). However, other studies showed superiority of CQ/DMPT over CQ/DMAEMA in generating free radicals (Teshima *et al.*, 2003). These conflicting results may have arisen because different monomer mixtures are used in those studies. There is no standard ratio of initiator to co-initiator concentrations and it is varied from 2:1 to 1:2 by weight (Asmussen and Vallo, 2009; Schneider *et al.*, 2009a). Any increase of the co-initiator concentration above the optimum concentration level will not improve the quality of polymerization (Yoshida and Greener, 1993) However, too much co-initiator will cause discolouration (yellowing) of the resin (Schneider *et al.*, 2009a) as well as compromising biocompatibility, as amines cause cytotoxicity (Bakopoulou *et al.*, 2009).

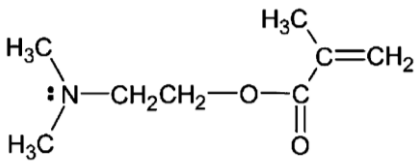


Figure 2.8 Chemical structure of DMAEMA

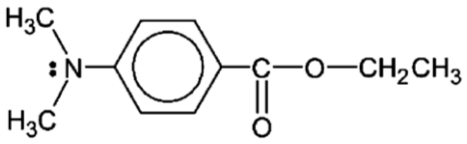


Figure 2.9 Chemical structure of EDAB

High concentrations of CQ have been reported to improve the DoC and mechanical properties of the resultant resin (Musanje *et al.*, 2009; Pfeifer *et al.*, 2009). However, it has been shown that above certain concentrations of CQ there is no further beneficial effect (Jakubiak *et al.*, 2001; Jan *et al.*, 2001; Musanje *et al.*, 2009). In addition, higher concentrations of CQ may lead to a yellow colour that contributes to poor aesthetics in dental resins. On the other hand, inadequate concentrations of the photoinitiators results in insufficient polymerization. This results in inferior biocompatibility, colour stability, physical and mechanical properties and wear resistance of the resultant polymer (Jan *et al.*, 2001; Musanje *et al.*, 2009)

One of the disadvantages of using CQ is the yellow colour which affects the colour of the resultant resins. To improve the aesthetic quality of dental composite resins and to optimize efficiency of polymerization, numerous alternative photo-initiator systems have been developed such as PPD and phosphine oxides.

B Phenylpropanedione (PPD)

The diketone PPD (see figure 2.10) has been introduced to improve the aesthetics of dental composite resins. It has been suggested that CQ may be mixed with or replaced by PPD to produce a resin with higher DoC and reduced yellowing effect (Park *et al.*, 1999). However, this depends on the type of LCU, as PPD has an absorption spectra near the ultraviolet (UV) region with a maximum absorption peak of PPD is 398 nm (Sun and Chae, 2000; Neumann *et al.*, 2006) (see Figure 2.10, Figure 2.12 and Figure 2.13). Therefore, it has been shown that PPD cured with a conventional LED LCU results in a lower DoC in comparison to CQ or CQ/PPD together (Brandt *et al.*, 2011). In addition, is slower to react and produce free radicals than CQ (Emami and Soderholm, 2005). However, PPD can photo-crosslink, which leads to higher mechanical properties than CQ in a mixture of BisGMA (Sun and Chae, 2000). It has been reported that photo-polymerisation of BisGMA in the presence of PPD does not depend on an activator like DMAEMA, compared to CQ which is highly dependent on the concentration of the co-initiator. Therefore in order to optimize curing efficiency of CQ and PPD, care should be taken in choosing the tertiary amine activator with these photo-initiators (Asmussen and Vallo, 2009).

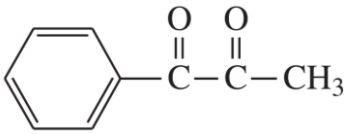


Figure 2.10 Chemical structure of PPD

C Acylphosphine ***oxide***

Acylphosphines represent a wide group of photo-initiators. They have a maximum absorption near UV light, also extending into the visible part of the spectrum (see Figure 2.11, Figure 2.12 and Figure 2.13(Neumann *et al.*, 2005). Some of them have been used in dental resins including (2,4,6- trimethylbenzoyl) diphenylphosphine oxide or TPO (LucirinTPO, BASF), a monoacylphosphine and bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide or Irgacure 819(Ciba-Geigy), a diacylophosphine.

Lucirin TPO photo initiator has advantages when compared to CQ and PPD in that it has a minimum effect on colour change of adhesive resins before and after polymerization, therefore resulting in better colour stability (Shin and Rawls, 2009). Another advantage of Lucirin over CQ is that Lucirin does not need a tertiary amine, however CQ needs a tertiary amine (Schneider *et al.*, 2009; Schneider *et al.*, 2012)..

Another advantage of Lucirin TPO is the ability to achieve a high DoC, with the reported DoC reaching as high as 75.7% (Arikawa *et al.*, 2009) and higher than CQ (Leprince *et al.*, 2011). This is due to Lucirin TPO being more reactive than CQ and PPD. It has a high quantum yield of polymerization, with the amount of monomer polymerized per absorbed photon of Lucirin TPO being greater than CQ and PPD (Neumann *et al.*, 2006). Each molecule of Lucirin generates two free radicals to initiate polymerization, compared to conversion of a molecule of CQ and PPD that generates one free radical (Neumann *et al.*, 2006; Leprince *et al.*, 2013). However the absorption spectra of TPO (380-430nm) is narrower than CQ (380-500 nm) and PPD (380-500nm) but has greater absorption at shorter wave lengths in a mixture of BisGMA and TEGMA (Neumann *et al.*, 2006; Arikawa *et al.*, 2009; Schneider *et al.*, 2012). The conventional LED LCU does not match the absorption spectra of Lucirin, and therefore a different LCU such as Bluephase should be used (see figures Figure 2.12 and Figure 2.13).

Despite the positive factors related to using Lucirin TPO, it has some disadvantages. It has been reported that phosphine oxide leads to a lower depth of cure than CQ (Leprince *et al.*, 2011; Miletic and Santini, 2012a; Schneider *et al.*, 2012). However, in these studies the light emission spectra were more suitable for CQ than to Lucirin TPO.

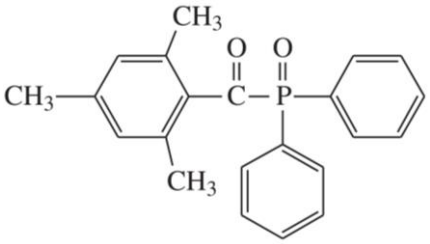


Figure 2.11 Chemical structure of Lucirin

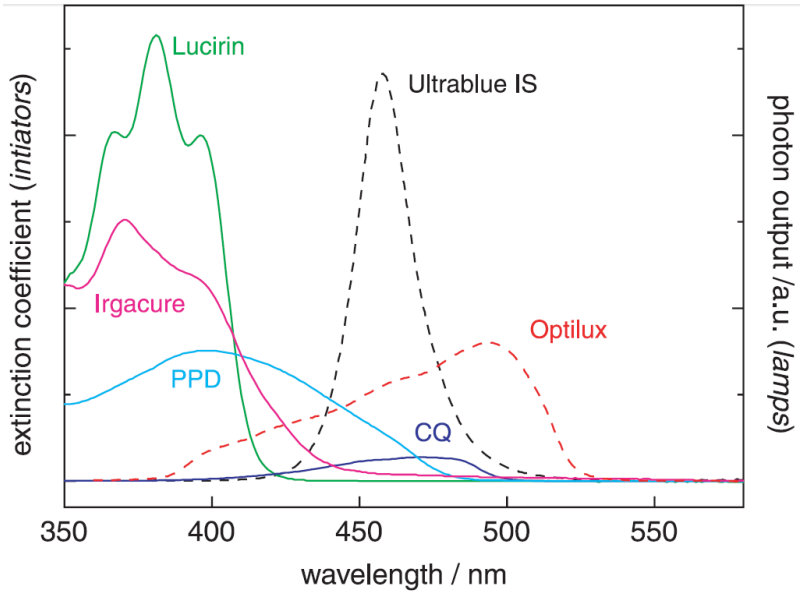


Figure 2.12 Extinction coefficients, molar absorption coefficient or molar coefficient, which are parameters defining how strongly a substance absorbs light at a given wavelength, per mass density or per molar concentration, respectively, of photoinitiators (solid lines), and photon output of the LCU (dashed lines) used. Ultrablue IS is an LED LCU while Optilux is Optilux 401 halogen LCU. The figure shows the maximum absorption of Lucirin at 371 nm followed by Irgacure photoinitator at 360 nm followed by PPD at 391 nm next is CQ at 470 nm. The maximum emission for LCU is Ultrablue IS LCU at 470nm followed by Optilux at 495nm (Neumann *et al.*, 2006).

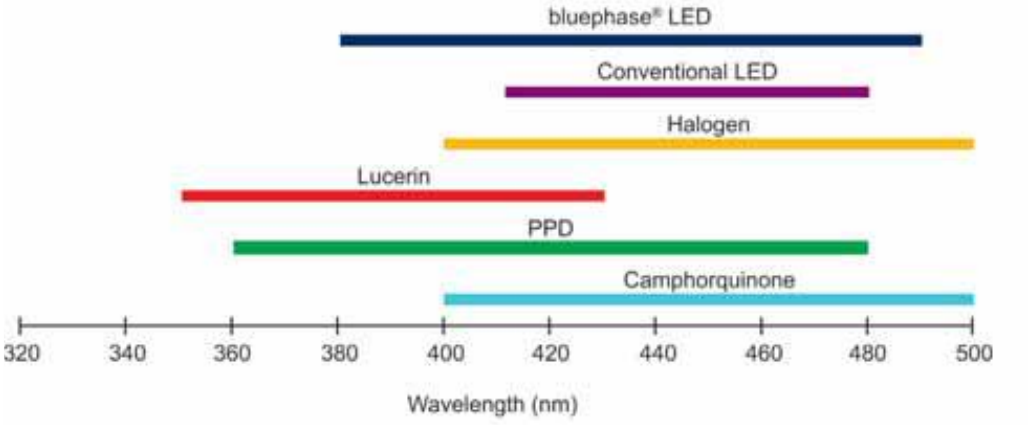


Figure 2.13 Absorption spectra of various LCUs and photo-initiators adopted from (Santini, 2010).

2.5 Polymerization reaction

Polymers are prepared by chemically interconnecting monomer units to produce high molecular weight molecules. There are two types of polymerization reactions, addition polymerization and condensation polymerization. In addition, polymerization, the reaction occurs without any by-products in four phases called activation, initiation, propagation, and termination. This type of polymerization can be seen with most of the acrylic resin materials (Yau *et al.*, 2002). Whilst in condensation polymerization, low molecular weight by-products are produced as a result of polymerization reaction. This type of reaction can be seen in some impression materials such as polysulfide (Craig, 2002).

There are several factors that affect polymerization efficiency which can be divided into intrinsic and extrinsic factors.

2.5.1 *Intrinsic factors*

The photoinitiator system used has been shown to affect photo-polymerization. In dental resins the most commonly used photoinitiator system is CQ. However, other photoinitiators systems have been developed to replace CQ such as PPD and Lucirin TPO. As previously described, each photoinitiator has its own maximum absorption spectra at specific range. In addition to that, the combination of the initiator with co-initiator type and quantity affect the overall photo polymerization.

In addition to the initiator system, the type and viscosity of the monomer mixture affect photo-polymerization. Monomers like TEGMA are less viscous than BisGMA, resulting in twice the higher maximum conversion at 60% vs 30% respectively. In addition, TEGMA reaches its maximum polymerization rate at 22% DoC in comparison to only 5% DoC for BISGMA. However, different co-monomer mixtures of the two monomers leads to intermediate values between them (Lovell *et al.*, 1999). Homopolymerization of UDMA is higher than BisGMA, the DoC of UDMA reaching 43% compared to 7% for BisGMA (Dickens *et al.*, 2003). It was shown that monomer mixture of UDMA/TEGMA has a higher DoC compared to BisGMA/TEGMA (Papakonstantinou *et al.*, 2013). However, in this study the BisGMA/TEGMA mixture used for comparison was commercial Transbond XT, rather than an experimental mixture.

Fillers also have an impact on photo-polymerization. It has been shown that the DoC decreases with increasing filler content, in a monomer mixture of BisGMA/TEGMA (Halvorson *et al.*, 2003; Garoushi *et al.*, 2008). It has been shown that even differences in filler size and geometry result in differences in DoC from 48% to 61% for a monomer mixture of

BisGMA/UDMA/TEGMA at a constant filler volume of 56.7% (Turssi *et al.*, 2005). Other studies have shown that light transmission through a composite might be diminished by higher filler content (Duangthip *et al.*, 2011) due to reduction in the mobility of free radicals (Almeida and Mothé, 2009).

2.5.2 *Extrinsic factors:*

There are some extrinsic factors that affect photo polymerization of adhesive resins. One factor is the light curing unit (LCU) and its emission spectra. In light cured adhesive resins to achieve optimum polymerization, the absorption spectrum of the photo-initiator should correspond to the radiation spectrum of the dental LCU used for photo-polymerization (Arikawa *et al.*, 2009; Leprince *et al.*, 2010a). Different types of LCU have been used for dental composites such as LED, halogen and plasma arc polywave LED LCU. It has been shown that conventional LED LCU has an emission spectra centred around the maximum absorption spectra of CQ, to polymerize CQ based materials, compared to halogen light which has a broad emission spectra see (Figure 2.13)(Nomoto *et al.*, 2009). Therefore curing CQ based composite resins with a conventional LED LCU leads to a higher DoC than a halogen light does. Conventional LED LCUs tend to emit light over a narrower wavelength compared to polywave LED LCUand halogen lights.

Light intensity, exposure time and radiant exposure are also factors that affect photo-polymerisation. Radiant exposure (J/cm^2) is the product of light intensity (W/cm^2) and exposure time (s) and it is defined as the total amount of energy delivered to the resin composite surface during the entire light curing procedure (Leprince *et al.*, 2013). The exposure reciprocity law is based on a concept that comparable material properties can be achieved as long as the radiant exposure is kept constant, irrespective of the light intensity and exposure time (Leprince *et al.*, 2013b). There is controversy amongst authors on the reciprocity law, some support radiant exposure as the major determinant factor regardless of the light intensity and exposure time (Miyazaki *et al.*, 1996; Price *et al.*, 2004; Emami and Soderholm, 2005; Erickson *et al.*, 2014). However, in the case of Miyazaki *et al.* (1996), only narrow ranges of moderate light cure intensity 100–400 mW/cm^2 and exposure times (30–120 s) were examined (Miyazaki *et al.*, 1996). Therefore, it cannot be generalized over all materials as a general rule.

However, several other studies have contradicted the reciprocity law and believe that reciprocity law cannot be used as a general rule (Musanje and Darvell, 2003; Feng *et al.*, 2009; Feng and Suh, 2009; Leprince *et al.*, 2010b; Leprince *et al.*, 2011). It has been shown that for some mechanical properties like flexural strength, no extra benefit is observed by increasing the light intensity above 1000 mW/cm^2 (Musanje and Darvell, 2003). In addition, it has been reported that despite an increase in the flexural strength and flexural modulus at increasing

radiant exposure, changing exposure time and light intensity resulted in significant change in the materials properties (Peutzfeldt and Asmussen, 2005).

The distance of the LCU tip to the material affects polymerization and DoC, as the farther the distance, the lower light intensity (Price *et al.*, 2004) and consequently the lower DoC. For example, DoC significantly decreases when the distance is increased from 0 or 3 mm to 7 mm in a sample of a micro-hybrid composite (Esthet- X), with a halogen light used at 400 and 600 mW/cm^2 (Fróes-Salgado *et al.*, 2009).

Another factor that affects photo-polymerization is the temperature during polymerization. It has been shown that increasing the temperature during polymerization from room temperature 22 °C to mouth temperature 35 °C results in superior DoC and mechanical properties of the material (Price *et al.*, 2011). A higher temperature will lead to increasing polymerization rate by improving the monomer conversion, encouraging more reaction to occur prior to vitrification (Lovell *et al.*, 1999; Trujillo *et al.*, 2004; Daronch *et al.*, 2006).

Finally oxygen inhibition that occurs during photo-polymerization is another extrinsic factor that affects photo-polymerization and the resultant polymer. Oxygen inhibition of polymerization has a detrimental effect on the properties of cured resin. Oxygen is a powerful inhibitor which reacts with free radicals to form unreactive peroxy radicals that retard and even terminate polymerization by reacting with themselves or other propagating radicals to form inactive products resulting in a poorly polymerized resin surface (Odian, 2004). Cold cure acrylic resin is also affected by air inhibition and retards curing time (Lee *et al.*, 2002). Different approaches have been used to avoid oxygen diffusion, including shortening the air exposure time prior to polymerization, optimising the mixing regime to decrease porosity and use of a matrix to block oxygen from the resin (Brantley and Eliades, 2000).

2.6 Mixing of experimental resin

Different types of mixing methods have been used for mixing experimental composites in laboratory studies including hand mixing, vacuum mixing and centrifugation. Many researchers have used hand mixing method for mixing experimental resins of their studies. However this method has some pitfalls such as a high chance of introducing air bubbles into the material, oxygen inhibition by inclusion of oxygen into the resin surface and increased risk of the operator to exposure to the volatile substances. It was found that 20 seconds of spatulation in air of a single paste light cured composite resin (Prisma-Fil) led to a mean porosity increase from 0.23% for minimally handled material to 1.53 % for hand spatulated material (McCabe and Ogden, 1987). Also there was an increase in the number of porosities after mixing the two

pastes of chemically activated material in comparison to each of the pastes alone (Fano *et al.*, 1995). Porosity can affect the mechanical and physical properties of the materials.

There is a high risk of bias in the comparison between experimental hand spatulated materials and commercial products. It is therefore difficult to extrapolate data based on these comparisons. Most researchers prepare experimental resins and report significant findings without mentioning the method of mixing (Marquis, 2003). However, it is possible their findings are inconsistent due to non-homogenous mixing. Inconsistent data may be apparent due to high standard deviations (SD). Therefore there is a need to optimize the mixing method of experimental resins to produce a standard, reproducible method to be used as a reliable method in order to precisely compare the data of experimental resins between researchers (Kumar and Shortall, 2011).

There is no published standardized method for mixing experimental composite resins. A study has been undertaken on the effect of the mixing method on flexural strength of an experimental resin based composite. The composite resin was composed of mixtures of BisGMA and TEGMA as monomers and barium alumina borosilicate and fumed silica glass as filler and hand mixing was compared to mechanical mixing with dual asymmetric centrifugation (DAC system) (Speed-Mixer™, DAC 150 FVZK, Hauschild Engineering, Germany). However the mixing time was not described. They reported that hand spatulation leads to more voids visible under SEM scan compared to mechanical mixing. In addition, mechanical mixing was shown to improve the mechanical properties including the biaxial flexural strength of the composite resin (Kumar and Shortall, 2011).

The DAC system is considered to be a suitable technology for mixing composite resin (Kumar and Shortall, 2011) One of the advantages of this method is the speed of mixing which can be increased up to 3500 rpm, significantly faster than can be achieved by hand mixing. This higher speed of mixing results in more homogenous paste. As it was shown increasing speed of mixing results in a more homogenous mixture (Massing *et al.*, 2008). Another advantage of this method is that DAC provides two types of rotation at the same time. One is clockwise centrifugation of the sample which tries to push the material in to the corner of the sample container. The second is counter-clockwise rotation of the container which takes place around container's own vertical axis and forces the material towards the center of the container (see Figure 2.14). These two types of rotations lead to shear forces and result in a more homogenous mix (Massing *et al.*, 2008). The DAC system has been used to prepare viscous mixtures such as liposomes and siRNA-liposomes (Massing *et al.*, 2008; Hirsch *et al.*, 2009) and also used as a preparation method for parenteral fat emulsions (Tenambergen *et al.*, 2013). It has also been used for mixing viscous components of polymer-based clay composites at 3000rpm (Kint *et al.*, 2005). The

DAC system has been used at different speed from 1300 -3500 rpm and for different durations of time from 1 to 5 minute to mix the whole composite resin component together to produce homogenous paste (Faltermeier *et al.*, 2007; Garoushi *et al.*, 2008; Schneider *et al.*, 2008; Schneider *et al.*, 2009a; Schneider *et al.*, 2009b). Therefore it is considered to be a suitable technology for mixing dental resin composites.

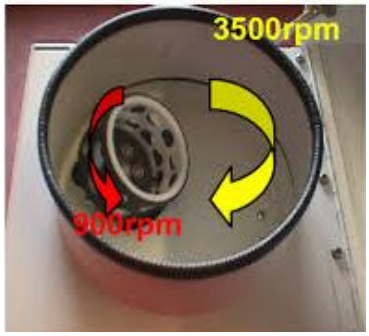


Figure 2.14 DAC system. The picture shows two types of rotation: the first rotation is clockwise centrifugation of the sample which reach maximum 3500 rpm and the second rotation around container's own vertical axis which reaches 900 rpm

2.7 Summary

Resin based composites are the materials most commonly used for orthodontic bonding, due to their high bond strength and low failure rate. However, conventional composite resin based orthodontic adhesives d not release fluoride. There is an issue of WSL during fixed orthodontic treatment which drives studies to develop orthodontic adhesives with the potential to release fluoride. There is evidence supporting the effectiveness of fluoride releasing orthodontic adhesives in reducing WSL during orthodontic treatment. Additionally, enamel loss during adhesive removal and debonding is reported and orthodontic adhesives that can be easily removed would be preferable. Therefore, a fluoride releasing orthodontic adhesive which can be easily removed would be a valuable addition to the current materials that are available.

The background of the present work is the continued development of a new fluoride releasing acrylic based orthodontic adhesive based on HEMA and MMA. NaF has been added as a source of fluoride. A copolymer of HEMA and MMA has previously been proposed as having potential to use for this purpose. Previous work has demonstrated promising characteristics in the developed material including, the setting characteristics, bond strength and fluoride releasing ability of the material (Su *et al*, 2010). Therefore, a copolymer of HEMA and MMA with NaF can be used to develop a new fluoride releasing orthodontic adhesive, by further developing the materials chemistry proposed by Su *et al*, 2010, working towards reducing existing issues of the current material such as high viscosity of the material, chemically curing with a long setting time and low bond strength particularly after water storage.

Chapter 3: **Aims and program of work**

3.1 Aims

The aim of this project is to develop a new fluoride releasing acrylic based orthodontic adhesive. To achieve this overall aim, a number of secondary aims have been identified:

1. To reduce the viscosity of the material to improve handling characteristics.
2. To reduce the curing time of the material through the use of different photo-initiator systems.
3. To improve the bond strength of the adhesive through the use of 4-META.

3.2 Objectives

To achieve the aims, it was important to establish the following objectives:

1. To establish the effect of acetone on certain key properties of the developed material as an orthodontic adhesive such as DoC, heat release and injectability.
2. To establish the effect of acetone on fluoride release of the developed material.
3. To establish the effect of different photo-initiator systems (CQ and Lucirin® TPO) on DoC of the developed material.
4. To establish the effect of 4-META on certain key properties of the developed material as an orthodontic adhesive such as DoC, water sorption and solubility.
5. To establish the effect of 4-META on fluoride release and recharging ability of the developed material.
6. To establish the effect of 4-META on SBS of the developed material.

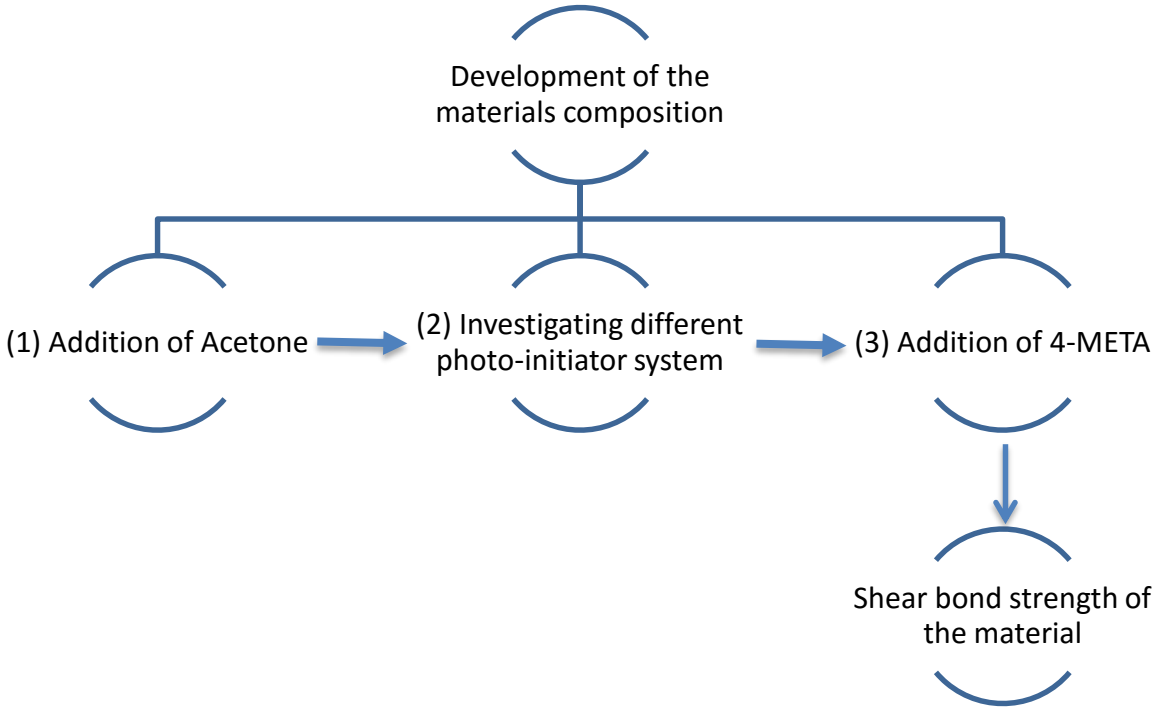
3.3 Hypotheses

The following hypothesis were tested:

1. The addition of acetone will result in decreasing viscosity of the material without decreasing DoC, heat release and deteriorating fluoride release of the material.
2. The degree of conversion (DoC) of the material will increase with increasing photo-initiator concentrations.
3. The addition of 4-META will increase the bond strength of the material without deteriorating the DoC, fluoride release and recharging ability of the material.
4. The the properties of the experimental materials will not differ significantly from those of the controls (Ketac-cement and Transbond XT)

3.4 Program of work

The plan of the study was designed to be conducted as below:



Chapter 4: **The effect of acetone on a new fluoride releasing orthodontic adhesives**

4.1 Introduction

This phase of the project was designed to develop the materials chemistry to provide better handling properties of the material. The handling characteristics of orthodontic adhesives have been linked to several factors such as ease of application, viscosity and setting kinetics (Papakonstantinou *et al.*, 2013). The first two parameters can be altered with the addition of a solvent. Acetone was chosen due to its common use in dental materials (Yiu *et al.*, 2005; Van Landuyt *et al.*, 2007; Ye *et al.*, 2007; Ekambaram *et al.*, 2015), in particular it has been shown to not reduce the bond strength of resin based adhesives to enamel (Reis *et al.*, 2003; Lopes *et al.*, 2006).

Consequently, the work described in this chapter involved analysing the effect that the addition of the solvent, acetone, had on a number of physical parameters of the materials. For measuring the rheological characteristics of the experimental materials, an injectability test (microcapillary rheometer) was developed to measure the force required to extrude the material from a simple disposable syringe. Injectability has been shown to be a reliable and reproducible method for quantitative rheological measurement of both Newtonian and Non-Newtonian rheological behaviours (Allahham *et al.*, 2004).

To investigate the effect of acetone on the setting characteristics of the materials, DoC and heat release were taken. Differential scanning calorimetry (DSC) was used to monitor heat produced during polymerization, as the polymerization reaction is an exothermic reaction. Consequently, the DoC can be obtained based on assumption that the heat produced during the setting reaction is proportional to the percentage of the monomers that contribute to polymerization (Cadenaro *et al.*, 2005; Emami and Soderholm, 2005). Fourier transform infrared spectroscopy (FTIR) was also used to measure DoC of the materials. The DoC is an important determinant of the physical and mechanical properties of dental resins (Ferracane and Greener, 1986; Calheiros *et al.*, 2008; Price *et al.*, 2011).

In addition to the handling and setting characteristics of the material, fluoride release from an orthodontic adhesive could help prevent WSL during orthodontic treatment. Consequently, fluoride release was measured from the developed adhesives using an ion selective electrode over a 160 day period of storage in an aqueous environment.

Therefore, the purpose of present work was to determine the effect of acetone on setting characteristics**,** injectability and fluoride release of the experimental orthodontic adhesives.

4.2 Aims and hypotheses:

4.2.1 *Aims*

Four aims were identified for this part of the project:

1-To investigate the effect of acetone on the degree of conversion (DoC).
2-To investigate the effect of acetone on the heat release of the material.
3-To investigate the effect of acetone on injectability.
4-To investigate the effect of acetone on fluoride release.

4.2.2 *Hypotheses*

1-Acetone will decrease the DoC of the experimental materials.
2-Acetone will decrease the heat released by the experimental materials.
3-Acetone will increase injectability of the experimental materials.
4-Acetone has no effect on fluoride release ability of the experimental materials.

4.3 Experimental Materials

Four experimental groups were prepared by mixing different ratios of MMA (methyl methacrylate, Sigma-Aldrich, UK), HEMA (2-hydroxyethyl methacrylate, Sigma-Aldrich), PMMA (polymethyl methacrylate, Esschem, UK) and NaF (sodium fluoride, Sigma-Aldrich), using CQ (camphorquinone, Sigma-Aldrich) as an initiator and DMAEMA (dimethylamino ethyl methacrylate, Sigma-Aldrich) as an activator as shown in (Table 4.1and Table 4.2). Four different concentrations of acetone were used to decrease viscosity of the material. For clarity four colours have been used to present the four groups as shown in Table 4.3.

Table 4.1 list of materials and their manufacturers that were used for preparation of experimental materials

Materials	Description	Manufacturer
PMMA	low molecular weight benzoyl peroxide free	Esschem Europe, County Durham, UK
NaF	Sodium fluoride	Sigma-Aldrich Company Ltd., Dorset, UK
MMA	Methyl methacrylate 99% (GC)	Sigma-Aldrich Company Ltd., Dorset, UK
HEMA	97% 2-Hydroxyethyl methacrylate	Sigma-Aldrich Company Ltd., Dorset, UK
CQ	97% Camphorquinone	Sigma-Aldrich Company Ltd., Dorset, UK
DMAEMA	98% 2- (Dimethylamino)ethyl methacrylate	Sigma-Aldrich Company Ltd., Dorset, UK
Acetone	Acetone	Sigma-Aldrich Company Ltd., Dorset, UK

Table 4.2 Composition of the experimental groups.

Groups	Group Label	PMMA %	NaF %	Acetone%	Other components
10:0 0%A	10:0	100	0	0	Liquid:
10:0 10%A	10:0	100	0	10	HEMA 60wt%
10:0 20%A	10:0	100	0	20	MMA 40%wt%
10:0 30%A	10:0	100	0	30	
10:0 40%A	10:0	100	0	40	Photo-initiator system:
9:1 0%A	9:1	90	10	0	CQ 0.6wt%
9:1 10%A	9:1	90	10	10	DMAEMA 0.8wt%
9:1 20%A	9:1	90	10	20	
9:1 30%A	9:1	90	10	30	
9:1 40%A	9:1	90	10	40	
8:2 0%A	8:2	80	20	0	
8:2 10%A	8:2	80	20	10	
8:2 20%A	8:2	80	20	20	
8:2 30%A	8:2	80	20	30	
8:2 40%A	8:2	80	20	40	
7:3 0%A	7:3	70	30	0	
7:3 10%A	7:3	70	30	10	
7:3 20%A	7:3	70	30	20	
7:3 30%A	7:3	70	30	30	
7:3 40%A	7:3	70	30	40	

MMA (methyl methacrylate), HEMA (2-hydroxyethyl methacrylate), PMMA (poly methyl methacrylate), CQ (Camphorquinone), DMAEMA (dimethylaminoethyl methacrylate).

Table 4.3 Colours used to present different groups.

Groups	Colours for tables	Colour for figures
10:0	Blue	
9:1	Red	
8:2	Green	
7:3	Purple	

4.3.1 *Preparing the Powder*

Four different ratios of PMMA, and NaF were weighed using an electronic balance (Mettler-Toledo Ltd., sensitivity 0.1mg, Switzerland) into a 20 g plastic jar (Synergy Devices Ltd, Germany) container (Table 4.2)

4.3.2 *Preparing the liquid*

All work preparing the liquid component was conducted using amber-glass bottles (500 ml, Sigma-Aldrich) to reduce the potential for accidental activation of the photoinitiator. The overall ratio of MMA to HEMA in the liquid component of the experimental materials was 60wt% to 40wt%. Where required, prior to mixing with MMA, 0.6wt% CQ and 0.8wt% DMAEMA were added to the HEMA and mixed for 60 minutes using a magnetic stirrer (VELP, Scientifica, Italy). Next, the MMA was added and mixed using magnetic stirring for 30 minutes. Then the liquid blend was stored in the amber bottles further wrapped with aluminium foil until use within a week.

4.3.3 *Mixing powder and liquid*

The liquid was mixed with powder by 1:2 by weight. 5g of the liquid was added to 10g of prepared powder in a container. Then acetone was added to the mixture according to the total weight of the liquid. Five different concentrations of acetone were used, namely 0%A, 10%A, 20%A, 30%A, 40%A, making 20 experimental resin formulations (Table 4.2). The container was then placed in a centrifugal mixer (SpeedMixer^{TM} DAC 150.1 FVZ, Hauschild Engineering, Germany) ready for mixing (). Unless otherwise stated, all formulations were mixed initially for 4 minutes mixing at 2000 rpm (first round mixing), followed by a further 4 minutes at 3300 rpm (second round mixing) with the aim of producing an homogeneous paste (Schneider *et al.*, 2012; Zahroon, 2014). Once mixing was complete, the containers were sealed with Parafilm (Parafilm®M, Bemis company, Inc., UK) and wrapped in aluminium foil to prevent accidental light exposure and then stored at 4°C until use. All materials were used only for single experiments and were used within a week of mixing.

Figure 4.1 SpeedMixerTM DAC 150.1 FVZ that used for mixing of the experimental materials.

4.4 Experimental Methods

4.4.1 *Investigating acetone loss*

In order to know the amount of acetone and monomer lost during mixing procedure, a preliminary study was conducted. The materials were mixed as discussed in section 4.3.3, except the CQ and DMAEMA were not included. Groups 10:0 and 7:3 each with 0% and 40% acetone were taken to investigate amount of acetone loss. 2 samples of each group were examined.

The weight of the containers that contained 10 g of powder was measured using a digital balance (Mettler AE 240, 0.01mg accuracy, Switzerland) before adding the liquid (monomers) and then following addition of the liquid and acetone. This measurement was repeated at the following times:

1- Immediately after adding acetone (as a reference).

2- After the first round of mixing, to investigate any weight lost through sealed containers after the first round mixing.

3- After the second round mixing, to investigate the amount of weight lost during the second round mixing.

4- After leaving the lid off the pots for 1, 2, 3, 4, 5, 10, 15 minutes after mixing, to investigate the effect of evaporation of components due to leaving the lid off.

To investigate the amount of weight lost during storage of the material, another preliminary study was conducted, in which the weight loss after 10 days storage was measured. Pots used

in this part of the study were stored in a refrigerator at 4°C and weighed daily to calculate the amount of weight lost.

4.4.2 *Degree of conversion (DoC)*

All degree of conversion measurements were conducted using an FTIR spectrometer (Spectrum One, PerkinElmer, Bucks, UK) with a diamond-crystal ATR attachment. Spectra were recorded at 4 cm^{-1} spectral resolution between 2000–750 cm^{-1} wavenumbers, using dedicated software (TimeBase, PerkinElmer). Specimens were placed in contact with the diamond crystal, to a thickness of 1 mm, using two glass microscope slides attached to the sides of the crystal and third glass to press the material to ensure 1 mm thickness and to minimise oxygen inhibition and acetone evaporation. The light guide tip of the curing light was positioned directly above the glass slide (1 mm) and perpendicular to the surface of the ATR crystal, see Figure 4.2. This technique has been used previously to monitor the photo-polymerization kinetics of resin based adhesives (Ye *et al.*, 2007; Cadenaro *et al.*, 2009; Abedin *et al.*, 2014; Zahroon, 2014).

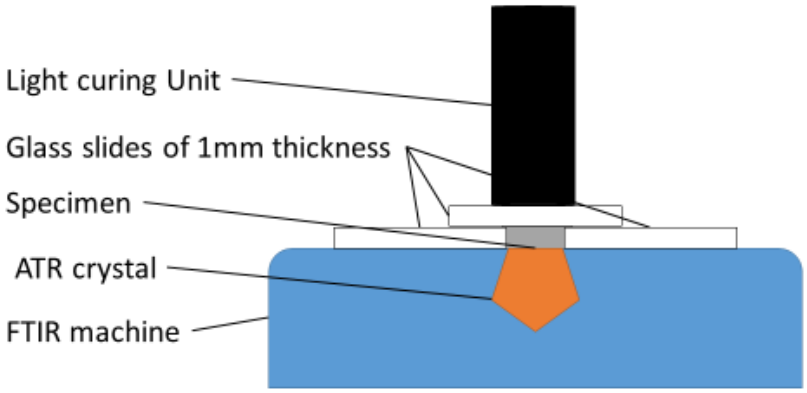


Figure 4.2 Schematic diagram of the FTIR.

For each specimen, spectra were measured before curing commenced to obtain the uncured state and then once the LED curing light was positioned on the specimen, a spectrum was measured after each 10s exposure of light. For all experiments, the same LED curing light unit (Coltolux® LED, Coltene, USA) with an intensity of 800-850 mW/cm^2 measured with an intensity meter (Coltolux LED, Sussex, UK) was used. In total the materials were exposed to 120 s of light, with 13 spectra measured for each specimen. For each experimental group 5 specimens were measured. All experimental procedures were carried out in a dark room to reduce the effects of ambient light on the photo-polymerisation.

The FTIR spectra collected from each specimen were the result of adding 13 scans together representing a spectra at uncured state and the 12 post cure interval using Spectrum TimeBase (Perkin Elmer Inc., Germany) and OMNIC (OMNIC^{TM} Series software, Thermo scientific) software and then converted into ASCII for exporting for processing using Microsoft Excel (Version 14, Microsoft Office Professional Plus 2013).The standard baseline method was used to assess the peak heights (Rueggeberg *et al.*, 1990). To calculate DoC the percentage of uncured carbon double bonds (%C=C) at any time was determined from the ratio of absorbance intensities of the aliphatic peak at 1638 cm^{-1} against an internal standard peak, the carboxyl group with a peak at 1715 cm^{-1} (Jafarzadeh Kashi *et al.*, 2007; Guo *et al.*, 2009; Abedin *et al.*, 2014), using Equation 4.1 and Equation 4.2:

Equation 4.1……..$(\%\mathrm{C}=\mathrm{C}) = \frac{[Abs\ (1638\ cm^{-1})/(\mathrm{Abs}\ (1715\ \mathrm{cm}^{-1})]\mathrm{polymer}}{[Abs\ (1638\ cm^{-1})/(Abs\ (1715\ cm^{-1})]monomer} \times 1$

From this the DoC could be calculated as:

Equation 4.2…….. $\mathrm{DC}\% = 100 - \%\ \mathrm{C}=\mathrm{C}$

After processing, all data were then imported into dedicated statistical software (SPSS 19 for windows, IBM SPSS Inc., USA) for analysis. Data normality was tested using the Shapiro-Wilk test. The data were not normally distributed therefore non-parametric tests were used to investigate statistical difference between groups. Thus a median DoC was calculated and the variability of the DoC was estimated using the interquartile range (IQR).

IQR= upper quartile-lower quartile.

Kruskal-Wallis H and Mann-Whitney U tests were used to determine significant differences between groups. A significance level of 5% was selected as a significant for all comparisons.

In order to consider the effects of each of the independent variables Acetone%, Fluoride%, exposure time on the DoC (dependant), a three way ANOVA was undertaken. As there is no non-parametric equivalent test to a three way ANOVA, the data was transformed to normal using a two-step transformation to normality in SPSS (Templeton, 2011) as previously described (Ramadas *et al.*; Mulcan *et al.*, 2015). Shapiro-Wilk test at ($P<0.05$) indicated the data to be normally distributed after transformation (see appendix 2).

4.4.3 ***Heat of polymerization (DSC)***

The heat flow measurement was performed using a differential scanning calorimeter (DSC) (Mettler Toledo, Switzerland) coupled to a photocalorimetry accessory. (Mettler Toledo, Switzerland) equipped with a halogen light curing unit (Heliomat H2, Vivadent, Austria) which had an intensity of 200-250 mW/cm^2 measured with an intensity meter (Coltolux LED, Sussex,

UK) see Figure 4.3. Five samples of approximately 10 mg of the experimental materials were placed in pre-weighed aluminium crucibles (Thorn Scientific Services Ltd., UK) and covered with a transparent polyethylene terephthalate (PET) film. The samples were placed in to the DSC chamber against an empty crucible. The weight of the empty crucibles and filled crucibles were measured using an electronic balance (Mettler AE 240, 0.01 mg accuracy, Switzerland). All measurements were performed isothermal at 37°C to represent the human oral temperature. The DSC chamber was sealed with a cover. The cover was used to isolate the sample and reference (empty) pans while still allowing curing lights to be positioned on the pans through two holes to guide the light on both equally see figure 4.3 and figure 4.4.

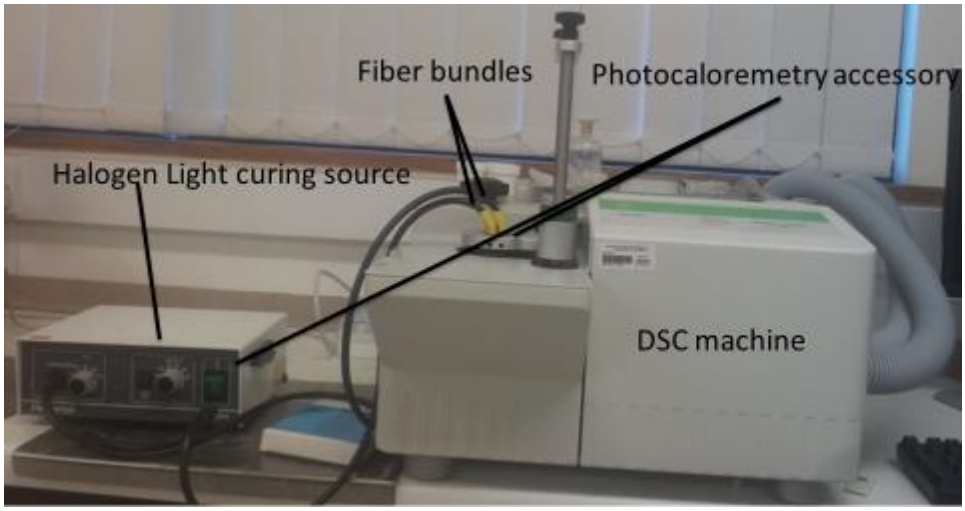


Figure 4.3 DSC with photocalorimetry accessory used in this study.

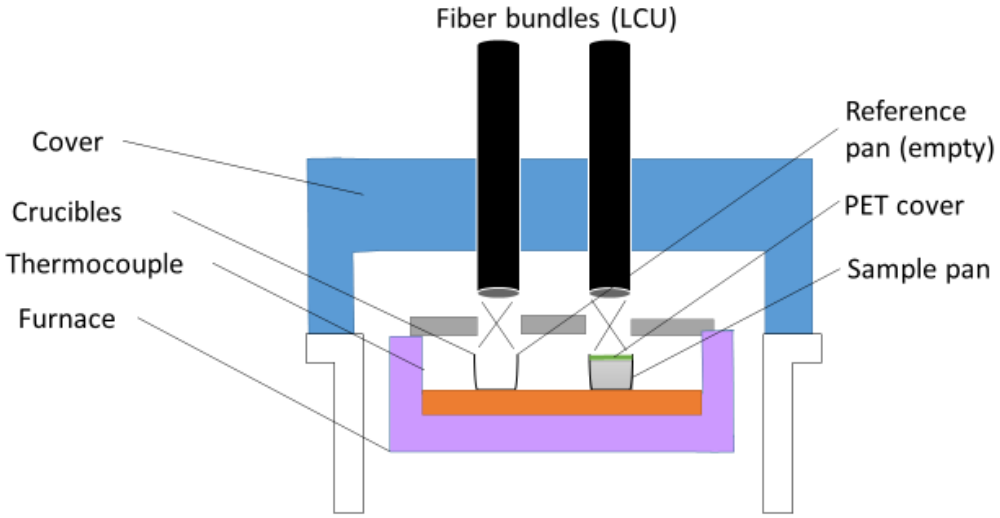


Figure 4.4 Schematic illustration of DSC apparatus.

The experiment was commenced after waiting for 2 minutes at the beginning to allow the temperature to equalize within the cell and to provide the same experimental condition for all

samples, then the samples were irradiated for 60 seconds every 3 minutes for 20 minutes to obtain 6 thermograms. Next, to measure the energy associated with the light source only, the samples were irradiated for an extra 10 minutes with a more powerful LED light curing unit (Coltolux® LED, intensity 800-850 mW/cm²). After this, it was assumed that no further polymerisation would occur. Then, two further thermograms were measured after exposing to 60 seconds of light exposure (using the halogen light) with 3 minute time interval. Five replications for each group were conducted. The area under each thermogram was integrated by the dedicated software (STAR^e SW 9.01, Mettler Toledo, Switzerland) in milliJoule (mJ). After changing the integration peak into Joule (J) and dividing by the mass of the specimen, gram (g), the heat release (enthalpy) J/g was recorded. The isothermal heat of polymerization was obtained by subtracting the average of the peak areas of light source only from the areas of the 6 peaks (Cadenaro *et al.*, 2008).

After processing, all data were analysed using statistical software (SPSS 19 for windows, IBM SPSS Inc., USA). The Shapiro-Wilk test was used to test normality of the data. The data were normally distributed. Therefore, mean heat release and standard deviations (SD) were calculated. Significant differences in heat release parameters of each fluoride and acetone subgroups and exposure time were identified using the Tukey post-hoc test. Three-way ANOVA was used to determine statistically significant differences between groups at the 5% level ($P<0.05$).

4.4.4 *Injectability test*

Preliminary studies:

Several pilot studies were conducted to develop a method to investigate injectability of the materials. First a load control method was used in which a maximum applied load of 400 N was used, and the resultant load rate measured as an estimate of viscosity. Secondly, load rate control method was used, in which loading rates of between 1 mm/min and 15 mm/min were tried.

The load control method proved difficult to standardise for the range of materials studied, with the lowest viscosity materials (group 7:3 40%A) extruding from the syringe immediately upon application of the force, while the most viscous materials (group 10:0 0%A) exhibited only small amounts of extruded from the syringe at this force.

For the loading rate control methods, the highest loading rates (5, 10 and 15 mm/minute) led to rupture of the syringes, figure 4.5, during testing with the 10:0 group. Consequently, a loading rate of 1 mm/min was selected for the injectability test, as no syringe ruptures were found with this rate.

Figure 4.5 Showing syringe failure at compression rate of 5, 10 and 15 mm/minute.

The method:

The experimental materials were prepared using the same method as described in section 4.2.3 except they were prepared in cartridge containers (Semco 2.5oz hd cartridge, Synergy Devices Ltd, Germany) and without addition of initiator system. Directly after mixing, the cartridge was put into the Semco 850 manual gun ready to dispense (Figure 4.6). 5 ml of the prepared material was introduced to a 5 ml syringe (disposable syringes, Omnifix®), with a 2 mm aperture, from the top and then sealed with cap seal ready for experiment. To make the syringes free of bubbles they were put in upright position for 30 minutes to aggregate all air bubbles at the top then pushing out. All tests were started immediately after 30 minutes from insertion into the syringes.

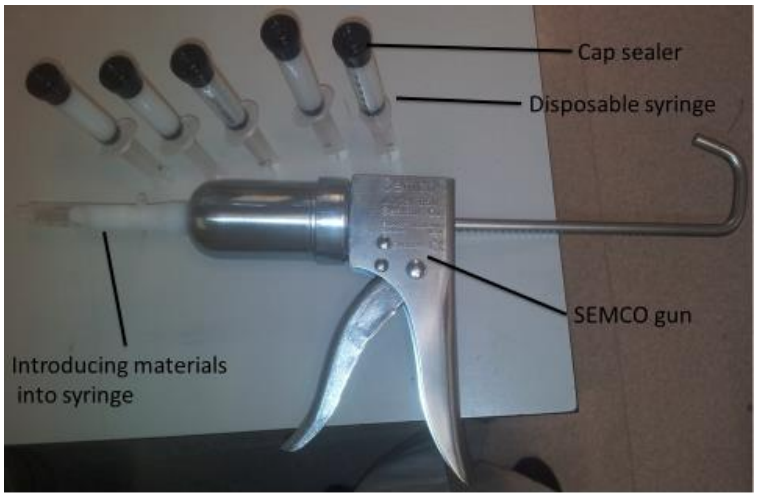


Figure 4.6 SEMCO manual gun and syringes ready to dispense material in to syringes.

The syringes were secured on the lower compartment of the test machine (model 5567, Instron, UK) within a clear acrylic tube (14 mm diameter, 30 cm length) holding them parallel to the loading direction of the test machine. A spirit level was used to ensure the syringe was level

before testing commenced (Figure 4.7). The acrylic tubes were held rigidly in place using retort stands and clamps.

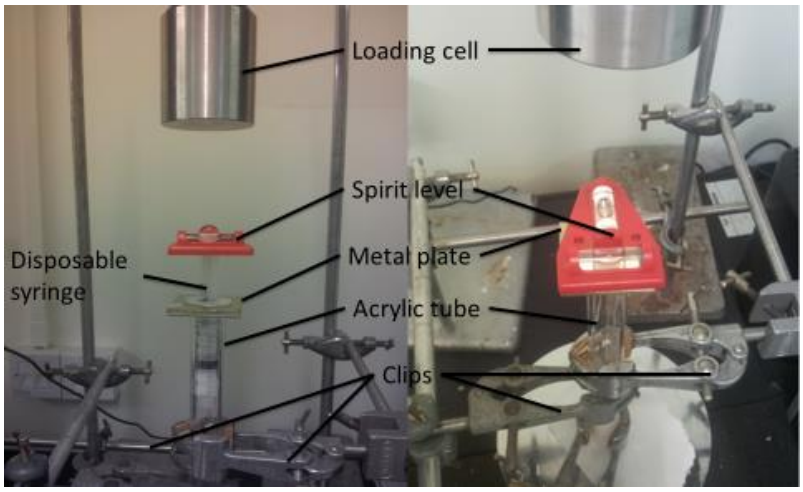


Figure 4.7 Using spirit level to keep the acrylic tube and plunger of the syringe level before starting test.

A universal test machine was used to apply pressure to the syringe plunger. A 1 kN load cell was mounted vertically on top of the plunger for 10 minutes at a compression rate of 1mm/min (figure 4.8). The load was recorded in Newton (N) as a function of the plunger run. The graph obtained was extrusion force in (N) against the plunger displacement in (mm). The maximum forces of extrusion were recorded for comparison.

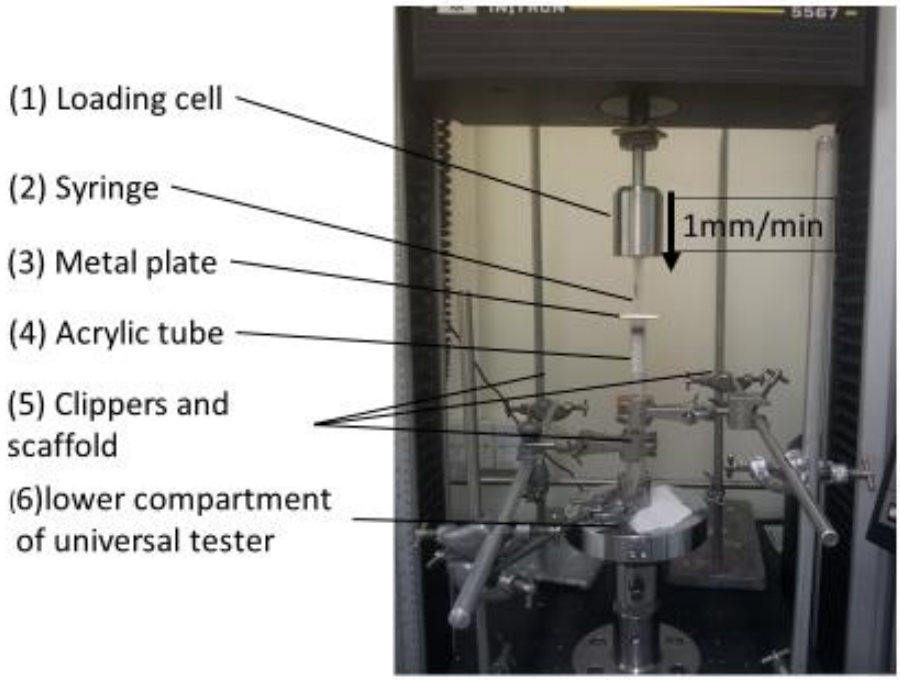


Figure 4.8 Experiment setup 1-1kN load cell 2-syringe 3- metal plate 4- acrylic tube 5- retort stand and clamp 6- lower compartment of universal tester.

A filled syringe could experience five cycles of extrusion (termed pushes subsequently) and these were investigated for specimens of the group 10:0. The results show no significant difference between the force-displacement behaviour of the first and second pushes (Table 4.4). Subsequent pushes showed differences in behaviour, particularly the final push, where it is likely that the proximity of the material to the syringe end caused a boundary effect. The coefficient of variation of the third and fifth push were so high, while the first and second push were less varied. Based on that it was decided to subject each syringes to 2 pushes with a three-minute time interval between each pushes.

Table 4.4 Mean extrusion force of the five pushes of the group 10:0.

Pushes	Mean extrusion force	SD	CV%
First	79	15	19
Second	79	12	14
Third	75	26	35
Fourth	88	12	13
Fifth	121	27	23

Injectability for five repetitions of each experimental material and three Newtonian fluids and water (see Table 4.5) were taken using the same method as described above.

Table 4.5 Newtonian fluids used in this study.

Newtonian fluid	description	Known viscosity mPa.s	Manufacture
Water	tap water	-	-
B29	PAO oli100%	28.81 mPa.s at 25°C with certification issued in 2009.	Brookfield engeering lab. Inc., Massachusetts, USA
B200	PAO oli100%	198.5 mPa.s at 25°C with certification issued in 2009.	
B10200	PAO oli100%	9959 mPa.s at 25°C with certification issued in 2010.	

All data were analysed using statistical software (SPSS 19 for windows, IBM SPSS Inc., USA). The Shapiro-Wilk test was used to test normality of the data. The data were normally distributed therefore parametric tests were used for statistical comparisons. A paired sample t-test was carried out to show the significances between first and second push. Two way ANOVA were

taken using the fluoride% (%F) and the Acetone% (%A) concentrations as the two factors. Post hoc Tukey method was used to determine any statistical significant differences between groups at ($P<0.05$).

4.4.5 *Fluoride release*

The experimental materials were placed into a plastic mould (10 mm diameter, 1 mm height), which was supported on a glass plate and transparent polyethylene terephthalate (PET) film (Goodfellow Cambridge Ltd., Huntingdon, Cambs., UK). A second strip and glass plate were then applied to the top surface of the mould. The moulds, covered with the glass plates was pressed to form flat disc shaped specimens, were light cured from both surfaces for 40 seconds each using an LED light curing unit (Coltolux® LED, Coltene, USA) with an intensity of 800-850 mW/cm² measured with an intensity meter (Coltolux LED, Sussex, UK).

Four specimens were prepared from each 0%A, 10%A, and 20%A acetone concentration. Based on previous experiments the two highest concentrations of acetone (30%A and 40%A) were excluded from the groups for fluoride release measurements due to inadequate curing.

After curing, the specimens were removed from the moulds and lapped using dry 1200-grit silicon carbide paper (Norton, Abrasive Technological Excellence, France). The diameter and thickness of the specimens were measured using digital Vernier callipers (Mitutoyo Digimatic, Japan), and weight was taken using a digital balance (Mettler AE 240, 0.01 mg accuracy, Switzerland). Specimens were stored in a sealed container together with a moist paper towel to produce 100% humidity in an incubator for 24 hours at 37°C (Gallenkamp, Riley Industries Ltd., UK).

Next, the specimens were placed into polyethylene vials (12 ml, VWR international Ltd.) containing 5 ml of distilled deionized water (DDW) and stored at 37°C. The containers were placed horizontally to allow full immersion of the specimens in the storage water while maintaining minimal contact with the walls (see figure 4.9). The water in the containers was changed daily for the first two weeks, then every 7 days up to 1 month and monthly thereafter.

Figure 4.9 Sample within 5ml of distilled deionized water.

An ion-selective electrode (Orion Research, Thermo Scientific, Waltham, MA, USA) connected to an ion analyser (Thermo electron corporation, Orion 4 star, USA) was used to measure fluoride ion release over 24 hour period daily for 14 days, then weekly up to 28 days, then at day 42, 70, 100 and 160. For weekly and monthly measurements, the storage water was replaced one day before measurement. At the time of fluoride measurement, each specimen was removed from its container and the storage solution decanted for analysis. The specimens were then washed with a DDW spray and dried in a paper towel then they were placed into fresh vials containing 5 ml of DDW for the next measurement.

The concentration reading of each storage (sample) solution was recorded after adding 0.5 ml of TISAB III (TISAB III concentrate with CDTA, Thermo Fisher science). The electrode was immersed into the solution and a magnetic stirrer (VELP, Scientifica, Italy) used to stir the solutions for three minutes prior to measurement (see figure 4.10).

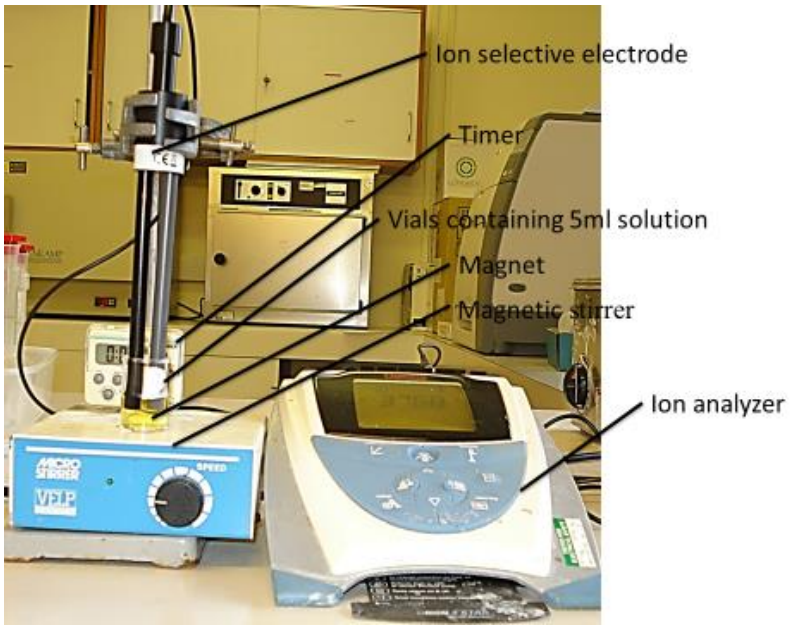


Figure 4.10 Ion selective electrodes used in this study.

The instrument was calibrated daily, therefore five standard fluoride solutions containing 0.01, 0.1, 1, 10, and 100 ppm F were prepared from a 100 ppm standard solution (activity standard solution for fluoride electrode 100 ppm as fluoride, Fluka, Sigma Aldrich). A new calibration curve was plotted every two hours. The concentration reading in milliVolts (mV) of each sample solution was recorded. A logarithmic equation was used to convert mV to corresponding fluoride concentrations in ppm as shown below. The ppm values were then converted into micrograms per unit surface area (calculated from the initial dimensions of the specimen). The final results were reported as daily fluoride-release rate (µg/cm²/day). All conversions were undertaken using Microsoft Excel software 2013.

The following equations were used to transfer mV into ppm of fluoride samples (Zahroon, 2014):

Equation 4.3 $$\frac{\mathrm{mV1}-\mathrm{mV2}}{logC1-logC2}=\frac{\mathrm{mVs}-\mathrm{mV2}}{logCs-logC2}$$

Equation 4.4 $$\frac{logCs-logc2}{logC1-logc2}=\frac{\mathrm{mVs}-\mathrm{mV2}}{\mathrm{mV1}-\mathrm{mV2}}$$

Equation 4.5 $$logcs-logc2=\left(\frac{\mathrm{mVs}-\mathrm{mV2}}{\mathrm{mV1}-\mathrm{mV2}}\right)*(\,logc1-logc2)$$

Equation 4.6 $$logCs=\left(\frac{\mathrm{mVs}-\mathrm{mV2}}{\mathrm{mV1}-\mathrm{mV2}}\right)logC1-\left(\frac{\mathrm{mVs}-\mathrm{mV2}}{\mathrm{mV1}-\mathrm{mV2}}\right)logC2+logC2$$

Equation 4.7 $$Cs=10^{logCs}$$

mV_1 and mV_2 represent *mV* of standard solutions, C_1 and C_2 represent concentration of standard solutions, *mVs* represents *mV* of testing sample, C_s represents concentration of testing sample, *Logcs* represents the concentration of testing sample in ppm, *mV* represents the milliVolts from the analyser reading, *ppm* represents the parts per million.

After processing, all data were then imported into dedicated statistical software (SPSS 19 for windows, IBM SPSS Inc., USA) for analysis. Data normality was tested using the Shapiro-Wilk test. The data were not normally distributed therefore non-parametric tests were used to investigate statistical difference between groups. Kruskal-Wallis H was used to find significant differences in the fluoride release for each fluoride and acetone group for each day. Mann-Whitney U test was used to characterise significant differences between groups at ($P<0.05$).

In order to consider the effects of each of the variables (Acetone%, Fluoride%, daily release) on the fluoride release, a three way ANOVA was undertaken. Therefore, the data was transformed to normal using a two-step transformation to normality in SPSS (Templeton, 2011). After transformation, the data was confirmed to be normally distributed using a Shapiro-Wilk test at ($P<0.05$)

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4.5 Results

4.5.1 *Investigating acetone loss*

The amount of weight lost for 10:0 40%A was 1.3% after 15 minutes exposure to air compared to 0.5% for 10:0 0%A see table 4.6. The percentage of weight lost for 7:3 40%A 1.6% was higher than 7:3 0%A 0.6% after 15 minutes exposure to air (see table 4.7). There was no weight change for all groups during the first and second round of mixing.

Table 4.6 Percentage weight loss of the material during preparation.

Experimental groups	First round mixing	Second round mixing	1 min	2 min	3 min	4 min	5 min	10 min	15 min	30 min
10:0 40%A	0	0	0.5	0.6	0.7	0.7	0.8	1	1	1.3
10:0 0%A	0	0	0.1	0.2	0.2	0.2	0.3	0.4	0.5	0.5
7:3 40%A	0	0	0.6	0.7	0.8	0.9	1	1.4	1.6	1.7
7:3 0%A	0	0	0.1	0.1	0.2	0.2	0.2	0.3	0.6	0.6

During storage of the materials no weight change occurred after 10 days storage for all groups see Table 4.7

Table 4.7 Percentage weight loss of the material during storage at different time intervals.

Experimental groups	First round mixing	Second round mixing	Day 1	Day 2	Day 3	Day 4	Day 5	Day 10
10:0 40%A	0	0	0	0	0	0	0	0
10:0 0%A	0	0	0	0	0	0	0	0
7:3 40%A	0	0	0	0	0	0	0	0
7:3 0%A	0	0	0	0	0	0	0	0

4.5.2 *Degree of conversion (DoC)*

Representative FTIR spectra of the experimental materials collected after different curing times are shown in figure 4.11. From this, the principal functional groups present in each experimental material can be identified. These are approximately 1720cm^{-1} C=O, 1640 cm^{-1} C=C, 1610 cm^{-1} Phenyl C=C, 1460 cm^{-1} CH_2CH_3 and 1118 cm^{-1} phenyl C-O-C. The absorption peak at 1638 cm^{-1} represents the methacrylate C=C which changes with polymerisation. While the absorption peak at 1715cm^{-1} represents C=O which does not change with polymerisation and therefore was taken as an internal standard. Therefore, a typical spectra focussing on the two key peaks, taken from one specimen at each time point, is shown in Figure 4.12. The graph shows the aliphatic C=C peak decreasing with light exposure however, the C=O peak remains relatively stable during polymerization.

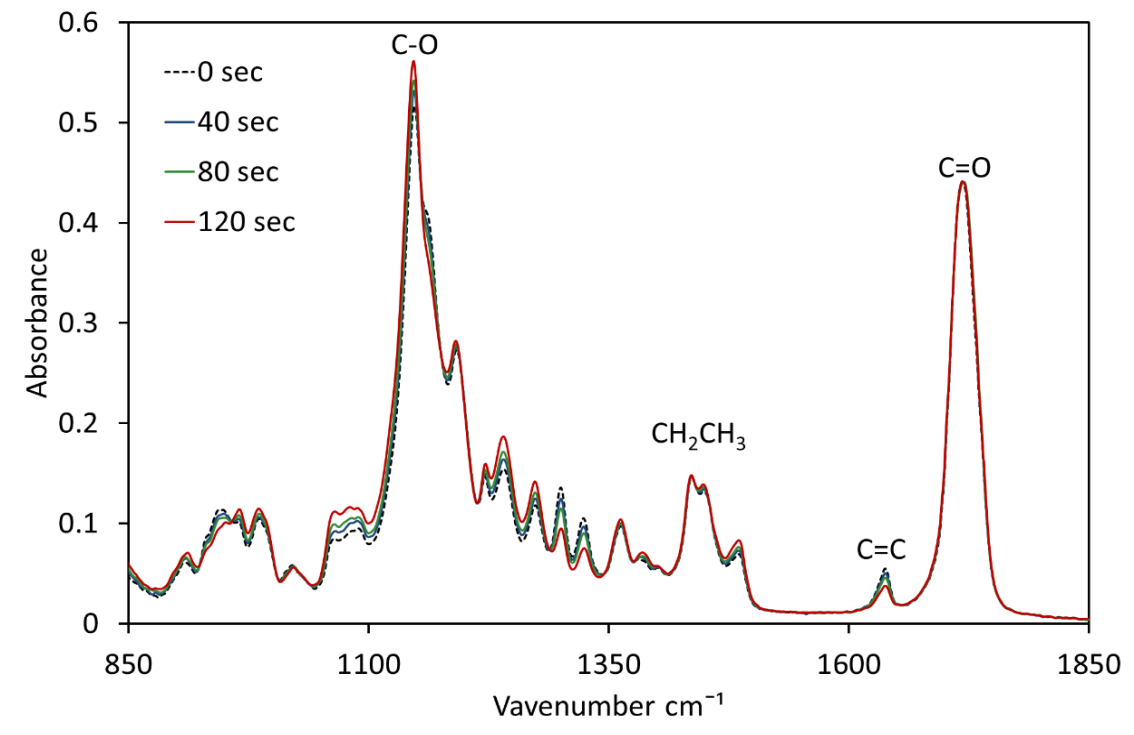

Figure 4.11 Representative FTIR spectra from 850 to 1850 cm^{-1} of the group 10:0 0%%A collected before and after different time of light exposure from 0 to 120 sec.

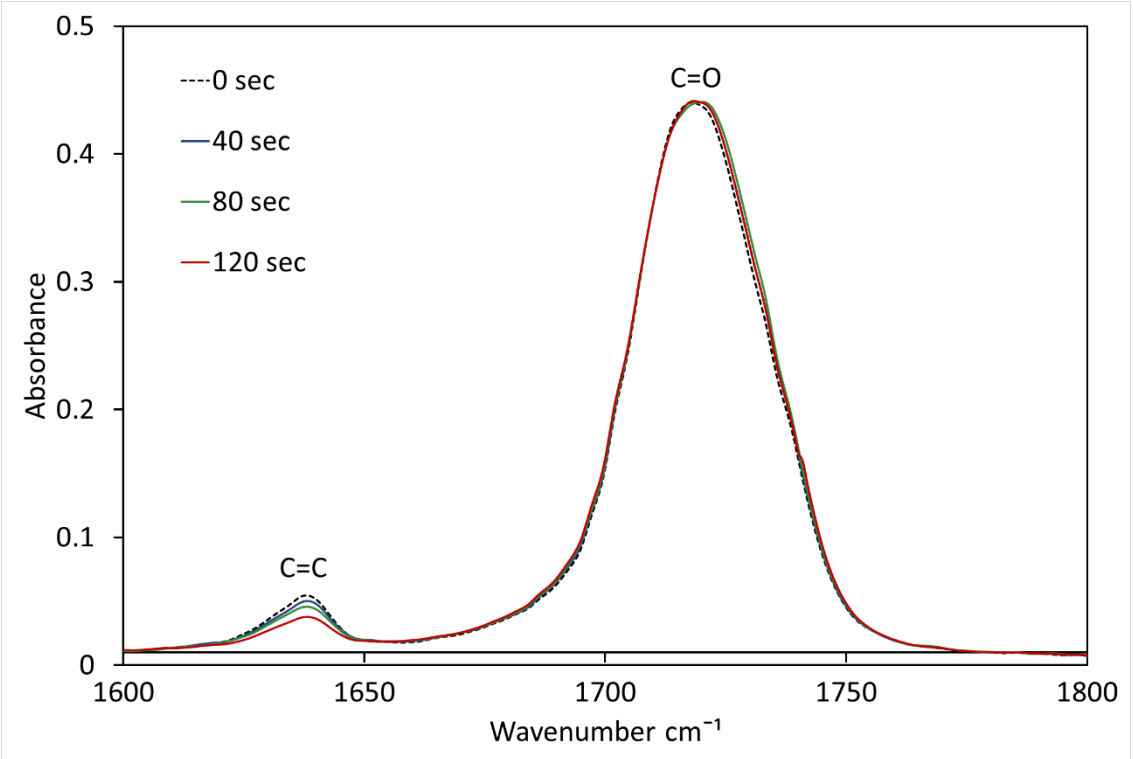

Figure 4.12 Representative FTIR spectra from 1600 to 1800 cm^{-1} from a specimen of group 10:0 0%A.

The median percentages of DoC of the experimental groups with different concentrations of acetone are shown in Table 4.8 and figure 4.13, 4.14, 4.15 and 4.16. At higher solvent content (30%A and 40%A) and after 40 seconds of light curing, DoC was significantly lower in all groups compared to the (0%A, 10%A and 20%A) except group 10:0 ($p<0.05$, Mann-Whitney U test) Table 4.8.

The results show that all 20%A groups had a significantly higher DoC compared to groups with 30%A and 40%A after 80 seconds light curing except for group 10:0 ($p<0.05$, Mann-Whitney U test), Table 4. 8.

After 120 second light curing, all groups with 20%A achieved significantly higher DoC compared to groups with 0%A and 10%A except group 7:3 which was not significantly different to the 0%A ($p<0.05$, Mann-Whitney U test) Table 4.8.

Table 4.8 Median degree of conversion (IQR) % of groups 10:0, 9:1, 8:2 and 7:3 with different concentrations of acetone, at different curing interval times.

Groups	% Acetone	Median (IQR) DC%		
		40 sec.	80 sec.	120 sec.
10:0	0%A	24 (8)^{ab}	29 (8)^{h}	35 (11)^{n}
	10%A	32 (5)^{a}	37 (7)^{h}	41 (6)^{n}
	20%A	44 (5)^{b}	55 (5)^{i}	60 (6)^{o}
	30%A	42 (8)^{b}	60 (1)^{i}	66 (1)^{o}
	40%A	16 (4)^{a}	34 (9)^{h}	51 (6)^{n}
9:1	0%A	43 (2)^{c}	48 (3)^{j}	50 (1)^{p}
	10%A	47 (6)^{c}	55 (7)^{j}	57 (6)^{p}
	20%A	38 (3)^{c}	60 (1)	64(3)^{q}
	30%A	22 (1)	44 (8)^{j}	63 (2)^{q}
	40%A	18 (7)	30 (13)	43 (16)^{pq}
8:2	0%A	36 (10)^{de}	41 (11)^{y}	43 (9)^{r}
	10%A	42 (4)^{d}	53 (5)^{k}	57 (5)^{s}
	20%A	27 (3)^{e}	56 (2)^{k}	64 (1)
	30%A	15 (4)	31.17 (5)^{y}	50 (7)^{rs}
	40%A	10.03 (2)	18.22 (4)	26 (4)
7:3	0%A	45 (4)	54 (4)^{l}	56 (5)^{tuv}
	10%A	34 (6)	54 (2)^{l}	58 (3)^{t}
	20%A	28 (5)^{f}	55 (4)^{l}	63 (1)^{u}
	30%A	12 (2)^{g}	24 (7)^{m}	37 (13)^{tuv}
	40%A	14 (4)^{fg}	26 (13)^{m}	41 (13)^{v}

The DoC values are median with IQR in the parenthesis. Values exhibited similar superscript letters indicate no significant difference within columns ($p > 0.05$) as determined using Mann-Whitney U.

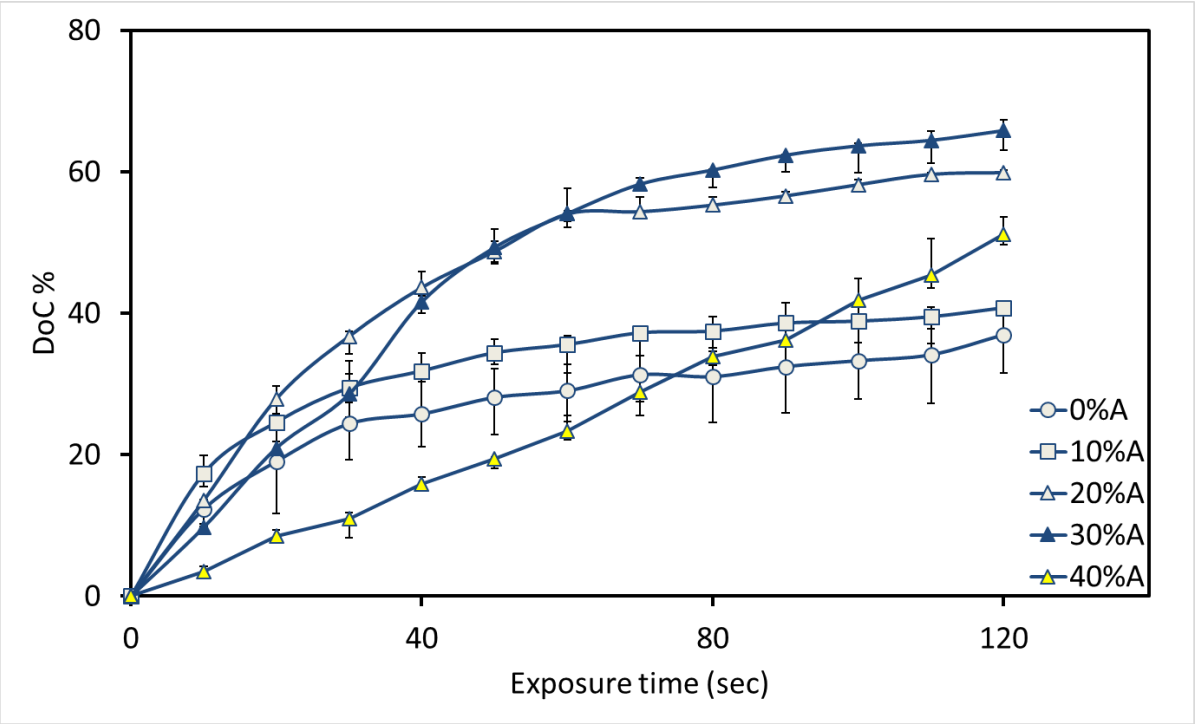

Figure 4.13 Median DoC for Group 10:0 with different concentrations of acetone. The figure shows the effect of acetone on DoC of group 10:0. The error bars represent IQR.

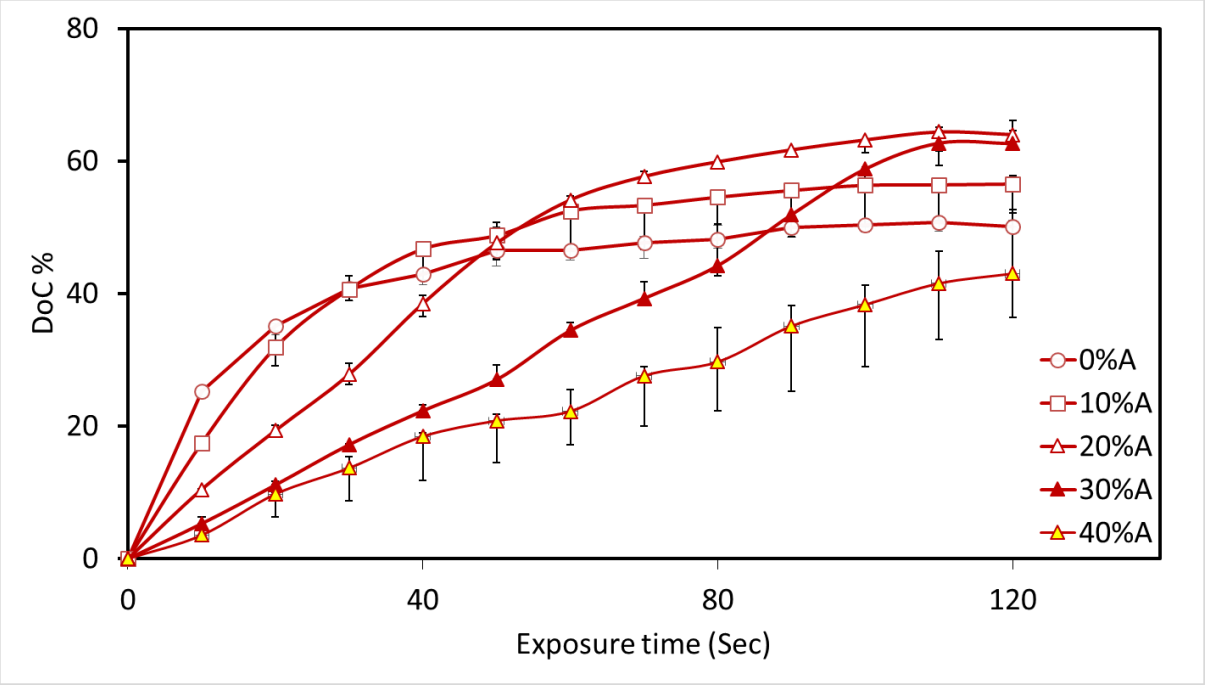

Figure 4.14 Median DoC for Group 9:1 with different concentrations of acetone. The figure shows the effect of acetone on DoC of group 9:1. The error bars represent IQR.

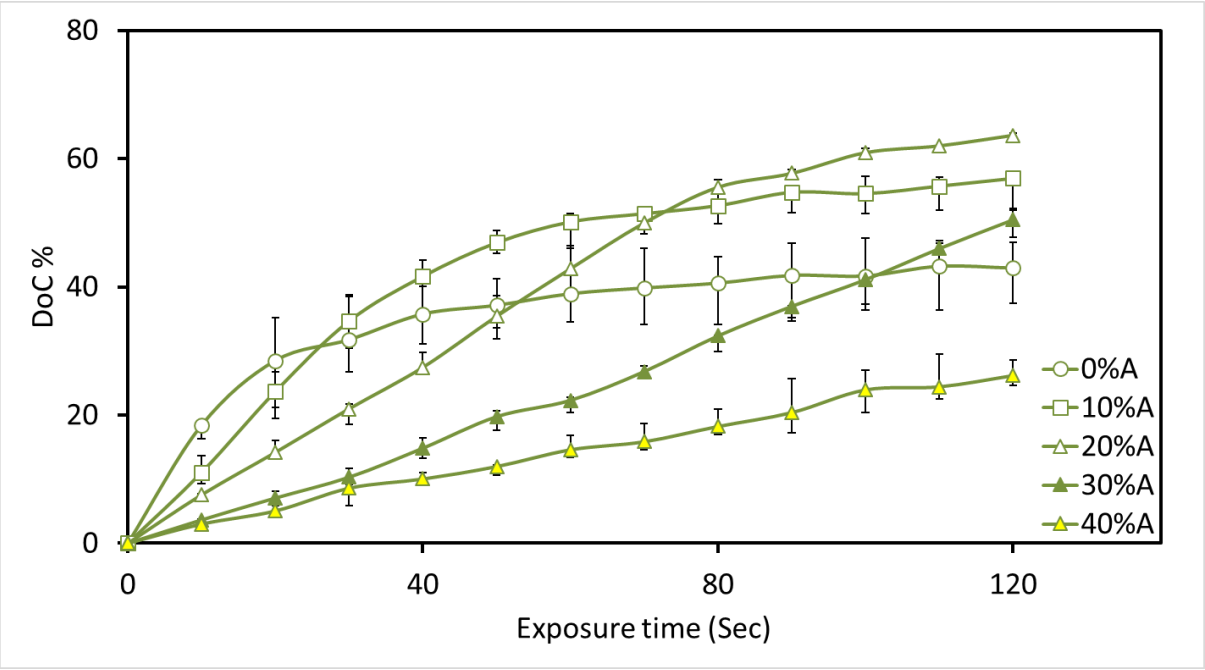

Figure 4.15 Median DoC for Group 8:2 with different concentrations of acetone. The figure shows the effect of acetone on DoC of group 8:2. The error bars represent IQR.

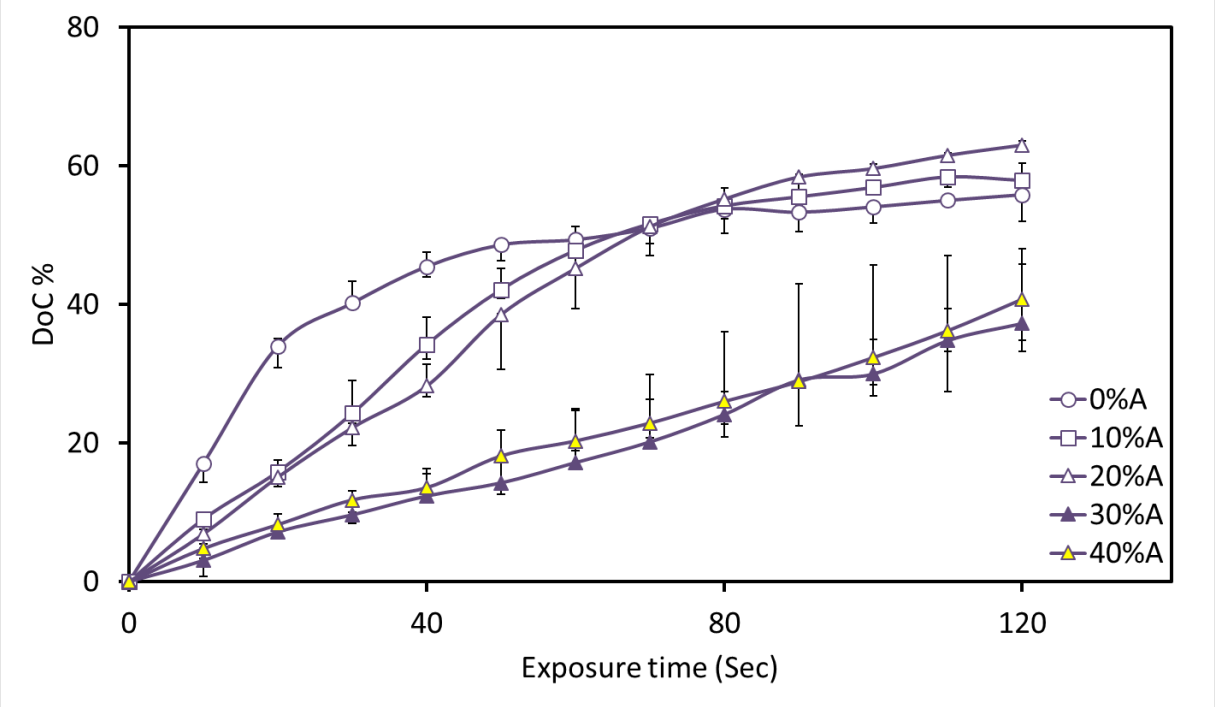

Figure 4.16 Median DoC for Group 7:3 with different concentrations of acetone. The figure shows the effect of acetone on DoC of group 7:3. The error bars represent IQR.

The data for the average value of DoC could also be presented as a function of fluoride and acetone concentrations, as illustrated in figures 4.17, 4.18, 4.19 and 4.20. A linear model was fitted to this data. Comparing DoC and acetone concentrations revealed the 10:0 group potentially showing a weak positive relationship and the 7:3 group potentially showing a weak

negative relationship between acetone concentration and DoC, however, no significant correlation was found for any group (P>0.05), see figure 4.19.

Similarly, no clear trend was evident indicating a relationship between fluoride concentration and DoC. While there was a significant correlation found for the 30%A specimens, and r values in excess of 0.6 for the 0%A, 10%A and 20%A, the trends were inconsistent between materials, suggesting that there is no clear relationship between these two parameters, see figure 4.20.

The results of three-way ANOVA showed that acetone, fluoride concentrations and exposure time had a significant effect on DoC at (P≤0.001), with a statistically significant interaction between fluoride%, acetone% and exposure time (P≤0.001).

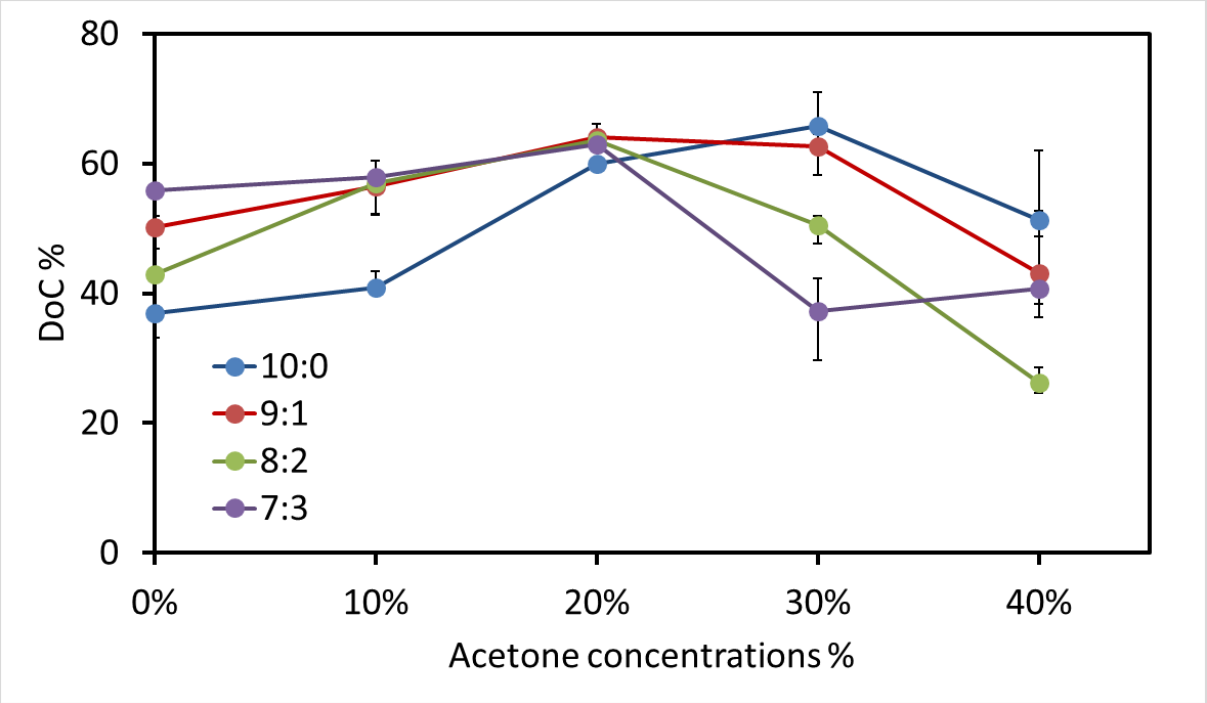

Figure 4.17 Median DoC of all experimental materials at different acetone concentrations after 120 seconds of light exposure. The error bars represent IQR.

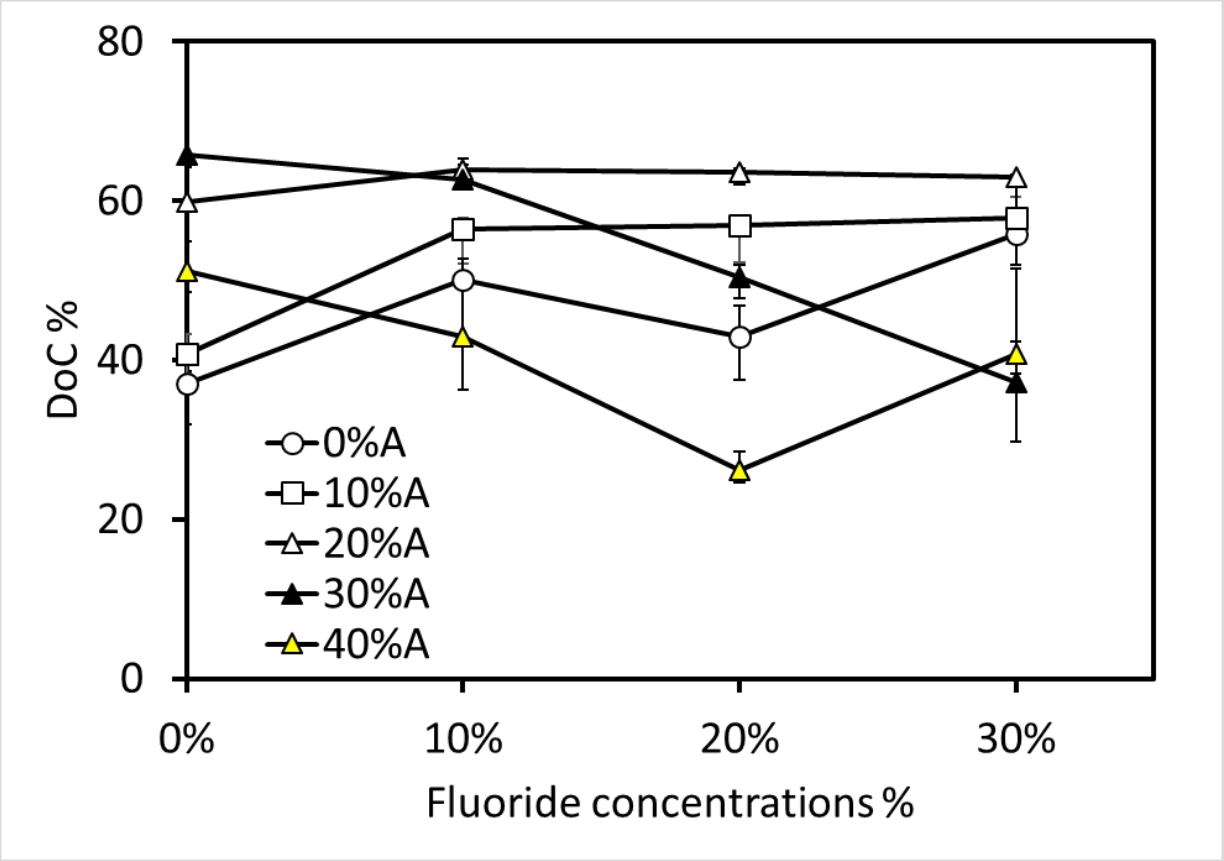

Figure 4.18 Median DoC of all experimental materials different fluoride concentrations after 120 seconds of light exposure. The error bars represent IQR.

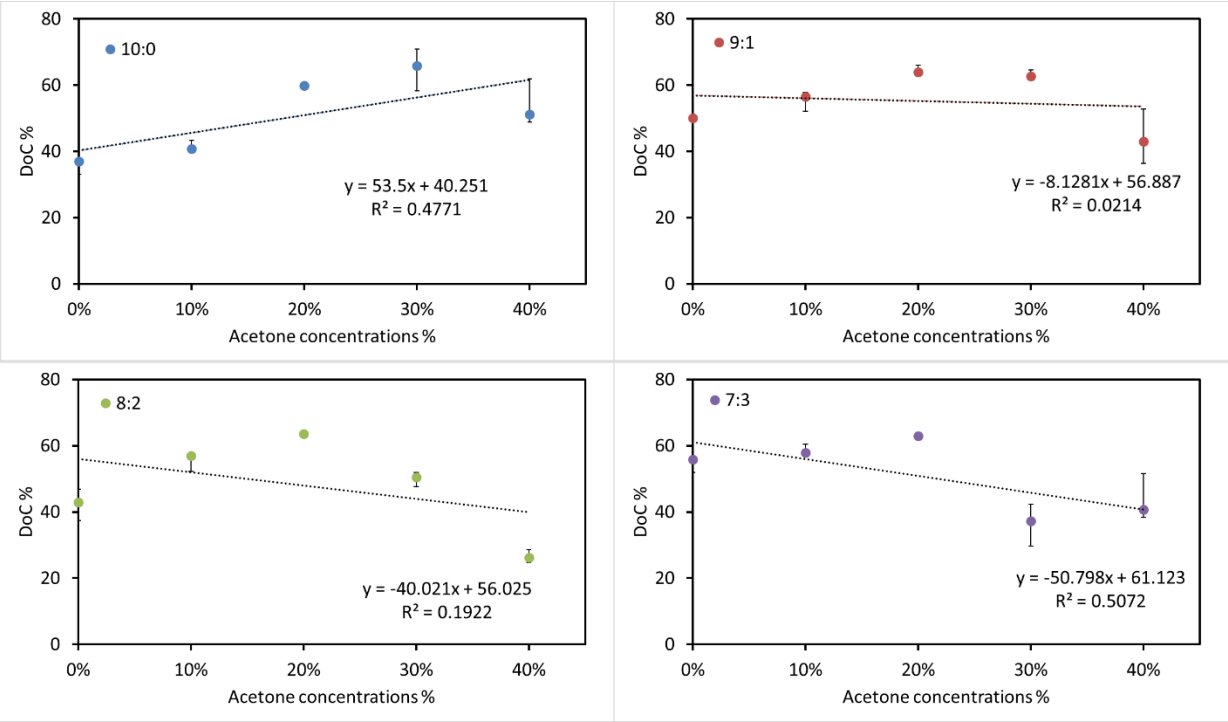

Figure 4.19 Relationship between DoC and acetone concentrations at 120 seconds of light curing. Data represents median value with error bars represent IQR. The r values are 0.68, 0.14, 0.43 and 0.71 for the groups 10:0, 9:1, 8:2 and 7:3 respectively.

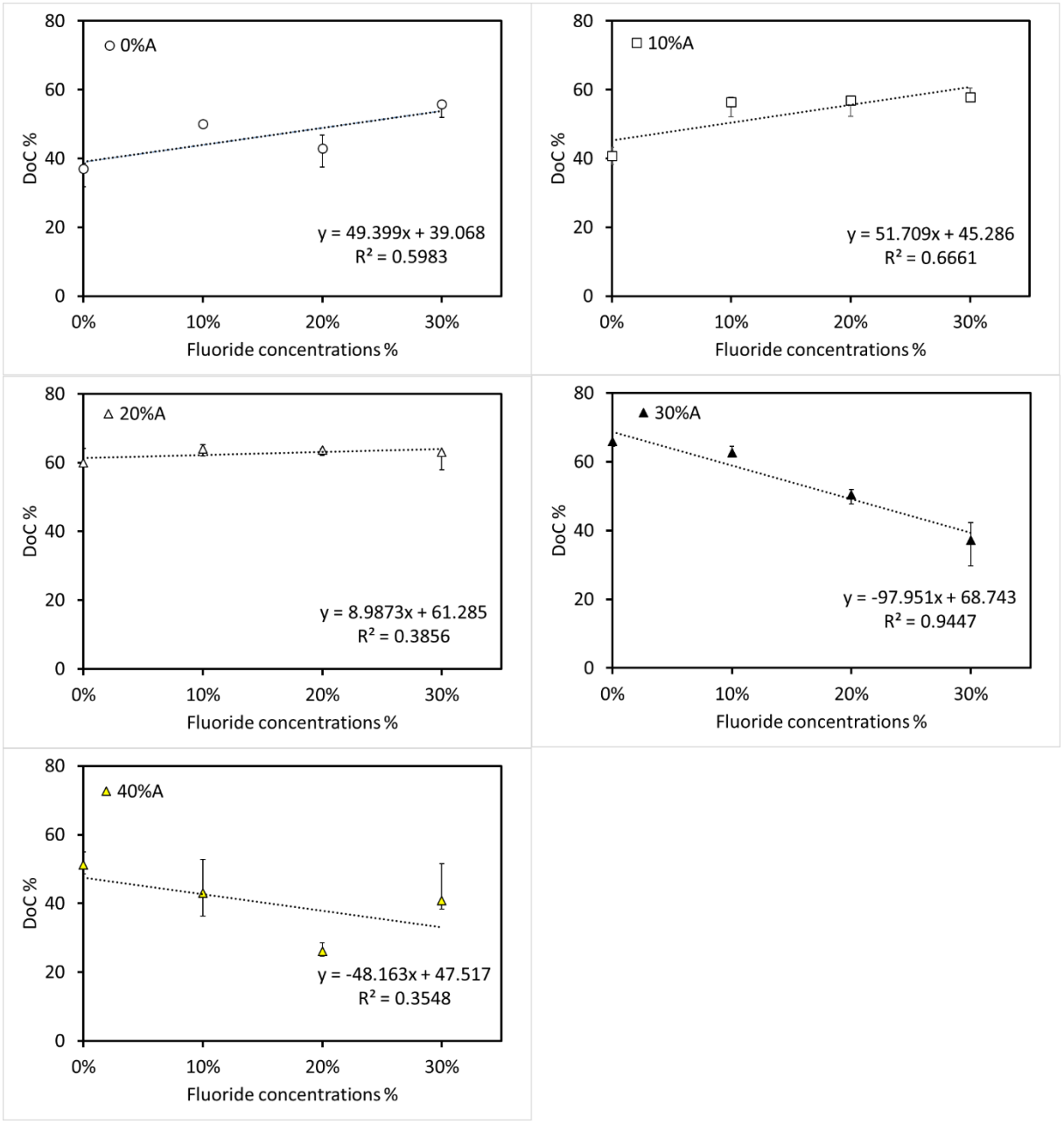

Figure 4.20 Relationship between DoC and fluoride concentrations at 120 seconds of light curing and at 0%A, 10%A, 20%A, 30%A and 40%A. Data represents median value with error bars represent IQR. The r values are 0.76, 0.81, 0.62, 0.96 and 0.59 of the 0%A, 10%A, 20%A, 30%A and 40%A respectively.

4.5.3 *Heat of polymerization (DSC)*

Representative isothermal DSC thermograms obtained during photo-calorimetry at 37°C of the samples of the group7:3 with 0%A, 10%A, 20%A, 30%A and 40%A are shown in Figure 4.21. The figure shows heat release decrease and extend with increasing acetone concentrations. The first six peaks (dotted lines) represent the exotherm generated by the polymerization of resin plus the heat released from the light source. The next two thermograms (solid lines) represent the energy from the light source only. The light source peaks were added to the 6 thermograms for simplicity.

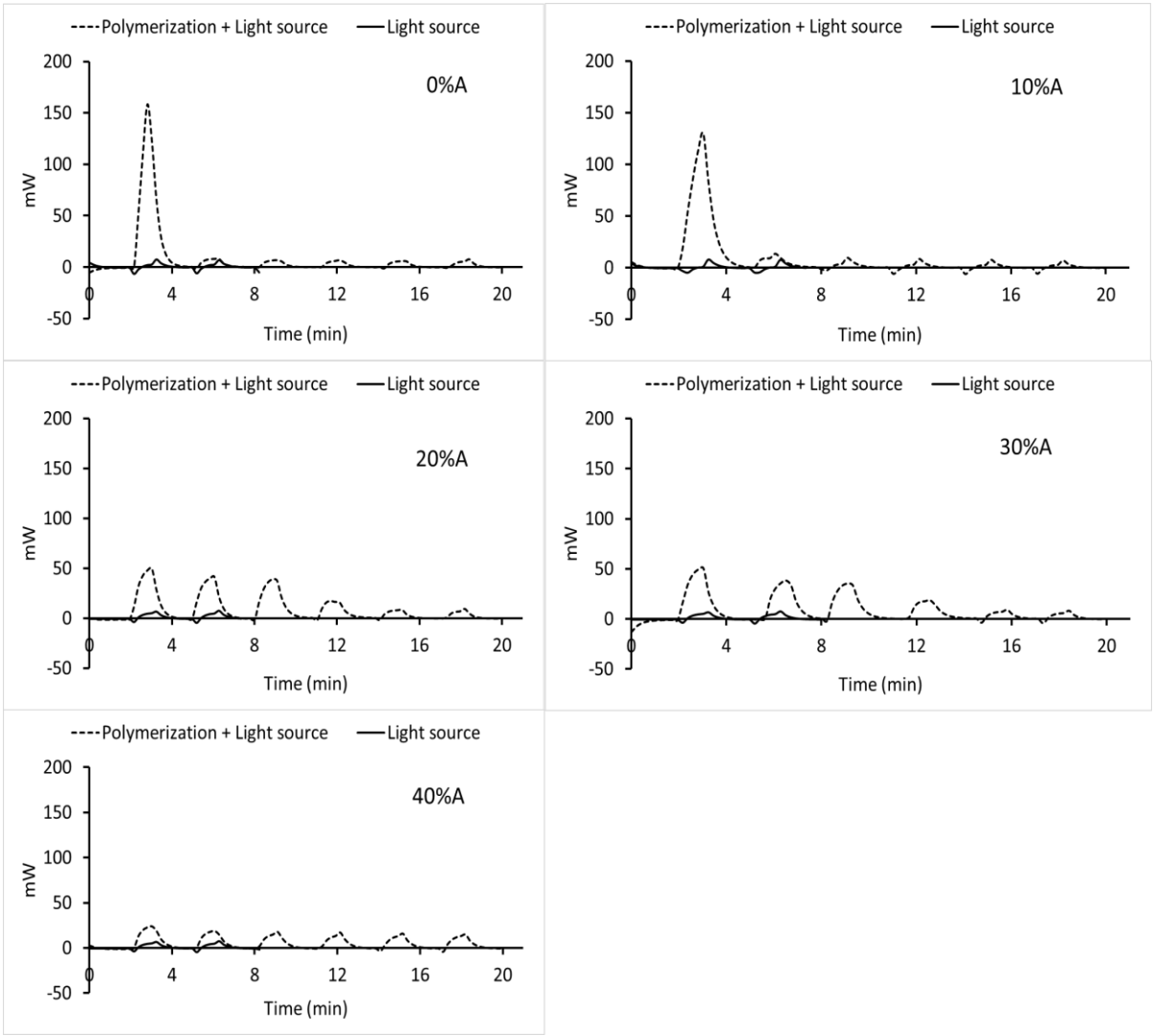

Figure 4.21 Representative isothermal DSC thermogram obtained during photo-calorimetry at 37C°of group 7:3 with different acetone concentrations. The dot line peaks represent heat of polymerization plus light source (six peaks). The solid line peaks represent the thermograms of the light sources only (two peaks).

The mean heat release from the experimental groups with different concentrations of acetone is shown in figures 4.21, 4.22, 4.23, 4.24 and table 4.9. All groups with 30% and 40% acetone

had significantly lower heat release at 60 and 120 seconds of light curing than groups with 0% and 10% acetone (Post hoc Tukey test, $p<0.05$). Groups 8:2 and 7:3 with 0%A had significantly higher heat release than 20%A at 60 and 120 seconds of light curing except group 8:2 at 60 seconds of light curing. However, there were no significant differences between 0%A and 20%A for groups 9:1 and 10:0 at (Post hoc Tukey test, $p<0.05$).

The effect of acetone and fluoride concentrations on heat release is shown in Figure 4.26 and 4.27. It was appearing that the addition of up to 20%A had no effect on the heat release until the concentration of NaF increased at least 20%A, after which there was a significant decrease in heat release as the acetone concentration increased (Post hoc Tukey test, $p<0.05$) see table 4.9.

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Table 4.9 Heat release values of groups 10:0, 9:1, 8:2 and 7:3 with different concentrations of acetone, at different curing interval times.

Groups	% Acetone	Mean (SD) of Heat release					
		60 sec	120 sec	180 sec	240 sec	300 sec	360 sec
10:0	0%	102(8)^{a}	105(9)^{ah}	106(9)^{c}	107(9)^{d}	108(9)^{e}	109(9)^{f}
	10%	109(8)^{a}	112(8)^{ahi}	114(7)^{cg}	115(6)^{dh}	116(6)^{e}	117 (5)^{f}
	20%	102(7)^{a}	108(6)^{cdh}	111(5)^{c}	112(6)^{d}	113(6)^{e}	114(7)^{f}
	30%	47(5)	87(9)^{ef}	114(9)^{c}	127(10)^{h}	130(11)^{i}	131(10)^{j}
	40%	39(4)	67(6)^{g}	90(9)^{g}	112(12)^{h}	129(11)^{i}	137(8)^{j}
9:1	0%	105(6)^{a}	108(6)^{aij}	111(6)^{d}	113(6)^{f}	114(6)^{j}	115(6)^{h}
	10%	112(9)^{a}	116(8)^{bj}	118(8)^{de}	120(8)^{fi}	121(9)^{jk}	122(10)^{hl}
	20%	108(5)^{a}	117(7)^{cj}	121(7)^{e}	124(6)^{i}	127(5)^{k}	129(4)^{l}
	30%	58(9)	98(10)^{ei}	118(5)^{de}	12(7)^{i}	128(8)^{k}	130(9)^{l}
	40%	40(5)	70(9)^{g}	96(11)	117(9)^{fi}	130(8)^{k}	135(10)^{l}
8:2	0%	108(4)	111(4)^{ak}	112(4)^{b}	114(4)^{c}	115(4)^{dj}	116(4)^{e}
	10%	87(7)	109(7)^{bk}	111(8)^{b}	114(8)^{cg}	115(9)^{dhj}	116(9)^{ei}
	20%	53(3)	102(4)^{dk}	117(4)^{b}	121(4)^{g}	123(4)^{h}	125(4)^{i}
	30%	39(6)	65(10)^{f}	91(14)	113(12)	123(8)^{dh}	126(7)^{ik}
	40%	30(3)	51(5)	68(7)	85(10)	102(13)^{j}	117(15)^{ek}
7:3	0%	104(8)^{a}	107(8)^{am}	108(8)^{cg}	108(8)^{d}	109(8)^{e}	109(8)^{f}
	10%	92(12)^{a}	105(4)^{bm}	108(4)^{c}	109(5)^{d}	110(5)^{e}	111(5)^{f}
	20%	40(2)^{h}	73(6)^{l}	108(8)^{cg}	116(11)^{d}	116(12)^{e}	114(12)^{f}
	30%	40(8)^{h}	71(21)^{l}	91(15)^{g}	106(8)^{d}	112(6)^{e}	112(6)^{f}
	40%	21(2)	36(4)	47(6)	57(8)	67(10)	76(11)

The heat release values are expressed as mean and SD in the parenthesis. Values exhibited similar superscript letters indicate no significant difference within columns within groups ($p > 0.05$) as determined using Post hoc test.

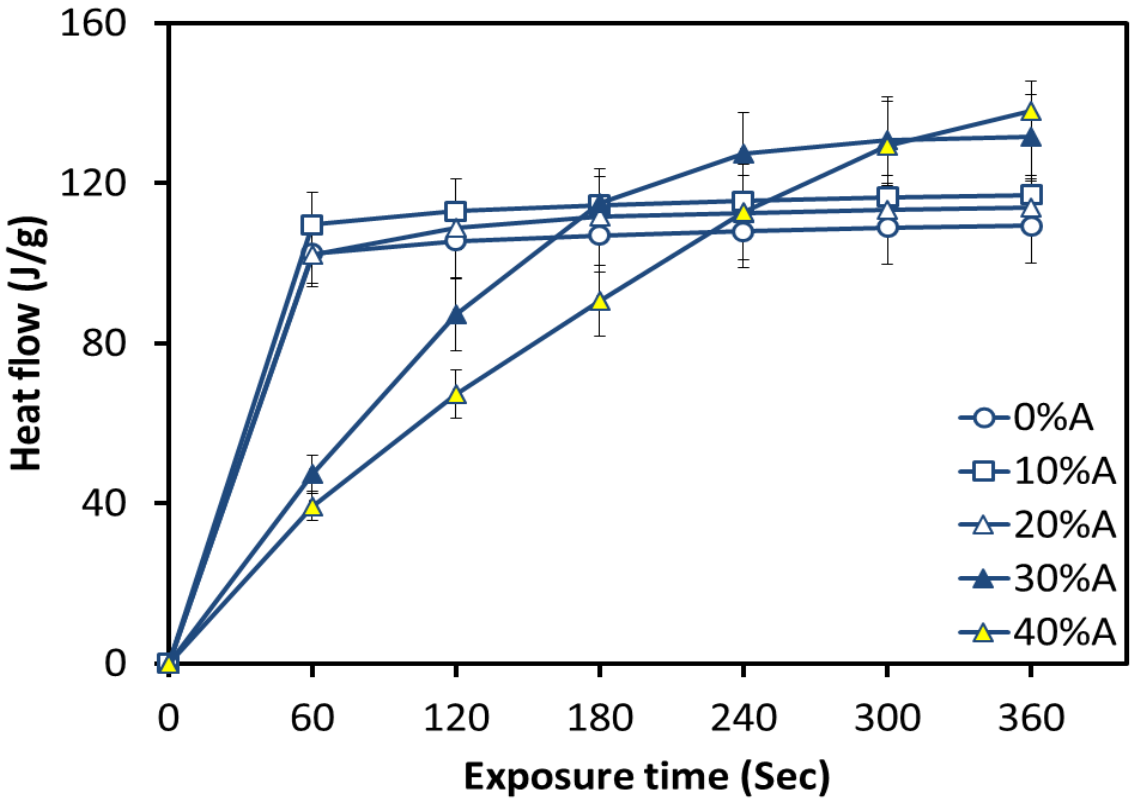

Figure 4.22 Mean heat release for Group 10:0 with different concentrations of acetone. The figure shows the effect of heat release of group 10:0. The error bars represent SD.

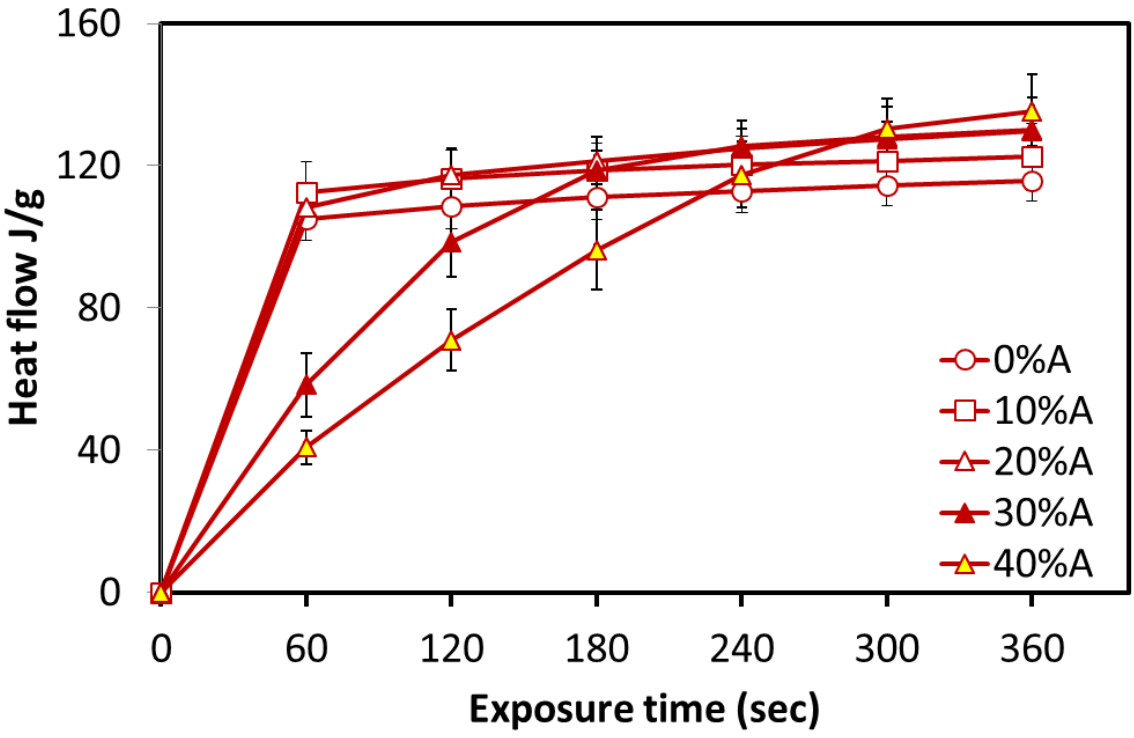

Figure 4.23 Mean heat release for Group 9:1 with different concentrations of acetone. The figure shows the effect of heat release of group 9:1. The error bars represent SD.

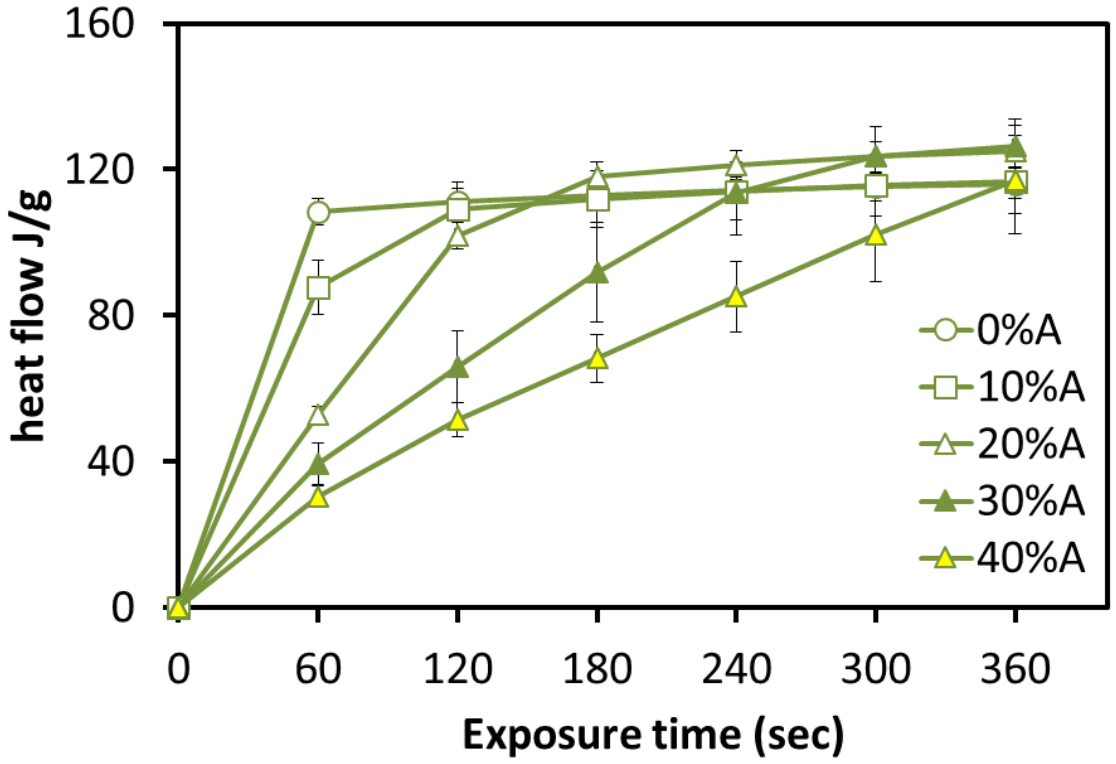

Figure 4.24 Mean heat release for Group 8:2 with different concentrations of acetone. The figure shows the effect of heat release of group 8:2. The error bars represent SD.

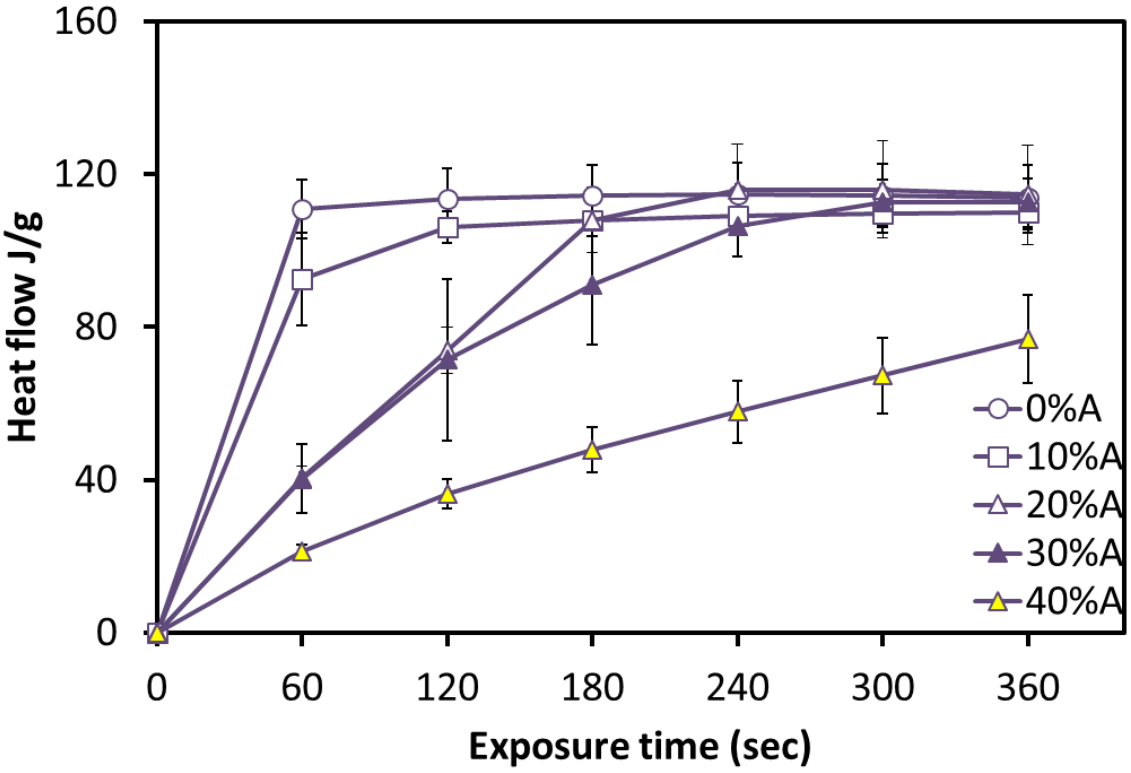

Figure 4.25 Mean heat release for Group 7:3 with different concentrations of acetone. The figure shows the effect of heat release of group 7:3. The error bars represent SD.

The data for the average value of heat release could also be presented as a function of fluoride and acetone concentrations at 120 seconds of light curing, as illustrated in figures 4.28 and 4.29. A linear model was fitted to this data. There was an inverse correlation between heat release and acetone concentrations. The relationship was significant for the groups 8:2 and 7:3 at $p<0.05$. The r values are 0.84, 0.77, 0.94 and 0.95 for the groups 10:0, 9:1, 8:2 and 7:3 respectively (Figure 4.28).

The correlation between heat release and fluoride concentration at 120 seconds of light curing are shown in figure 4.29. There was no relationship at 0%A, while when the concentrations of acetone (%A) increased an inverse relationship can be seen which becomes significant at 40%A at $p<0.05$.

The results of three way ANOVA showed that acetone and fluoride concentrations and exposure time had significant effect on heat release at ($P\leq0.001$). There was a statistically significant interaction between fluoride%, acetone% and exposure time ($P\leq0.001$).

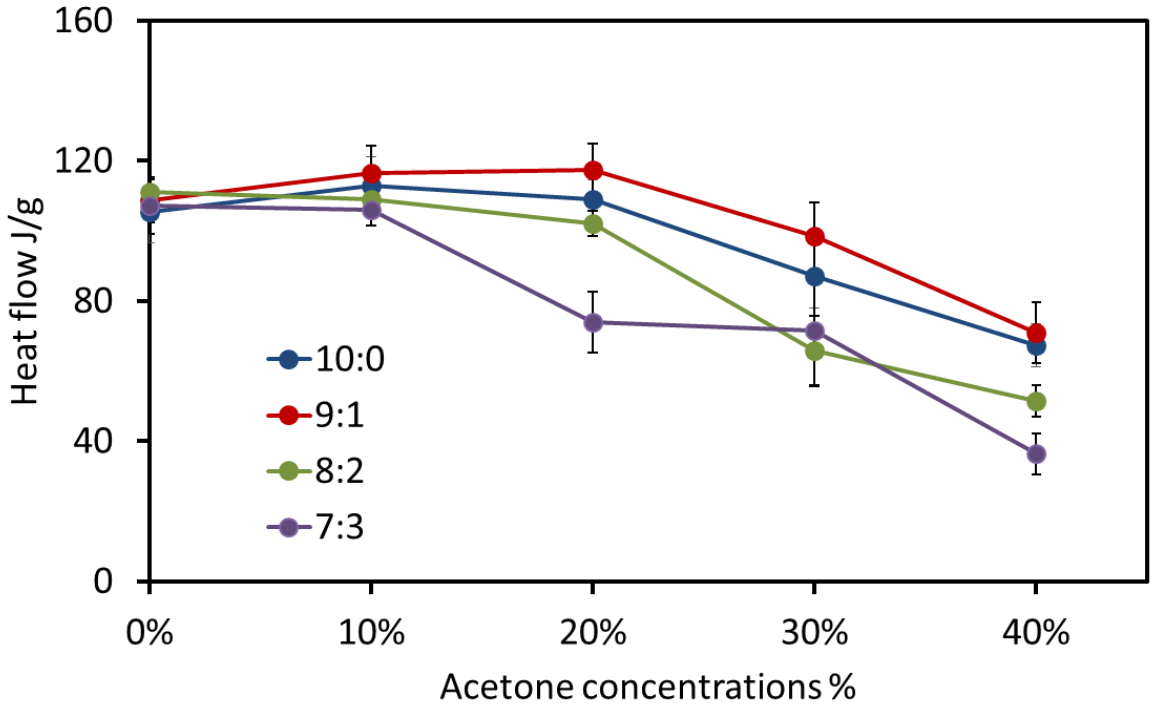

Figure 4.26 Mean heat release of all experimental materials at 120 seconds of light exposure. The error bars represent SD.

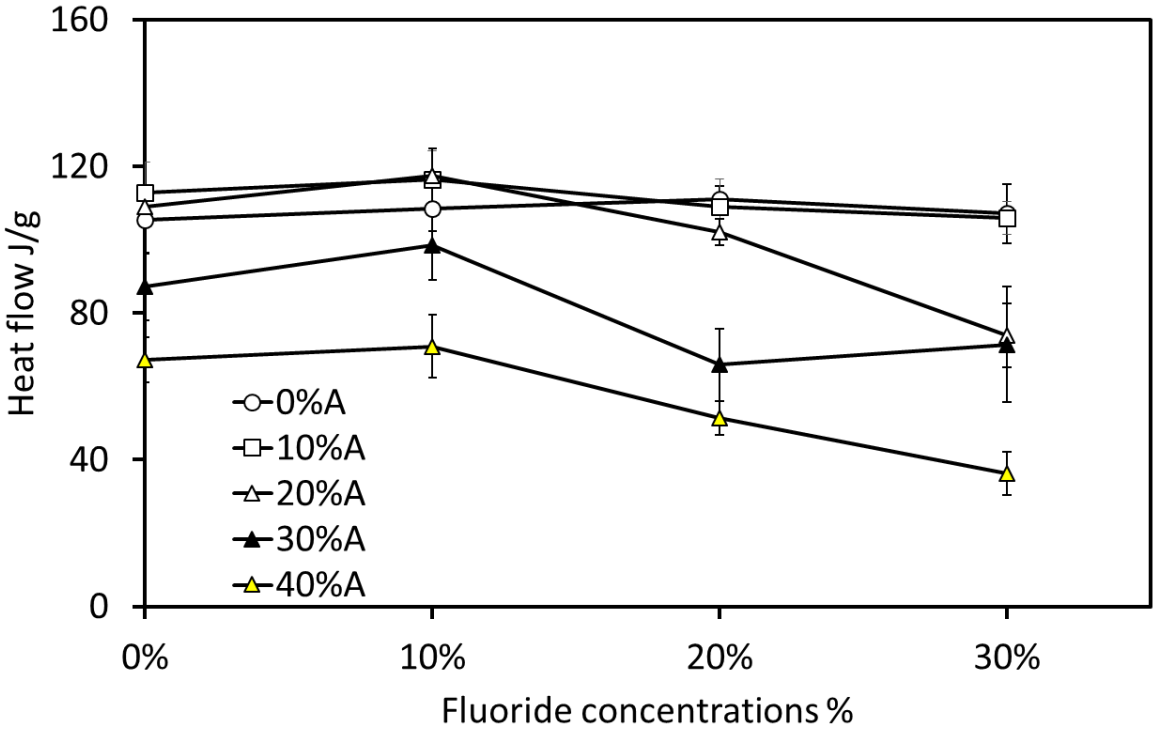

Figure 4.27 Mean heat release of al experimental materials at 120 seconds of light curing. The error bars represent SD.

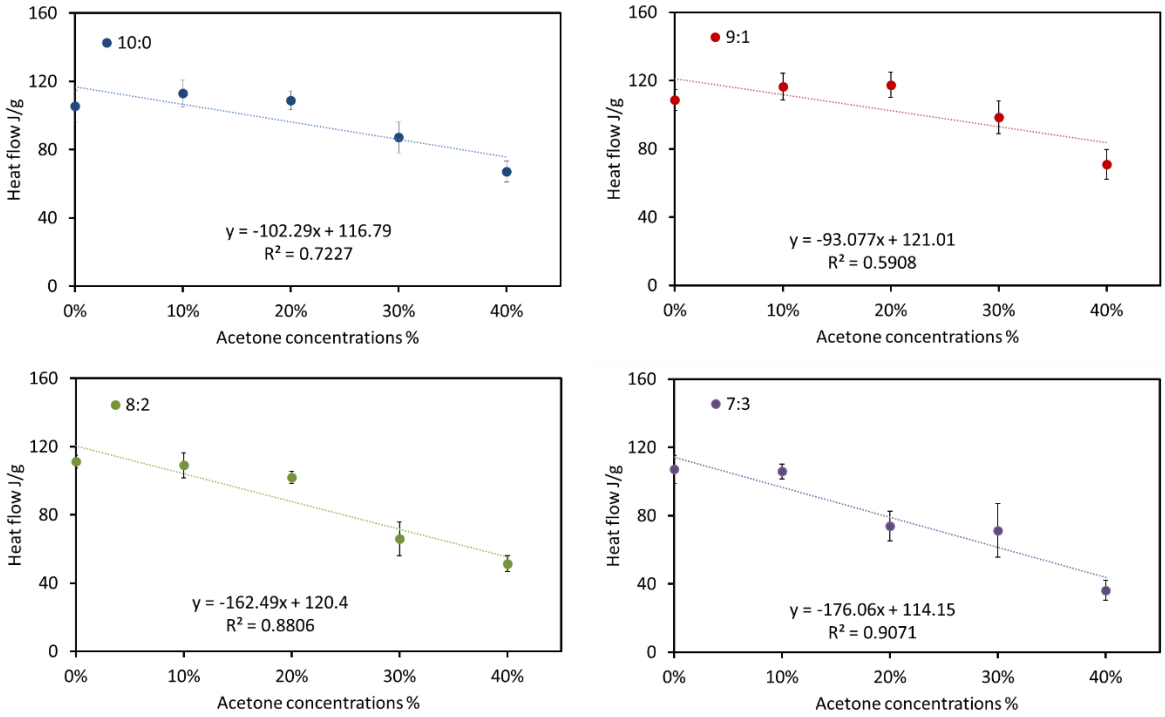

Figure 4.28 Relationship between heat release and acetone concentrations at 120 seconds of light curing. Data represents mean value with error bars represent SD. The r values are 0.84, 0.77, 0.94 and 0.95 for the groups 10:0, 9:1, 8:2 and 7:3 respectively.

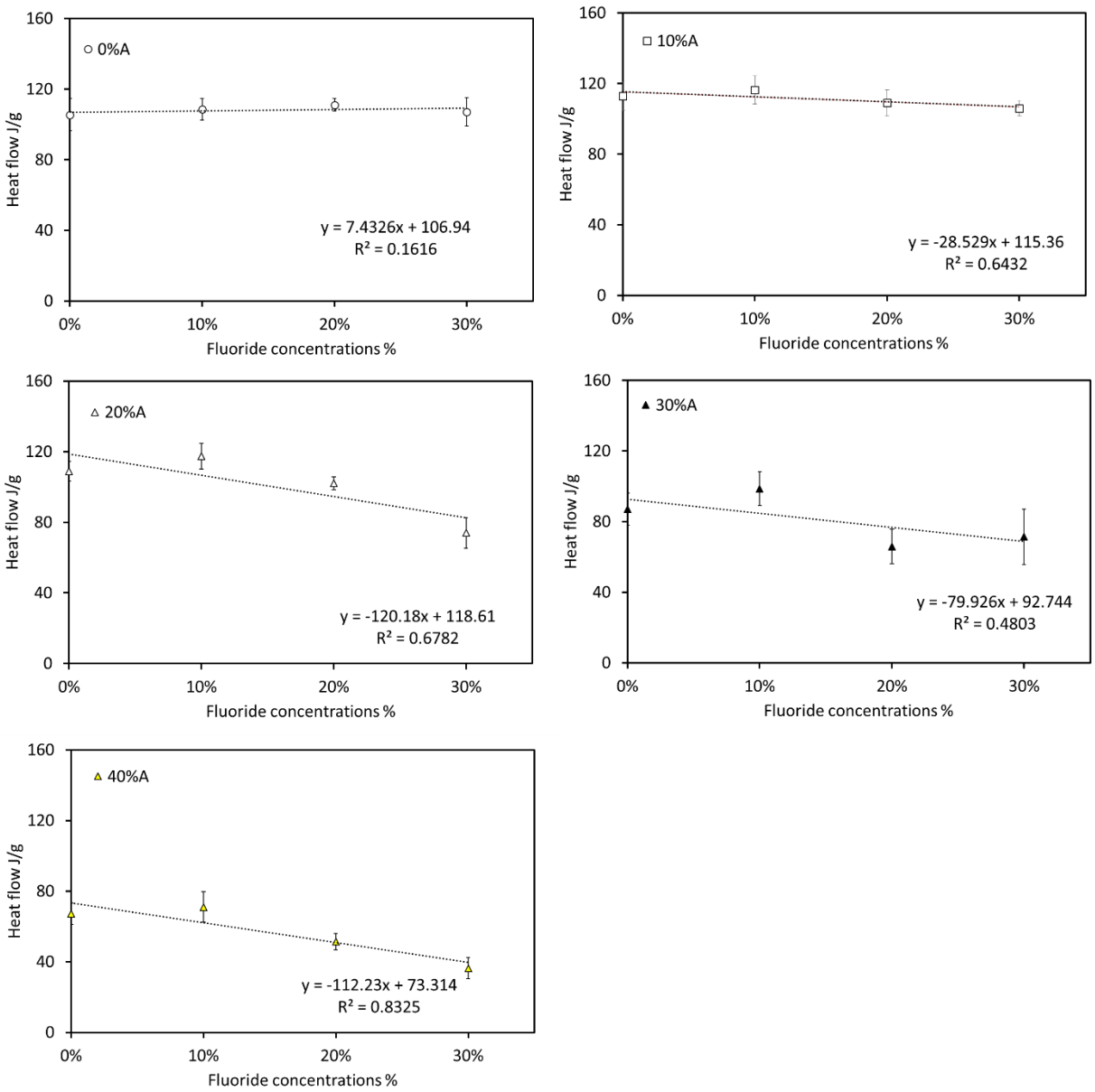

Figure 4.29 Relationship between heat release and fluoride concentrations at 120 seconds of light curing and at 0%A, 10%A, 20%A, 30%A and 40%A. Data represents mean value with error bars represent SD. The r values are 0.4, 0.8, 0.8, 0.69 and 0.91 of the 0%A, 10%A, 20%A, 30%A and 40%A respectively.

4.5.4 *Injectability test*

A representative force-displacement graph of group 10:0 at 0%A, 10%A, 20%A, 30%A and 40%A of one sample are shown in figure 4.30. There were two stages in the force displacement curves. The first stage consisted of an initial rapid increase of the applied load to reach the yield load, which corresponds to the load needed for the material to start flowing (extruding). In the second stage, the materials flow was in steady state at a constant load (injection load). Figure 4.30 shows that the extrusion force decreases with increasing acetone concentrations. These

representative graphs also show similar behaviour of first and second push. The maximum force of extrusion of the materials was taken as a comparison between groups.

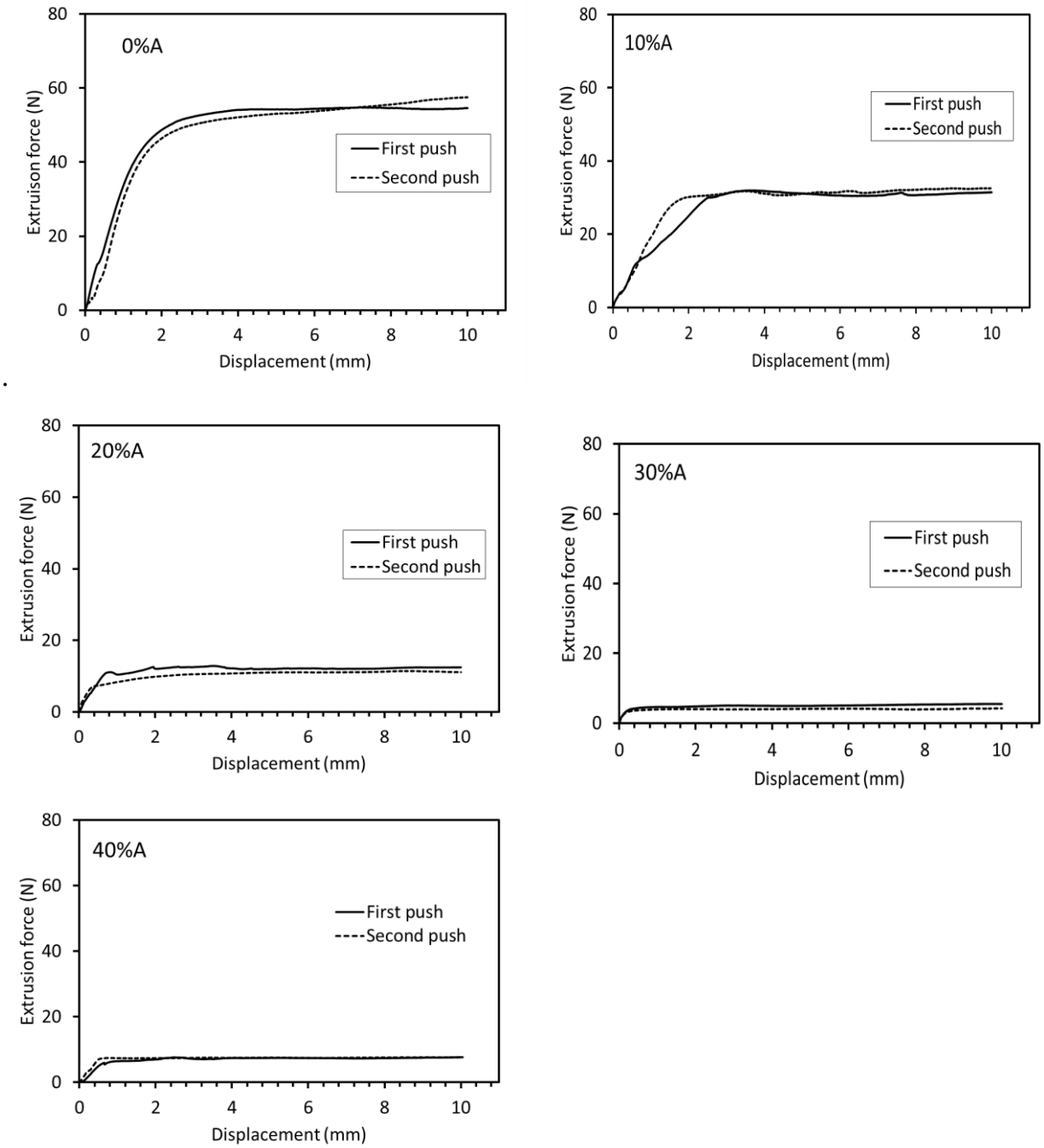

Figure 4.30 Representative extrusion force of group 10:0 at different acetone concentrations.

There was no significant difference between first and second push (Paired Sample t test, $p<0.05$) therefore the average was taken for comparison. The graphs of first and second push are shown in figures 4.31 and 4.32. The mean extrusion forces (N) with different concentrations of acetone for the first and second push and average of first and second push are shown in table 4.10 and figure 4.33.

The results show that the force required to extrude the materials varied according to different concentrations of NaF with 0%A the extrusion force decreased with increasing NaF concentrations, in which group 10:0 had high extrusion force followed by 9:1 and both were higher than the 8:2 group and all of them had higher extrusion force than the 7:3 group see figure 4.35 (Post hoc Tukey test, $p<0.05$).

For all groups there was a significant difference in the force of extrusion of the 0%A and groups with 20%A ,30%A and 40%A at ($P<0.05$) see figure 4.33. In addition, all groups at 10%A had significantly higher extrusion force than groups with 30%A and 40%A (Post hoc Tukey test, $p<0.05$).

Both NaF and acetone concentration up to 20% significantly affected injectability, with an increase in the concentration of either resulting in a significant decrease in the force required to extrude the material (Post hoc Tukey test, $p<0.05$).

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Table 4.10 Mean extrusion force and SD of first and second push of groups 10:0, 9:1, 8:2 and 7:3 with different concentrations of acetone.

Groups	% Acetone	Mean (SD) of extrusion force (N)		
		First push	Second push	Mean of first and second push
10:0	0%A	52.6(10.1)	62.4(11.9)	57.6 (11.7)
	10%A	32.5(6.9)	30.9(4.8)	31.7 (5.7)
	20%A	12.9(1.7)^{a}	13.1(1.7)^{b}	13 (1.6)^{r}
	30%A	11.9(2)^{a}	10.1(2.5)^{bc}	11 (2.3)^{r}
	40%A	10.3(2.1)^{a}	10.2(1.5)^{c}	10.2 (1.7)^{r}
9:1	0%A	33.5(5.2)	32.6(3.5)	33.1 (4.3)
	10%A	13.5(1.3)	14.3(2.6)	13.9 (2)^{a}
	20%A	8.4(1.4)^{d}	8.6(1.4)^{e}	8.5 (1.4)^{s}
	30%A	9.0(0.7)^{d}	9.1(2.4)^{e}	9.1 (1.6)^{s}
	40%A	8.0(1.3)^{d}	8.4(1.4)^{e}	8.2 (1.3)^{s}
8:2	0%A	20.2(1.2)	19.4(1.6)	19.8 (1.4)
	10%A	11.4(2)^{f}	12.5(1.2)^{i}	11.9 (1.8)^{t}
	20%A	9.6(0.9)^{fg}	10.0(1.3)^{ij}	9.8 9 (1.1)^{tu}
	30%A	7.9(1.3)^{gh}	7.3(1.7)^{jk}	7.7 (1.5)^{uv}
	40%A	7.3(1)^{h}	6.7(0.5)^{k}	7 (0.8)^{v}
7:3	0%	14.2(2.3)^{l}	14.1(3.2)^{o}	14.2 (2.7)^{x}
	10%	11.1(2.3)^{lm}	10.9(2.5)^{op}	11 (2.3)^{xy}
	20%	9.8(2.1)^{me}	9.6(1.5)^{p}	9.7 (1.8)^{y}
	30%	7.7(1)^{n}	7.5(1.1)^{q}	7.6 (1)^{y}
	40%	7.3(1.1)^{n}	7.4(0.7)^{q}	7.4 (0.9)^{y}

The entries are mean value with SD in the parenthesis. No differences were found between first and second push ($p > 0.05$ Using Paired Sample t test). Values exhibited similar superscript letters indicate no significant difference within columns within groups ($p > 0.05$) as determined using Post hoc Tukey method

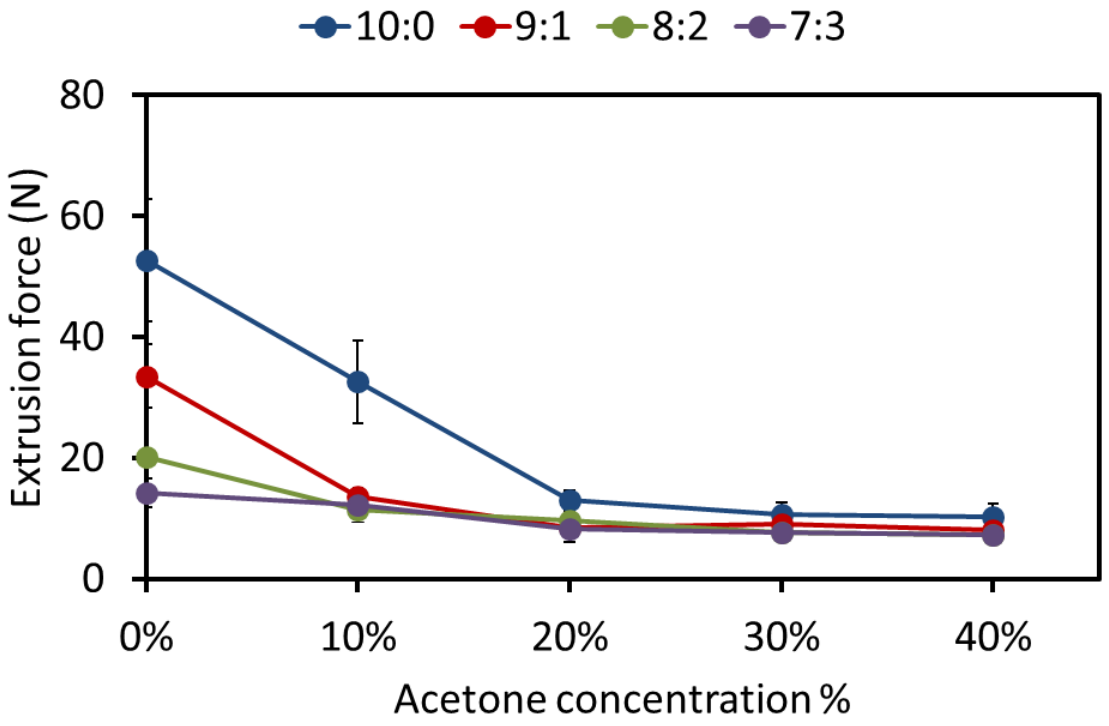

Figure 4.31 Mean extrusion force and SD of first push of groups 10:0, 9:1, 8:2 and 7:3 with different concentrations of acetone

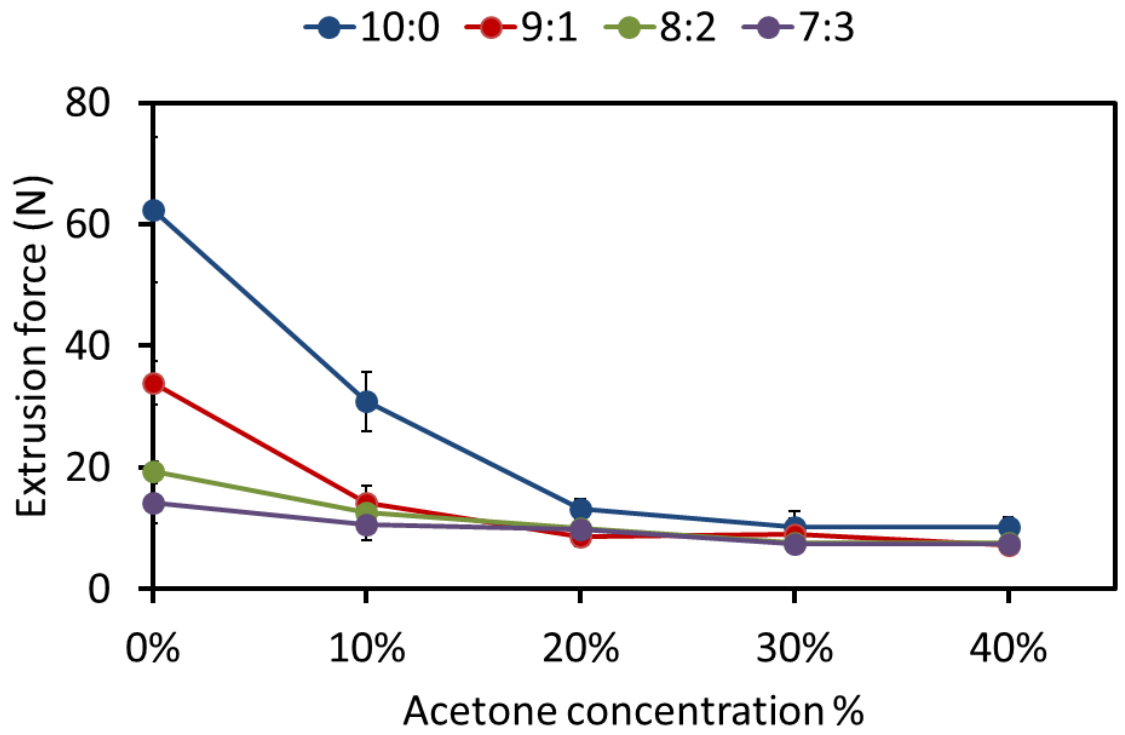

Figure 4.32 Mean extrusion force and SD of second push of groups 10:0, 9:1, 8:2 and 7:3 with different concentrations of acetone

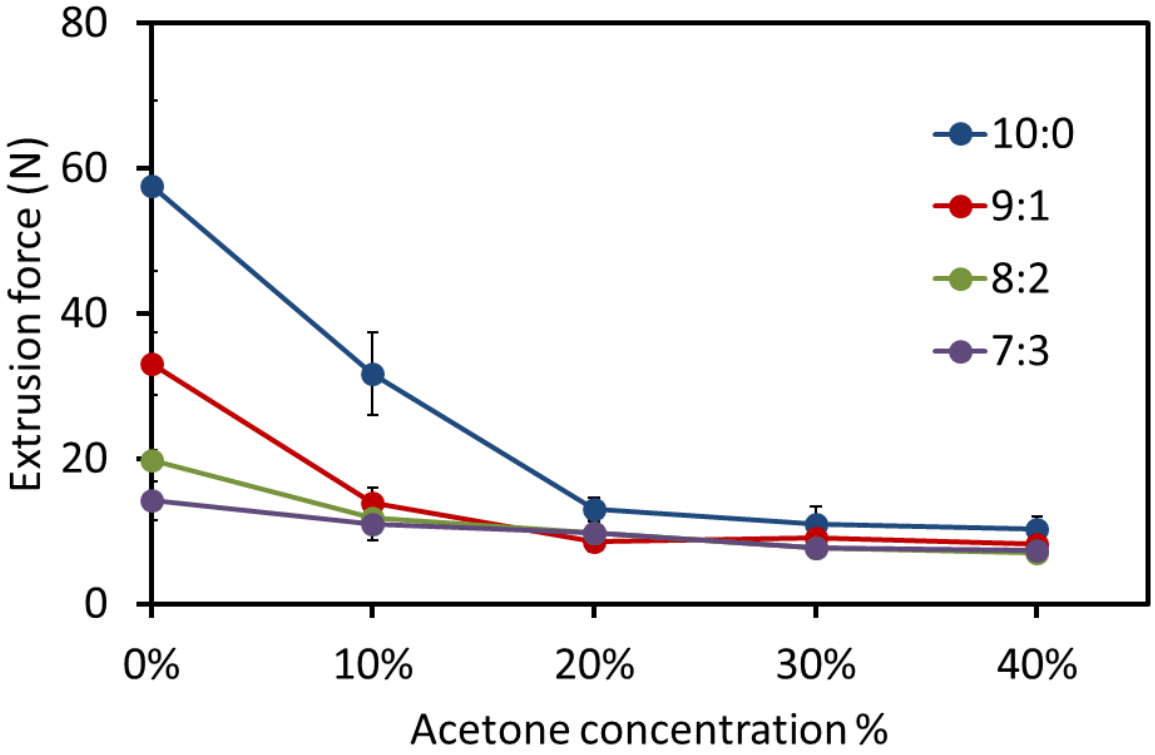

Figure 4.33 Mean extrusion force and SD of groups 10:0, 9:1, 8:2 and 7:3 with different concentrations of acetone.

The data for the average value of extrusion force could also be presented as a function of fluoride and acetone concentrations, as illustrated in figures 4.34 and 4.36. A linear model was fitted to this data. There was an inverse correlation between extrusion force and %A acetone concentrations (see figure 4.34). The relationship was significant for all experimental groups at $p< 0.05$. The r values are 0.89, 0.81, 0.91 and 0.95 for groups 10:0, 9:1, 8:2 and 7:3 respectively. The correlation between extrusion force and fluoride concentrations are shown in Figure 4.36. There was an inverse correlation between extrusion force and fluoride% concentrations at all acetone concentrations. The reduction in extrusion force with the addition of acetone was greater at lower concentrations of fluoride and vice versa.

The results of the two way analysis of variance test of the data showed that acetone and fluoride concentrations had significant effect on extrusion force at ($P \leq 0.001$). The effect of different levels of Acetone% depended on what level of Fluoride % was present. There was a statistically significant interaction between Acetone% and Fluoride % ($P \leq 0.001$).

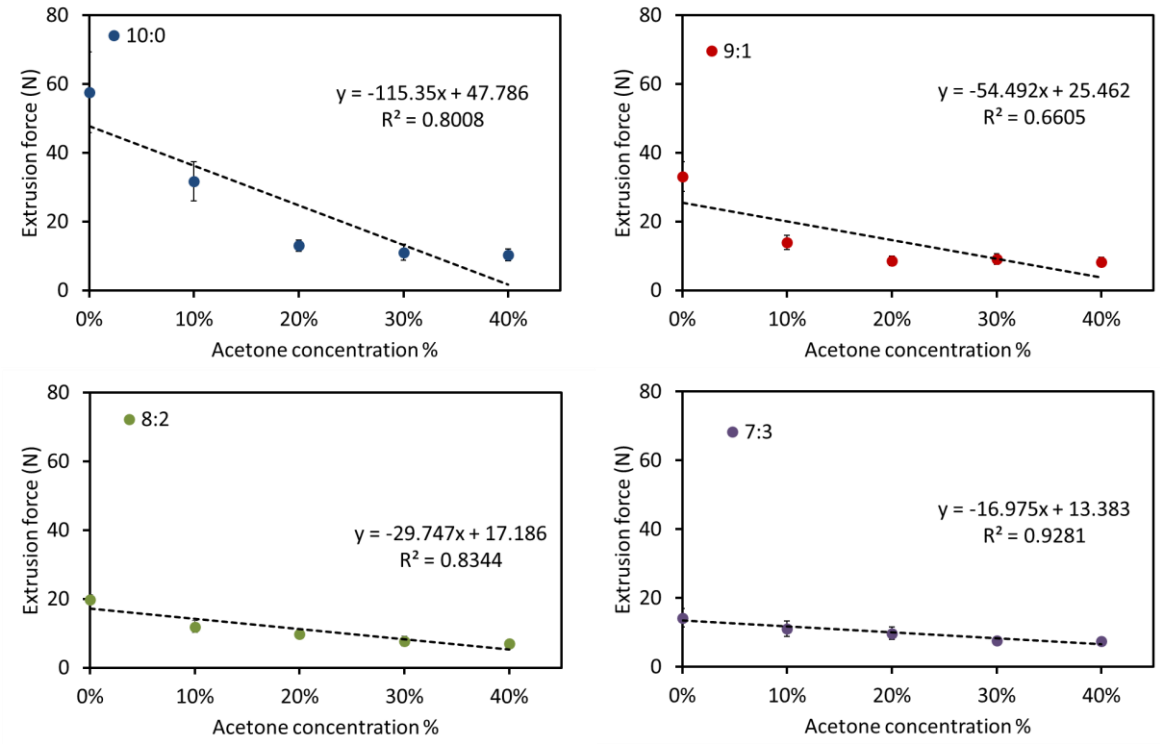

Figure 4.34 Relationship between extrusion force and acetone concentrations. Data represents mean value with error bars represent SD. The r values are 0.89, 0.81, 0.91 and 0.95 at (P = <0.001) for the groups 10:0, 9:1, 8:2 and 7:3 respectively.

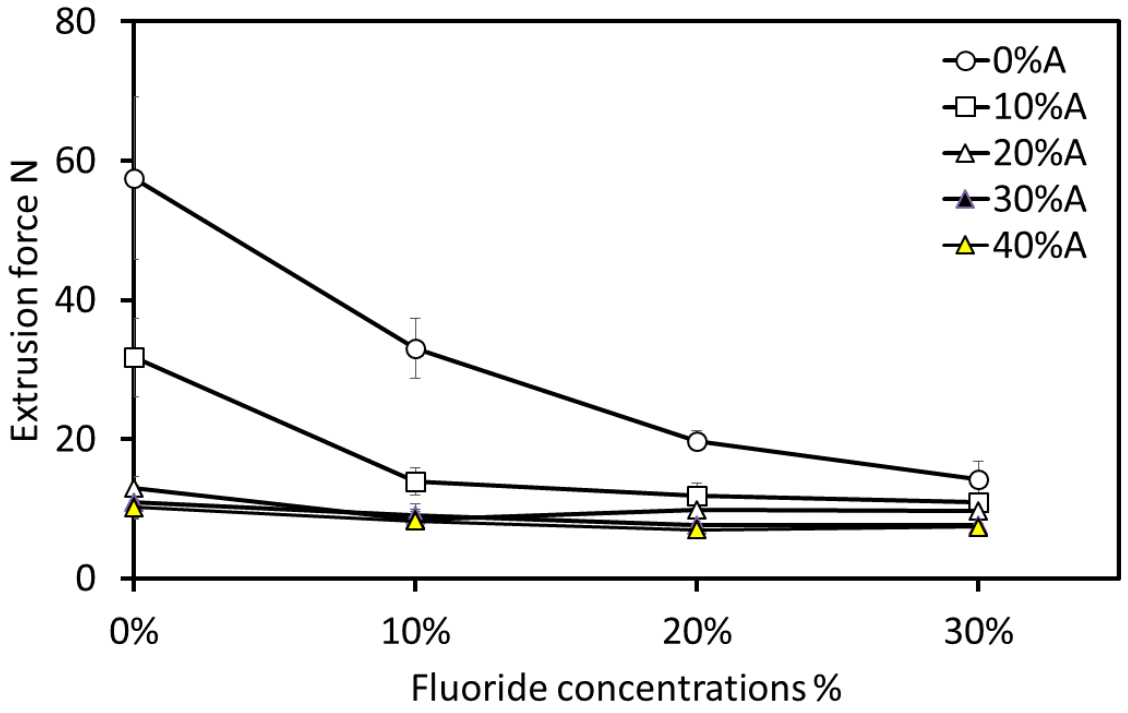

Figure 4.35 Mean extrusion force of all experimental materails at different fluoride concentartions.

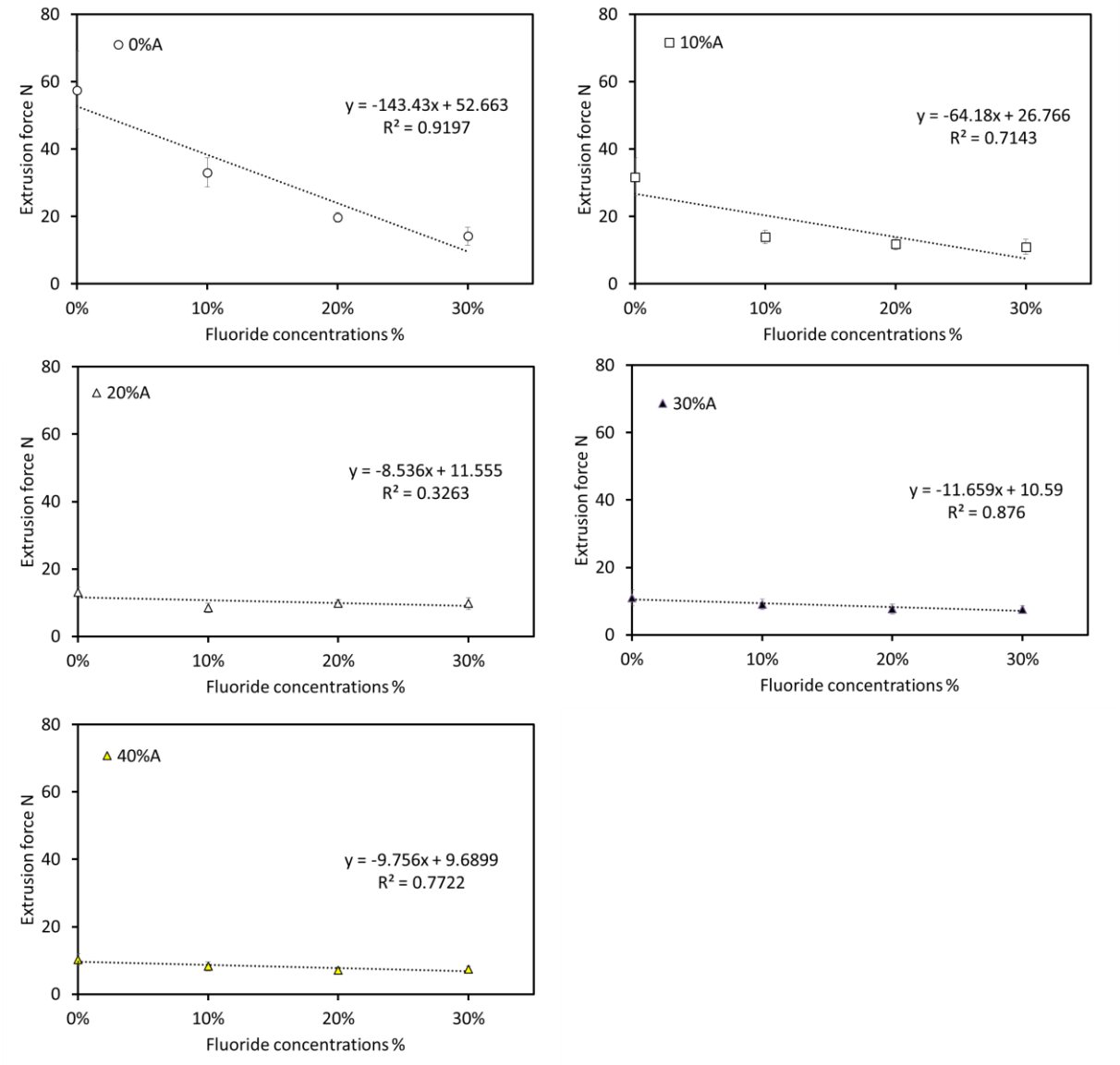

Figure 4.36 Relationship between extrusion force and fluoride concentrations at 0%A, 10%A, 20%A, 30%A and 40%A. Data represents mean value with error bars represent SD. The r values are 0.95, 0.84, 0.56, 0.93 and 0.87 of the 0%A, 10%A, 20%A, 30%A and 40%A respectively.

The mean extrusion force of Newtonian fluids are shown in table 4.11. There was high variation in the extrusion force of the samples of the water and Newtonian fluids. The graph obtained from Newtonian fluids (see figure 4.37) shows the yield force of first push was lower than the second push. There was no significant difference between these four fluids, despite the fact that they have different viscosities see table 4.11.

Table 4.11 Mean extrusion force of Newtonian fluids.

Newtonian fluids	First push	CV%	Second push	CV%	Viscosity at 25°C in mPa.s
Water	3.4 (1.3)	39	3.1 (1.1)	37	-
B29	4.7 (0.80	18	5.5 (1.1)	20	28.81
B200	4.1 (1)	24	5.1 (1.5)	30	198.5
B10200	4.6 (0.2)	6	4.5 (1.2)	26	9959

No significant differences were found bwteen Newtonian fluids (p> 0.05, ANOVA).

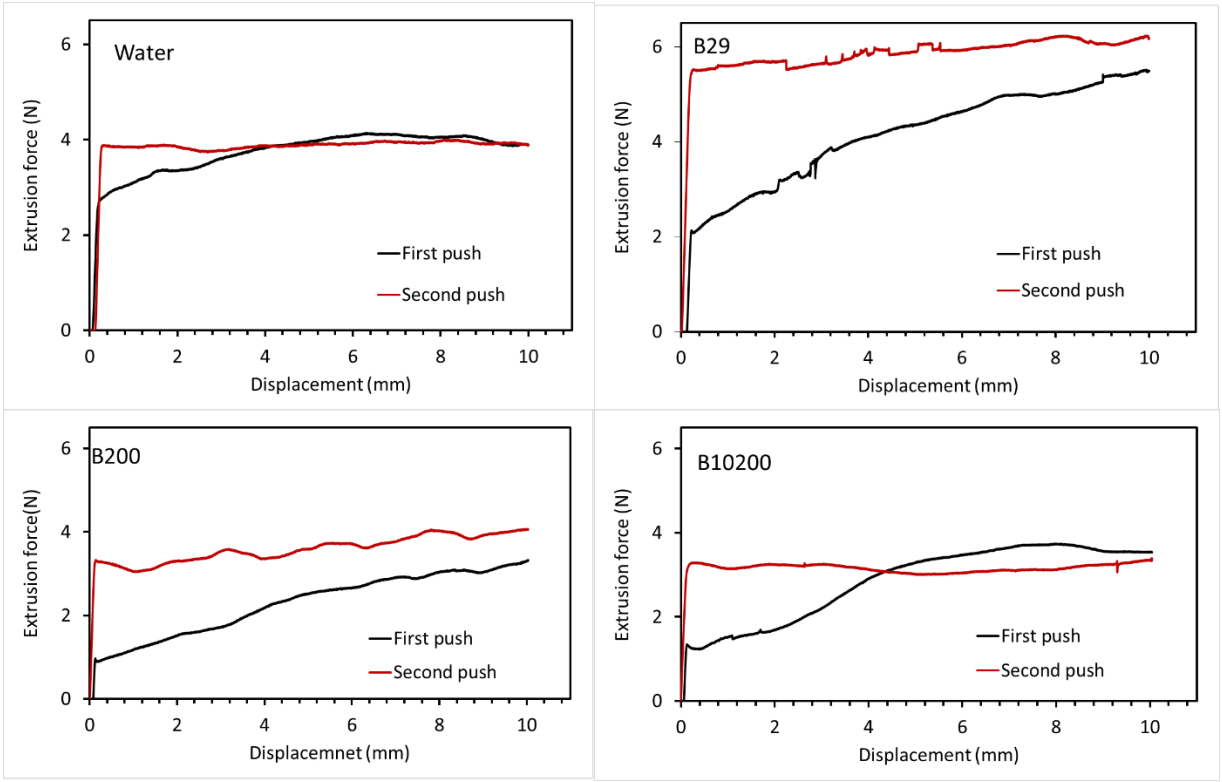

Figure 4.37 Representative force displacement curve for Newtonian fluids and water.

4.5.5 *Fluoride release*

The median fluoride release (IQR) values of all experimental materials at days 1, 7, 14, 21, 28, 42, 70, 100 and 160 are shown in table 4.12. Group 10:0 had small amount of fluoride release only at day 1, followed by a negligible amount of fluoride release.

Fluoride release of groups 9:1 at 10%A and 20%A were higher than 0% A till day 21 for 10%A and till day 70 except day 3 for 20%A (Mann-Whitney test, $P<0.05$). No significant differences found between 10%A and 20%A except at day 21 and 70 at ($P<0.05$, Table 4.12).

Fluoride release of group 8:2 at 20%A was significantly higher than 0%A and 10%A except at day 1 at ($P<0.05$). However, fluoride release at 10%A was significantly higher than 0%A till day 21 ($P<0.05$, Table 4.12)

Fluoride release of group 7:3 at 10%A released higher fluoride than 0%A except at day 2 at ($P<0.05$). However, at 20%A was significantly different from the 10%A only at day 1 and from 0%A at days 42 and 70 at ($P<0.05$). However, at 10%A released higher fluoride than 0%A except at day 2 at ($P<0.05$).

The pattern of fluoride release were similar for all experimental materials. All fluoride containing experimental materials 9:1, 8:2 and 7:3 had an initial high level of fluoride release for the first day. Fluoride release then decreased sharply from day 2 until day 14 and then after the first two weeks the amount of fluoride release became steady at a low level, gradually decreasing with time (see figures 4.38, 4.39, 4.40, 4.41, 4.42, and 4.43).

Table 4.12 Median fluoride release values of groups 9:1, 8:2 and 7:3 with different concentrations of acetone, at different days.

Groups	% Acetone	Median Fluoride release (IQR) µg/cm²/day								
		Day 1	Day 7	Day 14	Day 21	Day 28	Day 42	Day 70	Day 100	Day 160
10:0	0%	0.3	0	0	0	0	0	0	0	0
	10%	0.1	0	0	0	0	0	0	0	0
	20%	0.1	0	0	0	0	0	0	0	0
9:1	0%	122 (22.1)	21.2 (7.4)	4.1 (0.6)	3 (1.1)	1 (0)^{n}	0.5 (0.1)^{q}	0.3 (0.1)	0.2 (0.1)	0.1 (0.1)
	10%	149 (22)^{a}	24.6 (2.4)	8.4 (0.5)	4 (0.4)	1 (0.1)^{n}	0.54 (0.3)^{qr}	0.5 (0.4)	0.1 (0.1)	0.1 (0.2)
	20%	176 (17.5)^{a}	28.9 (4.4)	17.8 (7.1)	13 (2.2)	3 (1.3)	1 (0.3)^{r}	1.2 (0.2)	0.4 (0.1)	0.1 (0.1)
8:2	0%	308 (21)	26.2 (10.7)	5.8 (2.5)	5 (2)	2 (1)^{o}	2 (0.2)^{s}	1.7 (0.3)	0.7 (0.2)	0.5 (0.1)
	10%	456 (32)^{b}	43.9 (6.2)	13.3 (2.5)	9 (1)	3 (0)^{o}	1 (0.5)^{s}	1.1 (0.5)	0.3 (0.2)	0.6 (0.2)
	20%	457 (28)^{b}	82.4 (18.7)	34.3 (16.2)	21 (14)	12 (7)	6.25 (2)	6.5 (1.6)	1.1 (0.1)	0.6 (0.2)
7:3	0%	505 (164)^{cd}	77.9 (1.9)	29.9 (5.8)	14 (6)^{l}	6 (4)	3 (2)	3.1 (1.7)	2.1 (0.9)	1.1 (0.7)
	10%	579 (48)^{c}	85.1 (10.7)	44.8 (7.8)	35 (5)^{m}	19 (6)^{p}	8 (5)^{t}	8.1 (4.5)	2.6 (1.9)	1.8 (0.2)
	20%	497 (46)^{d}	63.2 (34.1)	28.2 (1.5)	21 (9)^{lm}	15 (2)^{p}	9 (2)^{t}	8.7 (2.1)	2.5 (0.1)	1.5 (0.4)

The entries are median value with IQR in the parenthesis. Values exhibited similar superscript letters indicate no significant difference within columns ($p > 0.05$) as determined using Mann-Whitney U.

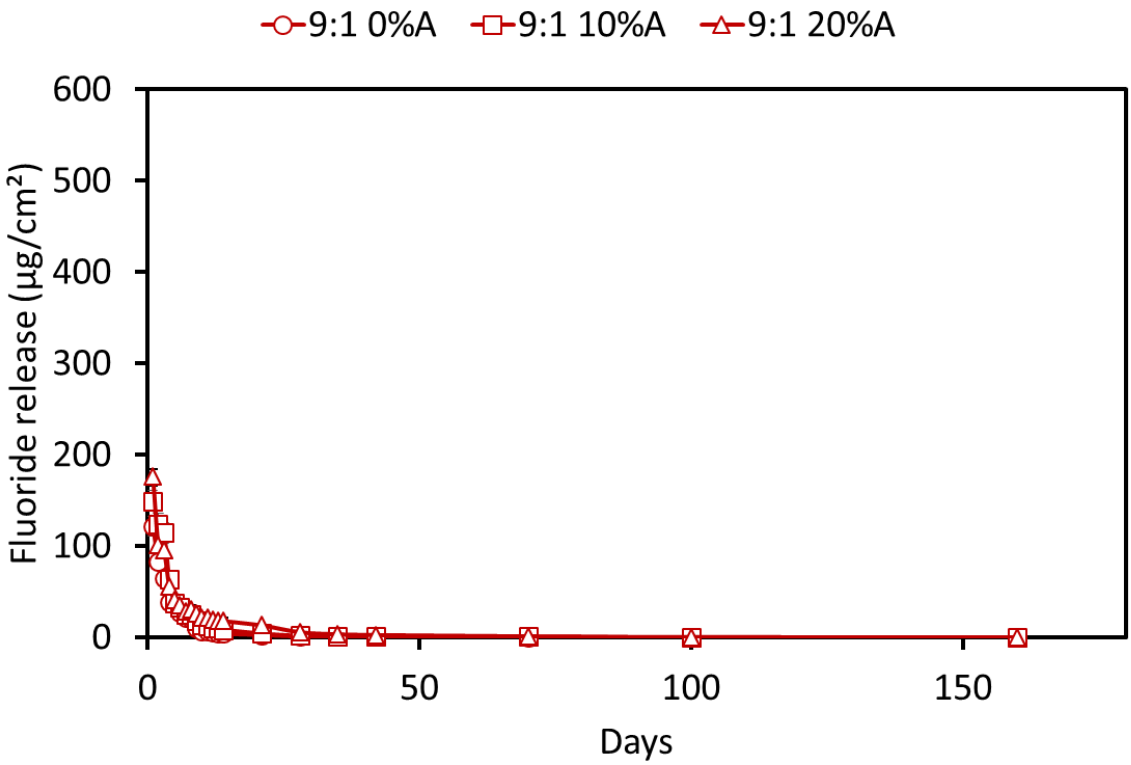

Figure 4.38 Median fluoride release for group 9:1 with different concentrations of acetone during 10 weeks study.

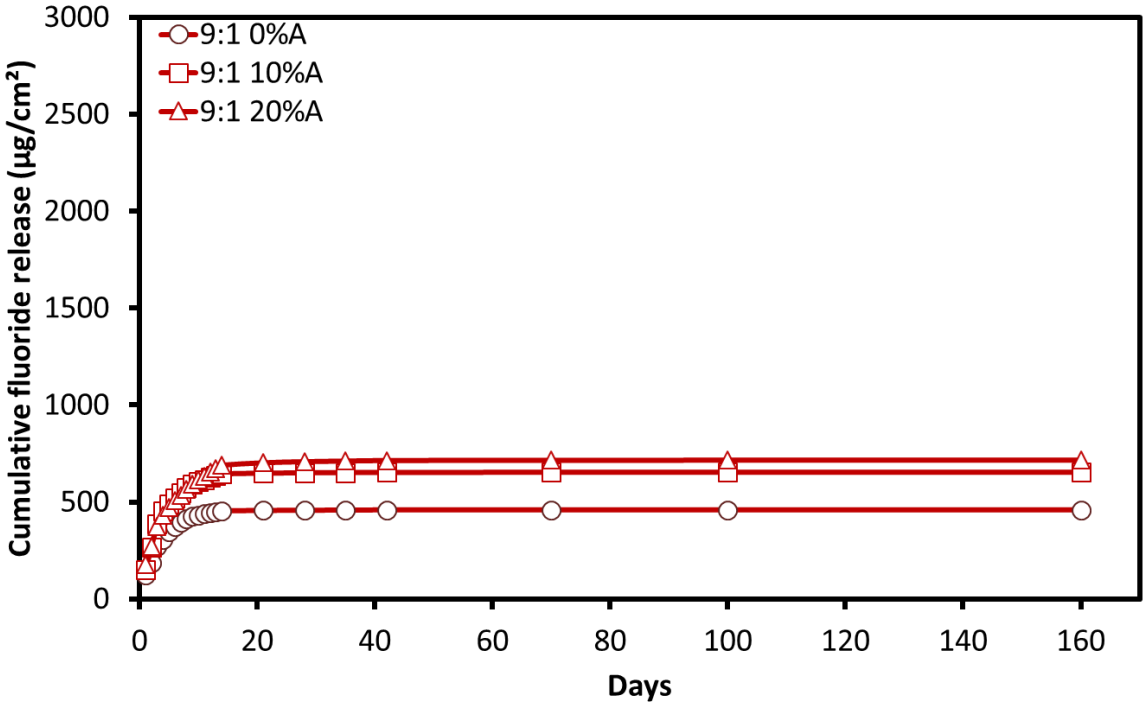

Figure 4.39 Cumulative fluoride release for the 9:1 group with different concentrations of acetone 0%A, 10%A and 20%A.

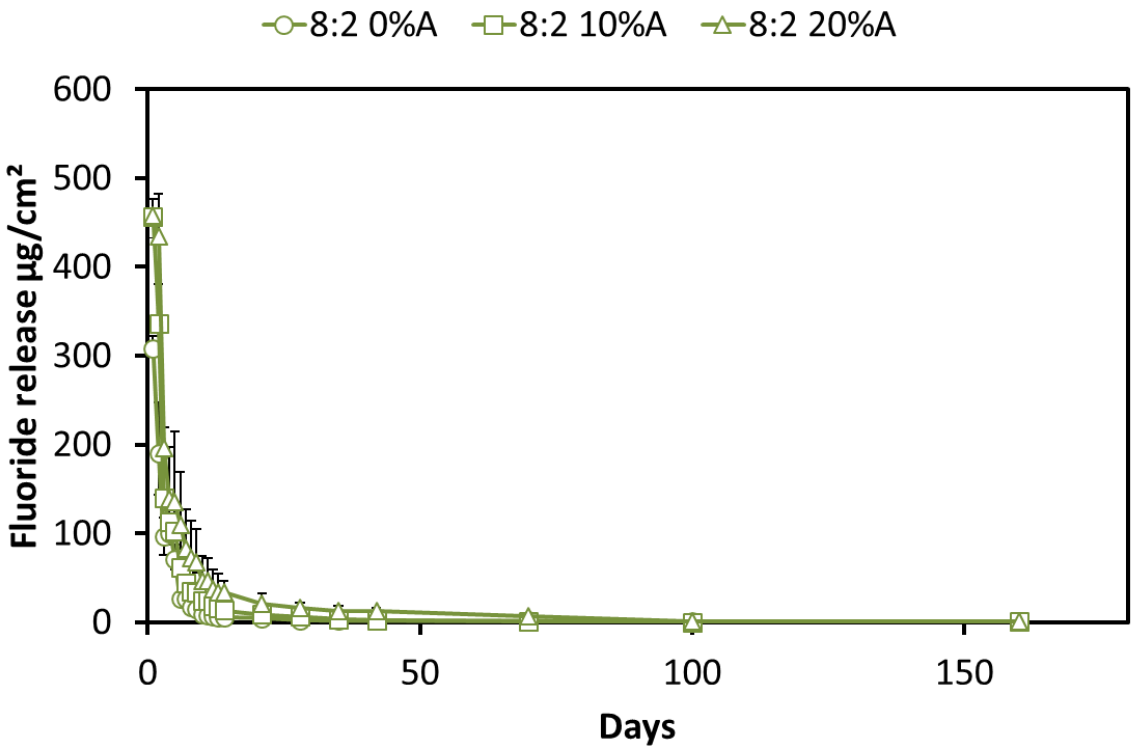

Figure 4.40 Median fluoride release for group 8:2 with different concentrations of acetone during 10 weeks study.

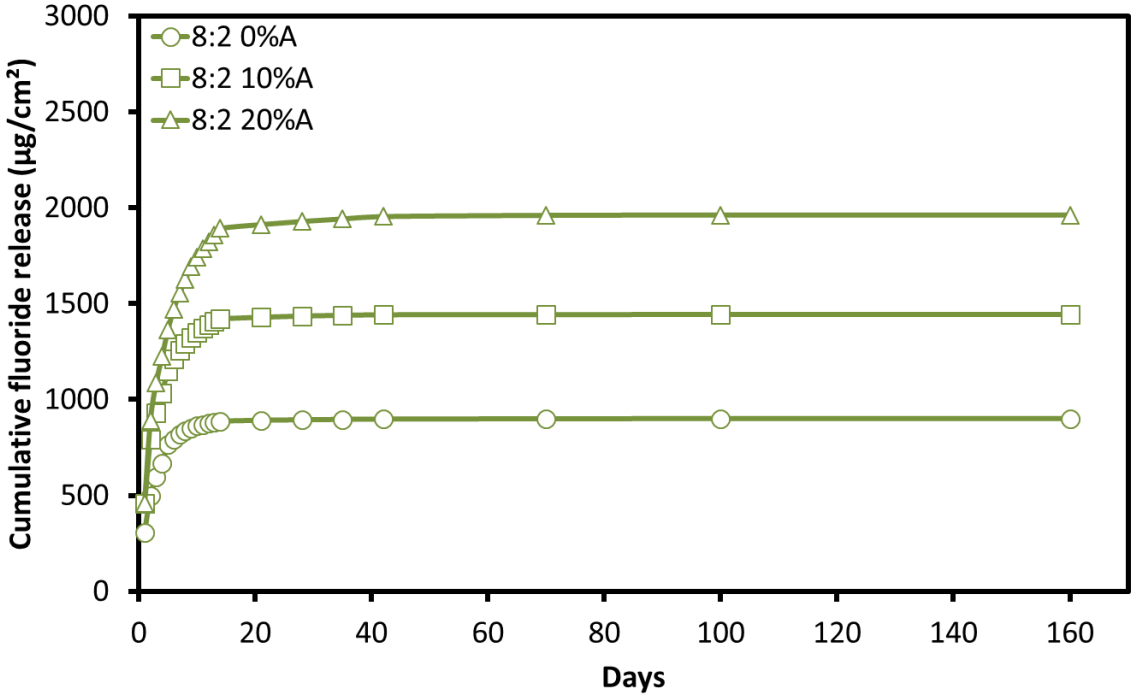

Figure 4.41 Cumulative fluoride release for the 8:2 group with different concentrations of acetone 0%A, 10%A and 20%A.

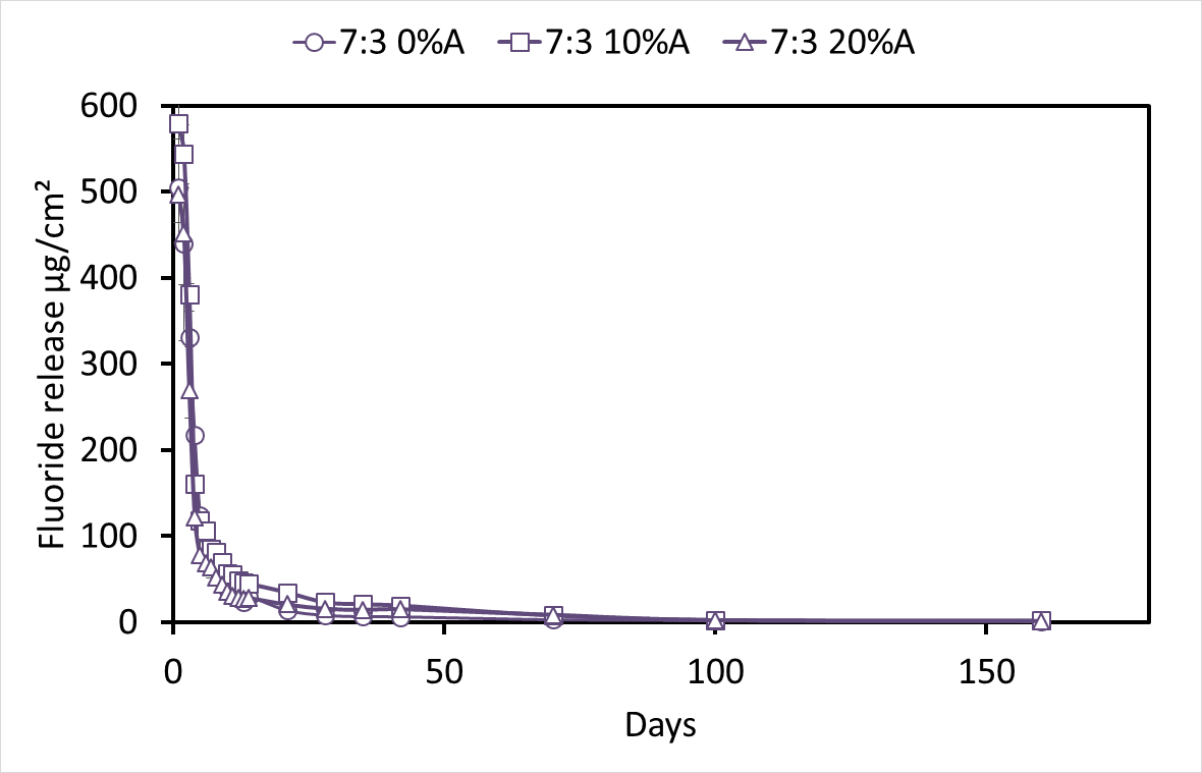

Figure 4.42 Median fluoride release for group 7:3 with different concentrations of acetone during 10 weeks study.

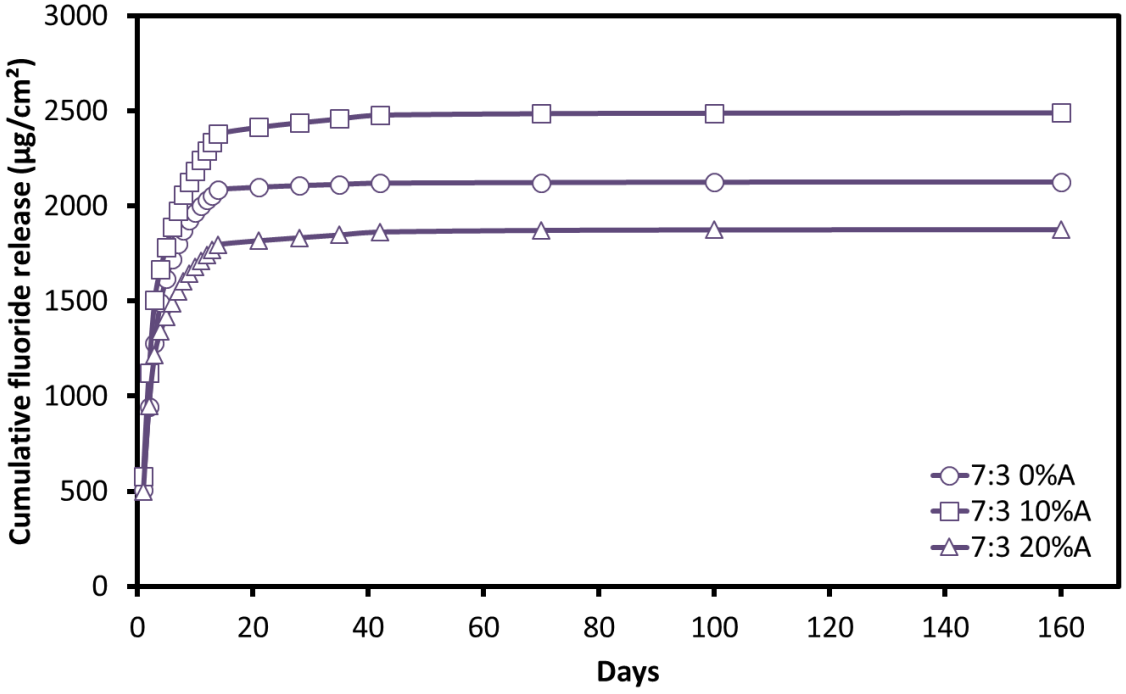

Figure 4.43 Cumulative fluoride release for the 7:3 group with different concentrations of acetone 0%A, 10%A and 20%A.

The data for the average value of fluoride release could also be presented as a function of fluoride concentrations, as illustrated in figure 4.45. A linear model was fitted to this data. The correlation between fluoride release and fluoride concentrations at day 28 are shown in figure 4.45. There was significant correlation at 0%A, 10%A and 20%A at $p < 0.05$. The r values are 0.92, 0.9 and 0.93 of the 0%A, 10%A and 20%A respectively.

The results of three way ANOVA showed that acetone and fluoride concentrations and storage time had significant effect on fluoride release at ($P \leq 0.001$). There was a statistically significant interaction between fluoride%, acetone% and storage time ($P \leq 0.001$).

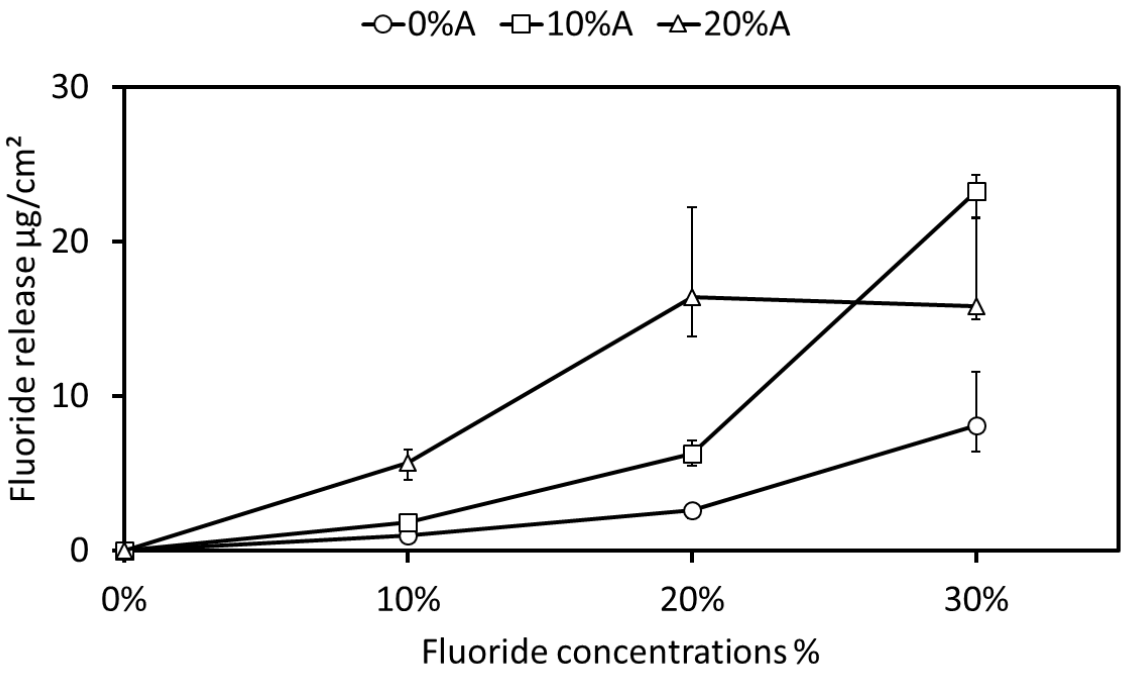

Figure 4.44 Relatioship between fluoride release and and fluoride concentrations at day 28. Data represents median value with error bars represent IQR.

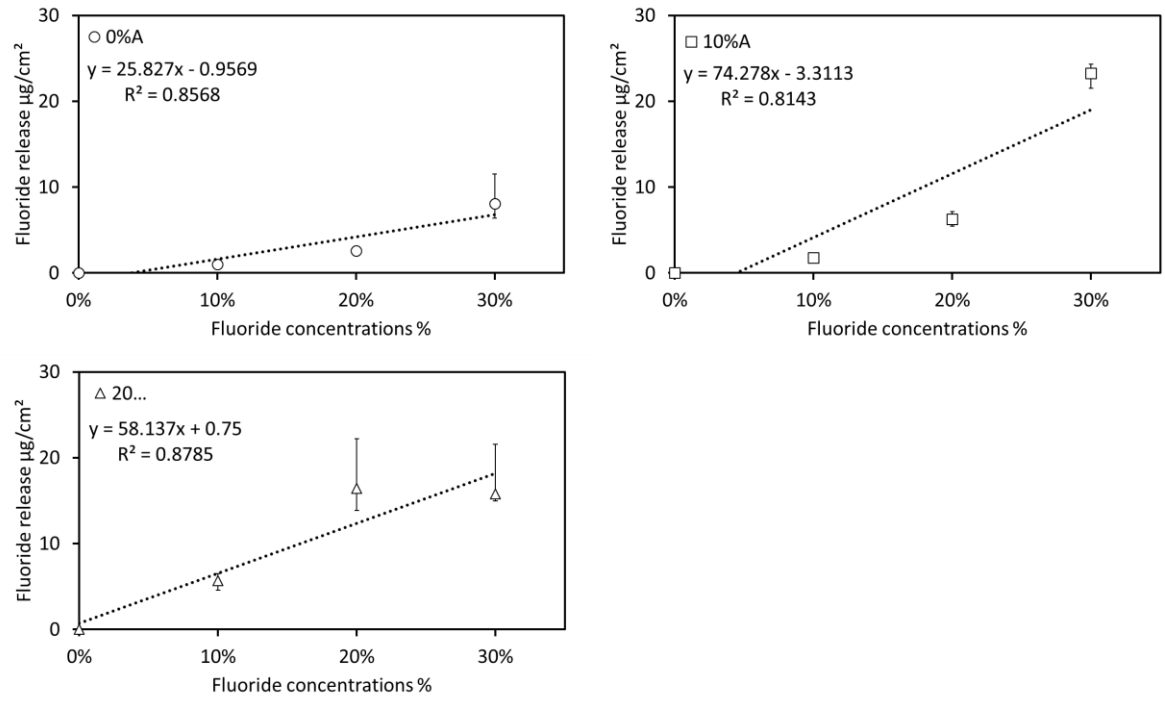

Figure 4.45 Relationship between fluoride release and fluoride concentrations at day 28 and at 0%A, 10%A, 20%A. Data represents median value with error bars represent IQR. The r values are 0.92, 0.9 and 0.93 of the 0%A, 10%A and 20%A respectively

4.5.6 *Summary of results*

The setting characteristics of experimental materials, DoC and heat release, were affected by the NaF and acetone concentrations. With an increasing in concentrations of both acetone and NaF together above 20% the effect was detrimental. However, the effect of curing time should not be neglected as DoC increased with increasing curing time.

Both NaF and acetone concentration up to 20% significantly affected injectability, with an increase in the concentration of either resulting in a significant decrease in the force required to extrude the material ($p<0.05$).

All fluoride contained groups had released fluoride for up to 160 days. The amount of fluoride release depend on the concentrations of NaF in each group the higher the NaF concentrations the higher fluoride release. Acetone had not detrimental effect on the fluoride release of the materials up to 20%A.

4.6 Discussion

A new fluoride releasing acrylic potential orthodontic adhesive has been developed. Orthodontic adhesives should have sufficiently low viscosity to allow easy positioning of brackets during treatment. The previously developed experimental materials were considered too viscous for orthodontic use, and therefore it was essential to improve the handling characteristics of the material by reducing its viscosity. Acetone was chosen for this due to its common use in dental materials (Yiu *et al.*, 2005; Van Landuyt *et al.*, 2007; Wiegand *et al.*, 2007; Ekambaram *et al.*, 2015), in particular it has been shown to not reduce the bond strength of resin based adhesives to enamel (Reis *et al.*, 2003; Lopes *et al.*, 2006).

There are some important properties for the developed materials to maintain after acetone addition such as setting characteristics and fluoride releasing ability. Therefore in order to investigate the effect of the acetone addition on the material a number of characteristics were measured, including injectability, setting characteristics and fluoride release. Four experimental groups were prepared in this study based on fluoride content including group 10:0 with no fluoride representing a control group, group 9:1 with 10% fluoride, 8:2 with 20% fluoride and 7:3 with 30% fluoride (Su *et al.*, 2010; Zahroon, 2014; Al-Sammarraie, 2015) . These groups were chosen as it has been shown they have fluoride release (except 10:0) up to 192 days in addition to having recharging ability when they are used as a fissure sealant (Zahroon, 2014). It was shown that the groups 10:0 and 9:1 have a comparable bond strength to commercial orthodontic adhesives in addition to having fluoride release (group 9:1) comparable to a commercial GIC (Su *et al.*, 2010).

Sodium fluoride (NaF) was used as a source of fluoride in this study as NaF is a very soluble salt and it is easily dissolves to free Na^+ and F^- ions (Nakajo *et al.*, 2009). NaF has been added to commercial MMA based acrylic orthodontic adhesives and it has been shown that the material can release fluoride for up to 6 months (Iijima *et al.*, 2013). Some studies have investigated other sources of fluoride including stannous fluoride (SnF_2) and calcium fluoride (CaF_2) as these sources are reported to provide continuous sustained level of fluoride for long time (Kodkeaw *et al.*, 2010). The solubility of NaF is not affected by the pH of the medium unlike fluorosilicate glass and calcium fluoride (Anusavice *et al.*, 2005; Shen *et al.*, 2007). Therefore, NaF was used in this study as there is a fluctuating pH in the oral environment. In addition NaF has been used before as a source of fluoride in orthodontic adhesives and in fissure sealants and it was shown fluoride release up to 192 days (Shen *et al.*, 2007; Zahroon, 2014).

To make the material more easily absorb water HEMA was used, as HEMA is hydrophilic and facilitates water sorption into the material. (Yiu *et al.*, 2006; Kodkeaw *et al.*, 2010). Polymers

of HEMA are flexible and porous (Tay *et al.*, 2002a) which might contribute to easy debonding at finishing. HEMA was used with MMA at 40:60wt% as it has previously been shown to be the best ratio to provide fluoride release after addition of NaF (Su *et al.*, 2010). MMA was chosen as a monomer and it is easily polymerizes. PMMA powder was used as an organic filler as it is compatible with MMA and it has been used before for denture construction. PMMA is a linear polymer with low density chains (Ferracane *et al.*, 1998; Ferracane, 2006) which results in a softer, more flexible and potentially weaker material (Gorelick *et al*., 1978). At the end of orthodontic treatment on average less enamel loss has been shown to occur during adhesive removal of an unfilled polymethylmethacrylate adhesive than removal of highly filled composite adhesive (Brown and Way, 1978; Su *et al.*, 2010). Less enamel fracture was seen after debonding an MMA based resin (Super-Bond and experimental MMA-based resin) in comparison to conventional Transbond XT (Kim *et al.*, 2014). Therefore, PMMA powder was used to make the experimental materials safe and easy removal during debonding.

It has been shown that photo-initiators like CQ can undergo polymerization under ambient light (Crivello, 2009). Therefore, for preparation of the experimental groups at first the liquids were prepared in dark amber bottles wrapped with aluminium foil to reduce the potential for accidental activation of the photo-initiator. The CQ and DMAEMA were mixed in monomers for 30 minutes in HEMA alone then 90 minutes in mixture of HEMA and MMA to allow thorough dissolution of the CQ and DMAEMA in the liquid as this has previously shown to be effective (Zahroon, 2014) and it has been shown that proper dissolution and homogeneous mixing are vital for a functional initiator system (Ogunyinka *et al.*, 2007).

The liquid and powder were mechanically mixed using a DAC system (dual asymmetric centrifugation) with the aim of producing a homogenous mixture (Massing *et al.*, 2008) and to reduce the chance of introducing air bubbles into the material, thereby reducing the oxygen content of the material, which could influence curing. The DAC system is considered to be a suitable technology for mixing of composite resin (Kumar and Shortall, 2011). One of the advantages of this method is the speed of mixing which can be set up to 3300 rpm which cannot achieved by hand mixing. This higher speed of mixing results in more homogenous paste. As it was shown increasing speed of mixing results in a more homogenous mixture (Massing *et al.*, 2008). Another advantage of this method is that DAC provides two type of rotation at the same time. One is clockwise centrifugation of the sample, which tries to push the material in to the corners of the sample container. The second is counter-clockwise rotation of the container, which takes place around container's own vertical axis which forces the material towards the centre of the container (See figure 2.14). These two types of rotations lead to shear forces and result in a homogenous mix (Massing *et al.*, 2008). The DAC system is recommended for

mixing experimental composite resins (Kumar and Shortall, 2011) and it has been used previously by many researchers for mixing experimental resins (Lee *et al.*, 2006; Faltermeier *et al.*, 2007; Garoushi *et al.*, 2008; Schneider *et al.*, 2008).

In order to consider the effects of each of the independent variables Acetone%, Fluoride%, exposure time on the DoC (dependant), a three way ANOVA was undertaken. There is no three way ANOVA for non-parametric data. Therefore, the data was transformed to normal using a two-step transformation to normality in SPSS (Templeton, 2011) as previously described (Ramadas *et al.*; Mulcan *et al.*, 2015). Shapiro-Wilk test at ($P<0.05$) indicated the data to be normally distributed after transformation. Another three way ANOVA was taken for untransformed data assuming as normally distributed. The results of both transformed and untransformed data showed the same interactions between each variables. The same procedure was done for the data of fluoride release taking fluoride, acetone and daily fluoride release as independent variables, see appendix 2.

4.6.1 *Acetone loss*

The experimental materials were prepared in sealed containers (pots) to prevent evaporation of the material (monomers and acetone). However, during opening the lids of the pots some weight loss is inevitable. Two preliminary studies were conducted to demonstrate the amount of monomer and acetone loss during preparation and storage for two samples of each 10:0 and 7:3 at 0% acetone and 40% acetone. It was found that material loss did not occur during storage and preparation. It only occurred during opening the lid of the pots, which was less than 1% and 2% of the total weight after 5 and 30 minutes respectively. However, in real life with good laboratory technique the lid is unlikely to be left off for more than 2 minutes at any one time. Therefore the minimal loss of acetone (and monomers) observed after 5 minutes of leaving the lid off is not considered important. This indicated acetone loss does not appear to be a significant factor.

The weight lost was likely to be due to evaporation of monomers and acetone and this is supported by comparison of the weight loss of 0%A to 40%A. The vapour pressure of acetone is very high. It has previously been shown that up to almost 80% of acetone evaporates within 10 minutes of exposure to air (Nihi *et al.*, 2009). However, in the mixed material less than 2% of the material weight was lost (acetone + monomers) after 10 minutes. This might be due in part to the presence of HEMA which has been shown to reduce acetone evaporation four-fold (Nihi *et al.*, 2009).

In order to maintain a consistent approach and for standardization all materials were prepared within a week of any experiment to be done. The lids of the pots were kept tightly shut whenever feasible. The materials were quickly dispensed from the pots for preparation of the samples.

4.6.2 *Degree of conversion*

ATR-FTIR was used for obtaining the DoC of the materials, as it is a commonly used technique for monitoring DoC (Alshali *et al.*, 2013; Leprince *et al.*, 2013; Al-Ahdal *et al.*, 2015). The DoC of a material is calculated by comparing the intensity of the carbon double bond in the aliphatic band, which is around 1638 cm^{-1}, relative to the peak of a bond that is not affected by polymerization; this is referred to as the internal reference peak. Previous studies on most dimethacrylate resins (like BisGMA ,TEGDMA and UDMA) use the aromatic band of the carbon-carbon double bond which is around 1608 cm^{-1} as the internal reference, as the aromatic band of the carbon-carbon double bond are not affected by the polymerization reaction (Chung *et al.*, 2002; Calheiros *et al.*, 2008; Al-Ahdal *et al.*, 2015). However, in the current study there was no aromatic band, therefore the carbonyl group of C=O at 1715 cm^{-1} was used as the internal standard (Pianelli *et al.*, 1999; Kashi *et al.*, 2007; Guo *et al.*, 2009). The C=O group was taken as internal standard as it does not participate in the polymerization reaction (Duray *et al.*, 1997) and has previously been used for monitoring the polymerisation of the HEMA monomer alone (Jafarzadeh Kashi *et al.*, 2007) and for monomer mixtures containing HEMA (Guo *et al.*, 2009; Abedin *et al.*, 2014). The carbonyl group peak was readily identifiable in the material, had no overlap with the other peaks and it appeared to be relatively stable during polymerization (see Figure 4.12).

It was shown that resin based adhesives that contain photo-initiator like CQ undergo polymerization under ambient light (Crivello, 2009). Therefore, all experimental procedures were carried out in dark room to reduce the effects of ambient light on the photo-polymerisation. For all experiments, the same LED curing light unit (Coltolux® LED, Coltene, USA) with an intensity of 800-850 mW/cm^2 was used. The LCU was returned to its battery charger after each use to make sure the LCU remained fully charged, as the charging is one of the factors which affects the LCU intensity (Jadhav *et al.*, 2011). In addition an intensity meter (Coltolux LED, Sussex, UK) was used every time to ensure the intensity of the LCU remained consistent throughout the experiment.

The current experimental materials were paste-like materials, therefore they were placed directly onto the ATR stage to enable measurement of changes in DoC in real time, for up to 120 seconds in increments of 10 seconds. This was to indicate the curing kinetics whilst monitoring the point at which the curing curve becomes flattened and to avoid post curing

effects between scans due to some continued reaction after the light unit was turned off, as it was shown that there is post curing polymerization (Par *et al.*, 2014; Al-Ahdal *et al.*, 2015) Therefore, a single scan FTIR spectra was taken to make sure that at this stage, we were not seeing some "post-curing effects" in the spectra due to some continued reaction after the LCU was turned off.

Fillers have been shown to have an impact on the DoC. The DoC has been shown to decrease with increasing filler content, in a monomer mixture of BisGMA/TEGDMA (Halvorson *et al.*, 2003; Garoushi *et al.*, 2008). It has been also shown that even differences in filler size and geometry result in differences in the DoC from 48% to 61% for a monomer mixture of BisGMA/UDMA/TEGDMA at a constant filler volume of 56.7% (Turssi *et al.*, 2005). This might be due absorption and scattering of a part of the light during the activation process consequently reducing the amount of energy absorbed by the materials and reducing the DoC of the material (Almeida and Mothé, 2009). This is due to refractive index of fillers which differs from the monomer mixture (Shortall *et al.*, 2008). The refractive index determines how much light is bent, or refracted, when entering a material. Whilst this study cannot be directly correlated to Almedia and Mothe 2009, I postulate that NaF and acetone both have a different refractive index to PMMA see Table 4.13. This will consequently be contributing to the refractive index change. This effect was seen at high fluoride concentrations, in particular when the concentration of acetone increased to 30%A and 40%A. Therefore, at these high fluoride and acetone concentrations the DoC decreased.

Table 4.13 Refractive index of the materials used in this study.

Materials	Acetone	PMMA	NaF
Refractive index	1.35 n	1.49 n (in the wavelength ranges 500-650nm)	1.32 n
References	(Sadek, 2004)	(Schubert *et al.*, 2005)	(Varner *et al.*, 2012)

The curing curves showed different materials reach a plateau (ie. curing slows because they have reached close to their maximal curing level) at different curing times depending on acetone and fluoride concentrations. It appears that for groups 8:2 and 7:3 at 30%A and 40%A the curing curve doesn't reach plateau during the illumination time of 120 seconds. This might be due to the combined effect of acetone and fluoride to extended curing. Therefore in the future, FTIR spectra should be recorded for a longer time.

The results show that the addition of acetone to the experimental acrylic resin affects the DoC of the material. As such, the first hypothesis which states "Acetone will decrease the DoC of the experimental resins" was partially supported by this. At the initial low acetone concentrations (up to 20% acetone) in the groups up to 20% fluoride, the DoC of the experimental acrylic resins increased, potentially due to increase diffusion of free radicals and more rapid growth of polymer chains after acetone addition (Cadenaro *et al.*, 2009; Malacarne-Zanon *et al.*, 2009). These results are similar to the results of previous study in which the DoC increased when between 2.5 and 5 M acetone was added to a BisGMA/TEGDMA mixture but above 5 M of acetone the DoC declined (Holmes *et al.*, 2007). Similarly, the addition of ethanol up to 20% led to an increase in DoC of a 40HEMA/60BisGMA mixture (Ye *et al.*, 2007).

However, at acetone concentrations greater than 20%A the rate and extent of polymerization were decreased and there may be several reasons for this. The first reason may be because of absorption by the solvent of the heat generated during the polymeric exothermic reaction (Lee *et al.*, 2004). Another possible explanation is that with increasing acetone concentration, there may be physical separation of free radicals, photoactivation constituents and growing polymer chains from each other thereby resulting in a reduced DoC (Holmes *et al.*, 2007).

Acetone has a relatively high specific heat capacity compared to other constituents (Table 4.14). The specific heat capacity of a substance is the amount of energy needed to change the temperature of 1 kg of the substance by 1°C. Therefore, as the acetone concentration increases, it will tend to absorb more of the heat during polymerization (Lee *et al.*, 2004), thereby reducing heat release and DoC at high acetone concentrations (30%A and 40%A). In addition to acetone, NaF has also a specific heat that is lower than PMMA. It appears that at 0% acetone concentrations the heat release is similar. While when both fluoride and acetone concentrations are increased the heat release changes accordingly.

Table 4.14 Specific heat capacity of some materials used in this study.

Materials	Acetone	PMMA	NaF
Specific heat $Jkg^{-1}K^{-1}$	2210	1446	1088
References	(Verma *et al.*)	(Iannone, 2014)	Sodium fluoride data sheet Materials Data from Crystran Ltd. Poole. UK

4.6.3 *Heat release*

DSC was used for monitoring thermodynamics of photo-polymerization as DSC is the most commonly used for this purpose (Maffezzoli *et al.*, 1995; Lovell *et al.*, 1999; Cotti *et al.*, 2011). An empty pan (crucible) was used as a reference against which to compare the sample, based on previous studies (Cotti *et al.*, 2011). A transparent cover was used to cover the samples to minimise acetone evaporation and oxygen inhibition on the surface of the samples, as it has been shown that oxygen decreases the heat release of dimethacrylate mixture measured by DSC (Nie *et al.*, 1998). The light source was adjusted to ensure 60 seconds of light exposure with the lights equally positioned above both the sample and reference pans. The 60 second light exposure was chosen because from the FTIR data it appeared that some groups took up to 60 seconds to reach a reasonable DoC (above 45%) and to monitor polymerization with time for a longer period of time.

The photo-polymerization of dental resin based adhesives are investigated at very low light intensity as low as 0.4 mW/cm² (Lovell *et al.*, 1999) others used different light intensities ranging from 1 mW/cm² to 1000 mW/cm² (Lovell *et al.*, 1999; Emami and Soderholm, 2005; Gatti *et al.*, 2007; Gao *et al.*, 2012). In the current study the light curing unit of the photocalorimetry accessory of DSC had a low intensity of 200-250 mW/cm^2. As increasing intensity increases polymerization reaction and heat release (Peutzfeldt and Asmussen, 2005). Therefore, some of the differences between the DoC data and heat release might attribute to the fact that higher intensity LED LCU (800 mW/cm^2) was used for FTIR data compared to the low intensity of light used for the DSC.

To calculate the heat release of the experimental materials only, the energy of light source must be subtracted from the total energy recorded. Some of previous studies have used the average of the peak areas under second and third thermogram as the energy from light sources only (Emami and Soderholm, 2005; Schneider *et al.*, 2008; Schneider *et al.*, 2009a). The reason that these previous studies used these peaks was based on assumption that no more polymerization happens after the first peak and the second and third peak are similar in height and referred to light sources only. However, this could not be used for the current experimental materials. As some of the experimental resins in this study (particularly those with 30% and 40%A) showed 6 peaks of similar low height peaks compared to groups with 0%A indicating these groups needed more time to fully polymerize. Previous work has used heat release of fully polymerized material to obtain the energy of light sources only, this is subtracted from the total heat release of the material to obtain heat release of the material only (Cook, 1992; Cadenaro *et al.*, 2005; Cadenaro *et al.*, 2008). Therefore, it was decided to further irradiate each specimen, after the

first 6 light exposure cycle, for an extra 10 minutes with a more powerful LED light with 800-850 mW/cm². A similar, constant peak was obtained after this extra irradiation time of each material, indicating they were fully polymerized and they were representing the energy of light sources only.

As mentioned earlier in section 1.4.2, some of the polymerization heat might be absorbed by acetone, NaF and PMMA, resulting in different levels of heat release. As each of these constituents have different specific heat capacity. Therefore, at 0% acetone concentration the heat release was similar as there was little difference in the heat capacity of PMMA compared to NaF that could not lead to differences in the heat release. While when both fluoride and acetone concentrations increased, the heat release decreased as some of the heat has been absorbed by the acetone (Lee *et al.*, 2004) and NaF. The experiment was carried out at a constant temperature of 37°C to keep the temperature of the cell consistent throughout the study and to simulate the oral temperature. Therefore, any differences observed might be due to different concentrations of each of these variables (Acetone, NaF and PMMA) within the materials. In addition these variables have different refractive indexes. As the materials photo-polymerize each of these variables will have affected reflection of light and the amount of energy which reaches the materials. Hence, the photo polymerization will have been affected differently.

All the experimental resins passed through three stages of polymerization, as described by Gatti *et al.* (2007) and Decker (1996), with differences in the contribution of each stage according to different concentrations of fluoride and acetone:

The first stage is the auto-acceleration stage, which occurs at the very beginning of the irradiation in which the reaction reaches its maximum value due to a rapid increase in viscosity of the material. It appeared that acetone prolonged and slowed down this process. This slowing down was significant at concentrations of acetone in excess of 30% for all experimental materials and in excess of 20% for groups 8:2 and 7:3.

The second stage is characterised by the material polymerizing at a constant rate. From the results it appeared that the experimental materials reached constant heat flow at a different times depending on acetone concentrations, with the presence of acetone slowing down reaching the constant rate of polymerisation. This may indicate acetone may acted as a physical barrier in reducing meeting free radicals, photoactivation constituents and growing polymer chains together (Holmes *et al.*, 2007). This effect was significant at higher acetone concentrations at 30% and 40%.

The final stage is auto-deceleration in which, due to increased viscosity, the propagation becomes diffusion controlled. However, as the addition of acetone decreased viscosity of the

materials propagation could continue for longer times without being diffusion controlled. It means acetone postponed auto-deceleration, in particular at higher acetone concentrations. The representative graph (Figure 4.21) shows that as the concentration of acetone increased the material continue to polymerize for longer times.

Overall, the results of DSC and FTIR analysis both support the conclusion that acetone affects the setting characteristics (DoC and heat release) of the materials. Up to 20%A this effect was not detrimental. Therefore, the second hypothesis which states "Acetone will decrease the heat released by the experimental materials" was partially accepted. However, there are some differences between the results of DSC (heat release) with that of FTIR (DoC). The differences may be attributed to the following reasons:

Firstly, DSC and FTIR are different techniques. FTIR monitors molecular changes occurring during polymerization, that is the conversion of C=C to C-C. While DSC measures heat release based on the exothermic polymerisation reaction of the material. Perhaps the presence of each of the variables acetone and fluoride affect these measurements differently. However, it has been shown that with both techniques the DoC is comparable (de la Caba *et al.*, 1998)

Secondly, different light sources were used for the polymerization of the materials, which was halogen light with 250 mW/cm² intensity for DSC and LED LCU with 800 mW/cm² for FTIR. It is known that the type of LCU affects polymerization reaction (Silva *et al.*, 2011). It has been shown that conventional LED LCU has an emission spectra centred around the maximum absorption spectra of CQ to polymerize CQ based materials compared to halogen light which has a broad emission spectra (Nomoto *et al.*, 2009). Another difference is the difference in the intensity of light used which was 250 mW/cm² for halogen light compare to 800 mW/cm² for LED all of these affect the results. As mentioned in the literature review in section (2.5.2), it has previously been shown increasing intensity increases polymerization reaction (Peutzfeldt and Asmussen, 2005) that is why most of the DoC curing curves flattened at only 80 s in comparison to heat release curves which took 120 s to flatten.

Thirdly, heat release by DSC was taken at 37°C however, FTIR spectra were measured at room temperature. It is known that temperature affects the polymerization reaction (Lovell *et al.*, 1999). Previous work has shown that increasing the temperature during polymerization from room temperature 22°C to mouth temperature 35°C results in an increasing DoC of the material (Price *et al.*, 2011). A higher temperature will lead to an increase in the polymerization rate by improving the monomer conversion, thereby encouraging more reaction to occur prior to vitrification (de la Caba *et al.*, 1998; Lovell *et al.*, 1999; Trujillo *et al.*, 2004; Daronch *et al.*, 2006). However, the DoC was not calculated from the heat release data to show whether the DoC from DSC data different from the FTIR data.

4.6.4 *Injectability*

A simple microcapillary rheometer was developed for measuring the injectability of the experimental materials. As it was discussed in section 2.3.3 a micro capillary rheometer can be used to measure the force that is required to extrude a material from a syringe termed the injectability (Ratier *et al.,* 2004). The pressure needed to extrude a material through a syringe can be predicted through measuring the viscosity of the material (Fatimi *et al.,* 2012). When the material is extruded at a constant rate the shear stress is related to the pressure required to depress the barrel of the syringe, whereas the shear rate is a function of the flow rate. Thus, a material of low viscosity requires only a low pressure to produce a high flow rate, whereas a more viscous material may require a high pressure to produce a relatively small rate of flow (McCabe and Walls, 2009). The force required to extrude the material was used to compare between groups, as it was interesting to determine the relative viscosity (injectability) of the material for comparison rather than going into detailed complex viscosity. For measuring complex viscosity of resin based adhesives different rheometrical techniques have been used such as steady shear sweep test, advanced rheometric expansion system and vertical oscillation rheometer (Lee *et al.,* 2007; Papakonstantinou *et al.,* 2013). However, the problems in using of these viscometers for the determination of the viscosity of orthodontic adhesives are complexity, adhesive evaporation, in addition to paste nature of the orthodontic adhesives that make it difficult to measure its viscosity.

Injectability is applicable and useful for testing the experimental materials. This technique has been used to measure extrusion force of non-setting paste of calcium phosphate bone cement which has a paste-like nature and has previously been reported to be a reproducible method for this purpose (Bohner and Baroud, 2005) which is similar in viscosity to the current materials. This method is very straightforward and seems to be a reproducible method as there was little variation between samples of each experimental group. It was used to compare the relative viscosity of the materials and to give an indication of the viscosity of the material, however, it was not used to give an absolute measurement of viscosity. It was interesting to know relative viscosity of the material for comparison to assess the impact of the altering the materials constituents. Finally, this method is more practical to measure injectability of the adhesives since it is more clinically relevant rather than just measuring viscosity, since currently most of the commercial orthodontic adhesives delivered in a sealed dark syringe (or compule). This makes quicker application and easy adjusting without excess material. The clinicians need to press the plunger of the syringe to extrude (inject) the adhesive.

The development of the injectability method was based on two pilot studies in which the two different methods were investigated that have been used in the literature for investigating injectability of calcium sulphate bone cement. The first method involved controlling the applied force, with the load rate determined by the materials viscosity (Wang *et al.*, 2006). It was shown that the extrusion force increases with increasing viscosity (Bohner and Baroud, 2005). As there was a wide range of viscosity of the experimental materials from very viscous to very low viscosity. Some experimental materials were so viscous they required a 400 N force to allow material extrusion, while other groups were so fluid they immediately dispensed when 400 N force applied. This high force also resulted in failure (rupture) of the syringes used. Therefore, it was decided not to follow this method.

The second technique trialled involved controlling the compression rate and measuring the force required to extrude the material. This was more useful as the rate of compression could be kept stable and the only difference between materials was the amount of force required to extrude the materials for a given displacement (Ginebra *et al.*, 2001; Bohner and Baroud, 2005; Bercier *et al.*, 2010; Fatimi *et al.*, 2012). Therefore this technique was adopted for measuring the extrusion force to allow comparison between groups.

In order to determine a suitable compression rate, different compression rates of 1, 5, 10 and 15 mm/minute were tested for those groups thought to be the most and the least viscous (10:0 without acetone and 7:3 40% acetone respectively). It was found that with group 10:0 with 5, 10 and 15 mm/minute the syringes ruptured and cracked (Figure 4.5). The extrusion force has been shown to increase with increasing compression rate (Allahham *et al.*, 2004; Fatimi *et al.*, 2012) and so it is likely that at these compression rates an excessive extrusion force was reached (300 N) leading to syringe failure. Therefore 1 mm/minute was used to minimise failure of the syringes.

Further preliminary work was undertaken to determine differences between the five different pushes per syringe for the group 10:0 as the most viscous group. No significant difference was found between the force-displacement behaviour of the first and second pushes. Subsequent pushes showed differences in behaviour, particularly the final push, where it is likely that the proximity of the material to the syringe end caused a boundary effect. There was no significant differences between first and second push and they were less varied looking at their SD. Therefore, the first and second push were taken for comparison between all groups. The maximum forces of extrusion were recorded for comparison. The friction due to the movement of the piston along the syringe was neglected for the calculation of the extrusion force, as only a relative measure of viscosity was required in this study. While this friction will clearly effect

the rate of extrusion of material, it is likely that this effect will be approximately constant for all of the materials studied here.

The syringes used in the injectability study were transparent. As CQ can polymerise under ambient light (Crivello, 2009), which would lead to an increase in the viscosity of the mixtures (Lovell *et al.*, 1999; Gao *et al.*, 2012), it was decided that for this part of the experimental work the mixtures would be made without either CQ or DMEAMA. As the concentrations of CQ and DMEAMA were less than 1 wt% of the total mixture, and the concentrations were identical for all mixtures the exclusion of these components was not considered to significantly affect the relative viscosities of the materials. In a previous study, in which the rheological properties of BisGMA-based composites a similar approach of excluding the photoinitator system was also followed (Lee *et al.*, 2006).

There was not a large difference in extrusion force measured between the Newtonian fluids used in this study, despite their different viscosities. This could be due to oily nature of these materials, which were very different from the experimental materials and this may also tend to lubricate the plunger of the syringe which will have an influence on the results. Another reason might be related to the diameter of the syringe opening. Previously, a micro-capillary rheometer was used to measure the viscosity and predict viscosity from extrusion force of Newtonian fluids such as B100, B50, B10 and Vaseline oil which are viscosity standards. (Allahham *et al.*, 2004; Fatimi *et al.*, 2012). However, the syringe opening in those studies was less than 0.8 mm while in the current study the opening was 2mm. Finally, this may indicate that this technique is not very precise (sensitive) in determining differences at low viscosity.

The current findings confirm that different concentrations of acetone lead to differences in the extrusion force of the experimental groups. As such, the extrusion force decreased with increasing acetone concentration. This was due to decreasing viscosity of the material. However, this reduction of extrusion force was up to certain concentration. There were little differences between the 20 and 40% acetone groups. This may indicate that this technique is not very precise (sensitive) in determining differences at low viscosity as it was seen for different Newtonian fluids.

Another interesting finding is that the extrusion force decreased with increasing NaF concentration. This indicates that the viscosity of the material decreased with increasing NaF concentration. This could be due to a reduction in the PMMA powder which absorbs monomer up 100% of its weight which would result in increased viscosity (McCabe and Walls, 2009). Another reason might be due to the particles of NaF which are smaller than those of PMMA and the smaller the particle size will result in a more injectable material (Bohner and Baroud, 2005).

4.6.5 *Fluoride release*

Fluoride release is a desirable property for an orthodontic adhesive to have to reduce demineralisation. Fluoride release values for different orthodontic adhesives vary in the literature with the type of storage medium also effecting the values. Previous studies have shown more fluoride release when specimens are stored in distilled water compared to storage in artificial saliva. This could be due to presence of organic components in saliva, which may act as a barrier and could interfere with the ion release process (McNeill *et al.*, 2001; Preston *et al.*, 2003). Other previous studies reported the influences of pH value of the solution on the release of fluoride ion (Yoda *et al.*, 2006). In the present study, DDW was used as a storage solution to investigate the general fluoride release behaviour of the experimental materials. DDW water was used to reduce the interference at the ion electrode surface that might be induced by ions and impurities. In addition, distilled water (Yoda *et al.*, 2006) and deionized water (Kodkeaw *et al.*, 2010; Dionysopoulos *et al.*, 2013) have been widely used for fluoride release measurement studies.

Samples were prepared using 80 seconds of light curing as the DoC data shows most of the groups reached almost 50% DoC by this time. However, as mentioned in section 2.3.3 there is no established DoC value for adequate clinical performance. The DoC of most orthodontic adhesives previously reported are between 43- 75% (Nithya *et al.*, 2009). 80 seconds cure time has been previously used for similar materials (Zahroon, 2014). However, at that curing time all of 30%A and 40%A groups reached less than 40% DoC. Therefore the groups with high acetone concentration 30% and 40% were omitted from fluoride release measurements.

The protocol used in this study was daily fluoride measurement for the first two weeks then weekly for a month, followed by monthly measurements. This has been used previously by many researchers (McNeill *et al.*, 2001; Cohen *et al.*, 2003; Su *et al.*, 2010; Zahroon, 2014; Al-Sammarraie, 2015). To avoid fluoride saturation of the samples by continued fluoride release (Forsten, 1990; Rix *et al.*, 2001a) the fluoride release measurement was taken after a 24 hour period at each time point, not cumulative fluoride release. This was achieved by changing the water 24 hours before weekly and monthly fluoride release measurements were taken (Rix *et al.*, 2001a) The fluoride release was measured for 160 days in order to get an insight into the long-term fluoride releasing ability of the material.

An ion selective electrode was used to measure fluoride release. This instrument is reliable, easy to use and has great selectivity and specificity for fluoride ions (McCabe *et al.*, 2002) Therefore it is most commonly used for fluoride release measurements. However, this instrument is highly sensitive to temperature and pH changes and it is not very accurate at very

low fluoride concentrations (Itota *et al.*, 2004a). Therefore, a magnetic stirrer was used to stir the solution as it was needed to stabilize the analyser reading (McCabe *et al.*, 2002) to optimise the analytic parameters of the electrode and to facilitate ion transmission through the electrode membrane. The instrument was calibrated every 2 hours during fluoride measurements using a standard solution in order to help account for any temperature change during the day, as temperature might have effect on fluoride release. TISAB was added to the solutions (standard and sample solutions) to de-complex fluoride ions (McCabe *et al.*, 2002; Itota *et al.*, 2004a; Itota *et al.*, 2004b) and prevent interference from other ions such as hydroxide ions (-OH) (McNeill *et al.*, 2001), as –OH has similar ionic charge and ion radius as fluoride ion (McCabe *et al.*, 2002; Rajković and Novaković, 2007). In addition, TISAB regulates the pH value of the solution in range of 5-7 (Rajković and Novaković, 2007).

The detection threshold of ion selective electrode is more than 0.01 $\mu g/cm^2$ of F^-, because the group 10:0 did not contain fluoride. The group 10:0 did not release sufficient fluoride to meet the detection threshold of the fluoride electrode except in the first day. The possible reason is due to contamination of the Teflon moulds that were used for preparation of the specimens. The other reason would be due to accumulation of fluoride ions around the electrode membrane. This was similar to the results of Zahroon in which fluoride was detected from non-fluoride containing materials during the first four days of fluoride measurement (Zahroon, 2014).

The patterns of fluoride release from all experimental materials were similar. In the first day the greatest amount of fluoride release was observed. This high level and rapid fluoride release is supposed to come mostly from surface 'wash-off' of the exposed surface of the material (Tay and Braden, 1988; Anusavice *et al.*, 2005) which was caused mostly by surface degradation (Khouw-Liu *et al.*, 1999). Fluoride release, then from day two decreased sharply until day 14 and then after the first two weeks the amount of fluoride release almost levelled-off at low level. This pattern of fluoride release is very similar to the result of (Kodkeaw *et al.*, 2010) in which 5% w/w NaF was added to a group of di-methacrylate copolymers contained HEMA. Also it was similar to the results of (Zahroon, 2014). The pattern of fluoride release from all experimental materials supported the two-phase diffusion theory. The first process relates to early rapid surface elution of short-term release. The second process relates to bulk diffusion resulting from prolonged slow elution and long-term release from the subsurface layers of the fluoride releasing materials (Tay and Braden, 1988; Verbeeck *et al.*, 1998; Anusavice *et al.*, 2005; Dionysopoulos *et al.*, 2013).

A higher fluoride concentration resulted in greater fluoride release. This was due to higher amount of NaF that dissolved to fluoride ions. NaF is a very soluble salt and it is easily dissolved to free Na and F ions (Nakajo *et al.*, 2009). The results also show that the addition of acetone

had increased fluoride release from the acrylic resin, which may be due to increased water sorption and solubility of the material. The results of section 6.2.2 confirm that. the water sorption of group 9:1 and 10:0 increased at 10% acetone. This may result in accelerated diffusion of fluoride ions within absorbed aqueous medium within first 12 – 24 h (Malacarne-Zanon *et al.*, 2009). In addition, inclusion of a solvent may influence on long term release of fluoride.

Based on the results of the current study, the fourth hypothesis "Acetone has no effect on fluoride release ability of the experimental materials" was not accepted. Acetone concentrations influenced the amount and rate of fluoride release from fluoridated experimental materials. However, the effect was not detrimental.

4.7 Summary

Using acetone as a solvent up to 20% increases injectability and does not negatively affect the setting characteristics and fluoride release of the experimental materials. Future work will focus on increasing the amount of initiator CQ and activator DMAEMA to increase DoC and decrease the time needed for curing the material.

Chapter 5: **Investigating the photo- initiator system of the experimental materials**

5.1 Introduction:

Previous work undertaken has demonstrated the effect of addition of acetone on the experimental materials setting characteristics and fluoride release. However, in this phase of the study, the photo-initiator composition and concentrations were altered in an attempt to polymerize the materials faster. In order to investigate the concentration and type of the photo-initiator system of the experimental materials in relation to the DoC of the materials, a number of combinations of photo-initiator and activator concentrations were examined, using different concentrations of acetone. Two photoinitiators were considered, camphorquinone (CQ) and diphenyl (2, 4, 6-trimethylbenzoyl) phosphine oxide (Lucirin® TPO). Where an activator was needed, two activators were considered, DMEAMA and EDAB (Table 5.2).

FTIR was used to monitor DoC of the material.

5.2 Aims and hypotheses

5.2.1 *Aims*

To investigate different photo-initiators to attempt to increase the DoC and reduce the setting time.

1- To compare the curing efficiency of different concentrations of CQ.

2- To compare the curing efficiency of CQ with different activators (DMEAMA, EDAB).

3- To compare the curing efficiency of Lucirin® TPO with CQ /activator system.

5.2.2 *Hypotheses*

1- DoC increases with increasing CQ concentrations.

2- DoC of groups CQ/DMAEMA will be higher than CQ/EDAB.

3- DoC of Lucirin® TPO group will be higher and maximum DoC reached quicker than CQ groups.

5.3 Materials and methods

Based on previous experiments 12 groups were chosen, each group with 0%A, 10%A and 20%A (see Table 5.1)**.** Six different concentrations of the photo-initiator system were used (see table 5.2). The experimental materials were mixed using the same method as discussed in chapter 4. The FTIR was used to monitor DoC using the same method as previously mentioned in 4.3.2 except 26 scans were taken. Due to the different excitation wavelengths of CQ and Lucirin TPO at 470 nm and 390 nm respectively, all experiments were conducted using an LED

curing light capable of emitting light at both these wavelengths which was bluephase®20i (Bluephase, Ivoclar, Germany). The light intensity was 1130 mW/cm^2 for all experiments, measured using a Coltolux® light meter. In total the materials were exposed to 260 s of light, with 27 spectra for each specimen. The same method was used to determine DoC from the FTIR data as described in section 4.3.2.

Microsoft Excel (Version 14, Microsoft office professional Plus 2010) was used to collate the data which was then imported into statistical software (SPSS 19 for windows, IBM SPSS Inc., USA) for analysis. Shapiro-Wilk test was used to test normality of the data. The data was not normally distributed therefore non-parametric tests were used to investigate statistical difference between groups. Kruskal-wallis H was used to determine statistical significant differences between groups at ($P<0.05$). Pairwise comparisons were performed using Dunn's (1964) procedure with a Bonferroni correction for multiple comparisons (Post hoc test).

Table 5.1 Experimental groups used in this study

Groups	Group Label	PMMA %	NaF %	Acetone	Other components
10:0 0%A	10:0	100	0	0	Liquid: HEMA 60wt% MMA 40%wt% Photo-initiator system: 6 different photo-initiators were used as shown in Table 5.2
10:0 10%A	10:0	100	0	10	
10:0 20%A	10:0	100	0	20	
9:1 0%A	9:1	90	10	0	
9:1 10%A	9:1	90	10	10	
9:1 20%A	9:1	90	10	20	
8:2 0%A	8:2	80	20	0	
8:2 10%A	8:2	80	20	10	
8:2 20%A	8:2	80	20	20	
7:3 0%A	7:3	70	30	0	
7:3 10%A	7:3	70	30	10	
7:3 20%A	7:3	70	30	20	

MMA (methyl methacrylate), HEMA (2-hydroxyethyl methacrylate), PMMA (poly methyl methacrylate), CQ (Camphorquinone), DMAEMA (dimethylaminoethyl methacrylate

Table 5.2 Experimental groups.

Experiments	Group Labels	CQ %	DMAEMA %	EDAB %	Lucirin TPO%
1- 0.6 CQ/0.8 DMAEMA	0.6CQ	0.6	0.8	-	-
2- 0.8 CQ/ 0.8 DMAEMA	0.8CQ	0.8	0.8	-	-
3- 1 CQ/ 1 DMAEMA	1CQ	1	1		
4- 1 CQ/1 EDAB	1EDAB	1		1	
5- 1% Lucirin TPO	1Lucirin				1
6- 1.5% Lucirin TPO	1.5Lucirin				1.5

CQ (camphorquinone), DMAEMA (dimethylaminoethyl methacrylate), EDAB (ethyl-4-(dimethylamino) benzoate), Lucirin® TPO (diphenyl (2, 4, 6-trimethylbenzoyl) phosphine oxide).

5.4 Results

In order to compare the efficiency of different photo-initiator systems they are presented in three sections. The first section describes the amount of the DoC obtained with different photo-initiator systems and at different light curing times. The second and third sections describe the effect of acetone and fluoride on the DoC. This is based on the amount of DoC achieved after 40 and 120 seconds of light curing. 40 seconds curing time was used for comparison as it is considered an acceptable time for curing clinically. A 120 second curing time was used to compare the results at long curing time measured.

5.4.1 *Photo-initiator systems and DoC*

The results of median DoC of all experimental groups are summarized in table 5.3, table 5.4, table 5.5 and table 5.6 for groups 10:0, 9:1, 8:2 and 7:3 respectively. A Kruskal-Wallis H test was run to determine if there were differences in median DoC between groups of each groups with different acetone and photo-initiator concentrations at 40s, 120s, and 260s of light curing. Median DoC were statistically significantly different between groups at 40 s, 120 s and 260s for all groups 10:0, 9:1, 8:2 and 7:3 (Kruskal-Wallis H, $p<0.05$).

The results show that at 40, 120 and 260 seconds of light curing the DoC of most groups with 10%A and 20%A of 0.8 CQ were higher than groups with 0.6 CQ (Kruskal-Wallis H, post hoc test, $p<0.05$). The results also showed that generally the 1 CQ groups were higher than 1EDAB at 40 second of light curing (Kruskal-Wallis H, post hoc test, $p<0.05$).

There were no significant differences between the 1 and 1.5 Lucirin at 0% acetone while when the concentration of acetone increased to 10% and 20%, the 1.5 Lucirin in most groups had

higher DoC than the 1 Lucirin using (Kruskal-Wallis H, post hoc test, $p<0.05$). However, the DoC of almost all groups with 1 and 1.5 Lucirin were higher than CQ groups using (Kruskal-Wallis H, post hoc test, $p<0.05$).

Median DoC of all experimental groups at different photo-initiator concentrations are shown in figures 5.1, 5.2, 5.3 and 5.4. These figures show that there are two stages in the curing process. The first stage consists of an initial rapid increase of the DoC, whilst in the second stage the DoC reaches a plateau. Analysis of these graphs demonstrates that the process of reaching the plateau in DoC curves varied according to different photo-initiator concentrations. The groups with 1 and 1.5 Lucirin reach the plateau after only 10 seconds of light curing irrespective of the concentration of the Lucirin. However, all CQ groups need more curing time before they reach the plateau. This time appears to depend on the concentrations of CQ and DMAEMA with increasing concentration of either agents resulting in more rapid first stage of curing and reaching the plateau sooner. However, CQ groups containing EDAB were generally more delayed in reaching the plateau in comparison to those with DMAEMA. In all of the CQ groups the curing curve delayed reaching the plateau with increasing acetone concentrations, in which higher acetone concentrations resulted in it taking a longer time to reach the plateau.

Table 5.3 Median DoC (IQR) of group 10:0 containing different photo-initiator systems and different acetone content at different curing times.

Experimental Groups	Acetone concentrations (%)	Median degree of conversion (IQR) at different curing time (s)		
		40 s	120 s	260 s
1.5Lucirin	0	53 (1.5)^{a}	58 (1.0)^{h}	62 (0.2)^{q}
	10	64 (0.7)^{b}	70 (0.4)^{ij}	73 (0.3)^{rs}
	20	70 (0.4)	76 (0.4)	79 (1.0)
1Lucirin	0	53 (2.6)^{a}	58 (1.2)^{hk}	62 (0.5)^{q}
	10	63 (3.2)^{b}	67 (3.3)^{jm}	71 (0.0)^{t}
	20	67 (2.1)	72 (2.0)^{i}	75 (1.1)^{r}
1CQ	0	43 (3.2)^{d}	52 (3.9)^{l}	54 (2.3)^{uv}
	10	51 (1.5)^{ae}	60 (2.2)	63 (1.1)^{q}
	20	50 (5.8)^{ae}	66 (2.5)^{m}	69 (4.1)^{sy}
1EDAB	0	43 (1.2)^{d}	50 (4.8)^{ln}	53 (1.4)^{ux}
	10	35 (7.8)^{df}	49 (4.1)^{n}	57 (1.2)^{v}
	20	18 (11.0) ^{g}	39 (7.8)^{o}	58 (1.1)^{v}
0.8CQ	0	44 (18.0)^{de}	53 (17.5)^{l}	56 (0.0)^{v}
	10	44 (5.2)^{de}	53 (2.2)^{l}	56 (0.6)^{v}
	20	39 (11.5)^{df}	65 (5.7)^{m}	71 (4.0)^{rt}
0.6CQ	0	33 (13.5)^{f}	44 (9.4)^{o}	45 (6.6)^{x}
	10	44 (9.3)^{de}	55 (9.0)^{h}	59 (8.5)^{qv}
	20	22 (0.9)^{g}	56 (0.7)^{h}	69 (1.2)^{ty}

The entries are median values with IQR in the parenthesis. Superscript letters indicate no significant difference within columns (Kruskal-Wallis H, post hoc test, $p<0.05$)

Table 5.4 Median DoC (IQR) of group 9:1 containing different photo-initiator systems and different acetone content at different curing times.

Experimental Groups	Acetone Concentrations (%)	Median degree of conversion (IQR) at different curing time (s)		
		40 s	120 s	260 s
1.5Lucirin	0	56 (1)[a]	61 (1.3)[g]	63 (0.2)[k]
	10	64 (1.6)[b]	69(1.6)[h]	73 (0.5)[l]
	20	66 (3.2)[b]	72 (5.1)[h]	76 (1)[o]
1Lucirin	0	54 (3.1)[ac]	60 (3.4)[g]	63 (3.8)[k]
	10	60 (1.2)	65 (1.9)[i]	67 (1.2)[m]
	20	66 (1)[b]	72 (1.2)[h]	77 (0.1)[o]
1CQ	0	48 (17.2)[cd]	54 (15.8)[g]	57 (13.8)[n]
	10	48 (07)[d]	63 (3.3)[i]	67 (3.2)[m]
	20	38 (12)[e]	69 (1.7)[h]	72 (2.1)[l]
1EDAB	0	45 (24.4)[cd]	51 (18.5)[gk]	56 (21.7)[n]
	10	21 (6.1)[f]	43 (3.2)[k]	52 (1.6)
	20	29 (10.4)[f]	56 (7)[g]	68 (0.9)[m]
0.8CQ	0	35 (13.1)[e]	42 (14.4)[k]	49 (11.8)
	10	48 (2.3)[d]	60 (1.3)[g]	66 (3.4)[km]
	20	33 (8.1)[e]	65 (0.3)[i]	70 (1)
0.6CQ	0	46 (2.4)[d]	54 (3.8)[g]	57 (2.7)[n]
	10	43 (9.7)[d]	57 (5.8)[g]	61 (5.1)[k]
	20	23 (5)[f]	59 (0.9)[g]	66 (2.7)[m]

The entries are median values with IQR in the parenthesis. Superscript letters indicate no significant difference within columns (Kruskal-Wallis H, post hoc test, $p<0.05$).

Table 5.5 Median DoC (IQR) of group 8:2 containing different photo-initiator systems and different acetone content at different curing times.

Experimental Groups	Acetone concentrations (%)	Median degree of conversion (IQR) at different curing time (s)		
		40 s	120 s	260 s
1.5Lucirin	0	56 (0.8)[a]	61 (1.9)[g]	64 (1.2)[m]
	10	64 (0.2)[b]	70 (0.6)[h]	72 (1.8)[n]
	20	68 (10.7)	74 (8.9)	77 (4.4)
1Lucirin	0	56 (2.6)[a]	60 (1.4)[g]	64 (1.7)[m]
	10	61 (0.5)	68 (1.6)[hj]	72 (2.3)[n]
	20	64 (3.1)[b]	70 (0.4)[h]	73 (2.9)[n]
1CQ	0	50 (2.7)[c]	57 (0.6)[i]	60 (2.2)[o]
	10	45 (6.1)[c]	62 (2.3)[g]	67 (4.0)[p]
	20	24 (4.4)[e]	67 (2.3)[j]	73 (1.3)[n]
1EDAB	0	42 (17)[c]	54 (15.6)[jk]	59 (14.3)
	10	36 (6.0)[d]	58 (4.3)[i]	64 (6.2)[m]
	20	21 (4.2)[e]	50 (3.6)[k]	71 (1.3)[n]
0.8CQ	0	37 (1.4)[d]	42 (1.3)	47 (2.9)
	10	45 (4.8)[c]	58 (3.6)[i]	64 (3.4)[m]
	20	27 (3.1)[e]	64 (1.2)[g]	70 (2.6)[n]
0.6CQ	0	46 (9.9)[c]	54 (9.3)[i]	57 (7.1)[o]
	10	36 (7.2)[d]	57 (0.5)[i]	61 (1.9)[mo]
	20	24 (2.8)[e]	57 (2.5)[i]	66 (0.6)[p]

The entries are median values with IQR in the parenthesis. Superscript letters indicate no significant difference within columns (Kruskal-Wallis H, post hoc test, $p<0.05$)

Table 5.6 Median DoC (IQR) of group 7:3 containing different photo-initiator systems and different acetone content at different curing times.

Experimental Groups	Acetone concentrations (%)	Median degree of conversion (IQR) at different curing time (s)		
		40 s	120 s	260 s
1.5Lucirin	0	54 (1)^{a}	59 (0.8)^{i}	61 (0.9)^{n}
	10	63 (0.4)^{b}	67 (1.2)^{j}	71 (1.7)^{o}
	20	64 (16.4)^{b}	69 (14.2)^{j}	73 (13.2)^{o}
1Lucirin	0	54 (3.6)^{a}	58 (2.1)^{i}	64 (3.6)^{n}
	10	61 (3.0)^{b}	67 (2.5)^{j}	68 (3.2)^{o}
	20	48 (13.6)^{c}	57 (7.7)^{i}	62 (10.1)^{n}
1CQ	0	49 (1.2)^{c}	59 (0.6)^{i}	62 (0.9)^{n}
	10	30 (6.4)^{d}	64 (1.2)^{k}	67 (2.8)^{np}
	20	20 (3.8)^{e}	65 (3.0)^{k}	71 (0.1)^{o}
1EDAB	0	28 (1.9)^{d}	42 (0.4)^{l}	45 (6.4)
	10	34 (1.4)^{d}	57 (1.6)i	66 (1.4)^{p}
	20	24 (3.1)^{ef}	50 (2.0)	67 (1.8)^{p}
0.8CQ	0	48 (2.1)^{c}	56 (1.1)^{i}	60 (1.2)^{n}
	10	28 (1.5)^{f}	59 (1.4)^{i}	64 (0.2)^{n}
	20	15 (4.9)^{g}	37 (2.8)	66 (6.7)^{pn}
0.6CQ	0	39 (5.3)^{h}	47 (9.2)^{l}	54 (8.6)^{n}
	10	35 (6.1)^{dh}	57 (3.3)^{i}	59 (4.2)^{n}
	20	15 (2.4)^{g}	46 (2.5)^{l}	64 (0.7)^{n}

The entries are median values with IQR in the parenthesis. Superscript letters indicate no significant difference within columns (Kruskal-Wallis H, post hoc test, $p<0.05$)

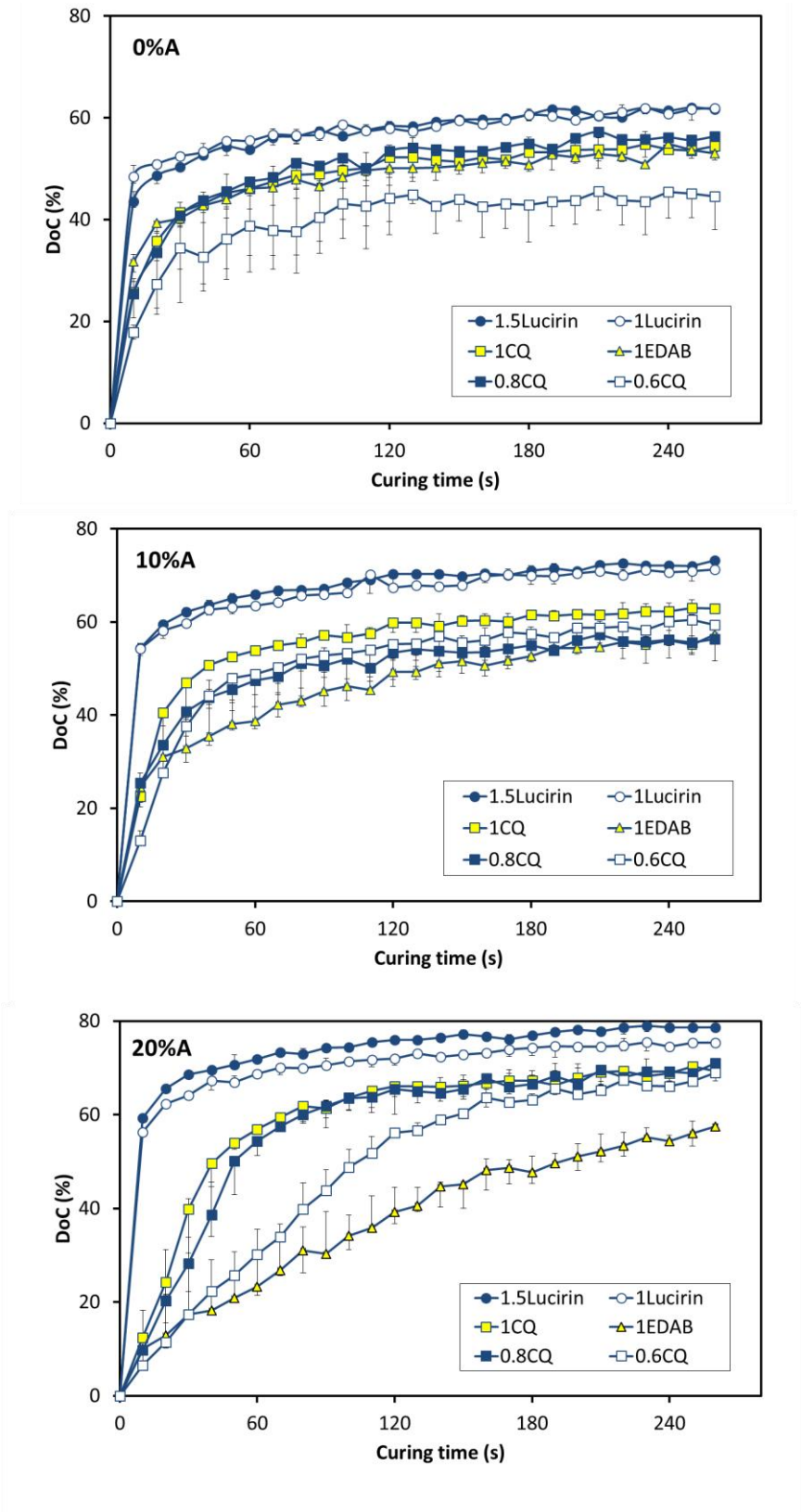

Figure 5.1 Median DoC of group 10:0 containing different photo-initiator systems and different acetone content at different curing times.

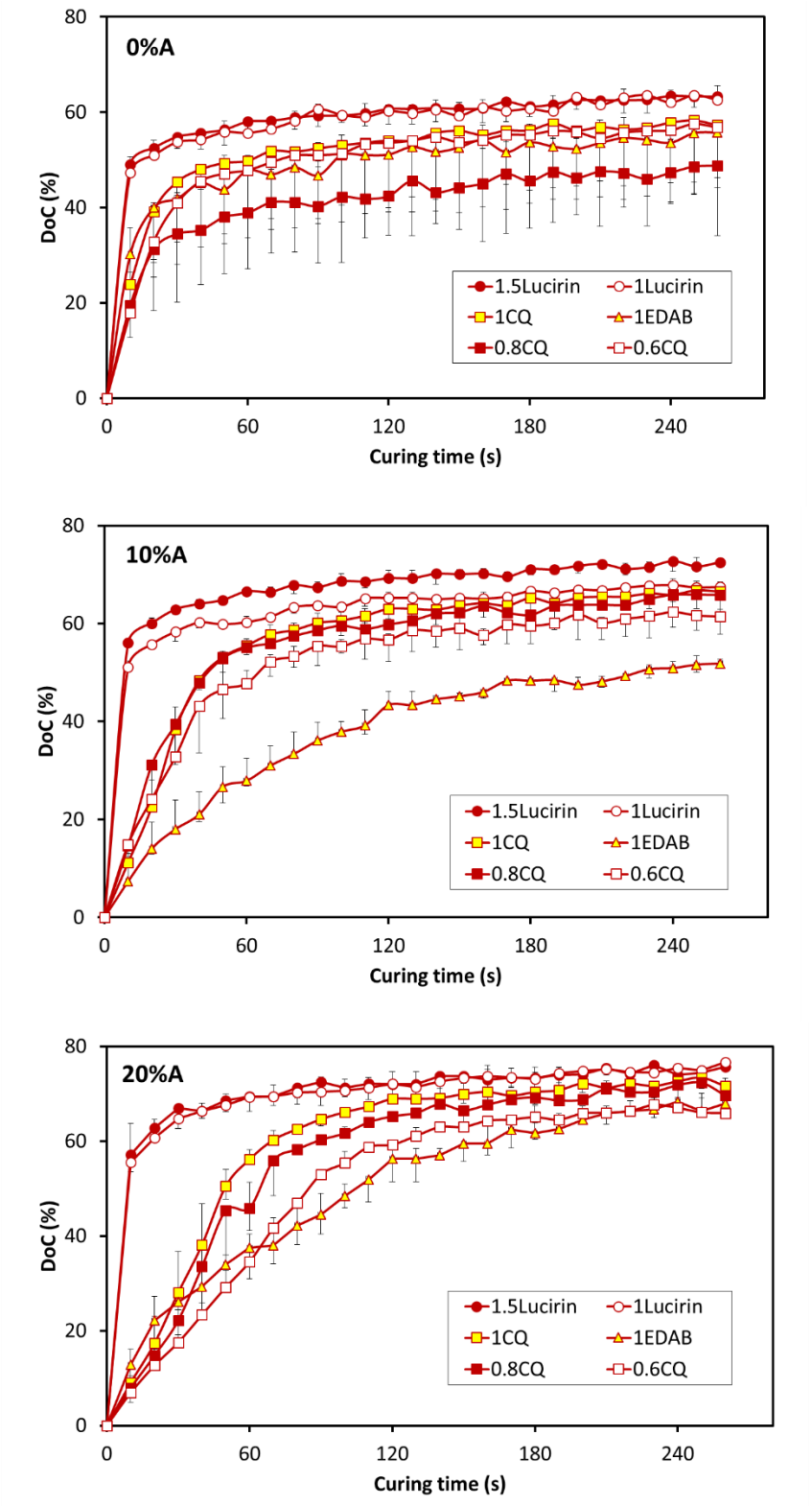

Figure 5.2 Median DoC of group 9:1 containing different photo-initiator systems and different acetone content at different curing times.

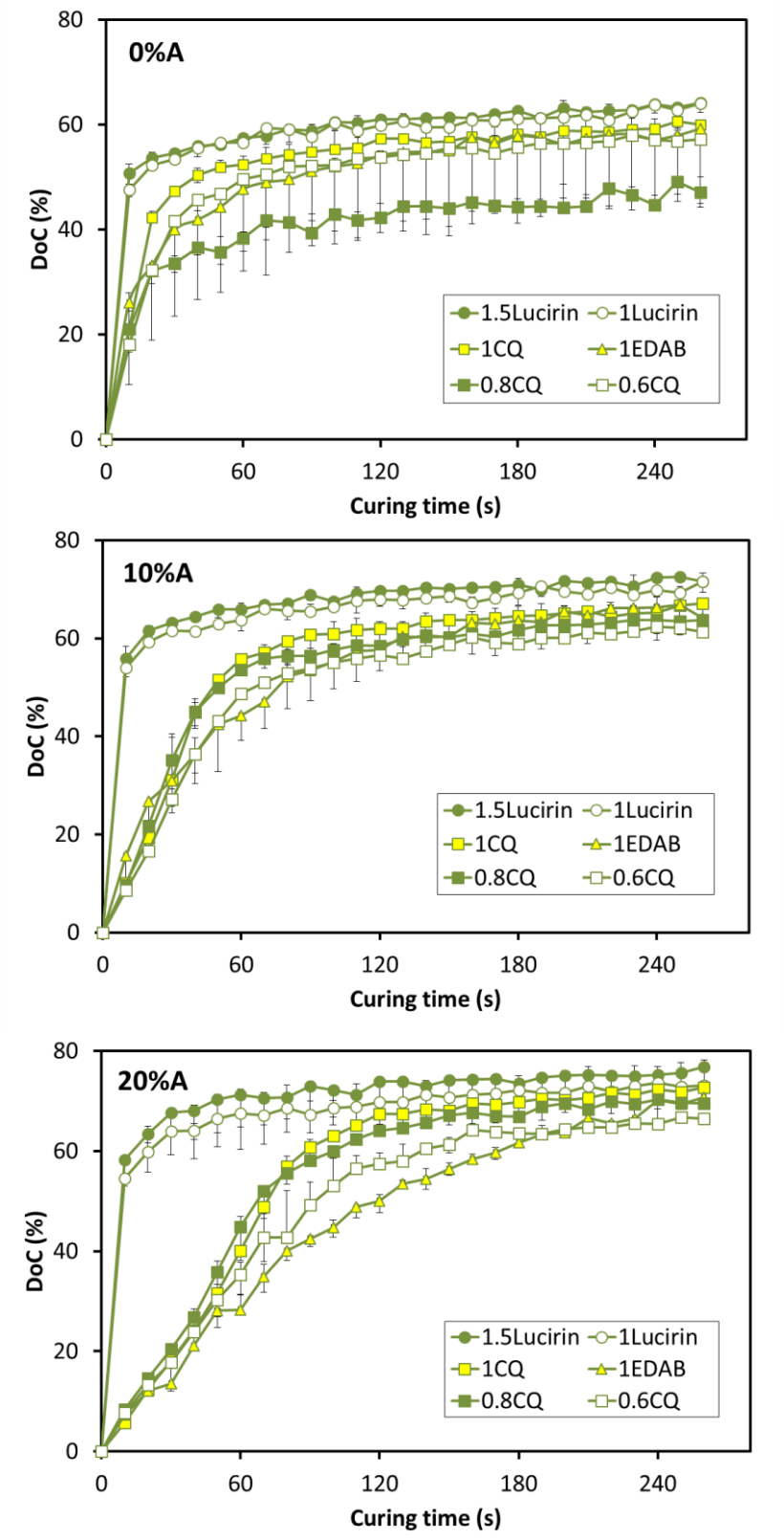

Figure 5.3 Median DoC of group 8:2 containing different photo-initiator systems and different acetone content at different curing times.

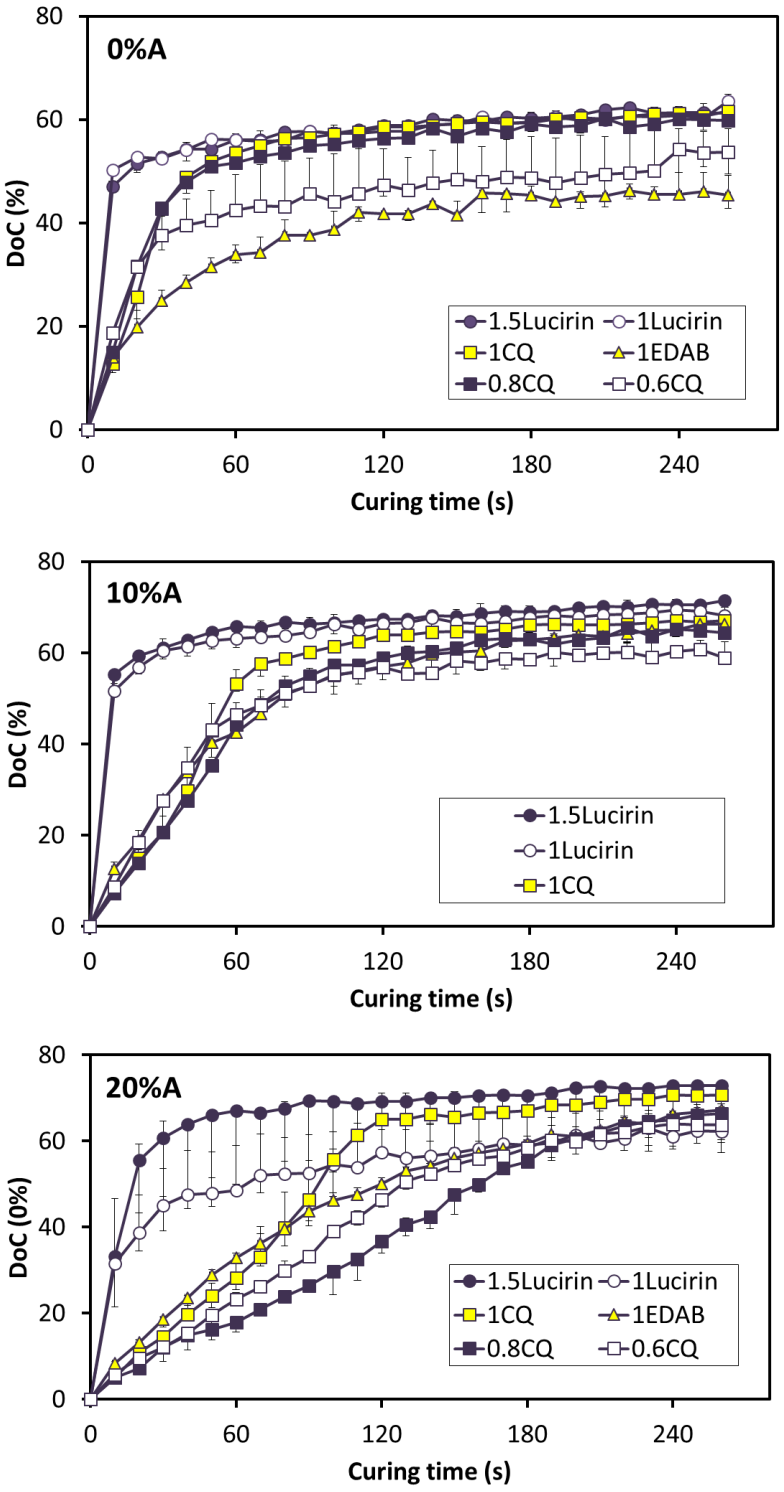

Figure 5.4 Median DoC of group 7:3 containing different photo-initiator systems and different acetone content at different curing times.

5.4.2 *Acetone concentrations and DoC in relation to photo-initiator systems*

At 40 and 120 seconds of light curing the DoC of all Lucirin® TPO groups increased with increasing acetone concentrations except in group 7:3 at 1 Lucirin the DoC decreased at 20%A (see Figure 5.5).

At 40 seconds of light curing the DoC of 1 EDAB decreased with increasing acetone concentrations (see Figure 5.5).

At 120 seconds of light curing the DoC of all CQ groups increased with increasing acetone concentrations except in group7:3 at 0.8 CQ the DoC decreased (see Figure 5.5)

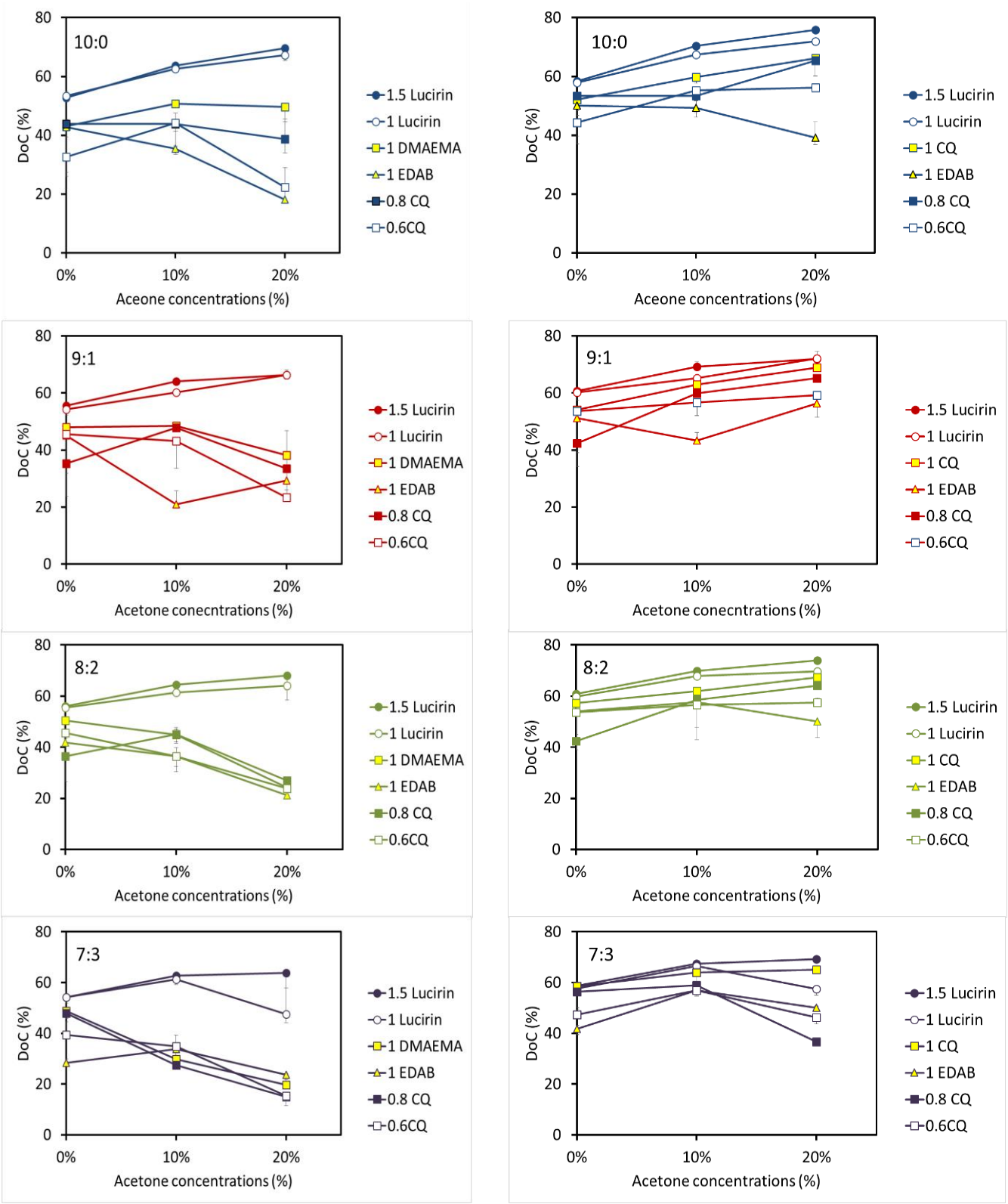

Figure 5.5 Representative DoC at two curing times (40 seconds (left) and 120 seconds (right figure) of all experimental groups containing different photo-initiator systems and different acetone content.

5.4.3 *Fluoride concentrations and Doc in relation to photo-initiator system*

Figures 5.6 and 5.7 showing the effect of fluoride concentrations on the DoC at 40s and 120s of light curing and at different acetone concentrations 0%A, 10%A and 20%A.

At 40 seconds of light curing the DoC of all Lucirin® TPO groups did not change with increasing fluoride concentrations except group 1Lucirin at 30% fluoride and 20%A where the DoC decreased. While for all CQ groups the DoC was not affected by increasing fluoride concentrations up to 10%A. At 20%A the DoC of all CQ groups decreased with increasing fluoride concentrations (see Figure 5.6)

At 120 seconds of light curing the DoC of all photo-initiator systems was not affected by increasing fluoride concentrations (see Figure 5.7).

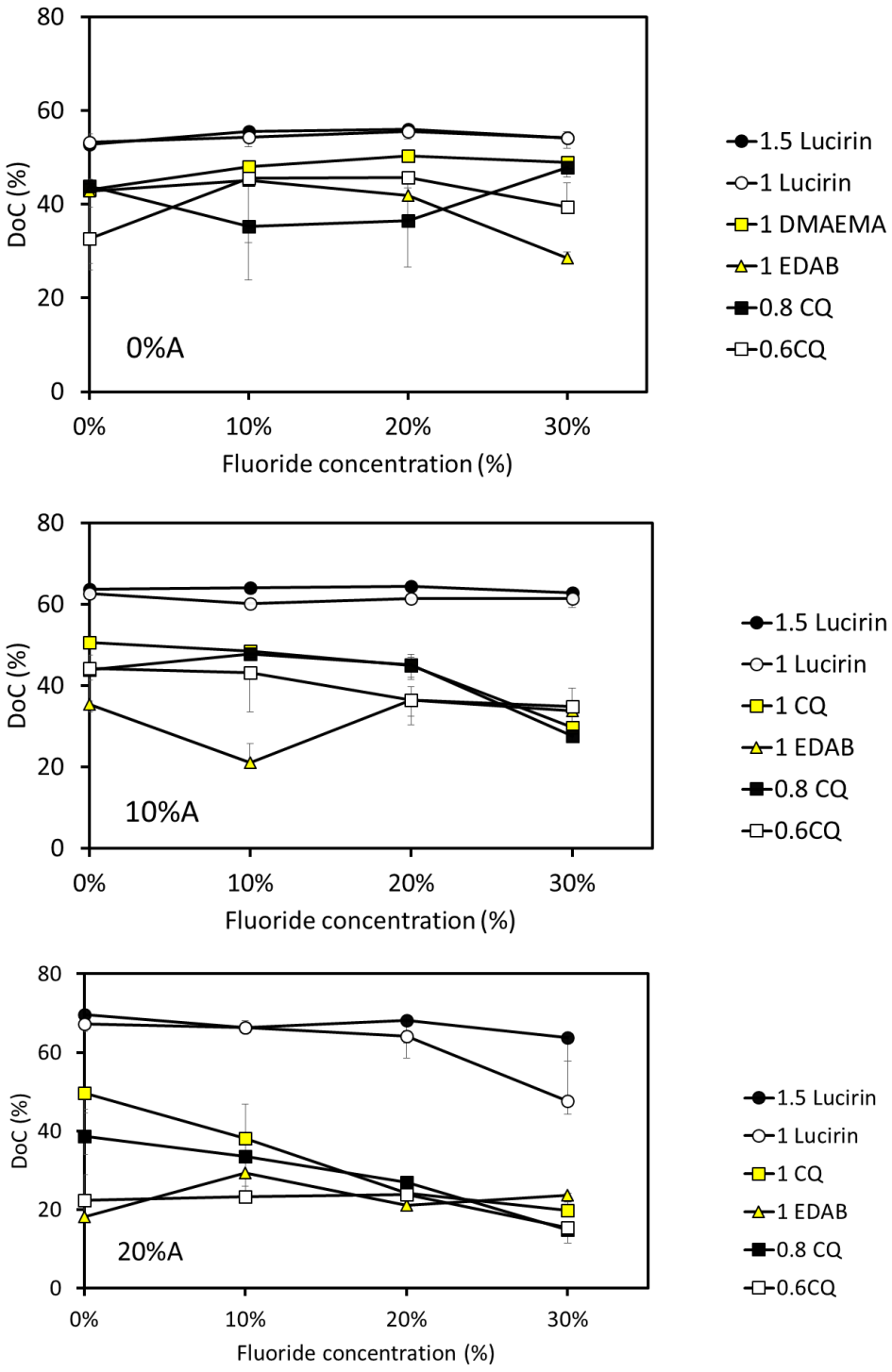

Figure 5.6 Representative DoC at 40 seconds curing time of all experimental groups containing different photo-initiator system and different fluoride content.

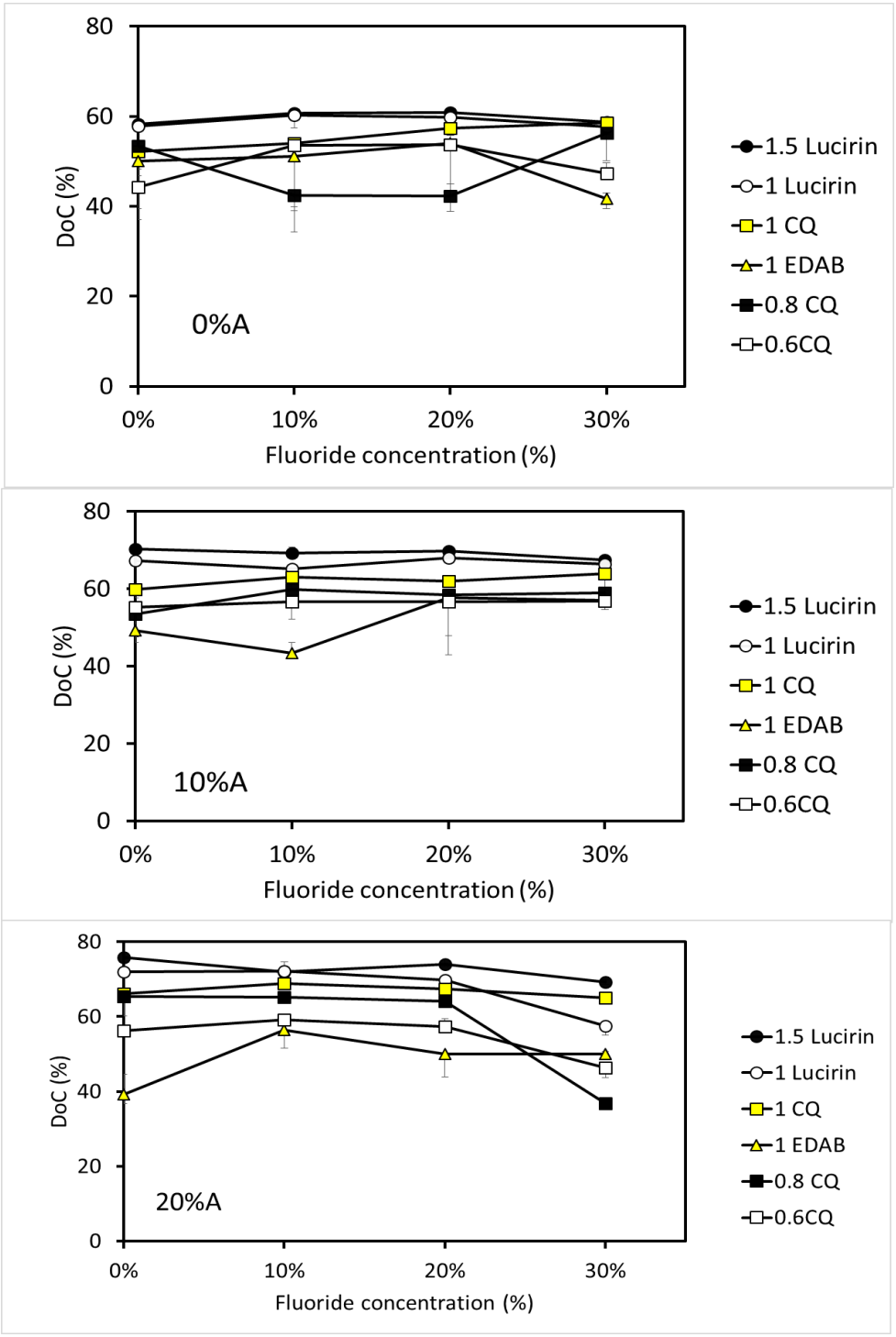

Figure 5.7 Representative DoC at 120 seconds curing time of all experimental groups containing different photo-initiator system and different fluoride content.

5.4.4 *Summary of the results*

DoC increased with increasing CQ concentrations.

Generally the DoC of CQ groups with 1% DMAEMA were higher than those containing 1% EDAB.

The DoC of all groups with Lucirin® TPO was higher and polymerized faster than CQ containing groups.

5.5 Discussion:

Lucirin® TPO is currently a relatively new material developed for use as a photo-initiator. It produces greater colour stability than CQ (Arikawa *et al.*, 2009; Shin and Rawls, 2009). Unlike CQ, Lucirin® TPO does not need a tertiary amine to activate the polymerization that contributes to a greater yellowing effect (Schneider *et al.*, 2009a; Schneider *et al.*, 2012). Lucirin® TPO also leads to higher DoC than CQ (Arikawa *et al.*, 2009; Leprince *et al.*, 2011). Despite these positive aspects of using Lucirin® TPO, it has a low depth of cure compared to CQ (Leprince *et al.*, 2011; Miletic and Santini, 2012a; Schneider *et al.*, 2012). CQ is still the most commonly used photo-initiator in dental resins and composites (Sun and Chae, 2000; Jakubiak *et al.*, 2003; Leprince *et al.*, 2013), despite its tendency to discolour.

The same methodology was used for measuring DoC as discussed in previous chapter section 4.3.2. However, the FTIR spectra were measured for a longer curing time (260 seconds) in order to investigate the effect of each photo-initiator for a longer exposure time and to continue curing until the curing curve flattened, because in previous work for some experimental compositions the curing curve was not flattened indicating curing may still be continuing at the point where the experiment was ceased. The light source was also different, for this experiment a poly-wave LCU bluephase®20i was used. This was to cover the absorption spectra of Lucirin® TPO as well as the CQ. The bluephase®20i has two emission peaks one around 470 nm to cover the absorption spectrum of CQ and the other around 400 to cover the spectrum of Lucirin® TPO (Price *et al.*, 2010)(see Figure 5.8). Lucirin® TPO has exhibits maximum absorption near UV light, also extending into the visible part of the spectrum (380-430 nm), which is narrower than CQ (380-500 nm) but has greater absorption at shorter wave lengths (Neumann *et al.*, 2005; Neumann *et al.*, 2006; Arikawa *et al.*, 2009; Schneider *et al.*, 2012). The absorption range of CQ is about 380-500 nm with a peak absorbance wavelength at around 470 nm (Schroeder *et al.*, 2008; Arikawa *et al.*, 2009). In the previous chapter a conventional LED LCU (single wave) with intensity of 800 mW/cm² was used while in this chapter the higher intensity polywave LCU bluephase®20i with an intensity of 1130 mW/cm² was used. As it has previously been shown that increasing intensity increases the rate of the polymerization reaction (Peutzfeldt and Asmussen, 2005). Therefore, there might be some differences in the values of the results between the previous chapter and this chapter but trends should be similar. The results of this chapter confirms the results of previous experiments which show that acetone and fluoride had an effect on DoC. These were discussed in chapter 1.

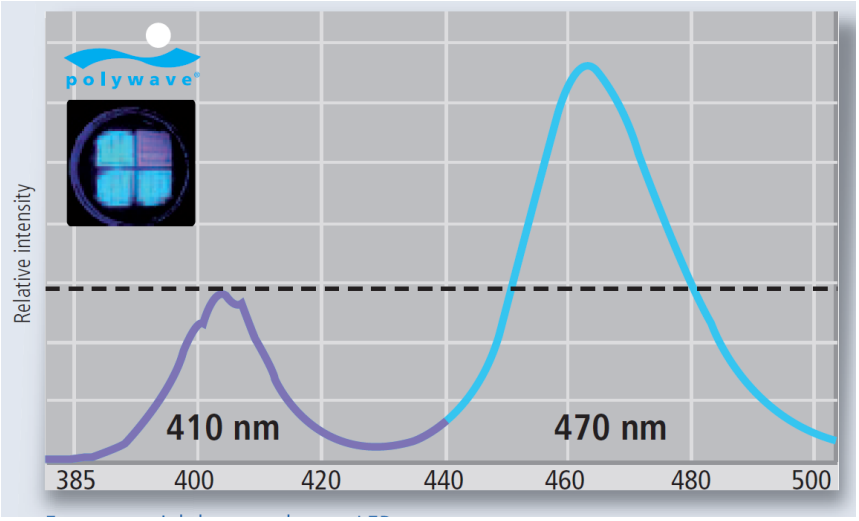

Figure 5.8 The emission spectra of bluephase®20i as shown by manufacture.

Ideally, the concentration of the photo-initiator molecules in any photo-polymerized resin based systems should be limited to the amount that is necessary to bring about a satisfactory DoC within a clinically acceptable curing time. Previous studies experimented with various concentrations of CQ in dental composites (Taira *et al.*, 1988; Asmussen and Vallo, 2009; Musanje *et al.*, 2009). Some have used different concentrations to find optimal CQ concentrations from 0.17 to 1.03 wt% of the resin (Taira *et al.*, 1988) whilst others suggested that at 1%CQ a resin composite of TEGDMA/BisGMA/UDMA reaches maximum DoC, compared to a range of CQ concentrations from 0.1-1.6 wt% (Musanje *et al.*, 2009). Therefore, in the present study 0.6%, 0.8% and 1%CQ were used to determine the amount needed to potentially maximise DoC. The results of the current study showed that generally DoC increased with increasing photo-initiator concentrations at 10% and 20%A acetone concentrations. High concentrations of CQ have been reported to improve the DoC and mechanical properties of the resultant resin (Musanje *et al.*, 2009; Pfeifer *et al.*, 2009). However, it was shown that above certain concentrations additional CQ has no further beneficial effect (Jakubiak *et al.*, 2001; Jan *et al.*, 2001; Musanje *et al.*, 2009). Within the limitations of the current study the first hypothesis "DoC increases with increasing CQ concentrations" was accepted as generally the DoC increased with increasing CQ concentrations.

Two tertiary amines (DMAEMA and EDAB) have previously been widely used with CQ as activators (Yoshida and Greener, 1993; Teshima *et al.*, 2003; Emami and Soderholm, 2005; Musanje *et al.*, 2009; Furuse *et al.*, 2011) and these were therefore used in this study. Some studies have used CQ with either EDAB or DMAEMA at 1:1wt% in monomer mixture of BisGMA/TEGDMA (Asmussen and Vallo, 2009). Our results showed that almost all CQ

groups with DMAEMA had higher DoC than EDAB. This could be due to increased activity of DMAEMA over EDAB. It has been shown that consumption of CQ and PPD in combination with DMAEMA is more rapid than that of the photoinitiators combined with EDAB in a mixture of BisGMA/TEGDMA (Asmussen and Vallo, 2009). In addition, DMAEMA interacts strongly with monomers which have a methacrylate functional group capable of copolymerization with the matrix monomer (Jan *et al.*, 2001). Therefore, the second hypothesis "DoC of groups CQ/DMAEMA will be higher than CQ/EDAB" was accepted as DoC of groups CQ/DMAEMA higher than CQ/EDAB.

Lucirin® TPO was used in two concentrations at 1 wt% and 1.5 wt% without an activator. Previous studies have used Lucirin® TPO at 1.5 wt% (Arikawa *et al.*, 2009) and it was found that in a mixture of BisGMA/TEGDMA the DoC reaches 80% with both a halogen light and a custom made light curing unit with an emitting spectra from 390-430 nm (Arikawa *et al.*, 2009). It has been shown that the curing curve reaches a plateau at 1.08 wt% and 1.5 wt% Lucirin® TPO in a mixture of BisGMA/TEGDMA using a polywave LED LCU (Miletic and Santini, 2012b). In another study it was found that using Lucirin® TPO alone at 1wt% produces higher DoC than using TPO with CQ and an activator like EDAB at 0.4% (Miletic and Santini, 2012a). It has also been reported that there is no significant change in DoC after addition of activator like EDAB in a mixture of BisGMA/TEGDMA with Lucirin® TPO as the photo-initiator (Schneider *et al.*, 2012). This might be due to the chemistry of Lucirin® TPO as it undergoes fast photolysis of the carbon-phosphorus bond, generating benzoyl and phosphonyl radicals, independent of a tertiary amine (activator) (Kajiwara *et al.*, 1993; Medsker *et al.*, 1998).

The results of the current study showed that all groups with the CQ initiator system had lower DoC and a slower reaction than groups containing Lucirin® TPO. This has been shown in previous literature in mixtures of BisGMA/TEGDMA (Arikawa *et al.*, 2009; Leprince *et al.*, 2011). Therefore, the third hypothesis was accepted "DoC of Lucirin® TPO group will be higher and polymerized faster than CQ groups". Various factors may contribute to this difference.

Firstly, CQ has a lower molar absorptivity (molar absorption coefficient or molar coefficient, molar extinction coefficient), which are parameters defining how strongly a substance absorbs light at a given wavelength, per mass density or per molar concentration, respectively, than Lucirin® TPO this means that the probability for CQ to absorb light at the peak of its absorption range is much lower than Lucirin® TPO (Neumann *et al.*, 2006; Schneider *et al.*, 2008). Secondly, CQ has a lower quantum yield conversion, which is the ratio of the number of converted photoinitiators to the number of photons absorbed by the initiators (Chen *et al.*, 2007), in comparison to Lucirin® TPO. It has been shown that the quantum yield of CQ combined with dimethylaminoethyl methacrylate is 0.07, this means that the absorption of 14

photons is necessary for the conversion of one CQ molecule (Chen *et al.*, 2007). However, much higher initiation quantum yield values were reported for Lucirin® TPO. Thirdly, each converted CQ molecule can only generate one free radical to initiate polymerization, whereas Lucirin® TPO generates two active radicals (Neumann *et al.*, 2006) see Table 5.7.

CQ and Lucirin® TPO have different initiation mechanisms. Initiation of CQ involves the presence of an activator (DMAEMA, EDAB), due to its diketone grouping. In this case only one active radical is expected, as only the alpha radicals are derived from the activator, which are considered effective for polymerization initiation (Teshima *et al.*, 2003; Neumann *et al.*, 2006). However Lucirin® TPO undergoes fast photolysis of the carbon-phosphorus bond, generating benzoyl and phosphonyl radicals, which are both very reactive and capable of initiating vinyl monomer polymerization (Kajiwara *et al.*, 1993; Medsker *et al.*, 1998).

Table 5.7Characteristics of the photoinitiators used in this study.

Photoinitiators	UV-Visible absorptions		Quantum yields (mole/Einstein^{-})	Quantum yield efficiency (photons: converted photoinitiator molecule)	Number of initiating radicals	Source
	Absorption range/max (nm)	Molar extinction coefficient at λmax (L mol−1 cm−1)				
CQ	400-550/470	28	6.61X10^3	0.07 (14:1)	1	(Neumann *et al.*, 2006)
		40				(Chen *et al.*, 2007)
		46				(Neumann *et al.*, 2005)
						(Schneider *et al.*, 2008)
						(Leprince *et al.*, 2011)
Lucirin® TPO	300-430/381	520	31.64X10^3	0.35 (3:1)	2	(Neumann *et al.*, 2006)
		660				(Neumann *et al.*, 2005)
						(Leprince *et al.*, 2011)
						(Leprince *et al.*, 2013)

Whilst Lucirin® TPO provided a higher DoC and faster polymerization than CQ, the 1%CQ was chosen for further development of the materials. Lucirin® TPO is known to have a low depth of cure and this might be an important issue for orthodontic adhesives which polymerize under metallic brackets and therefore require a high depth of cure. The height and width of

orthodontic brackets are different from one manufacture to another generally they are between 1.5 - 4 mm. There is no study up to my knowledge on depth of cure of orthodontic adhesives under brackets. However, there is one study investigated the issue of depth of cure of a light cured adhesive cement for metallic orthodontic bands (Namura *et al.*, 2006). There are some studies on comparing micro-leakage of orthodontic adhesives under metallic and ceramic adhesives. The highest micro-leakage was found of the adhesives under metallic brackets compared to ceramic bracket, they postulated that incomplete polymerization of the adhesives under metallic brackets was the cause (Arikan *et al.*, 2006; Tancan *et al.*, 2008) due to metallic brackets not conducting light while, ceramic brackets do.

Additionally, CQ is the most commonly used photo-initiator in most dental adhesive systems and it is suitable for curing with all LED LCU unlike Lucirin® TPO which requires special LCU to cover the absorption spectra of the material which is near UV light. Regarding acetone concentrations, the 0%A and 10%A were chosen for further development of the experimental materials composition as at 40 seconds of light curing the DoC of all experimental materials up to 10%A was minimally affected, apart from group 7:3, which showed a significant reduction in DoC with 10%A. (see Figure 5.5). The 40 seconds of light curing was chosen for comparison of the materials. It was considered suitable for further testing because it is considered an acceptable curing time for orthodontic bonding. In addition, in most of orthodontic bond strength studies 40 seconds of light curing has been used (Oesterle *et al.*, 1995; Evans *et al.*, 2002; Usumez *et al.*, 2004; Mavropoulos *et al.*, 2008), although many recent studies focus on decreasing curing time of orthodontic adhesives to 5s or even less by increasing the intensity of LCU (Erion and Banu, 2011), however, this was not considered the focus of this research.

5.6 Summary

Lucirin® TPO is an effective photo-initiator which can be used to increase the rate and amount of polymerization of the material compared to a CQ photo-initiator system. However, 1% CQ was chosen for further development of the materials composition for several reasons. Firstly, CQ is still the most commonly used photo-initiator in dental adhesives. Secondly, there are some problems with using Lucirin® TPO reported in the literature like low depth of cure and the requirement for a specific and non-standard LCU. 1 wt% CQ had higher DoC than other concentrations of CQ and activator. Regarding acetone concentrations, the 0%A and 10%A were chosen for further investigation because at 40 seconds of light curing up to 10%A the DoC was not significantly affected apart from group 7:3. Regarding fluoride concentrations, all experimental groups were taken for further investigation as at this stage I felt it was important to explore fluoride release in all groups.

The next phase of this study focuses on the addition of an adhesive promotor 4-methacryloyloxyethy trimellitate anhydride (4-META) to the material to increase the bond strength of the material to brackets and to enamel.

Chapter 6: **Investigating the effect of 4-META on the developed materials**

6.1 Introduction

Bond strength is one of the important parameters that determines the success and efficacy of orthodontic adhesives. Orthodontic adhesives should provide sufficient bond strength to retain brackets throughout treatment. Insufficient bond strength leads to bond failure of brackets during treatment, consequently retarding treatment, which is costly in terms of time, material, and patient inconvenience (Mandall *et al.*, 2003). Once the bracket bond has failed, the adhesive residue should be removed, which in addition to being time consuming, can also lead to the removal up to 50 µm of enamel surface (Al Shamsi *et al.*, 2007).

A previous study by (Su *et al.*, 2010) showed that the bond strength of the developed material decreased after storage in water for 30 days. In this chapter, as part of further developing the materials, 4-META was added to increase bond strength of the materials as an adhesion promoting monomer. The 4-META monomer is able to adhere to hydroxyapatite and form an ionic bond with calcium in hydroxyapatite (Yoshida *et al.*, 2004). Therefore, a 4-META containing adhesives potentially will provide significantly higher bond strength than the conventional orthodontic adhesives (Clark *et al.*, 2003; Rikuta *et al.*, 2008). 4-META has also been used to improve bond strength of brackets to amalgam, gold alloy, metal alloys and porcelain in conjunction with conventional orthodontic resins (Ohno *et al.*, 1992; Björn *et al.*, 1995; Büyükyilmaz *et al.*, 1995; Zachrisson *et al.*, 1996; Minami *et al.*, 2013). 4-META is commonly used together with MMA in the form of 4-META/MMA-TBB adhesives and it is available as a commercial product as Superbond C&B, whose polymerization is initiated by tri-n-butylborane (TBB).

Previously, the handling characteristics of the materials were developed through the addition of acetone to decrease materials viscosity and the investigation of different photo-initiator systems. In this phase of the study, 4-META was added to the developed materials as an adhesion promoting monomer to increase bond strength of the material. Consequently, the work described in this chapter involved analysing the effect that the addition of the adhesion promoting monomer, 4-META, had on a number of physical parameters of the materials. Therefore the aim of this chapter is to investigate the effect of 4-META on DoC, fluoride release, fluoride recharge, water sorption and solubility of the developed material.

6.2 Aims and hypothesis

6.2.1 *Aims*

1-To investigate the effect of 4-META on DoC and compare the DoC with commercially available Transbond XT.

2- To investigate the effect of 4-META on water sorption and solubility of the material and compare this to Ketac-cement and Transbond XT.

3- To investigate the effect of 4-META on fluoride release and compare this with the Ketac-cement.

4- To determine the fluoride recharging ability of 4-META containing experimental acrylic resins after application of a fluoride source and comparison of fluoride release with that of a commercially available GIC based material.

5- To investigate the effect of 4-META on surface morphology of experimental samples after being in water for 28 days.

6.2.2 *Hypotheses*

1- 4-META does not deteriorate DoC of the experimental materials.

2- 4-META increases water sorption and solubility of the material

3- 4-META increases fluoride release of the experimental materials.

4- 4-META increases the fluoride recharging ability of the material.

6.3 Materials and methods

Based on previous results all experimental groups based on NaF concentrations of 0%, 10%, 20% and 30% were used. Acetone was added at two concentrations (0%A and 10%A). An adhesion promoting monomer (4-META) was added at two concentrations namely 0%M and 5%M. The material was mixed using the same procedure as described in chapter 4, with the 5% 4-META added to the liquid to encourage its dissolution, because it is supplied as a powder. A total of 16 experimental groups were prepared (see Table 6.1). Transbond^{TM} XT (3M Unitek, UK) and Ketac-cement (Ketac^{TM} Cem, 3M ESPE, Germany) was used as a commercial comparator. Four experiments were undertaken including, DoC, water sorption and solubility, fluoride release and fluoride recharge. SEM images were taken for all experimental materials immediately after specimen preparation (fresh) and after immersion in water for 28 days (aged).

Table 6.1 Composition of experimental groups

Experimental Materials	PMMA%	NaF%	Acetone%	4-META%	Other components
10:0 0%A 0%M	100	0	0	0	Monomers: 40% HEMA 60% MMA Photo-initiator system: 1% CQ 1% DMAEMA
10:0 0%A 5%M	100	0	0	5	
10:0 10%A 0%M	100	0	10	0	
10:0 10%A 5%M	100	0	10	5	
9:1 0%A 0%M	90	1	0	0	
9:1 0%A 5%M	90	1	0	5	
9:1 10%A 0%M	90	1	10	0	
9:1 10%A 5%M	90	1	10	5	
8:2 0%A 5% M	80	2	0	0	
8:2 0%A 5%M	80	2	0	5	
8:2 10%A 0%M	80	2	10	0	
8:2 10%A 5%M	80	2	10	5	
7:3 0%A 0%M	70	3	0	0	
7:30%A 5%M	70	3	0	5	
7:3 10%A 0%M	70	3	10	0	
7:3 10%A 5%M	70	3	10	5	

6.3.1 *Degree of conversion (DoC)*

The DoC of the experimental materials and Transbond™ XT (3M Unitek, UK) as a commercial comparator were taken using FTIR-ATR (Spectrum 100, PerkinElmer, Bucks, UK). 10 specimens of each material were prepared by placing the material into washers of (6.4 mm internal diameter and 0.8 mm thick) (A2 stainless steel plain washer metric BS4320), which were light cured for 40 seconds using bluephase® 20i LCU, emitting 1130 mW/cm^2 intensity (measured using Coltolux Intensity Meter, Germany). The polymerized specimens were directly placed on the diamond crystal of a horizontal attenuated total reflectance attachment stage (ATR) using a clamp to obtain contact between the sample and diamond disc**.** For each material 5 spectra were measured in the unpolymerized state, which the material were placed in the washers on the ATR-sensor. The upper surface of the specimen was covered with a Mylar sheet and a glass slide of 1mm thickness and slightly pressed against the ATR to ensure the good contact of the specimen. The FTIR spectrometer was operating under the following

conditions: 4000–750 cm^{-1} range, 4 cm^{-1} resolution, and 32 co-added scans, using dedicated software (Spectrum, PerkinElmer).

The same method as described in section 4.4.2 was used for analysis and calculation of the DoC, except for Transbond XT group where the aromatic band of C-C at 1607cm^{-1} peak was taken as the internal standard. After processing, all data was imported into dedicated statistical software (SPSS 19 for windows, IBM SPSS Inc., USA) for analysis. The Shapiro-Wilk test was used to test normality of the data. The data were normally distributed. One-way ANOVA and post-hoc Tukey tests were used to determine statistically significant differences between groups at the 5% level ($P<0.05$). In order to consider the effects of each of the variables (Acetone%, Fluoride%, 4-META%) on the DoC, a three way ANOVA was undertaken.

6.3.2 *Water sorption and solubility*

Circular discs were prepared of all experimental materials, Transbond XT and Ketac-cement. The materials were prepared using a Teflon mould of 1 mm thick and 10 mm in diameter, and light cured for 40 seconds using bluephase®20i LCU. The Ketac-cement samples were prepared by mixing the powder and liquid (3:8:1 w/w) ratio according to the manufacturer's instructions, placed into the same Teflon mould and left for 24 hours to set. Samples were then polished with 12000 grit sandpaper to obtain a smooth surface. Samples were then placed into a desiccator containing dried silica gel and placed into an oven at 37°C for 24 hours. The desiccator was then removed from the oven and all specimens weighed using an analytical electronic balance (Mettler AE 240, 0.01mg accuracy, Switzerland). A constant weight was considered to have been achieved when the mass change of each specimen did not exceed 0.1 mg in any 24 hour period, and this weight was designated as w1.

Samples were stored in 5 ml distilled water in an oven at 37°C for 28 days. The water was changed daily for the first two weeks then each week for the next two weeks. At 28 days, samples were removed from the water, blotted dry until the surface appeared free of visible moisture, air dried for 15 seconds (by waving it gently while it is being held by tweezers) and weighed. The saturated weight was designated as w2. They were then reconditioned to a dry constant mass using a desiccator as described above. The constant mass was designated as w3. Sample volume (V) was calculated in mm^3 after measuring the diameter and thickness of each sample. Thickness was measured in the center of each sample and at 4 equally spaced points around the circumference to allow calculation of the average thickness of each sample. Water sorption and solubility was then calculated in ($\mu g/mm^3$) using the following Equation 6.1 and Equation 6.2.

Equation 6.1……. $\text{Water sorption } (\mu g/mm^3) = \frac{W2-W1}{V}$

Equation 6.2…….. $\text{Water Solubility } (\mu g/mm^3) = \frac{W3-W1}{V}$

All data were analysed using statistical software (SPSS 19 for windows, IBM SPSS Inc., USA). The Shapiro-Wilk test was used to test normality of the data. The data were normally distributed. Two individual one-way ANOVA and Tukey post hoc (one for water sorption and the other for solubility data), using the materials as the main factor was used to determine statistically significant differences between groups at the 5% level ($P<0.05$).

6.3.3 *Fluoride release:*

10 specimens were prepared of each of the fluoride containing experimental materials using the same method described in chapter 4.3.4, except that curing was undertaken for this experiment using the bluephase®20i LCU. For preparing Ketac-cement the powder and liquid were mixed using 3.8:1 w/w powder to liquid ratio according to the manufacturer's instructions. The prepared material was then placed into the same mould as used for the experimental materials and compressed to expel excess material. The specimens were left in the mould for 24 hours to set. Samples were then polished with 12000 grit sandpaper to obtain a smooth surface.

Fluoride release measurements were taken using the same method as described in chapter 4 except they were taken for only 28 days. After fluoride measurement, all data were then imported into dedicated statistical software (SPSS 19 for windows, IBM SPSS Inc., USA). The Shapiro-Wilk test was used to test normality of the data. The data were normally distributed. One-way ANOVA and post hoc Tukey test were used to determine statistically significant differences between groups at the 5% level ($P<0.05$).

6.3.4 *Fluoride recharge:*

The recharging ability of all fluoride contained experimental groups and Ketac-cement commercial GIC were tested. 10 specimens for each group were prepared using the same method as mentioned in section 6.3.3. All specimens were stored in cylindrical vials containing 5ml of deionized distilled water (DDW) for 28 days before recharging commenced. The water was changed every week to prevent saturation.

One day before recharging, fluoride release measurements of all specimens were taken using the same procedure described in section 6.3.3. For recharging, the specimen disc was immersed in 5 ml of a 1000 ppm fluoride solution, made by dissolving 2.21 g of NaF in 100 g water, for three minutes in an ultrasonic bath to simulate the weekly mouth wash. Samples were then rinsed with DDW, dried with paper towel and stored in 5ml of fresh DDW. Daily fluoride measurements were taken for seven days after recharging, after which the specimens were left in DDW for a week before repeating the recharge process for a further 2 cycles. The DDW was replaced a day before starting each recharge cycle.

All data were imported into dedicated statistical software (SPSS 19 for windows, IBM SPSS Inc., USA). The Shapiro-Wilk test was used to test normality of the data. The data were normally distributed. A paired sample t-test was carried out to show the significances between pairs of samples of the same group for each recharge cycle. In all tests, a significance level of 5 per cent was used.

6.3.5 *SEM observation*

Three aged and three freshly made specimens from each fluoridated experimental group and Ketac-cement were observed under SEM (Stereoscan S40, Cambridge Instruments, UK). Aged specimens were examined following immersion in water for 28 days with daily water change for the first two weeks and weekly for the two following weeks. Fresh and aged specimens were made using the same procedure used in preparation of fluoride releasing samples and stored at 37°C in an incubator for 24 hours in relatively 100% humidity. After 24 hours these surfaces were lapped using 1200 grit paper (Norton, Abrasive Technological Excellence, France).

Aged and fresh specimens were dried in a desiccator for seven days then mounted on an aluminium stub and coated with gold (standard 15 nm) using a Polaron SEM coating unit. SEM images were taken at two different magnification powers. Approximately 50X and 500X were applied to examine the surfaces of both fresh and aged specimens.

6.4 Results

6.4.1 *Degree of conversion (DoC)*

The DoCs of all experimental materials are shown in Table 6.2. All experimental groups had higher DoC than Transbond XT except group 8:2 0%A 5%M ($p<0.05$, one-way ANOVA). Group 10:0 0%A 0%M had significantly higher DoC than all experimental groups except group 7:3 0%A 0%M ($p<0.05$, one-way ANOVA).

In group 10:0, addition of either acetone or 4-META results in lowering DoC as illustrated in Figure 6.1 ($p<0.05$, one-way ANOVA).

In groups 9:1 and 8:2, no differences were found after addition of either acetone or 4-META or a combination of both ($p<0.05$, one-way ANOVA) see Figure 6.2and Figure 6.3.

In group 7:3, addition of either acetone or 4-META alone results in decreasing DoC, while when both 4-META and acetone added together no differences were found ($p<0.05$, one-way ANOVA) see figure 6.4.

Figure 6.5 shows that all experimental groups had DoC more than 50%, with group 10:0%A 0%M had higher DoC than the rest except 7:3 0%A 0%M ($p<0.05$, one-way ANOVA).

The data for the average value of DoC could also be presented as a function of fluoride concentrations, as illustrated in figure 6.6. A linear model was fitted to this data. Weak

correlations were observed between DoC and fluoride concentrations at (0%A 5%M) and (10%A 0%M) (r=0.50, 0.60 for (0%A 5%M) and (10%A 0%M) respectively. No relationship was seen at (0%A 0%M) and (10%A and 5%M)

The results of three way ANOVA showed that there was a statistically significant interaction between Fluoride%, Acetone% and 4-META% (P = 0.002).

Table 6.2 Show mean DoC of all experimental groups

Experimental Materials	Mean DoC (%) at 40 seconds
10:0 0%A 0%M	71 (2)[a]
10:0 0%A 5%M	63 (2)[bg]
10:0 10%A 0%M	62 (5)[bg]
10:0 10%A 5%M	61 (3)[bg]
9:1 0%A 0%M	59 (4)[b]
9:1 0%A 5%M	57 (1)[b]
9:1 10%A 0%M	62 (5)[bg]
9:1 10%A 5%M	61 (2)[bg]
8:2 0%A 5% M	56 (4)[bc]
8:2 0%A 5%M	50 (7)[bh]
8:2 10%A 0%M	62 (5)[bg]
8:2 10%A 5%M	62 (3)[bg]
7:3 0%A 0%M	66 (4)[ag]
7:3 0%A 5%M	55 (4)[c]
7:3 10%A 0%M	53 (9)[c]
7:3 10%A 5%M	60 (6)[bcg]
Transbond XT	43 (4)[h]

The entries are mean values with SD in the parenthesis. Similar superscript letters indicate no significant differences between groups (ANOVA, post-hoc Tukey test, p> 0.0

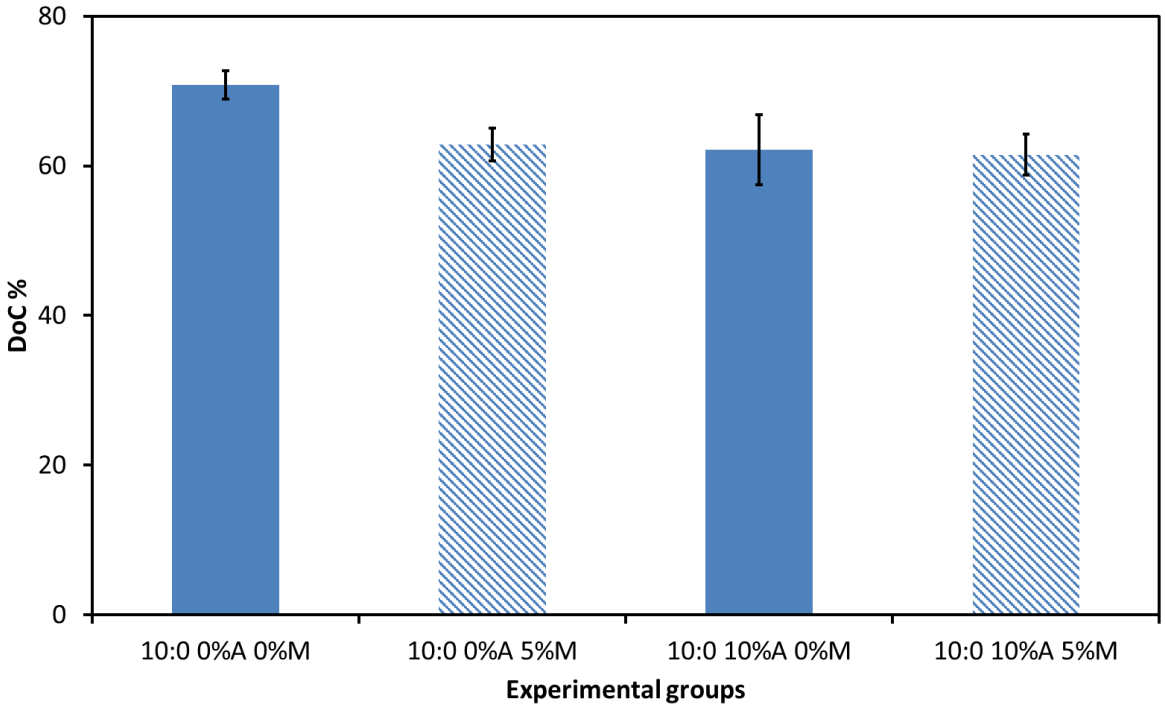

Figure 6.1 Mean degree of conversion of the group 10:0 with and without 10% acetone and 5% 4-META. Error bars represent SD

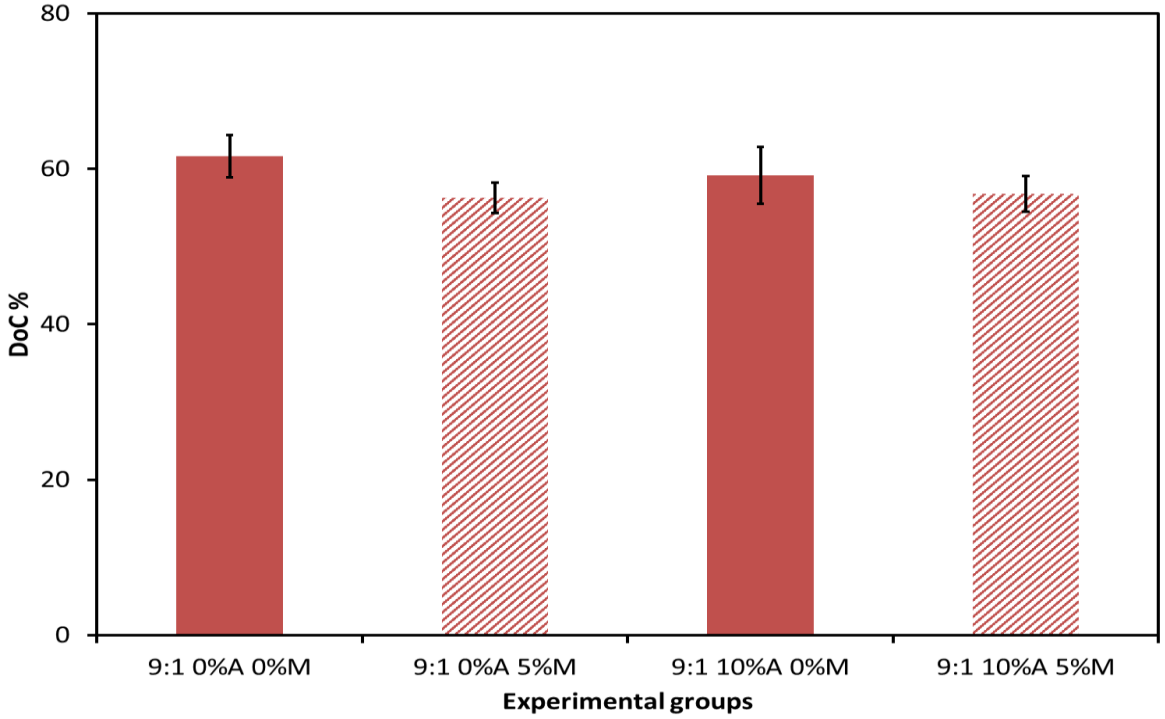

Figure 6.2 Mean degree of conversion of the group 9:1 with and without 10% acetone and 5% 4-META. Error bars represent SD.

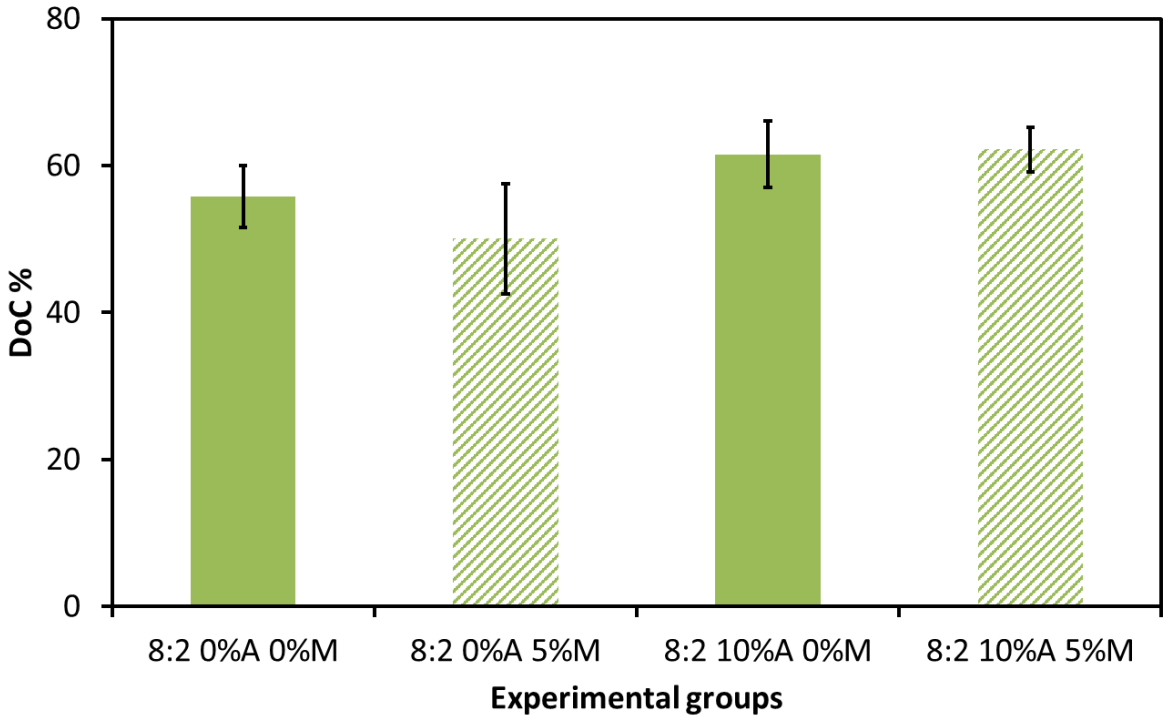

Figure 6.3 Mean degree of conversion of the group 8:2 with and without 10% acetone and 5% 4-META. Error bars represent SD.

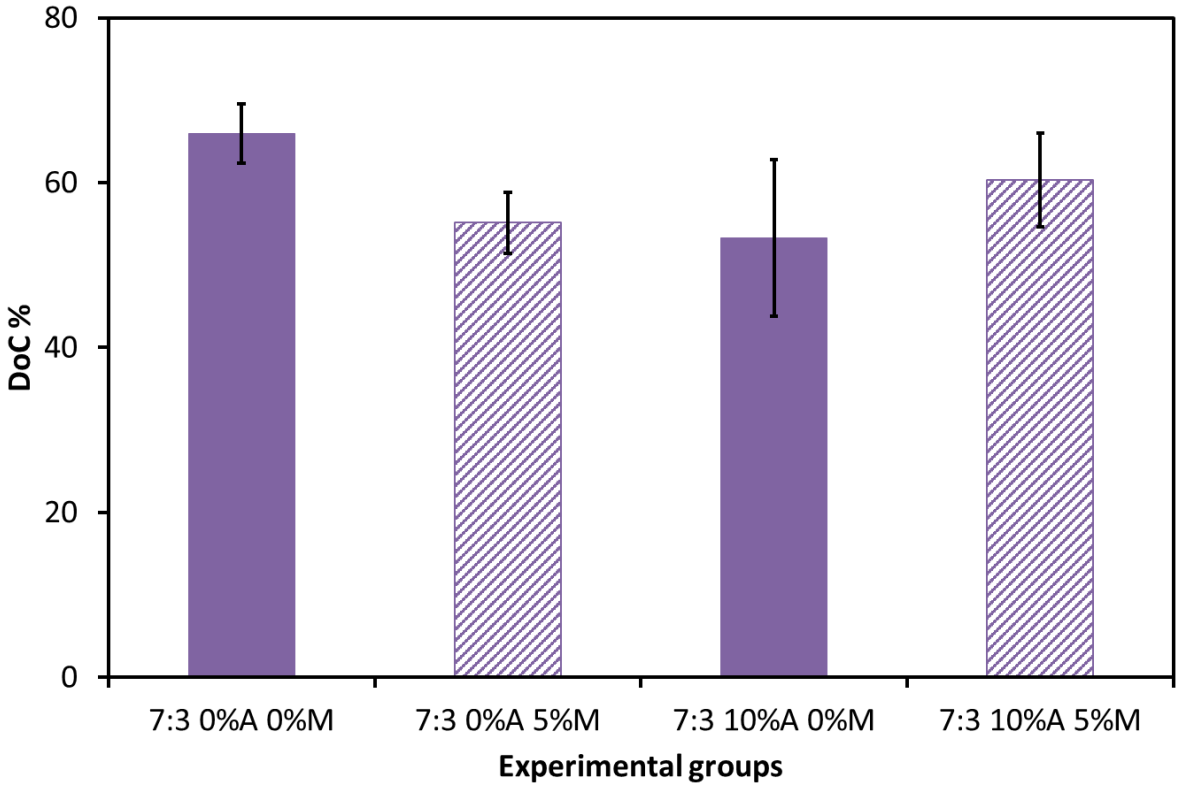

Figure 6.4 Mean degree of conversion of the group 7:3 with and without 10% acetone and 5% 4-META. Error bars represent SD.

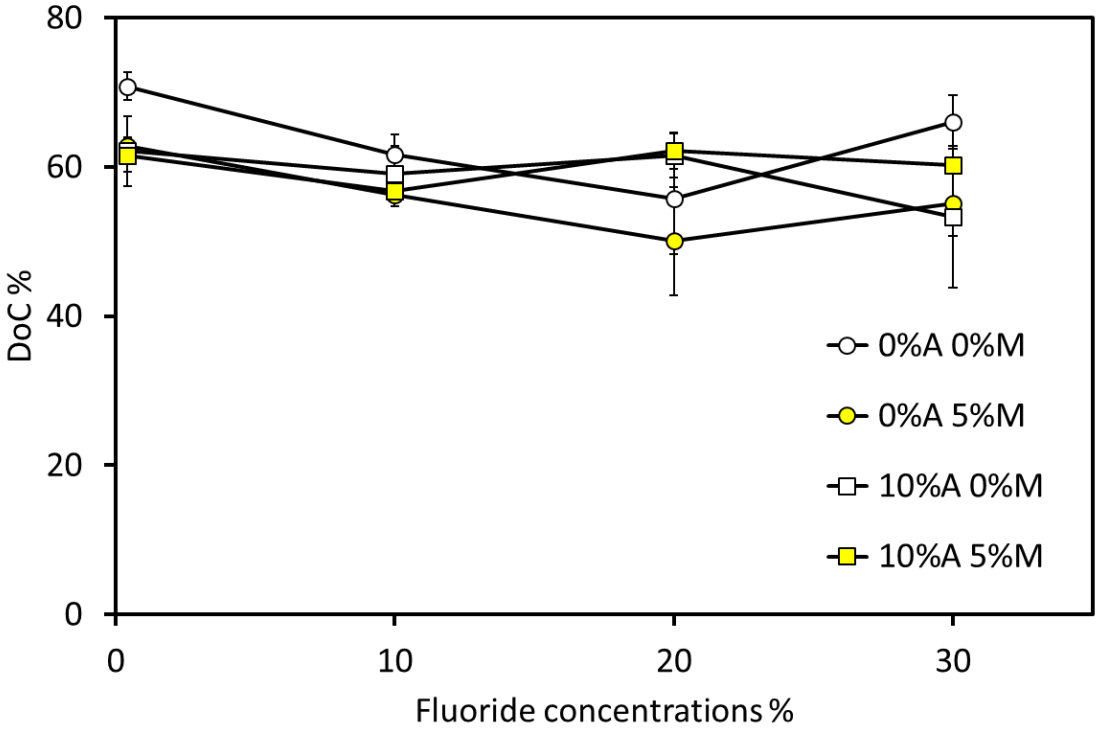

Figure 6.5 Mean DoC of all experimental groups based on different fluoride, acetone and 4-META concentrations. Error bars represent SD.

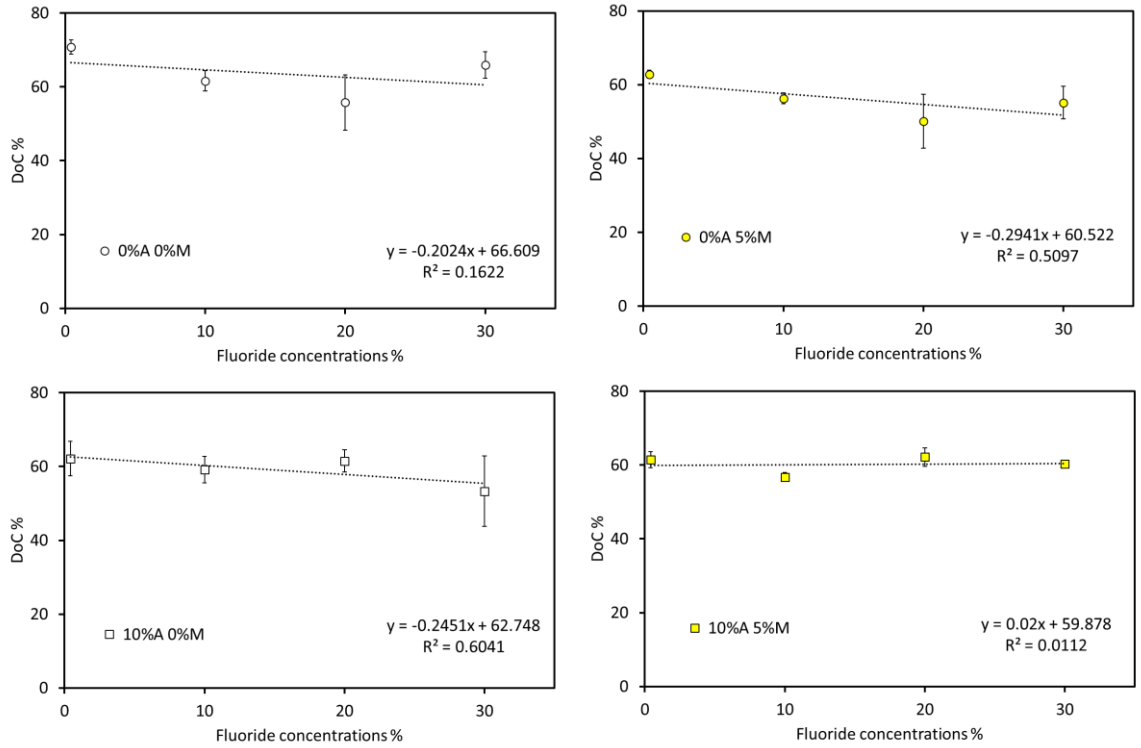

Figure 6.6 Relationship between DoC and fluoride concentrations at 40 seconds of light curing and at 0% and 5% and 10% acetone and 4-META. Data represents mean value with error bars represent SD.

6.4.2 *Water sorption and solubility*

The water sorption and solubility values are summarized in table 6.3. Solubility significantly increases with increasing NaF concentration irrespective of the acetone and 4-META concentrations ($p<0.05$, ANOVA, Tukeys test). Transbond XT had the lowest solubility ($p<0.05$, one-way ANOVA).

All experimental groups with 10%A 0%M had significantly higher solubility than the rest of the groups ($p<0.05$, one-way ANOVA) see figure 6.7.

In groups 10:0 and 9:1 all samples containing 10%A 0%M had significantly higher water sorption than the rest ($p<0.05$, one-way ANOVA) see figures 6.8 and 6.9.

The water sorption and solubility of group 7:3 Ketac-cement and Transbond XT are shown in figure 6.10 and 6.11.

The relationship between water sorption and fluoride concentration of all experimental materials is shown in figure 6.12. The figure shows that water sorption depends on fluoride and acetone and 4-META content of the material.

The relationship between water solubility and fluoride concentration of all experimental materials is shown in figure 6.13. The figure shows that solubility increases with increasing NaF concentrations.

The data for the average value of solubility could also be presented as a function of fluoride concentrations, as illustrated in figure 6.14. A linear model was fitted to this data. There was a significant correlation at $p<0.01$ between solubility and fluoride concentrations. The r values are (0.97, 0.98, 0.93 and 0.96) of the groups (0%A 0%M, 0%A 5%M, 10%A 0%M and 10%A 5%M) respectively.

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Table 6.3 Water sorption and solubility.

Materials	Water sorption µg/mm³ Mean (SDV)	Solubility µg/mm³ Mean (SDV)
10:0 0%A 0%M	44 (7)^{A}	16 (4)^{ae}
10:0 0%A 5%M	36 (7)^{A}	18 (3)^{ab}
10:0 10%A 0%M	68 (9)^{A}	45 (6)^{bck}
10:0 10%A 5%M	35 (5)^{A}	33 (8)^{cbd}
9:1 0%A 0%M	53 (15)^{A}	43 (6)^{bef}
9:1 0%A 5%M	63 (12)^{A}	48 (3)^{ckg}
9:1 10%A 0%M	133 (56)^{B}	125 (31)^{h}
9:1 10%A 5%M	46 (9)^{A}	54 (5)^{dgk}
8:2 0%A 5% M	29 (4)^{A}	87 (13)^{l}
8:2 0%A 5%M	88 (14)^{A}	111 (32)^{hl}
8:2 10%A 0%M	45 (22)^{A}	154 (25)^{o}
8:2 10%A 5%M	39 (14)^{A}	97 (12)^{l}
7:3 0%A 0%M	4 (10)^{C}	147 (15)^{ho}
7:30%A 5%M	11 (5)^{C}	154 (24)^{o}
Ketac-cement	15 (10)^{C}	138 (34)^{hmo}
Transbond XT	12 (3)^{C}	2 (3)^{a}

The entries are mean value with SD in the parenthesis. Values exhibited similar superscript letters indicate no significant difference within columns ($p > 0.05$)

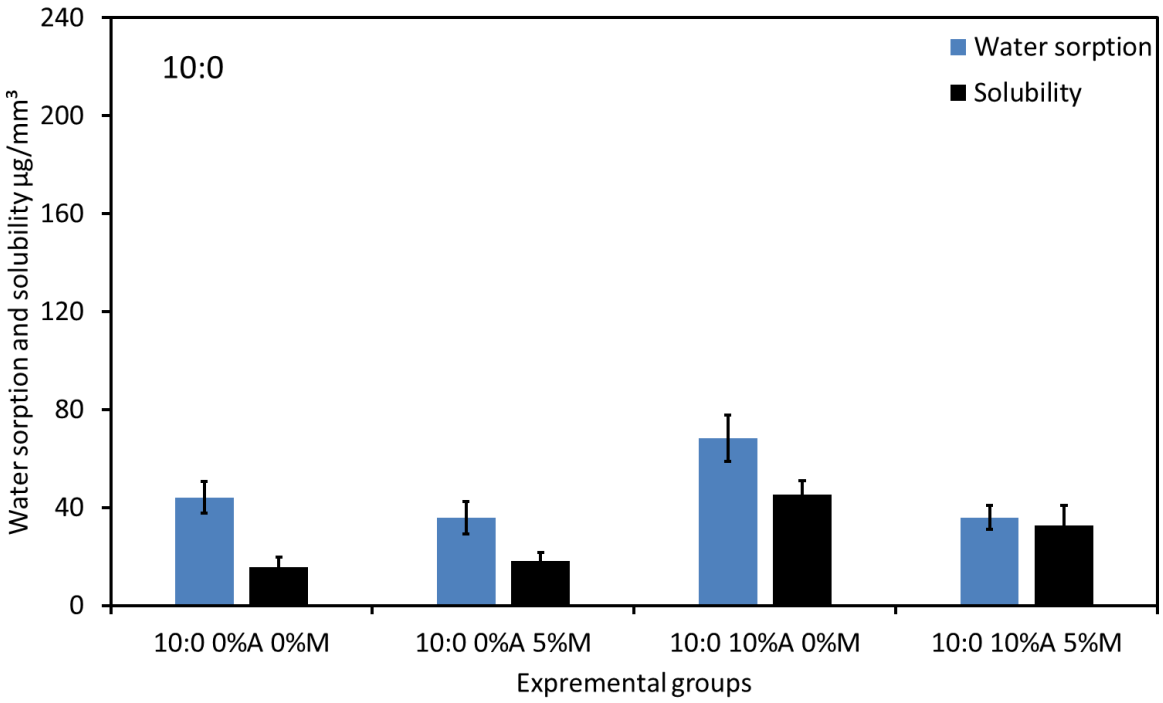


Figure 6.7 Mean water sorption and solubility of group 10:0 with and without acetone (10%) and 4-META (5%). Error bars represent SD.

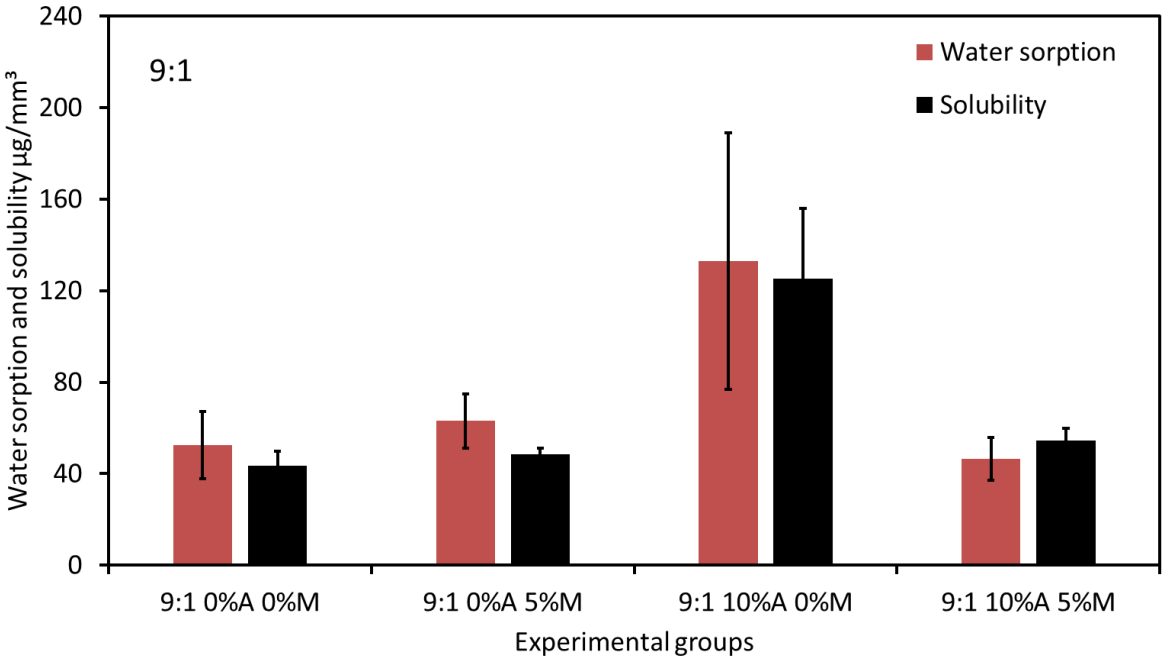


Figure 6.8 Mean water sorption and solubility of group 9:1 with and without acetone (10%) and 4-META (5%). Error bars represent SD.

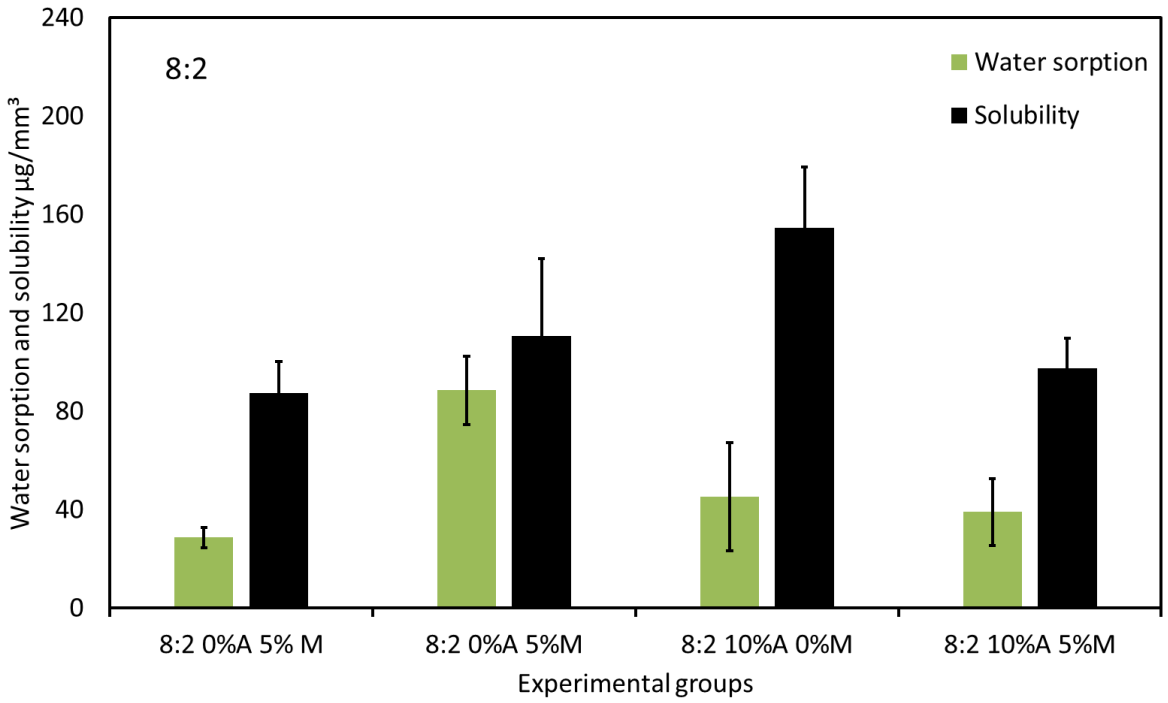


Figure 6.9 Mean water sorption and solubility of group 8:2 with and without acetone (10%) and 4-META (5%). Error bars represent SD.

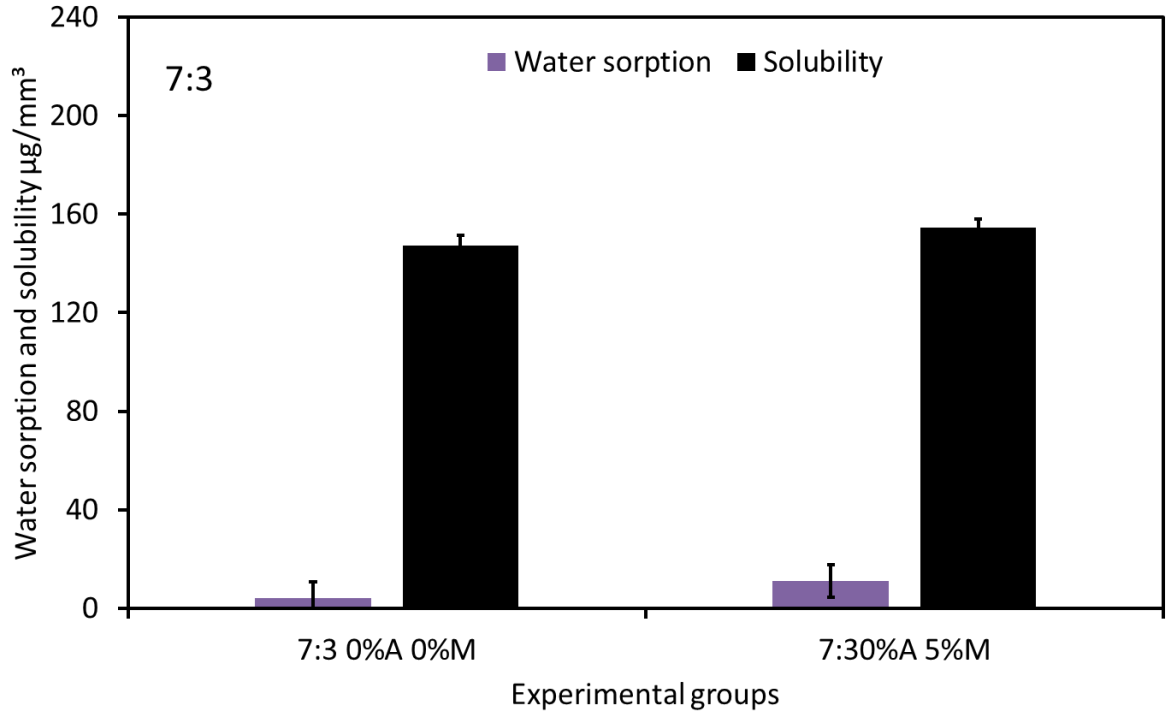


Figure 6.10 Mean water sorption and solubility of group 7:3 with and without 4-META (5%). Error bars represent SD.

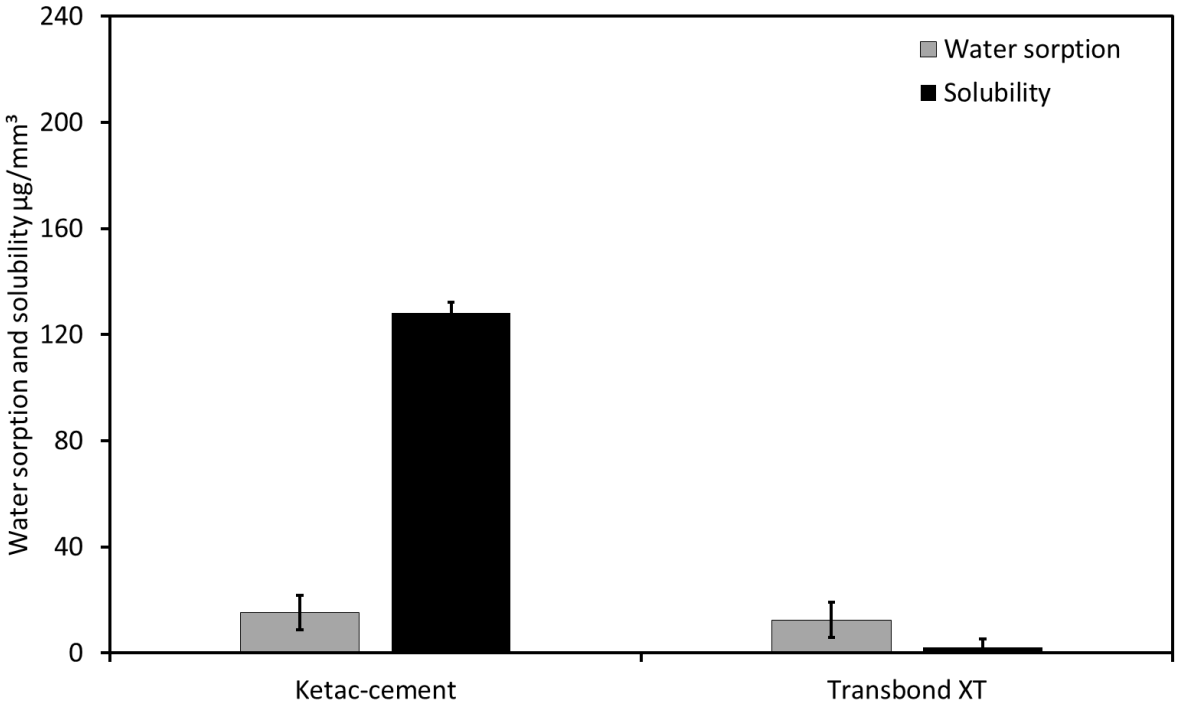


Figure 6.11 Mean water sorption and solubility of ketac-cement and Transbond XT. Error bars represent SD.

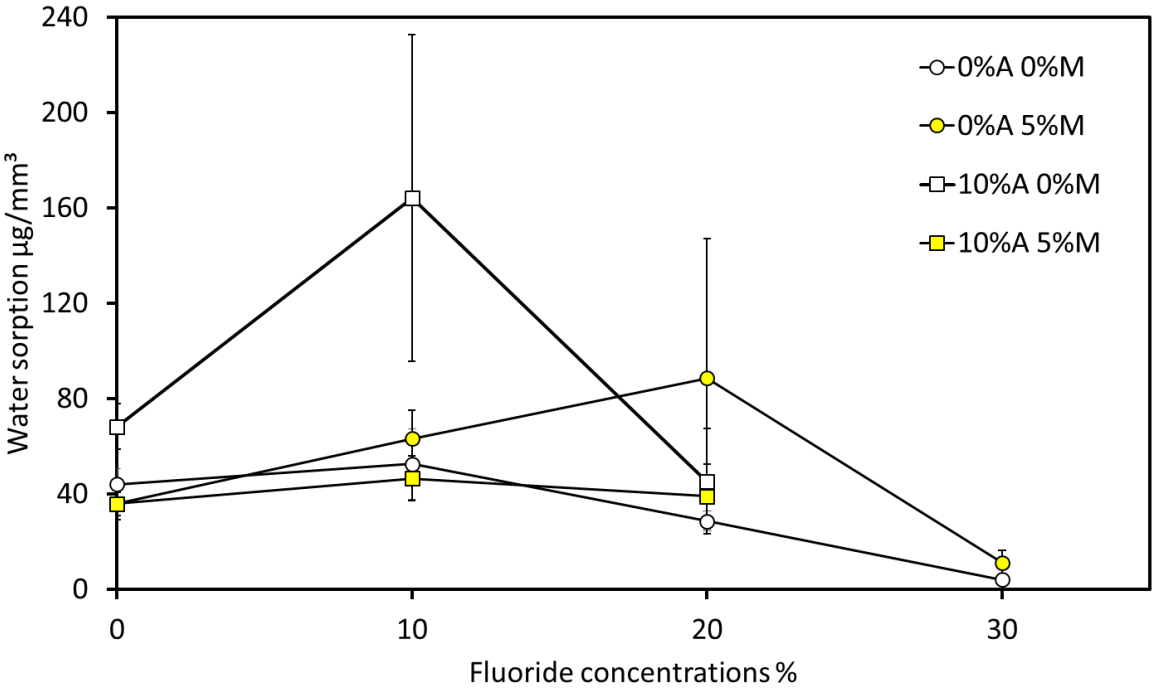


Figure 6.12 Mean water sorption of all experimental materials. Error bars represent SD.

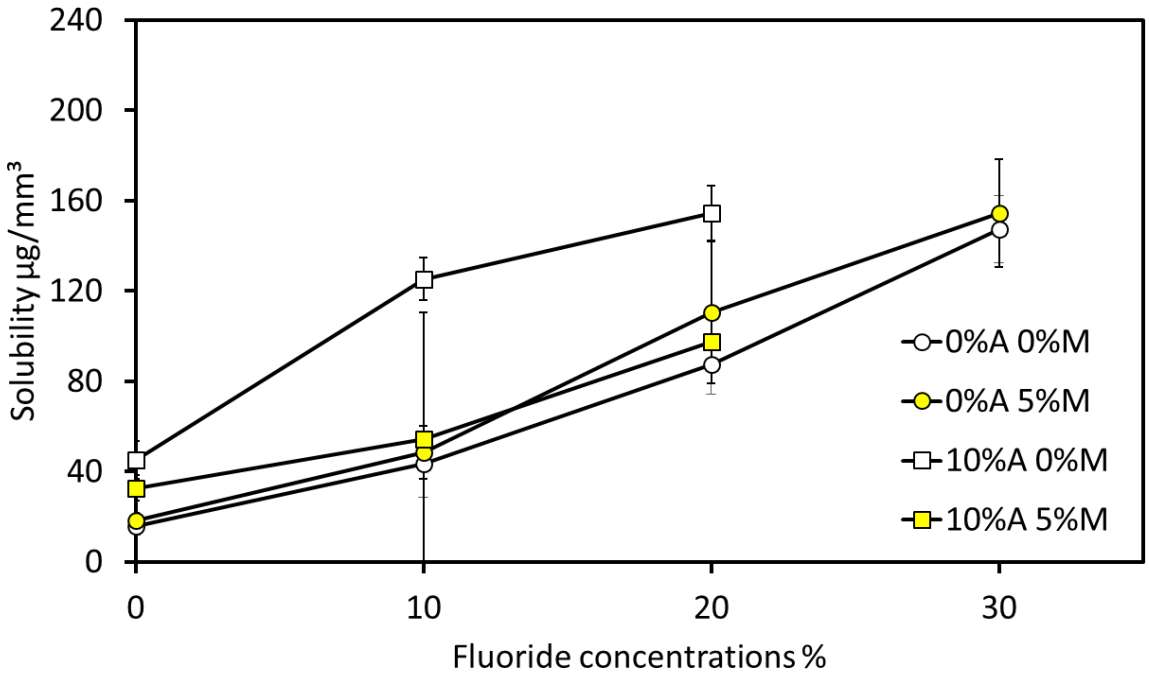


Figure 6.13 Relationship between water solubility and fluoride concentrations of all experimental materials. Error bars represent SD.

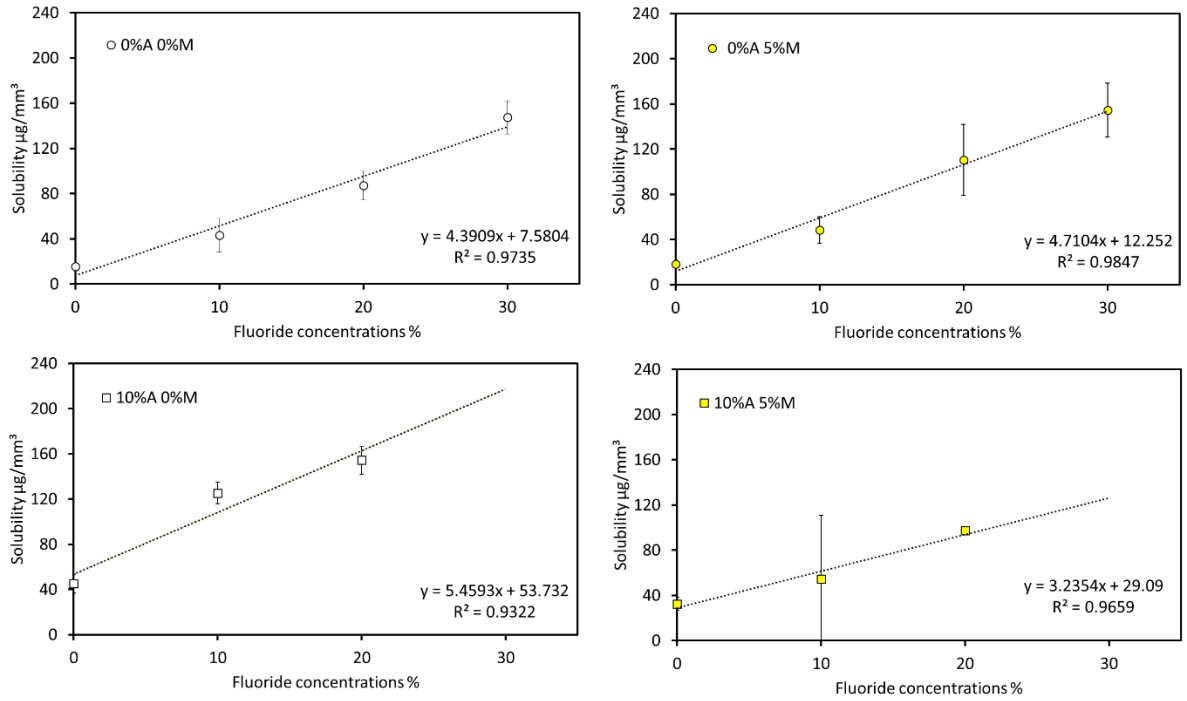


Figure 6.14 relationship between Solubility and fluoride concentrations. Data represents mean value with error bars represent SD.

6.4.3 *Fluoride release*

All experimental materials had significantly greater fluoride release than Ketac-cement at days 1, 2 and 7 ($p<0.05$, one-way ANOVA), with the groups with the 10%A 0%M exhibiting the highest amount except in group 8:2 and 7:3 see table 6.4.

At day 28, all experimental groups with the 0%M had significantly higher fluoride release than the 5% M and the Ketac-cement specimens ($p<0.05$, one-way ANOVA) see table 6.4.

The pattern of fluoride release was similar for all experimental materials and Ketac-cement. All materials had an initial burst-effect fluoride release followed by decreasing with time see figures 6.15, 6.16, 6.17, 6.18, 6.19, 6.20, 6.21 and 6.22.

In comparison between groups, group 7:3 released significantly higher fluoride at days 1 and 2 than all groups in each measurement point, followed by group 8:2 which showed significant greater release than group 9:1 ($p<0.05$) see table 6.4.

The fluoride release measurement at day 1 and 28 are shown in figures 6.23 and 6.24 at day 1 the figure shows groups with 10%A 0%M had higher fluoride release than other groups while on day 28 all groups with 0%M had higher fluoride release than those with 5%M.

The cumulative fluoride release for the 28 days are shown in figure 6.25, which shows groups 9:1 and 8:2 with 10%A 5%M have lower fluoride release than 10%A 0%M.

Table 6.4 Show the mean fluoride release of the fluoride containing groups and Ketac-cement at day 1, 2, 7, 14, 21st and 28th.

Materials	Mean Fluoride release (SDV) µg/cm²/day					
	Day 1	Day 2	Day 7	Day 14	Day 21	Day28
9:1 0%A 0%M	148 (12)^{ab}	85 (17)^{fg}	20 (4)^{j}	10 (2)^{op}	9 (2)^{v}	12 (2)^{z}
9:1 0%A 5%M	143 (15)^{ab}	85 (9)^{fg}	15 (3)^{j}	5 (1)^{oq}	4 (1)^{vw}	4 (1)^{A}
9:1 10%A 0%M	196 (23)^{b}	130 (20)^{g}	70 (18)^{k}	26 (8)^{r}	16 (4)^{x}	12 (4)^{z}
9:1 10%A 5%M	108 (16)^{a}	61 (11)^{f}	19 (8)^{j}	6 (1)^{oq}	5 (1)^{v}	3 (1)^{A}
8:2 0%A 0%M	297 (29)^{c}	278 (22)^{h}	47 (5)^{l}	27 (4)^{r}	31 (6)^{y}	21 (3)^{B}
8:2 0%A 5%M	417 (55)^{d}	246 (122)^{hi}	68 (46)^{kl}	19 (7)^{s}	24 (13)^{x}	14 (3)^{z}
8:2 10%A 0%M	394 (59)^{d}	296 (36)^{h}	85 (21)^{km}	37 (7)^{t}	22 (6)^{x}	23 (3)^{BC}
8:2 10%A 5%M	250 (69)^{c}	218 (35)^{i}	43 (9)^{l}	14 (2)^{ps}	21 (4)^{x}	12 (2)^{z}
7:3 0%A 0%M	613 (90)^{e}	456 (52)^{f}	101 (6)^{n}	59 (4)^{l}	47 (4)	37 (3)
7:3 0%A 5%M	573 (52)^{e}	517 (72)	91 (16)^{mn}	39 (4)^{t}	35 (6)^{y}	25 (3)^{C}
Ketac-cement	18 (5)	8 (4)	4 (1)	3 (1)^{q}	3 (1)^{w}	3 (1)^{A}

The entries are mean value with SD in the parenthesis. Values exhibited similar superscript letters indicate no significant difference within columns ($p > 0.05$) as determined using Tukey HSD.

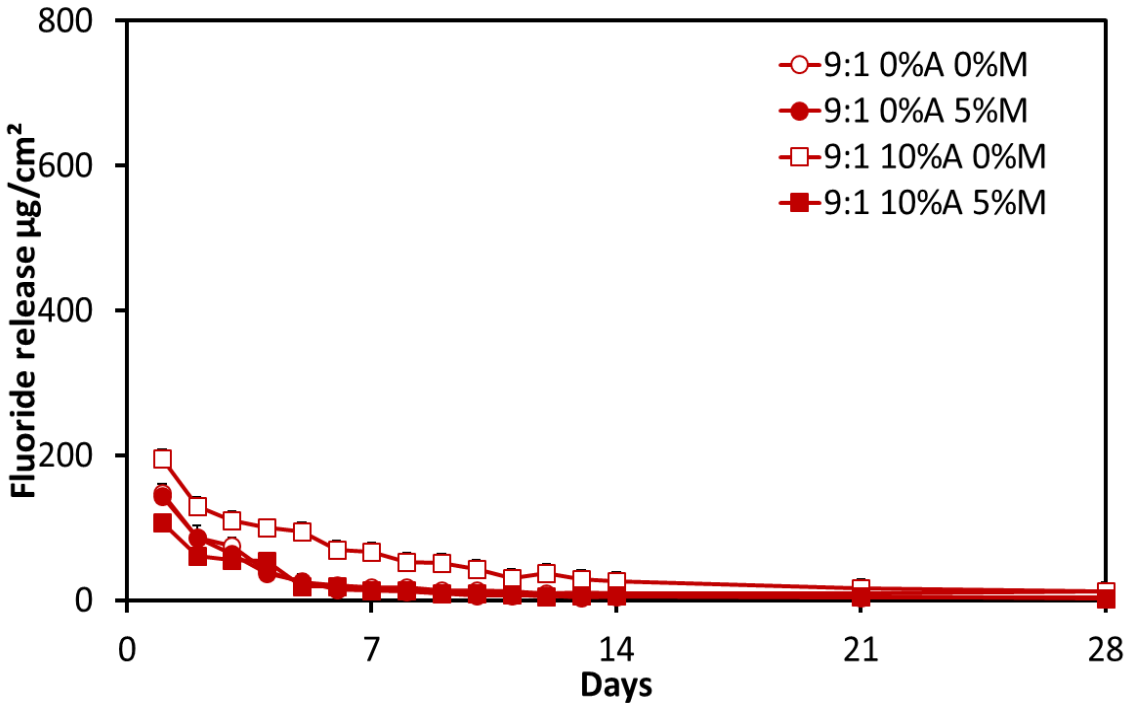


Figure 6.15 Mean fluoride release of all group 9:1 with and without acetone (10%) and 4-META (5%). The figure shows the burst effect pattern of fluoride release from the materials. The error bars represent SD of the mean fluoride release.

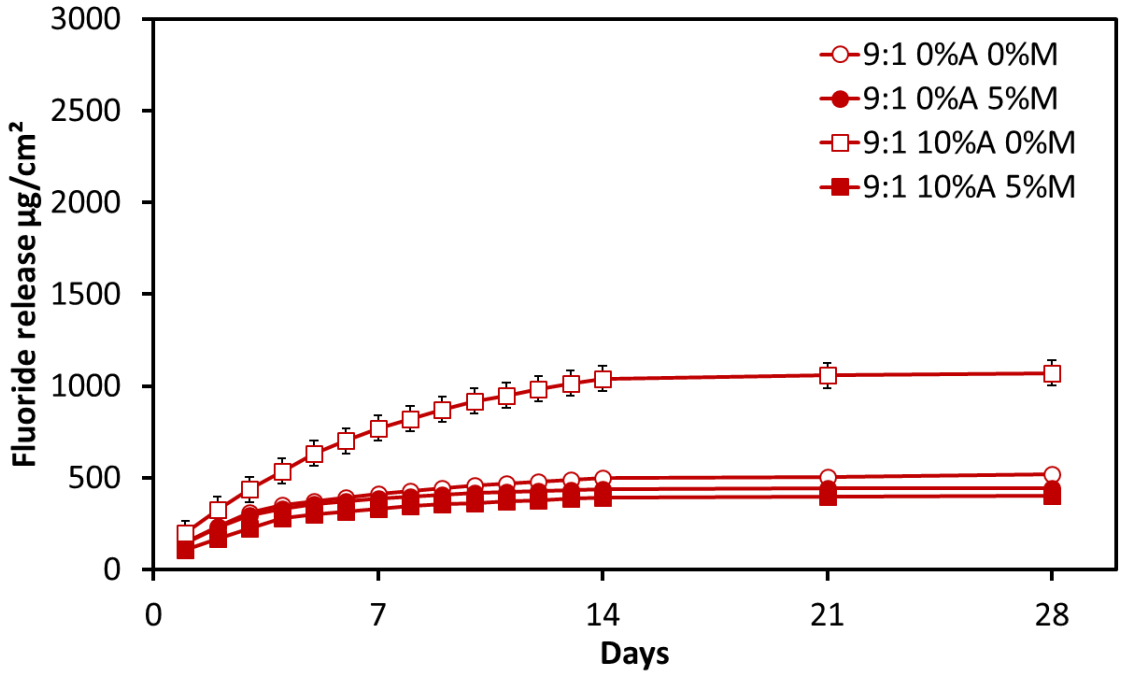


Figure 6.16 Cumulative fluoride release of all group 9:1 with and without acetone (10%) and 4-META (5%).

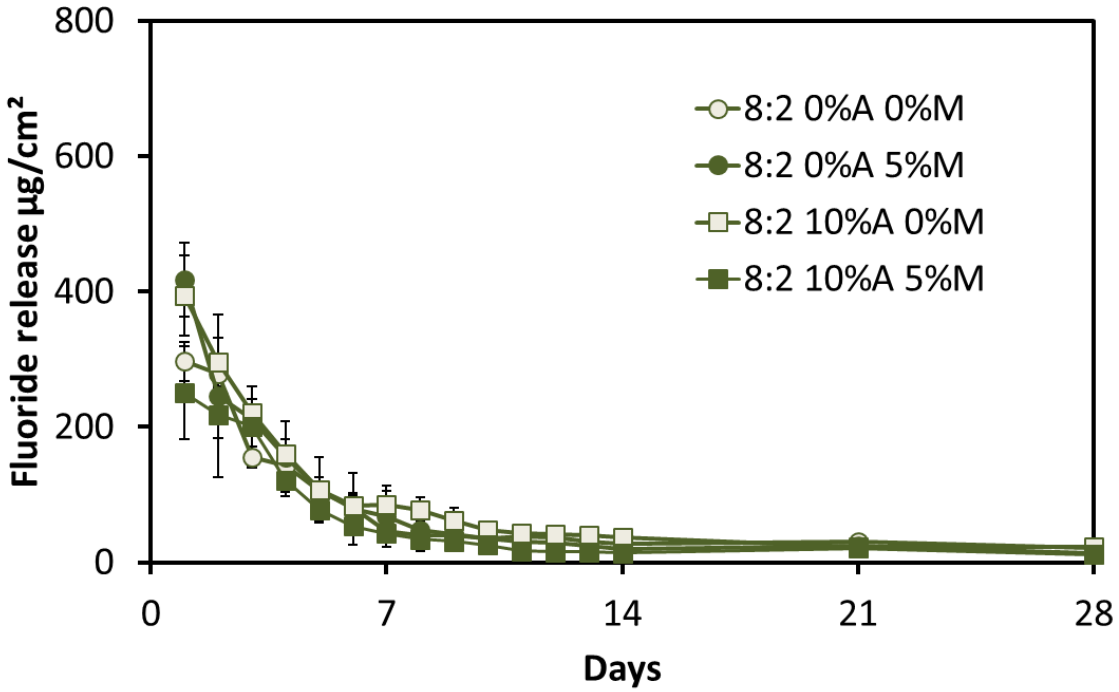


Figure 6.17 Mean fluoride release of Group 8:2 with and without acetone (10%) and 4-META (5%). The figure shows the burst effect pattern of fluoride release from the materials. The error bars represent SD of the mean fluoride release.

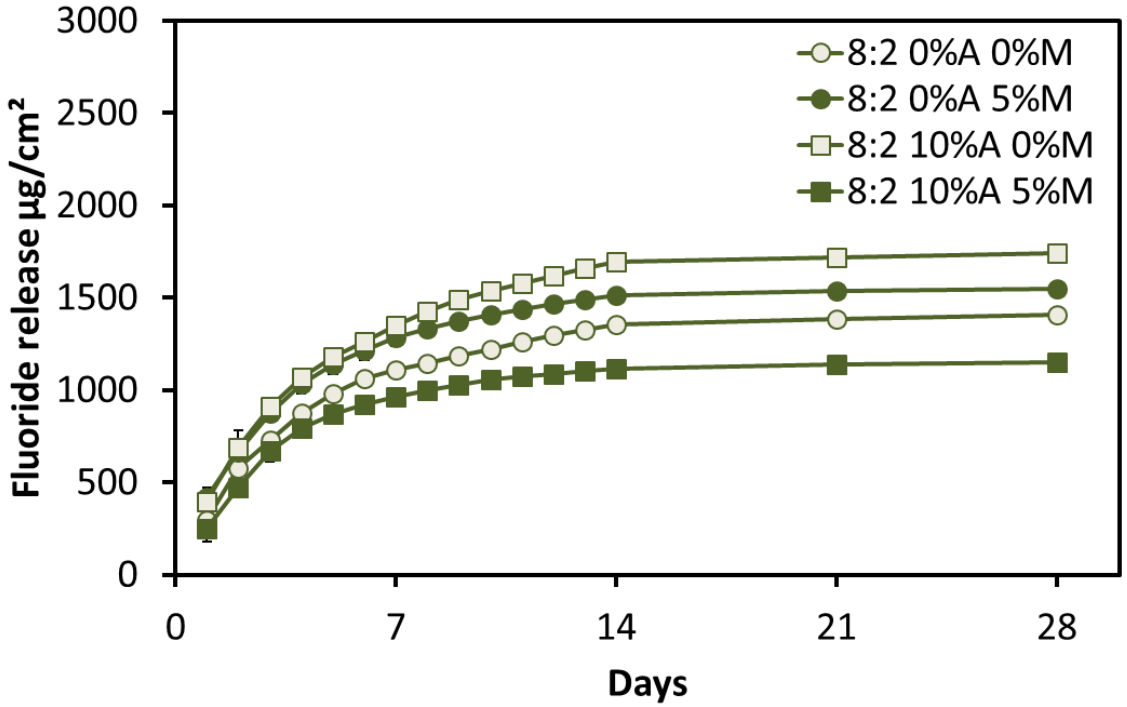


Figure 6.18 Cumulative fluoride release of all group 8:2 with and without acetone (10%) and 4-META (5%).

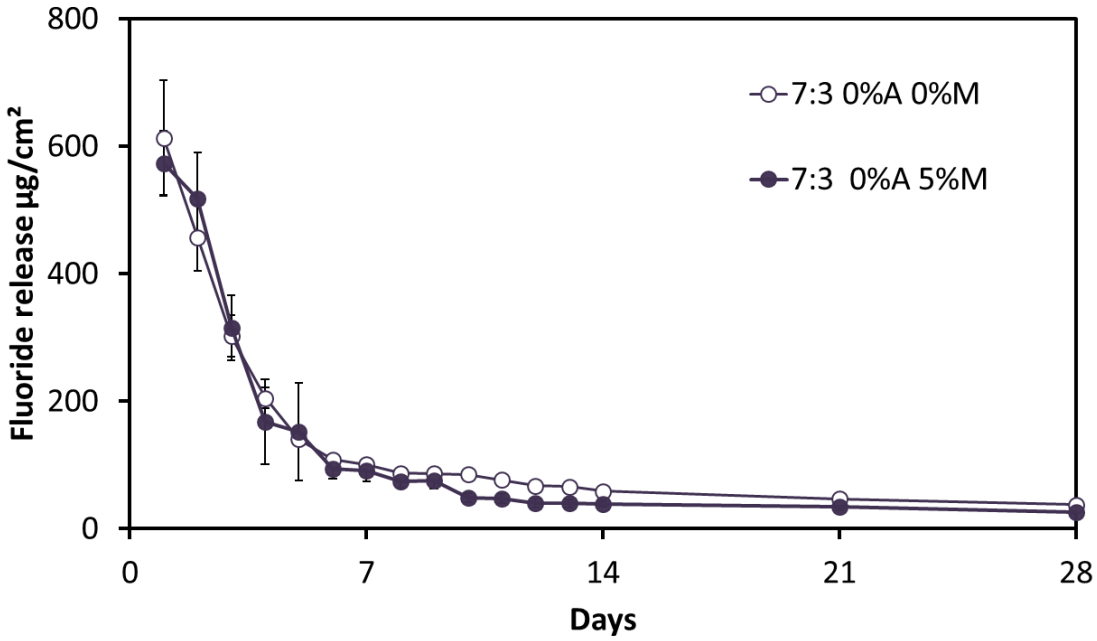


Figure 6.19 Mean fluoride release of group 7:3 with and without 4-META (5%). The figure shows the burst effect pattern of fluoride release from the materials. The error bars represent SD of the mean fluoride release.

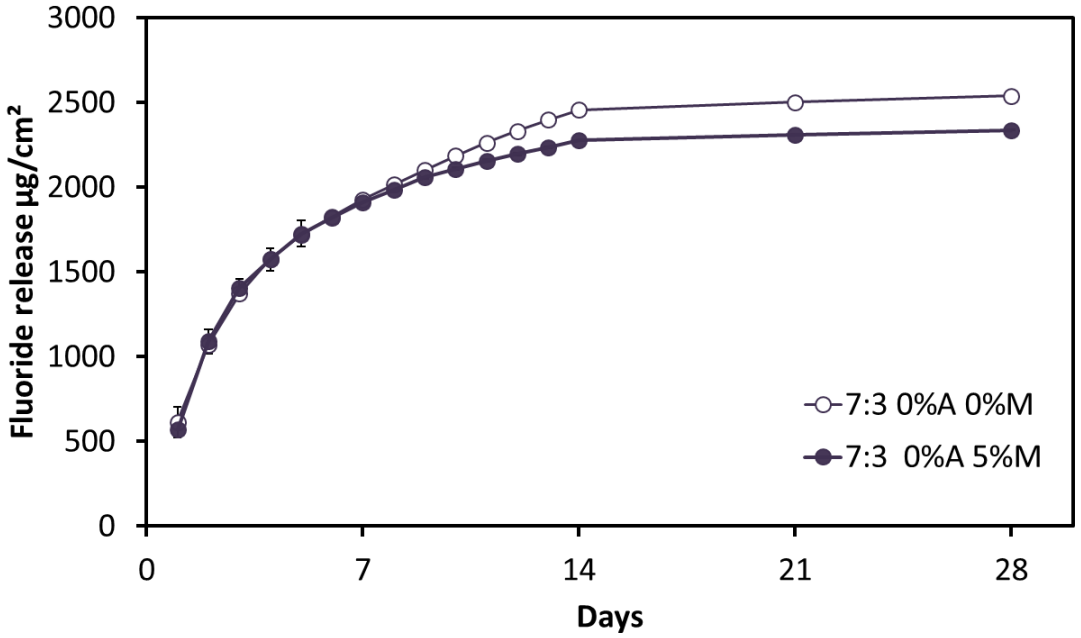


Figure 6.20 Cumulative fluoride release of all group 7:3 with and without 4-META (5%).

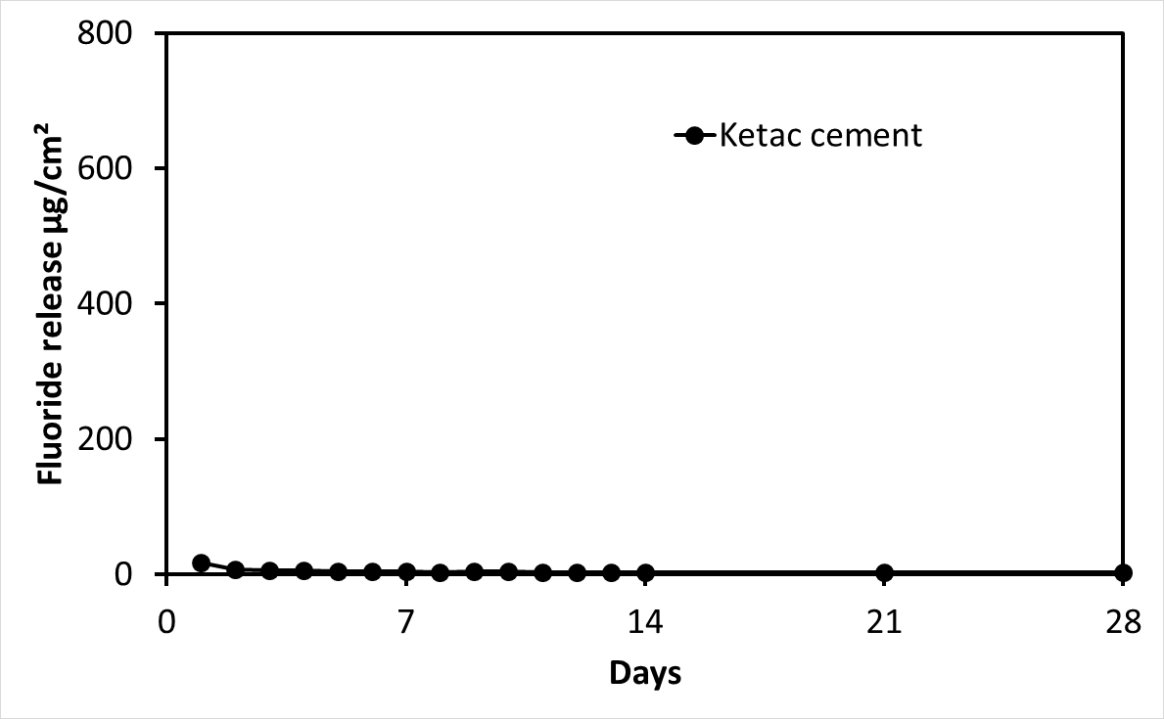


Figure 6.21 Mean fluoride release of Ketac-cement. The error bars represent SD of the mean fluoride release.

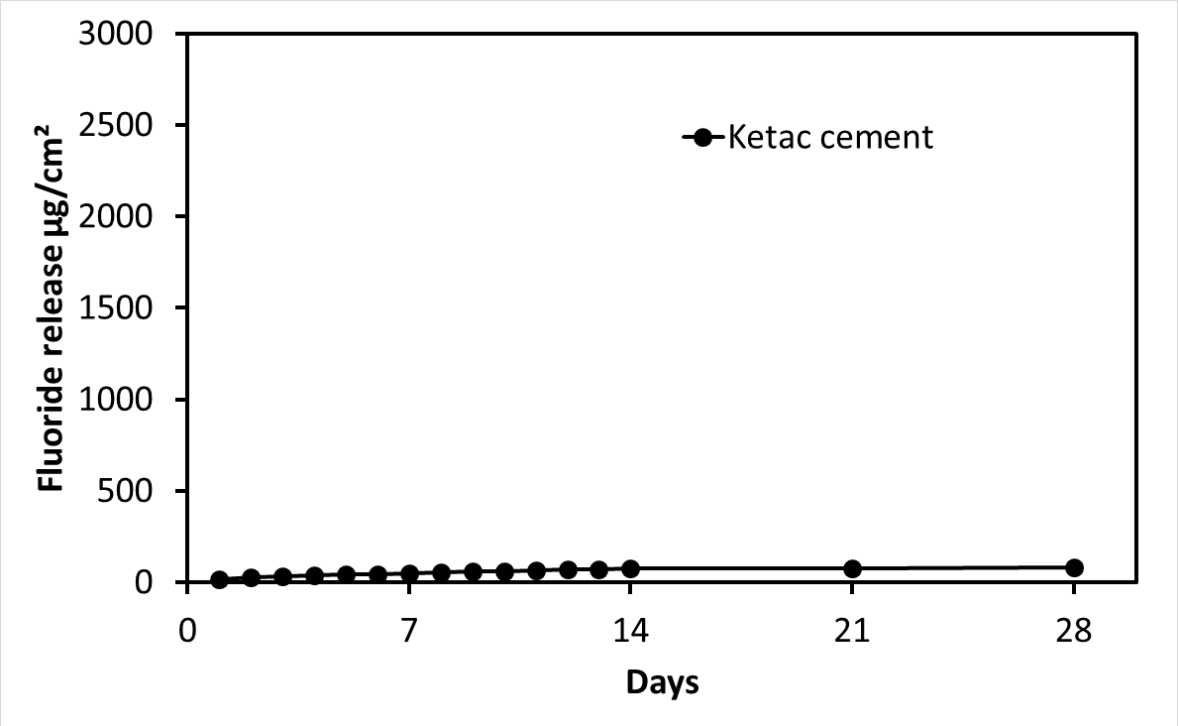


Figure 6.22 Cumulative fluoride release of Ketac-cement.

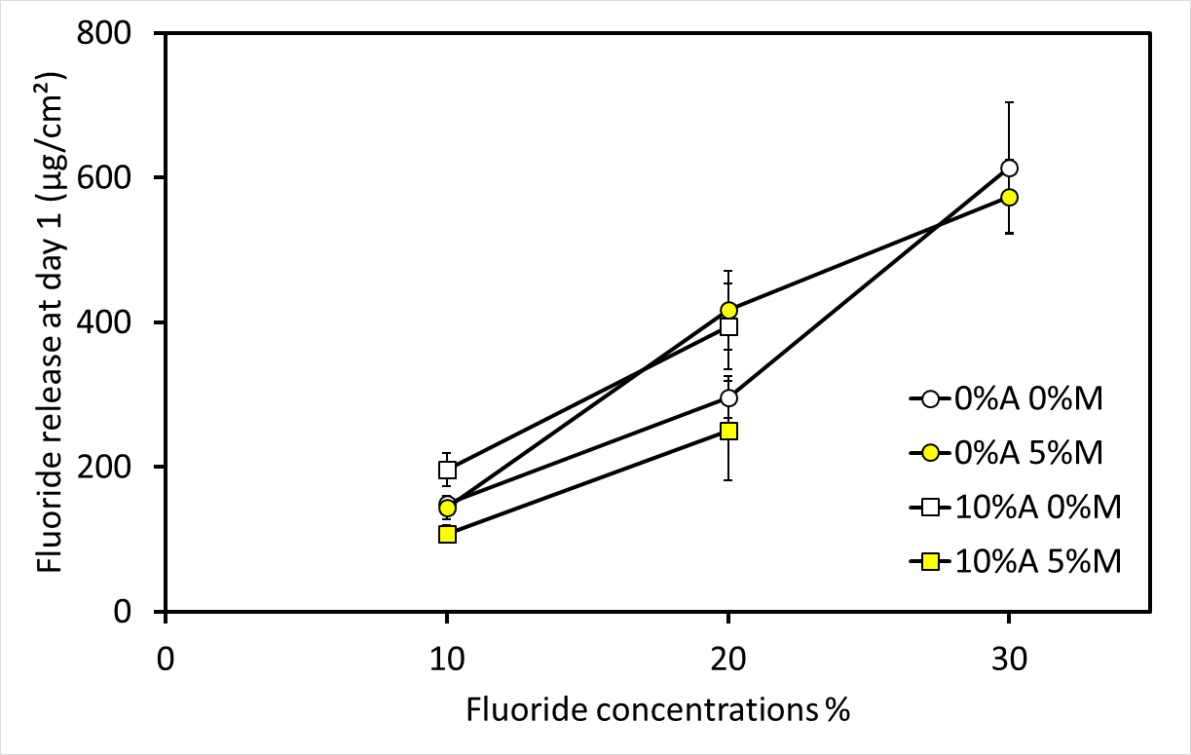


Figure 6.23 Fluoride release at day 1. Fluoride release increased with increasing fluoride concentrations.

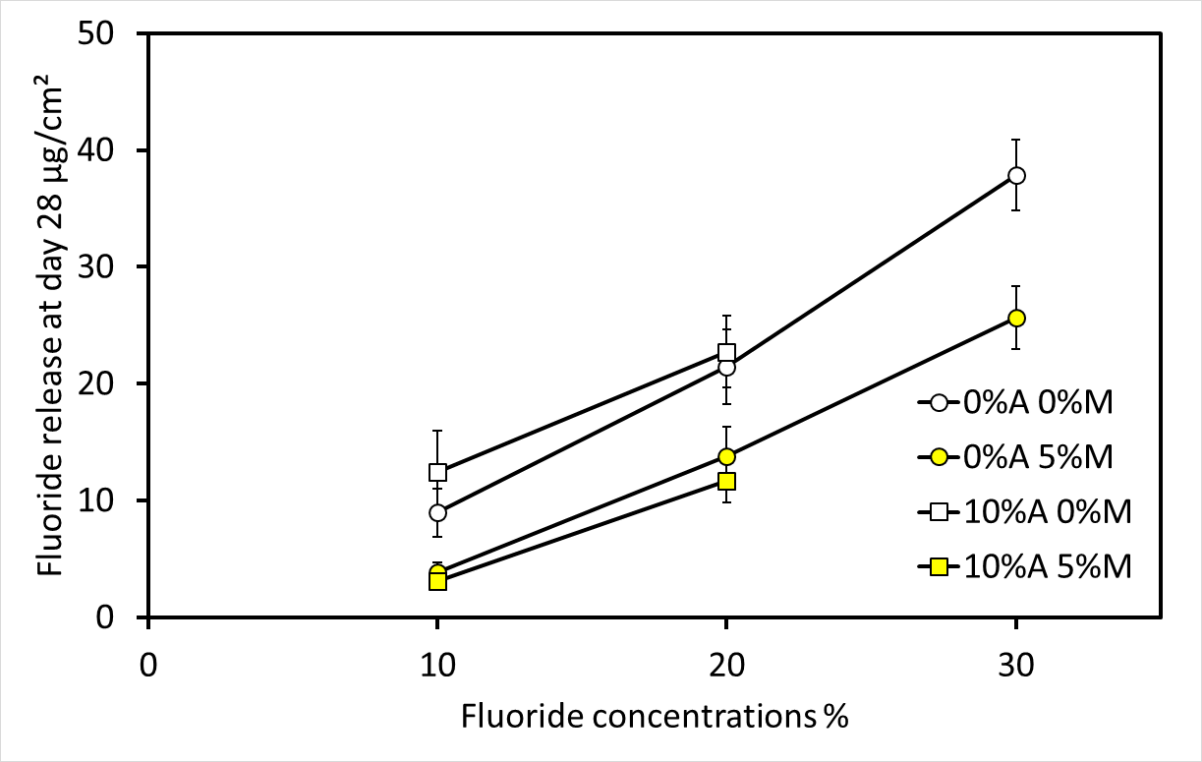


Figure 6.24 Fluoride release at day 28. Showing fluoride release increase with increasing fluoride concentrations. Fluoride release decreased with addition of 4-META.

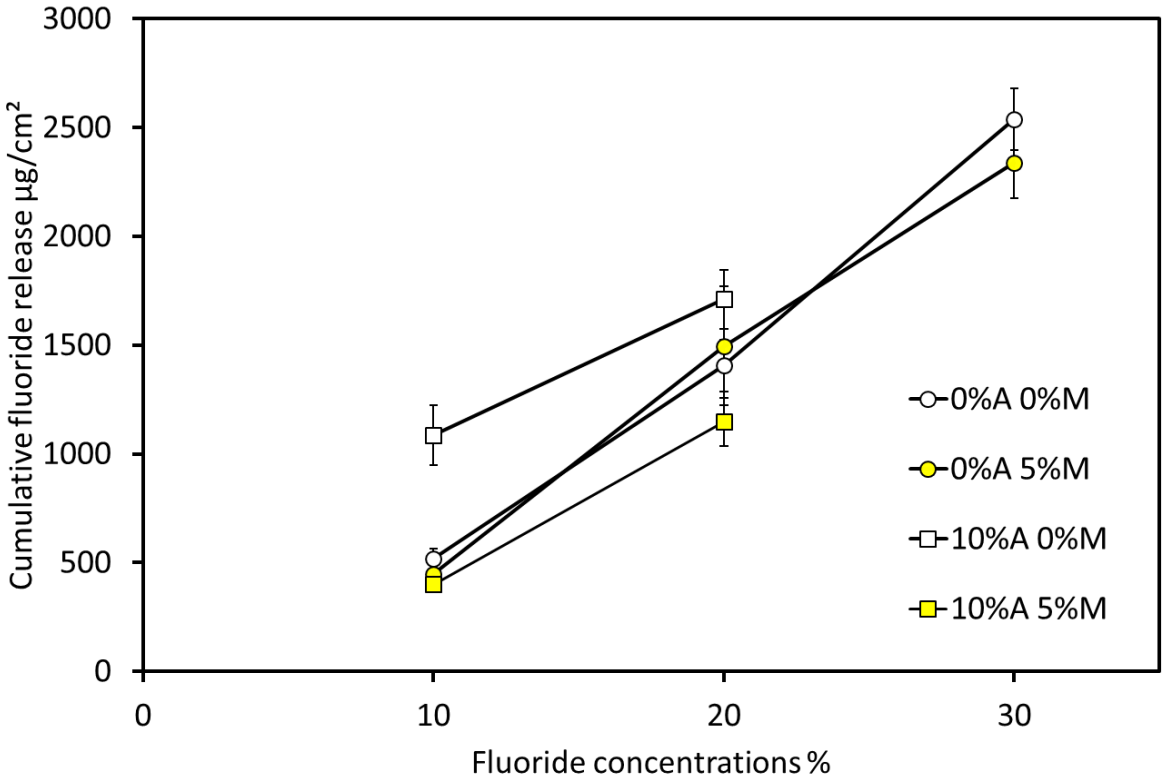


Figure 6.25 Cumulative fluoride release of all experimental materials and at day 28. The graph shows increasing fluoride release with increasing fluoride concentrations.

6.4.4 *Fluoride recharge*

The mean amounts of fluoride release pre and post three recharge cycles of all experimental groups and Ketac-cement are presented in Table 6.5. The fluoride re-release after recharging is greater in all experimental groups, however, the release was significant in the third recharging cycle for experimental groups and the second recharging of all experimental groups except 9:1 and 8:2 at 10%A 0%M and 8:2 0%A and 0%M (at $p<0.05$, paired sample t test). The group 9:1 also significantly increased at all recharging cycles except 10%A 0%M at first and second cycle (at $p<0.05$, paired sample t test). Ketac-cement also showed significant increase in fluoride release after recharging compared to before recharging in all recharging cycles (at $p<0.05$, paired sample t test).

The pattern of fluoride recharge from the experimental materials is shown in figures 6.26, 6.27, and 6.28. These show a fluctuating or oscillating manner of re-release for a week after exposure to the recharge solution with the peak re-release at the third, fourth or fifth day after recharge. While Ketac-cement showed a peak level of re-release 24 hours after recharge, the level of fluoride re-release from Ketac-cement during the second day after recharge exposure dropped back to a lower level than that recorded before recharge as shown in figure 6.29.

Table 6.5 Mean fluoride release of experimental materials containing fluoride and Ketac-cement.

Materials	Mean fluoride recharge µg/cm^2/day (showing day before and after recharge) Mean (SD)					
	1stround		2ndround		3rdround	
	Before	After	Before	After	Before	After
9:1 0%A 0%M	8 (1)	13 (3)	7 (1)	10 (2)	4 (1)	8 (1)
9:1 0%A 5%M	4 (1)	8 (1)	4 (1)	9 (2)	2 (0)	8 (1)
9:1 10%A 0%M	13 (4)^{a}	15 (3)^{a}	12 (3)^{b}	13 (6)^{b}	6 (1)	11 (1)
9:1 10%A 5%M	2 (1)	4 (1)	3 (1)	5 (1)	1 (0)	5 (0)
8:2 0%A 0%M	19 (2)	21 (2)	20 (3)^{e}	21 (2)^{e}	11 (2)	15 (2)
8:2 0%A 5%M	14 (2)	17 (2)	14 (2)	16 (1)	8 (2)	14 (2)
8:2 10%A 0%M	30 (4)^{g}	31 (6)^{g}	25 (4)^{h}	26 (3)^{h}	15 (1)	19 (2)
8:2 10%A 5%M	12 (2)^{i}	12 (2)^{i}	9 (2)	10 (2)	6 (1)	9 (1)
7:3 0%A 0%M	37 (3)^{l}	39 (7)^{l}	36 (3)	44 (5)	21 (2)	28 (2)
7:3 0%A 5%M	32 (7)^{m}	32 (7)^{m}	26 (3)	29 (3)	17 (1)	24 (2)
Ketac-cement	2 (1)	5 (1)	1 (0)	5 (1)	2 (0)	5 (1)

The entries are mean values with SD in the parenthesis. Values exhibited similar superscript letters indicate no significant difference within rows ($p > 0.05$) as determined using Paired Sample t test**.**

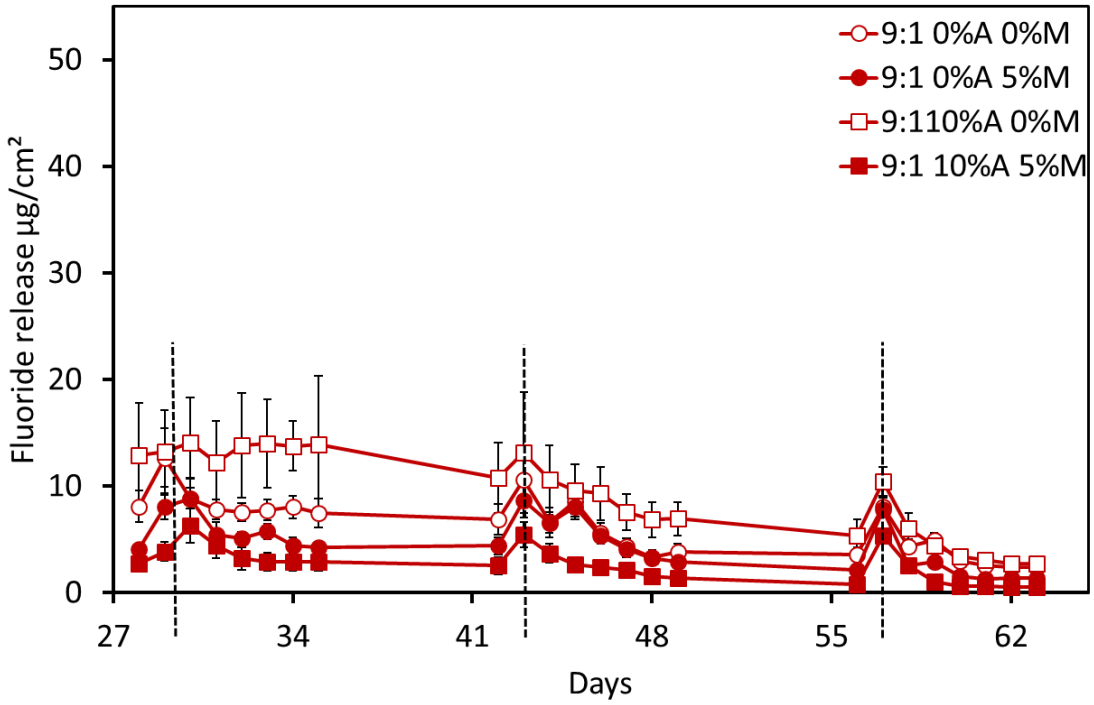


Figure 6.26 Mean fluoride recharging of group 9:1 with different acetone and 4-META concentrations. The dotted lines indicate fluoride release during the first day after recharging. The peaks represent an increase in the fluoride release levels after 24 hours post exposure to the recharging solution. (The error bars represent SD of the mean fluoride release).

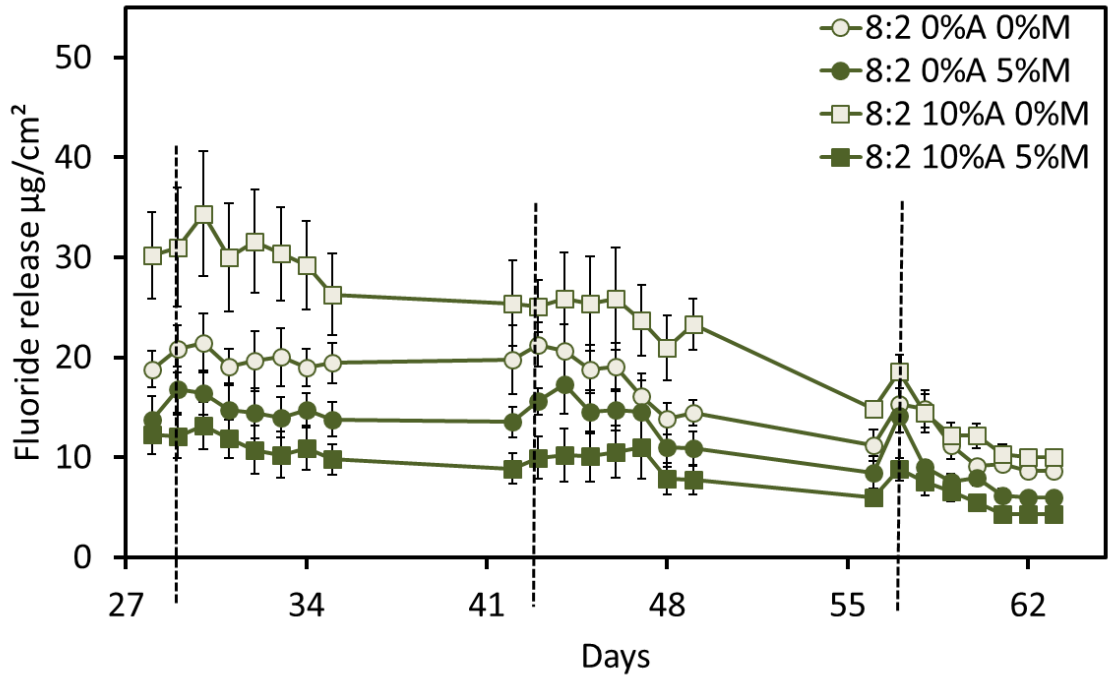


Figure 6.27 Mean fluoride recharging of group 8:2 with different acetone and 4-META concentrations. The dotted lines indicate fluoride release during the first day after recharging. The peaks represent an increase in the fluoride release levels after 24 hours post exposure to the recharging solution. (The error bars represent SD of the mean fluoride release).

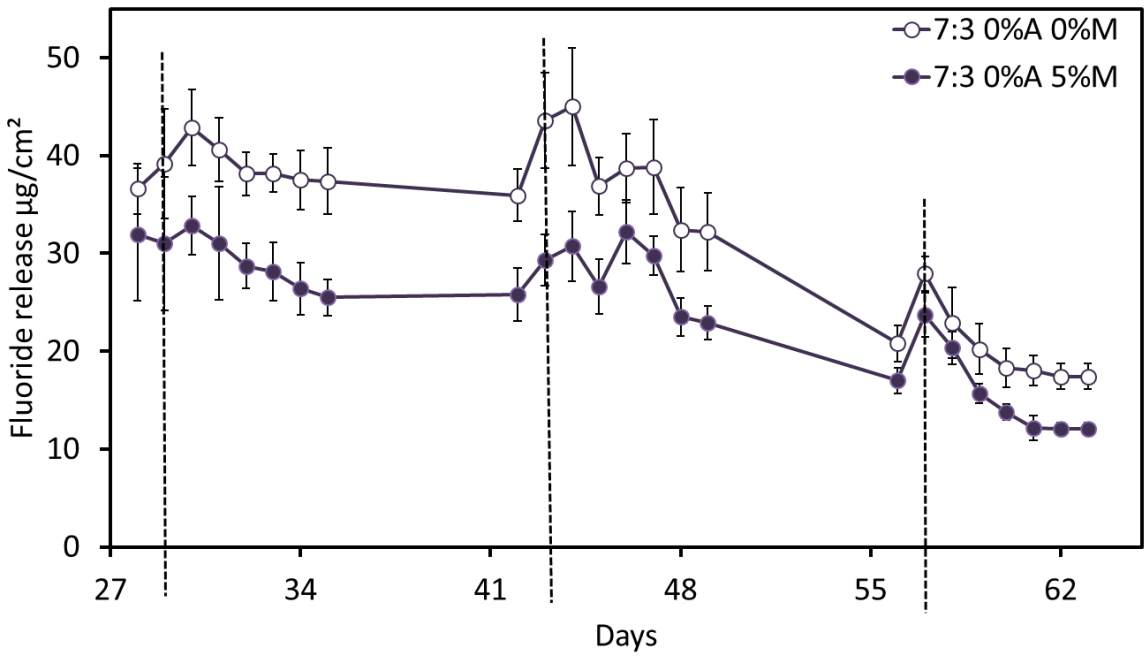


Figure 6.28 Mean fluoride recharging of group 7:3 with different 4-META concentrations. The dotted lines indicate fluoride release during the first day after recharging. The peaks represent an increase in the fluoride release levels after 24 hours post exposure to the recharging solution. (The error bars represent SD of the mean fluoride release).

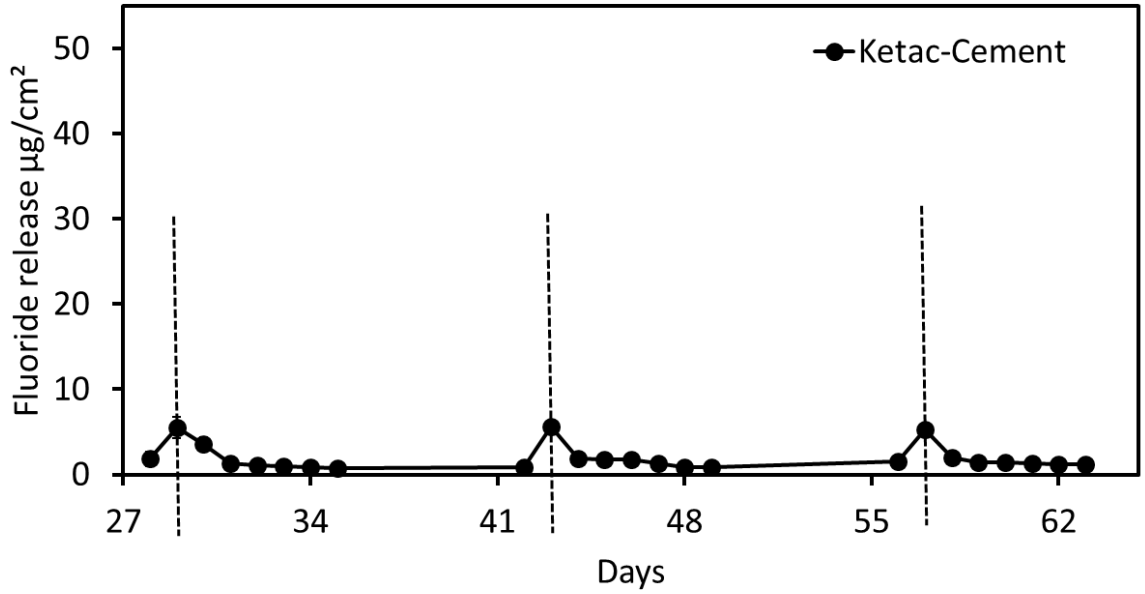


Figure 6.29 Mean fluoride recharging of Ketac-cement. The dotted lines indicate fluoride release during the first day after recharging. The peaks represent an increase in the fluoride release levels after 24 hours post exposure to the recharging solution. (The error bars represent SD of the mean fluoride release).

6.4.5 *SEM observation*

SEM images of fresh samples are shown in figures 6.30, 6.32, 6.34, 6.46, 6.38, 6.40, 6.42, 6.44, 6.46 and 6.48. Aged samples which have been exposed to 28 days in water are shown in figures 6.31, 6.33, 6.35, 6.37, 6.39, 6.41, 6.43, 6.45, 6.47 and 6.49. All images of experimental materials are shown at two magnifications (50× and 500×).

The images of freshly made specimens revealed smooth surfaces and all groups appeared to be similar. There are some scratches, which are due to lapping the specimens during preparation with 1200 grit silicon carbide paper. Cracks are also seen which are likely to have formed during desiccation of the samples for SEM analyses.

The images of aged specimens revealed pores on the surface of specimens. The pores are of oval, irregular and round shapes. The number of these pores appear to increase with increasing NaF concentrations. In addition, cracks are also seen which are likely to have formed during desiccation of the samples for SEM analysis.

SEM images of Ketac-cement fresh and aged specimens are shown at two magnifications (50X and 500X) in figures 6.50 and 6.51. The images of fresh and aged samples show cracks and the cracks were more marked in the aged specimen compared to the fresh specimen.

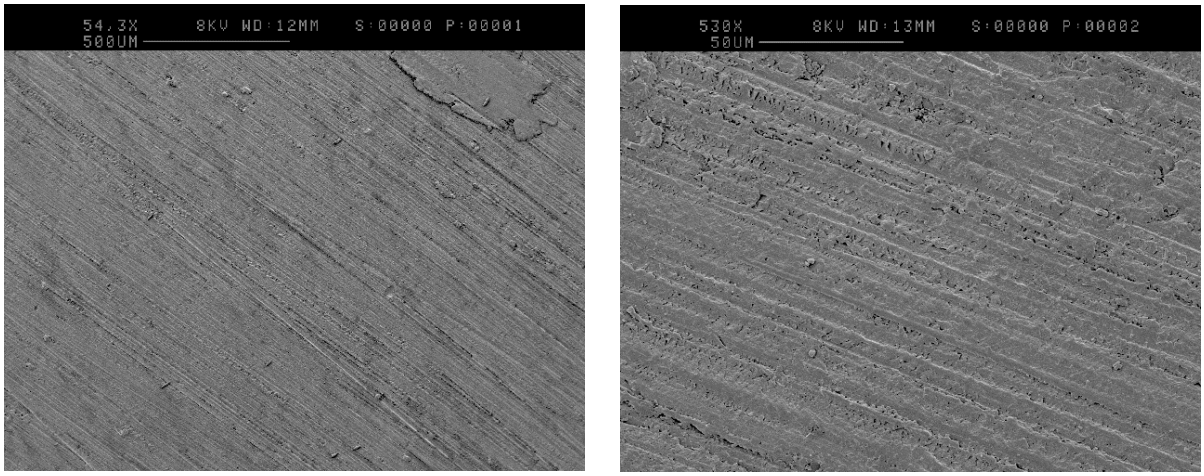


Figure 6.30 SEM images of fresh specimens of group 9:1 0%A 0%M at two magnifications 50X (left side) and 500X (right side).

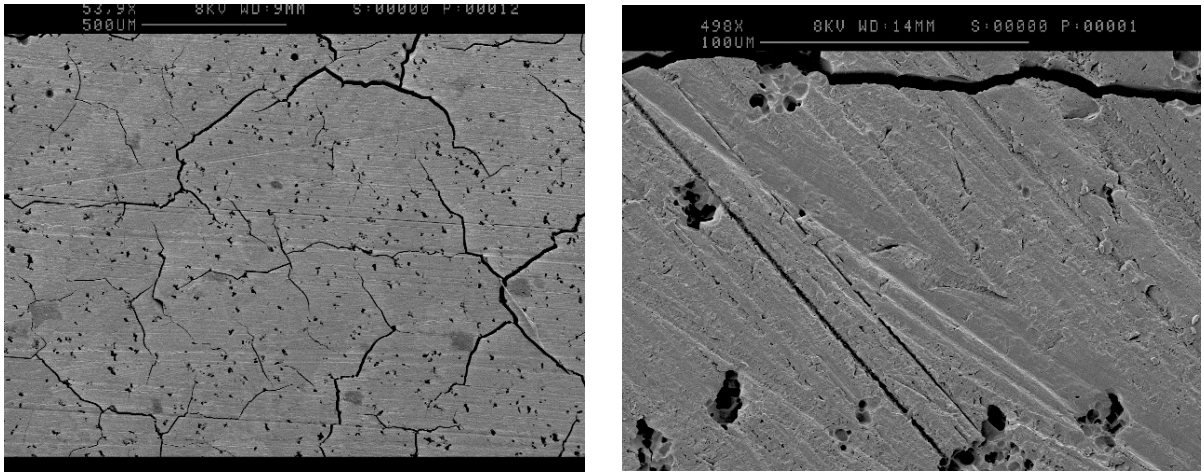


Figure 6.31 SEM images of aged specimens of group 9:1 0%A 0%M at two magnifications 50X (left side) and 500X (right side).

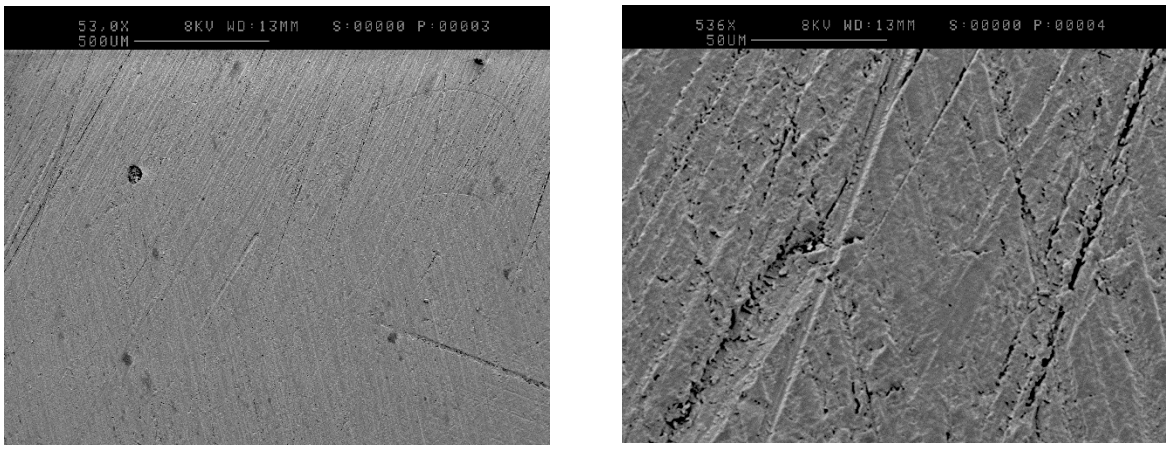


Figure 6.32 SEM images of fresh specimens of group 9:1 0%A 5%M at two magnifications 50X (left side) and 500X (right side).

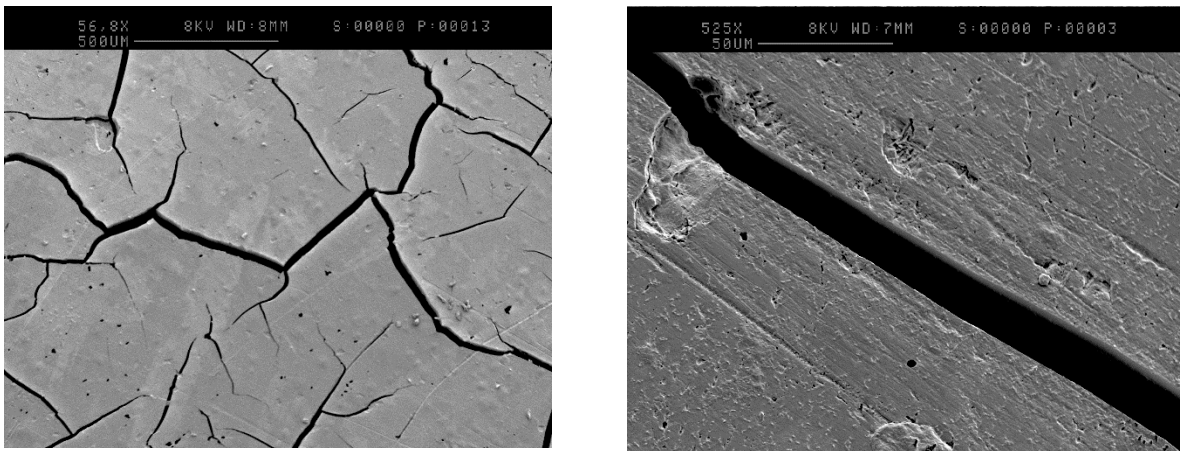


Figure 6.33 SEM images of aged specimens of group 9:1 0%A 5%M at two magnifications 50X (left side) and 500X (right side).

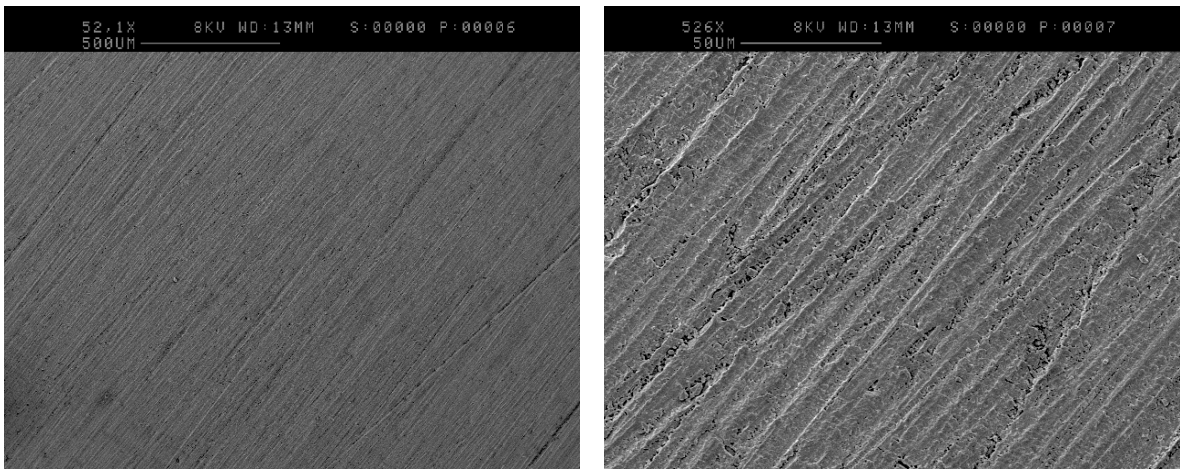


Figure 6.34 SEM images of fresh specimens of group 9:1 10%A 0%M at two magnifications 50X (left side) and 500X (right side).

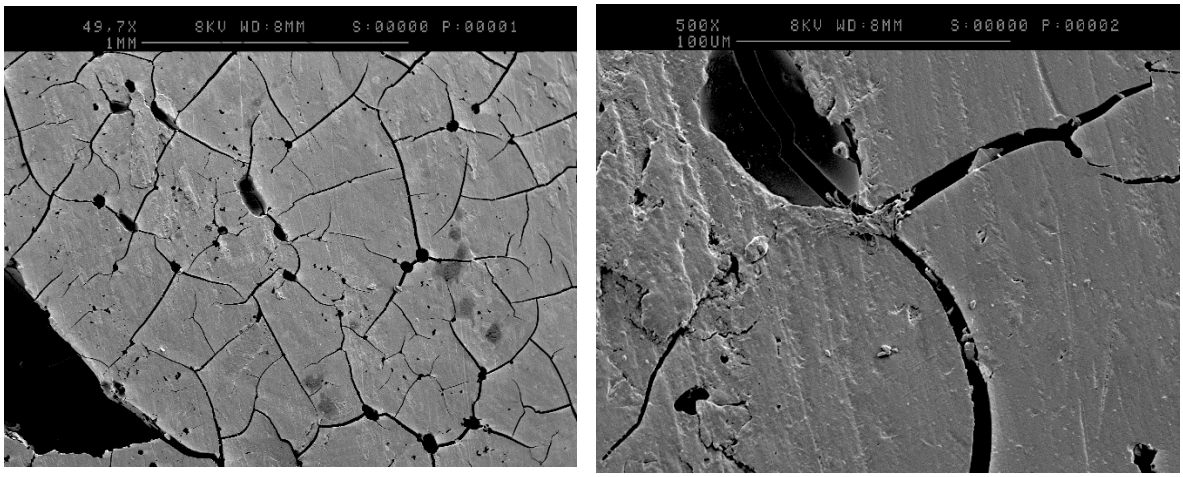


Figure 6.35 SEM images of aged specimens of group 9:1 10%A 0%M at two magnifications 50X (left side) and 500X (right side).

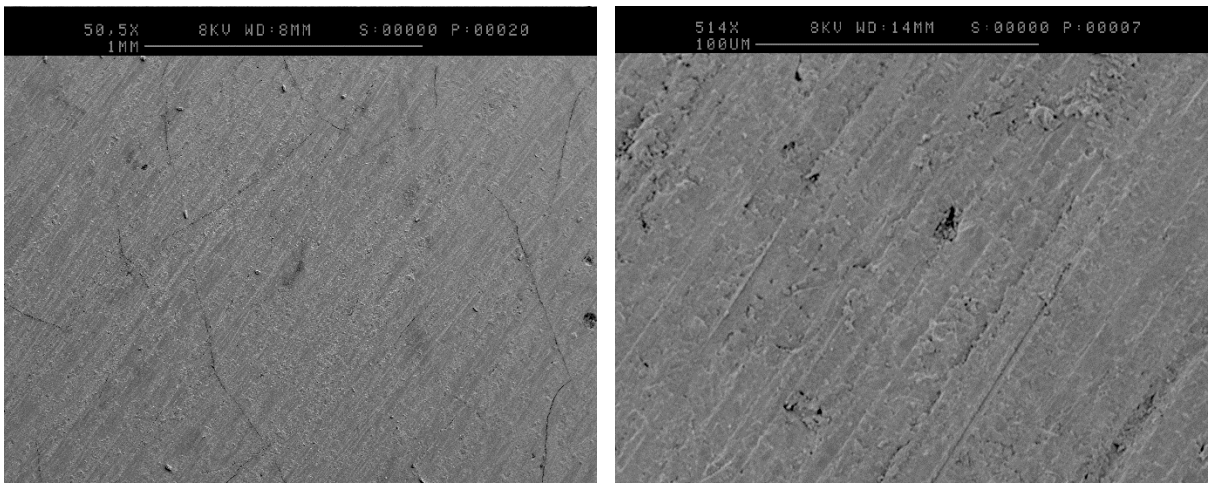


Figure 6.36 SEM images of fresh specimens of group 9:1 10%A 5%M at two magnifications 50X (left side) and 500X (right side).

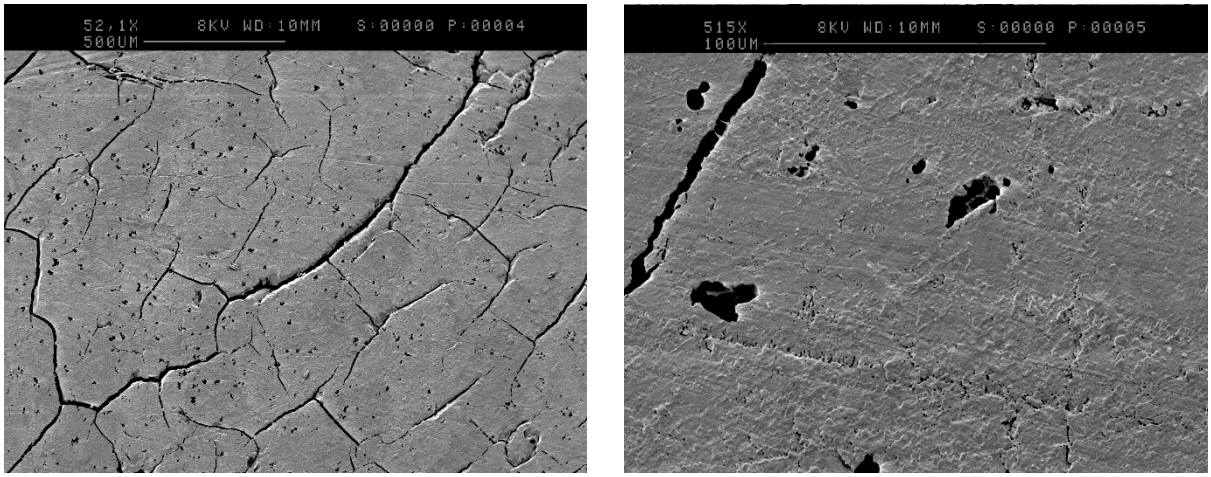


Figure 6.37 SEM images of aged specimens of group 9:1 10%A 5%M at two magnifications 50X (left side) and 500X (right side).

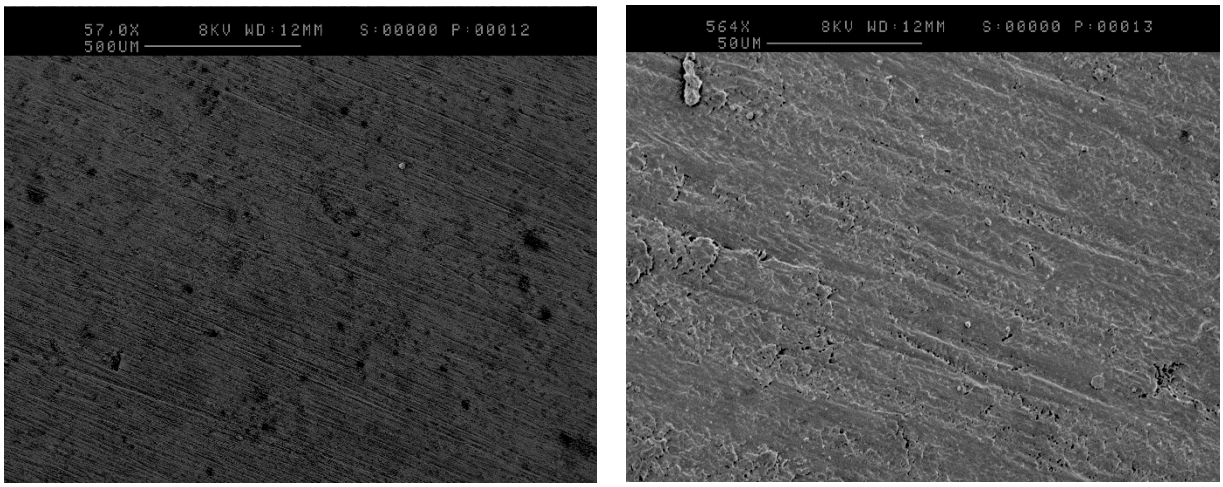


Figure 6.38 SEM images of fresh specimens of group 8:2 0%A 0%M at two magnifications 50X (left side) and 500X (right side).

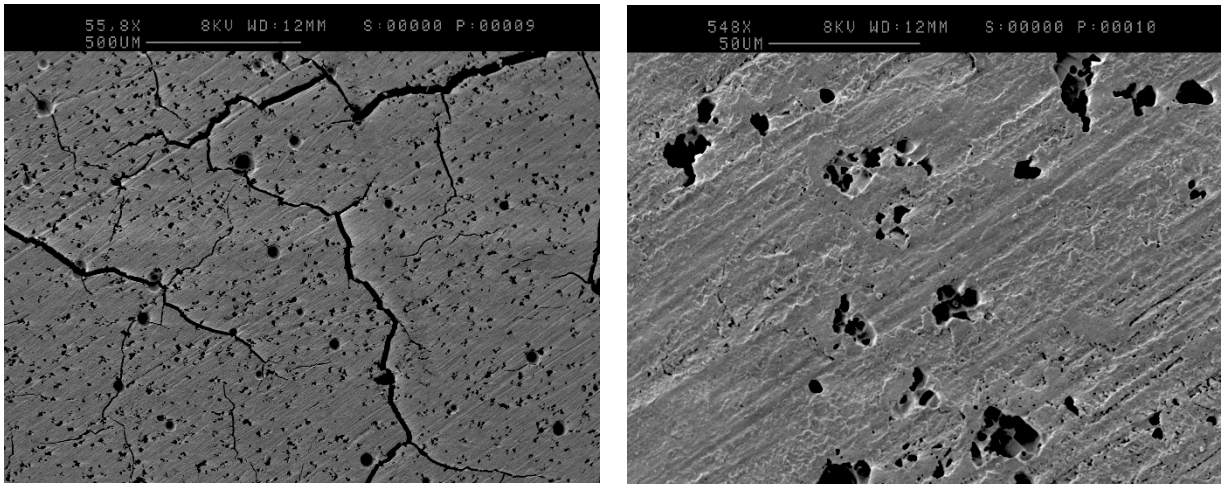
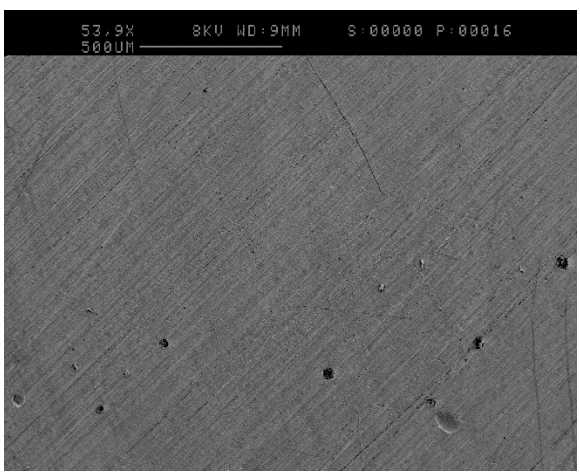


Figure 6.39 SEM images of aged specimens of group 8:2 0%A 0%M at two magnifications 50X (left side) and 500X (right side).



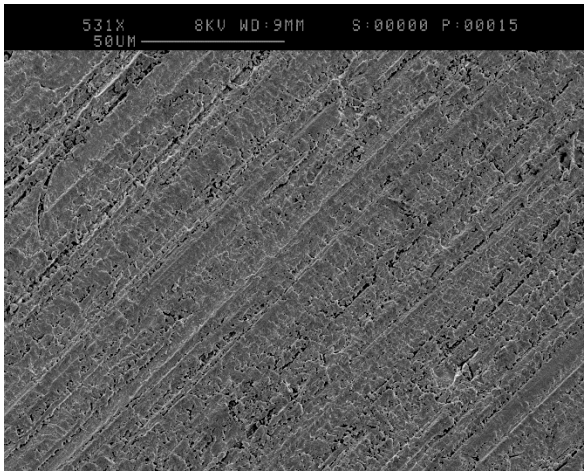
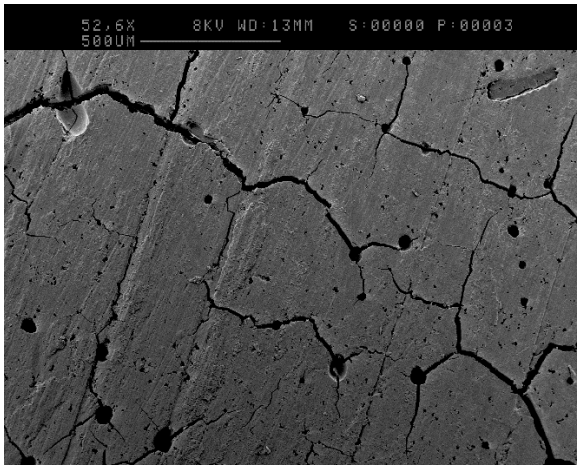


Figure 6.40 SEM images of fresh specimens of group 8:2 0%A 5%M at two magnifications 50X (left side) and 500X (right side).



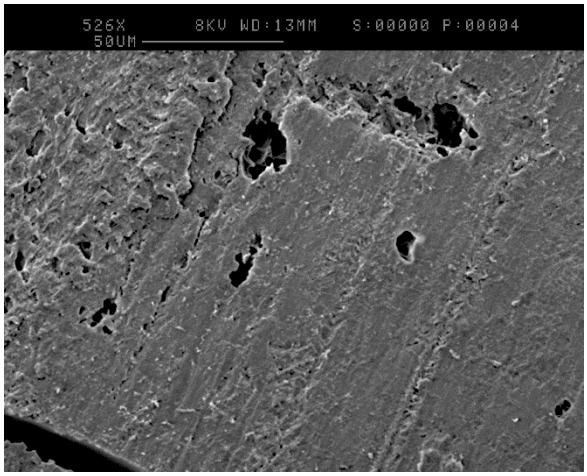


Figure 6.41 SEM images of aged specimens of group 8:2 0%A 5%M at two magnifications 50X (left side) and 500X (right side).

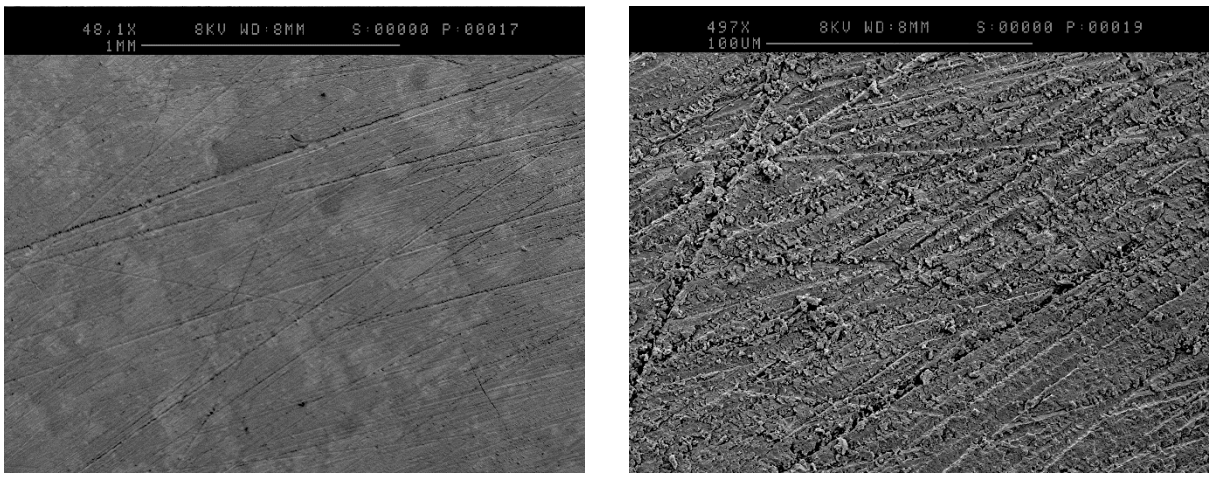


Figure 6.42 SEM images of fresh specimens of group 8:2 10%A 0%M at two magnifications 50X (left side) and 500X (right side).

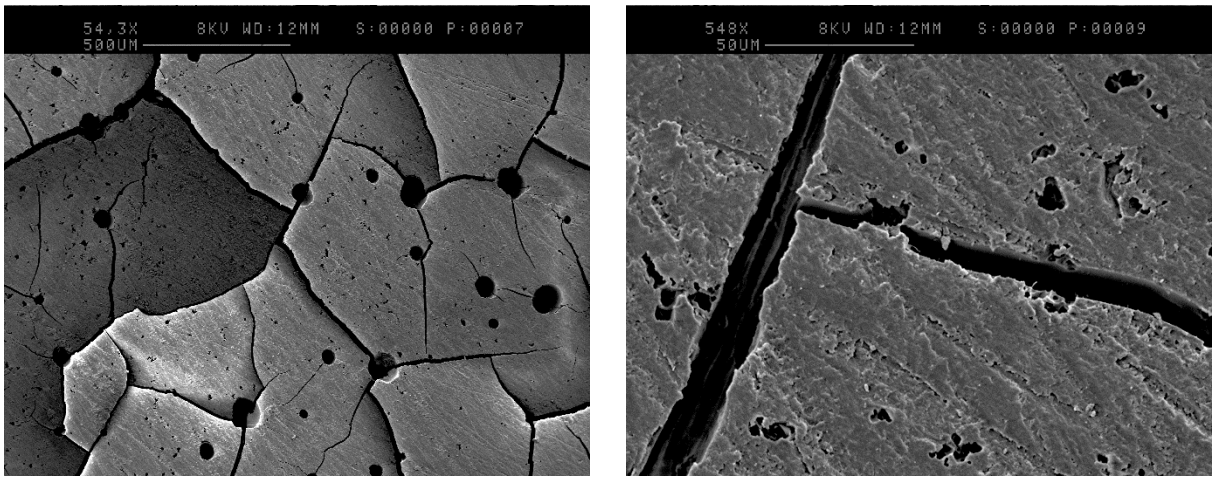


Figure 6.43 SEM images of aged specimens of group 8:2 10%A 0%M at two magnifications 50X (left side) and 500X (right side).

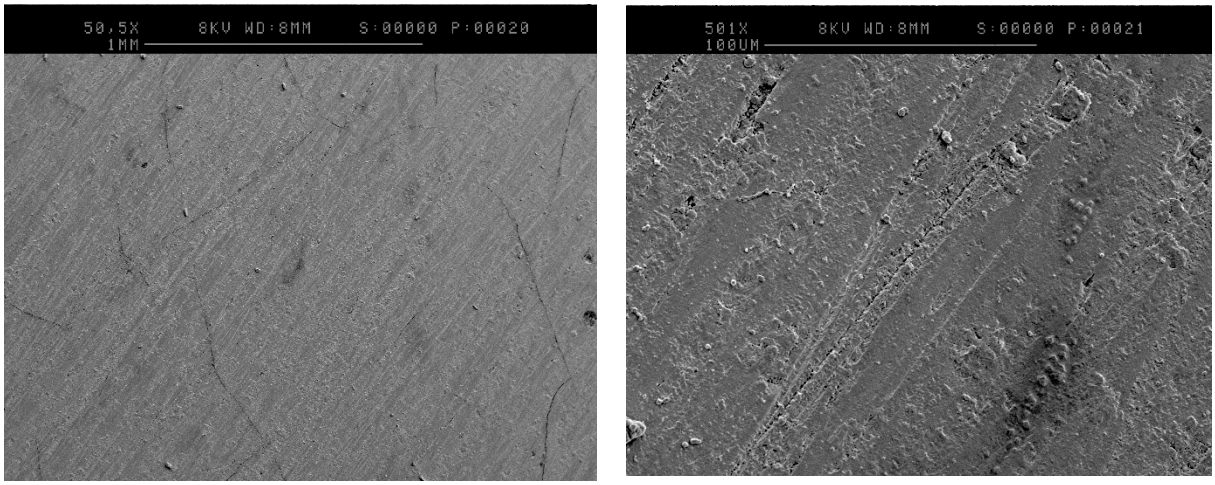


Figure 6.44 SEM images of fresh specimens of group 8:2 10%A 5%M at two magnifications 50X (left side) and 500X (right side).

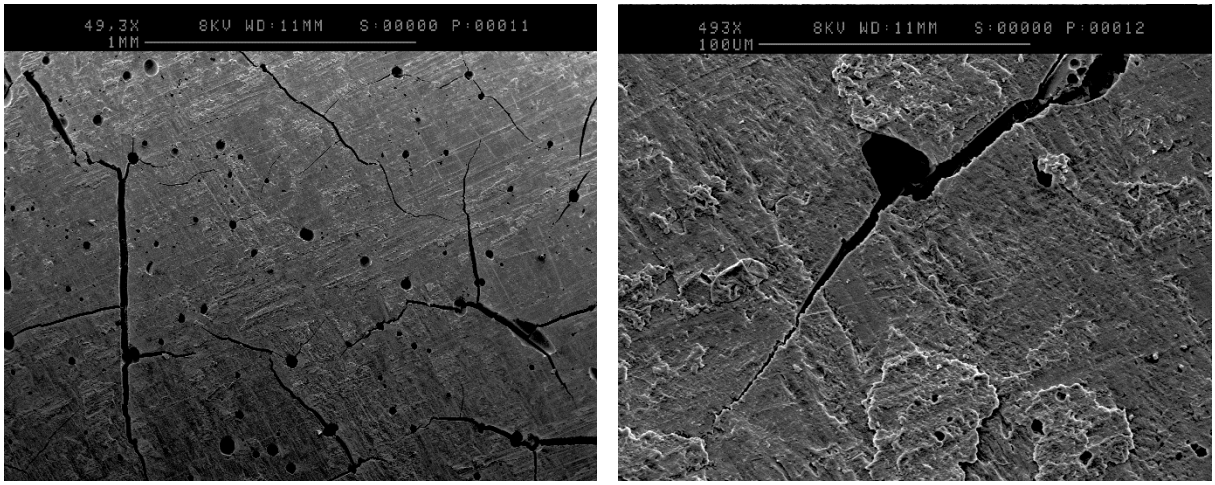


Figure 6.45 SEM images of aged specimens of group 8:2 10%A 5%M at two magnifications 50X (left side) and 500X (right side).

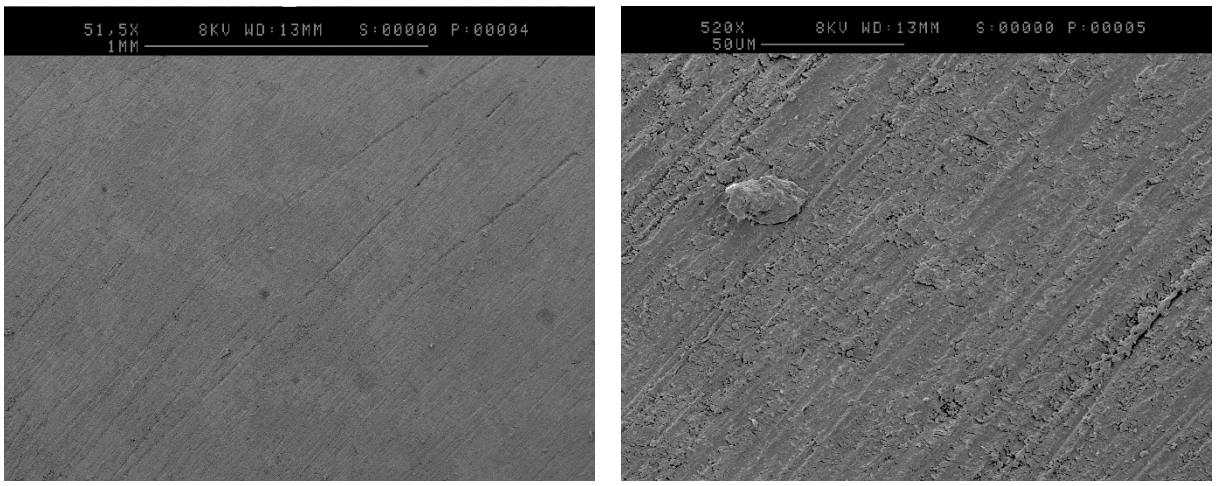


Figure 6.46 SEM images of fresh specimens of group 7:3 0%A 0%M at two magnifications 50X (left side) and 500X (right side).

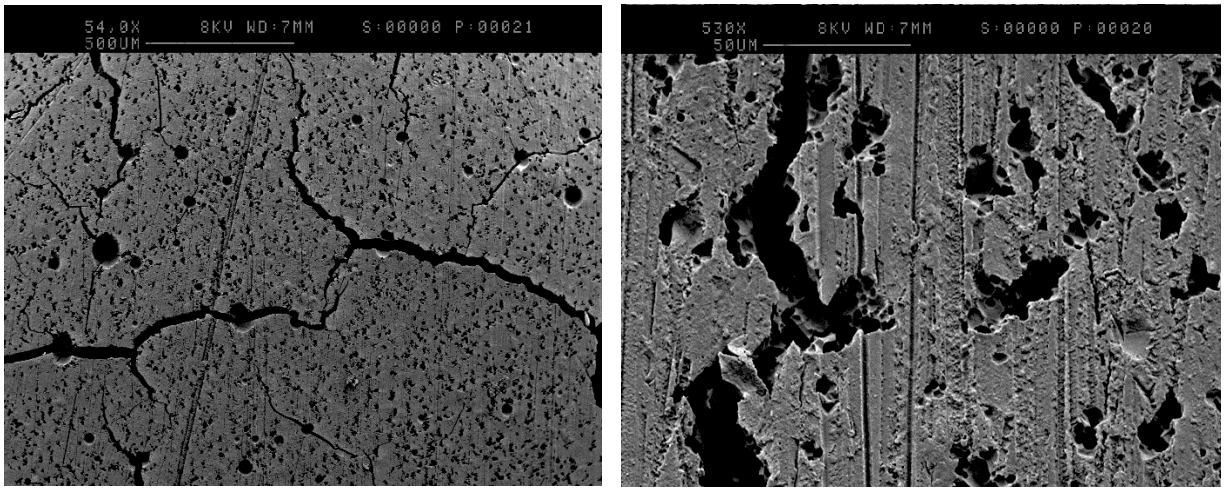


Figure 6.47 SEM images of aged specimens of group 7:3 0%A 0%M at two magnifications 50X (left side) and 500X (right side).

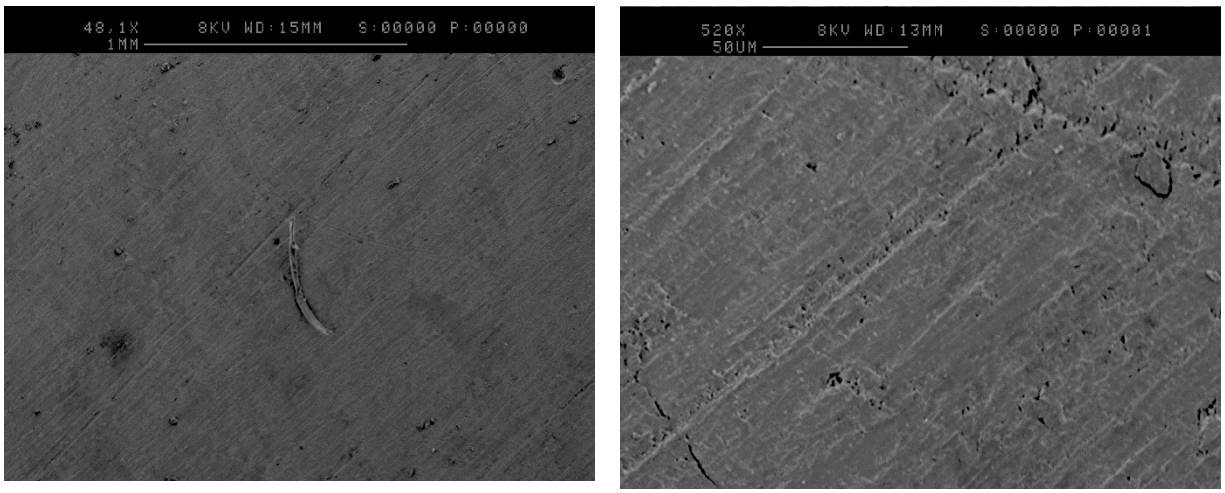


Figure 6.48 SEM images of fresh specimens of group 7:3 0%A 5%M at two magnifications 50X (left side) and 500X (right side).

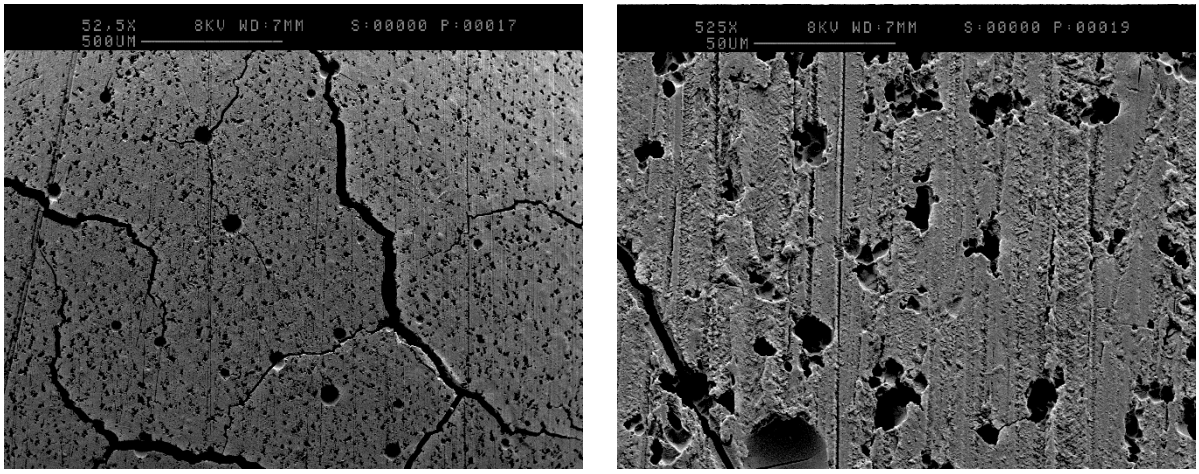


Figure 6.49 SEM images of aged specimens of group 7:3 0%A 5%M at two magnifications 50X (left side) and 500X (right side).

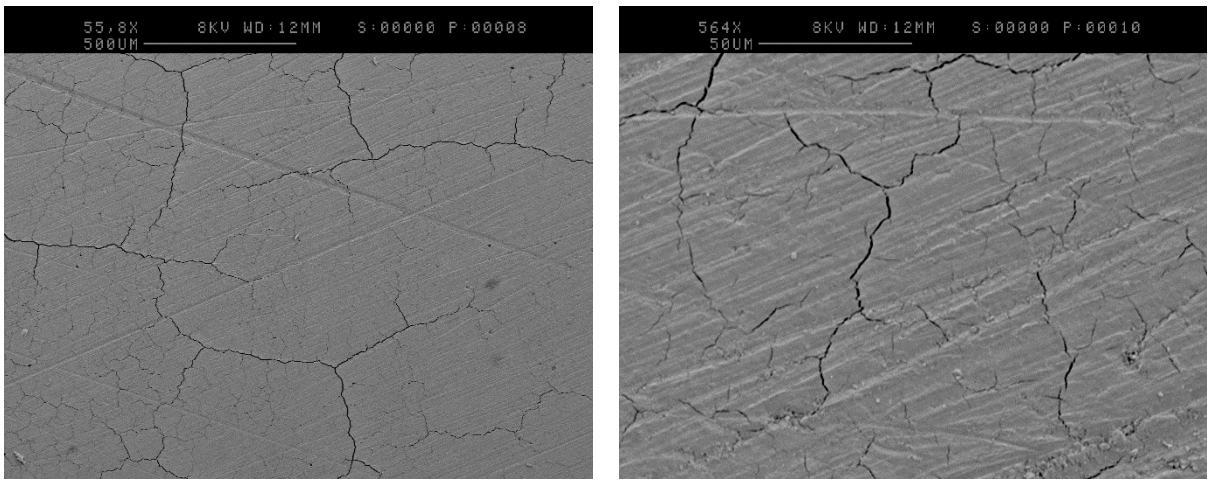


Figure 6.50 SEM images of Ketac-cement fresh specimens at two magnifications 50X (left side) and 500X (right side).

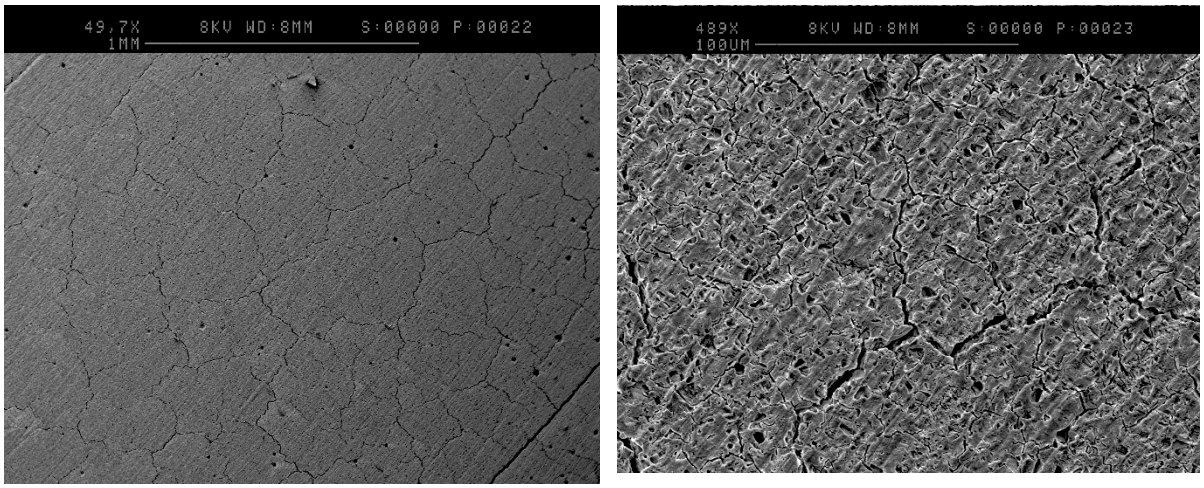


Figure 6.51 SEM images of Ketac-cement aged specimens at two magnifications 50X (left side) and 500X (right side).

6.4.6 *Summary of the results*

The DoC of experimental materials was not significantly affected by the addition of 4-META and it was higher than DoC of Transbond XT.

The solubility of experimental materials increased with increasing NaF concentrations. However, solubility was not affected by the addition of 4-META.

All experimental materials had fluoride releasing and recharging ability comparable to Ketac-cement.

6.5 Discussion

In this chapter 4-META was added to the experimental materials as an adhesion promoter, to increase the bond strength of the materials. It has been shown that 4-META containing adhesives had higher SBS than composite resin based orthodontic adhesives like Transbond XT (Clark *et al.,* 2003). 4-META was used at 5% as primer to increase tensile bond strength of 4-META/MMA-TBB resin to dentine (Nakabayashi and Hiranuma, 2000).

There are some key properties which it is important that the experimental materials maintain after the addition of 4-META such as setting characteristics and fluoride releasing ability. It is also important to investigate the water sorption and solubility of the developed materials after the addition of 4-META. This was to understand the fluoride release and recharge of the materials. As it was known that fluoride release of most orthodontic adhesives is controlled by diffusion/dissolution mechanism (Verbeeck *et al.*, 1998). In addition fluoride recharging is also important to ensure sustained fluoride release and thereby minimise WSL. Therefore in order to investigate the effect of the addition of 4-META to the experimental materials a number of characteristics were measured, including DoC, water sorption and solubility, fluoride release and recharging ability in addition to observing the surface characteristics of the fluoride releasing samples after being in water for 28 days.

6.5.1 *Degree of conversion (DoC)*

In previous chapter the method used for measuring the DoC of the materials was directly applying the experimental materials on to the ATR stage of the FTIR then light curing in place. It was impossible to use this method after the addition of 4-META because the materials are likely to adhere to the ATR stage and removal could cause scratching and permanent damage to the crystal of the ATR. As 4-META containing adhesives strongly adhere to metals and stainless steel (Björn *et al.*, 1995; Yoshida *et al.*, 1996; Hayakawa and Nemoto, 2003). Therefore, in this chapter a more conventional methodology was used to measure the spectra, which has been previously used by many researchers (Silikas *et al.,* 2000; Furuse *et al.*, 2011). In contrast to the single scan per spectrum method used in the previous chapter, in this

experiment 32 co-addition scans were taken to increase signal to noise ratio (Furuse *et al.*, 2011; Loguercio *et al.*, 2011; Rastelli *et al.*, 2012). Regarding calculation of the DoC the same method was used as described before (chapter 4.3.2) using aliphatic C=C for comparison and carbonyl group C=O as the internal standard. However, for calculating the DoC of Transbond XT, which is composed of dimethacrylate based monomers like BisGMA and TEGDMA, the aromatic band of C=C around 1607cm^{-1} was taken as the internal standard as it does not participate in polymerization reaction and has been widely used before (Chung *et al.*, 2002; Calheiros *et al.*, 2008; Al-Ahdal *et al.*, 2015).

The results of this chapter confirm the results of first and second chapter in which acetone and NaF were seen to have an effect on the DoC of the experimental materials. However, the results of this chapter showed that the DoC of the experimental materials behave differently according to different fluoride and 4-META concentrations. For groups 9:1 and 8:2 no significant differences were found after acetone and 4-META addition while with group 10:0 the DoC decreased with acetone and/or 4-META addition while for group 7:3 the DoC decreased with addition of either acetone or 4-META. The results of group 10:0 10%A contradicted those found in the previous chapter, in which the DoC increased after acetone addition. These differences might be attributed to the following reasons:

Firstly while the spectra measured in the first chapter were measured in real time, as the specimen polymerized, in this chapter the specimens were polymerized and then analyzed at a later time. Potentially, the delay between light exposure and analysis could have led to some post-curing of the specimens (Par *et al.*, 2014; Al-Ahdal *et al.*, 2015).

Secondly the difference might arise from differences in the pressure applied on the samples during the ATR measurement. It has been shown that pressure has effect on FTIR spectra. In a study to investigate structure of kaolinite, clay minerals, it was found that with increasing applied pressure the ATR spectra of Si-O silicon-oxygen bond shifted in addition the intensity of the bonds increase with increasing pressure (Friedrich and Weidler, 2010). For the single scans the tip of the LCU was used to apply pressure on the sample, because of the short timeframe between curing and taking an FTIR measurement (every 10 seconds), whilst in this experiment the ATR accessory clamp was used to press the sample against the crystal of ATR stage at 90 -120 MPa.

Finally in this chapter 32 co-added scans were taken to increase SNR (signal to noise ratio) compared to a single scan in previous chapter. It is suggested that for spectra with 100 co-added spectra would have SNR ratio 10 times better than a single scan (Perkins, 1987; Griffiths and De Haseth, 2007; Smith, 2011). However, the single scan was taken in the previous chapter to

make sure, at this stage, that no post-curing effects were present in the spectra due to some continued reaction after the LCU turned off.

Based on the results of the current study, the first hypothesis "4-META does not deteriorate DoC of the experimental materials." was partially accepted. For some groups like group 10:0 the DoC decreased with 4-META addition while for other groups (9:1 and 8:2) no differences were found after 4-META addition. Therefore, 4-META concentrations influenced the DoC of some of the experimental materials. However, the DoC of all experimental groups were higher than Transbond XT and all experimental groups had satisfactory DoC more than 50%. Generally, DoC of dental resins is between 43- 75% (Lovell *et al.*, 1999; Moraes *et al.*, 2008).

6.5.2 *Water sorption and solubility*

The kinetics of water sorption depend on two processes, water diffusion and diffusion of soluble fraction out of the sample, see figure 2.3 (Van Noort, 2013). When an acrylic resin or resin composite is soaked in water two processes occur. Firstly, a rapid elution of unreacted monomers and other dissolving elements within the resin takes place. Secondly, water is absorbed by the resin, and occupies the holes left by eluting monomer and the space between the polymer chains (Costella *et al.*, 2010); this process is time dependant, slow and diffusion controlled (Sideridou *et al.*, 2007). There are two mechanisms through which water diffuses into polymeric materials. Firstly, infiltration into free spaces which is controlled by the free spaces available. The commonly occurring micro-voids and other morphological defects, increasing free space should result in increasing water uptake and diffusivity (Unemori *et al.*, 2003). The second mechanism is diffusion by molecular interaction. This is controlled by the available hydrogen bond at hydrophilic sites of the monomer that formed the polymer. The water sorption is the net gain of the weight of a specimen as a result of the ingress of water molecules and egress of monomers and other molecules (Chai *et al.*, 2004; Sideridou *et al.*, 2007).

In the current project the experimental materials were prepared like fluoride releasing samples. The specimen sizes used were disks of 10 mm diameter and 1 mm thickness and they were put in to 5 ml water as used for fluoride releasing procedure. The reason for this was to simulate the fluoride releasing condition in order to understand the fluoride releasing behaviour. In addition these dimensions have been used previously to study water sorption and solubility of a range dental composite restorative materials (Rahim *et al.*, 2012).

The experimental materials contained NaF at different ratios. This was 30% for the 7:3 group, 20% for the 8:2 group and 10% for the 9:1 group. NaF is a very soluble salt and easily dissolves into Na^+ and F^- ions (Nakajo *et al.*, 2009). The highest amount of NaF present in the materials

the highest amount of fluoride dissolved and leached out. Once the fluoride leached out it was replaced by water and water has a lower molecular weight than NaF. Therefore, the net weight change for the 7:3 group appeared to be lower than 8:2 and both were lower than the group 9:1. Therefore, in order to know the effect of 4-META on water sorption each experimental group should be taken individually based on the percentage of NaF.

The rate and extent of water sorption depends on resin polarity, dictated by the concentration of polar sites available to form hydrogen bonds with water (Unemori *et al.*, 2003; Malacarne *et al.*, 2006). The monomer 4-META is hydrophilic and it has been previously shown that for materials based on 4-META and PMMA there is a significant correlation between the 4-META concentration and water sorption (Unemori *et al.*, 2003). However, in the current study there was no significant difference between groups with and without 4-META. This might be due to the fact that there was roughly equal content of hydrophilic monomers in all materials because when adding 4-META the concentration of HEMA, also a hydrophilic monomer, (Arima *et al.*, 1995; Van Landuyt *et al.*, 2007; Su *et al.*, 2010) was reduced. All experimental groups containing 10% acetone without 4-META showed increased water sorption compared to those that did have 10% acetone and 5% 4-META. It has been shown that presence of solvents results in increasing water sorption of adhesive resins (Malacarne-Zanon *et al.*, 2009).

The results of this study also showed that solubility did not change with the addition of 4-META. This is in accordance with other studies on the effect of addition of 4-META on solubility of MMA/4-META resin (Unemori *et al.*, 2003). Solubility of materials containing 10% acetone without 4-META increased, this might be due to increasing micro-voids within the materials as a result of acetone evaporation, increasing water diffusion (as shown by increased water sorption) and consequently increased solubility.

Solubility also increased with increasing NaF concentrations, materials with higher NaF content unsurprisingly showed greater solubility. This was due to leaching out of fluorides after being in water, the more fluoride content the more fluoride leached out. Therefore, the solubility of group 10:0 was lower than group 9:1 as there was no fluoride to leach out. Increasing NaF concentrations from 10% to 20 % the solubility increased by two-fold and then three-fold to 30% fluoride accordingly except groups with 10% acetone without 4-META. Interestingly all groups with 10%A and 5% 4-META had lower solubility compared to groups with 10%A without 4-META. Thus, it appeared that addition of 5% 4-META to the groups with 10%A controlled solubility of the materials. The solubility of all the 9:1 groups except at 10%A are within the acceptable range which is (30-50 µg/ mm^3) (Van Noort, 2013).

The results of this study showed low water sorption and solubility for Transbond X, which was lower than experimental materials. This was due to a highly cross-linked nature of

dimethacrylates, such as BisGMA and UDMA (Braden *et al.*, 1976; Söderholm, 1981), which slow down the transportation rate of water and ions in the polymer (Asmussen and Peutzfeldt, 2002). Also there was no soluble fractions apart from unreacted monomers. There are some studies which have looked at water sorption and solubility of a range of experimental and commercial filled and unfilled composite resin based on dimethacrlaytes like BisGMA, UDMA and TEGDMA. They found water sorption and solubility in deionized water between (5.16 - 37 µg/mm³)(Gerdolle *et al.*, 2008; Uysal *et al.*, 2008; Sunbul *et al.*, 2015). However, a different methodology was used, as the size of the prepared discs was different from the current study and water sorption and solubility was taken for different times compared to the current study. All these results show that the water sorption and solubility of Transbond XT in the current study are comparable to previous studies and it was within a range that considered acceptable (30-50 µg/ mm³) (Van Noort, 2013).

6.5.3 *Fluoride release*

The same method of fluoride measurement was used as mentioned before. The specimens were prepared using the same method as described in chapter 4.4.5. The only difference was using Bluephase®20i which had greater intensity 1130 mW/cm^2 compared to Coltolux 800 mW/cm^2. Group 7:3 with 10%A was omitted because the samples remained soft after preparation. Group 10:0 was not included for fluoride release measurements as there was no fluoride in this group to be released and the results of first chapter showed no fluoride release for this group. WSL can develop within one month of appliance placement (O'Reilly and Featherstone, 1987; Gorton and Featherstone, 2003), and therefore fluoride release is important in the first month after appliance placement to prevent WSL. Therefore, fluoride release measurements were taken for only 28 days. This protocol has been used in a number of previous studies (Wheeler *et al.*, 2002; Vahid-Dastjerdi *et al.*, 2012).

The pattern of fluoride release of the experimental materials was seen to be comparable to Ketac-cement. The current findings were also similar to all published data on GIC, RMGIC and compomers (Verbeeck *et al.*, 1998; Xu and Burgess, 2003) in which the highest levels of fluoride are released during the first 24-48 hours (Creanor *et al.*, 1994; Chatzistavrou *et al.*, 2010). The highest amount of fluoride was followed by a rapid decrease in level. In the present study, an initial high release from Ketc-cement on day 1 was due to the well-documented burst of fluoride released from the glass particles when reacting with the polyalkenoic acid during the setting reaction (Wiegand *et al.*, 2007; Dionysopoulos *et al.*, 2013).

The results of this chapter confirm those of the first chapter in which addition of 10%A resulted in increasing fluoride release, which was thought to be due to increasing water soprtion of the

materials (Malacarne-Zanon *et al.*, 2009) and the presence of greater porosity after acetone evaporation. These factors result in higher water diffusion and therefore greater leaching of NaF. The addition of solvents has been shown to increase water sorption in adhesives (Malacarne-Zanon *et al.*, 2009), which may result in accelerating diffusion of fluoride ions within absorbed aqueous medium. It was suggested that the kinetics of fluoride elution is a diffusion-dissolution mechanism (Verbeeck *et al.*, 1998). This means fluoride elution depends on dissolution of the additive fluoride source, NaF, which was added to the material by the water diffusion. Therefore the mechanism must be water absorption and then diffusion of fluoride to its surroundings.

The addition of 4-META generally led to a reduction in fluoride release irrespective of whether acetone was present or not. Despite 4-META being a hydrophilic monomer it did not increase water sorption of the experimental materials, most likely due the fact that the overall content of hydrophilic monomers was not changed. Interestingly, 4-META seemed to regulate the fluoride release of the experimental materials even in the presence of 10% acetone. Whilst it is not clear what the reason for this is, the 4-META containing adhesives still exhibited significantly greater fluoride release than the Ketac-cement. Based on the results of the current study, the fourth hypothesis "4-META increases fluoride release of the experimental materials" was rejected. 4-META concentrations influenced the amount and rate of fluoride release from fluoridated experimental materials. However, it appeared that 4-META addition may make materials release a low level of fluoride for longer, therefore, the effect was not detrimental.

6.5.4 *Fluoride recharge*

In addition to the fluoride release of orthodontic adhesives, fluoride recharging is another interesting property of fluoride releasing orthodontic adhesives. Fluoride releasing orthodontic adhesives can take up fluoride from the oral environment to replace the fluoride that has been lost. Fluoride release is important to prevent WSLs after appliance placement then fluoride recharging is important to top up the fluoride release of the materials after its internal fluoride content is exhausted. This results in sustained fluoride release for a long period of time and consequently prolonged prevention.

There is no standard recharging protocol. Different studies have been done *in vitro* to measure fluoride recharge of orthodontic adhesives, through exposing the tested material to an external fluoride source to study fluoride uptake of a material (Lim *et al.*, 2011). Fluoride has been used at different concentrations from 200 ppm to 1000 ppm (Coonar *et al.*, 2001; Lim *et al.*, 2011). In the present study the recharging ability (fluoride uptake) of the experimental materials were tested after exposing the materials to 1000 ppm NaF solution for three minutes over three

recharging cycles two weeks apart. A 1000 ppm NaF solution was used as it was shown fluoride rinsing with 1000 ppm NaF has been found to be effective in recharging of orthodontic adhesives (Ahn *et al.*, 2011). This was to represent a weekly mouthrinse. An ultrasonic bath was used to simulate the weekly mouth wash and to enhance dispersion of fluoride (Zahroon, 2014). NaF was used as a source for fluoride recharging in the present study because it is the most commonly used source in different dentifrices and mouthwashes (Preston *et al.*, 1999; Preston *et al.*, 2003). The NaF was used in neutral solution as it is recommended to use neutral sodium fluoride gel for home use in patients with GICs and composite restorations. This is to maintain the material integrity and minimize surface degradation (El-Badrawy *et al.*, 1993; Diaz-Arnold *et al.*, 1995).

The recharge samples were soaked in water for 28 days before starting the fluoride recharge treatment. This was to give the materials 28 days of high initial burst fluoride release as there was a high amount of fluoride release during the first 28 days of water immersion. There might be some differences between the value of fluoride recharging samples at day 28 compared to the standard fluoride releasing experiment at same time of immersion in water. This could be due to the changes in the frequency of water changes. For the fluoride releasing experiment the water was replaced daily for the first 14 days while for the recharging specimens the water was changed weekly. These differences have been reported previously in similar experiments (Zahroon, 2014).

The pattern of fluoride release after exposure to supplemental fluoride is a burst-effect (Attar and Turgut, 2003; Cohen *et al.*, 2003). A high amount of fluoride is released in the first day then the fluoride release returns to pre-exposure level after 2 to 3 days (Young *et al.*, 1996). This behaviour was similar to Ketac-cement in the current study, with fluoride release levelling off by the third day (Figure 6.29). Whilst for the experimental materials there were peaks at third, fourth, even fifth day after recharge (see Figure 6.26, Figure 6.27and Figure 6.28).

The reason for this delayed pattern of fluoride release after recharging is not completely understood. However, there are some suggestions regarding the mechanism of fluoride recharging. Firstly, it is suggested that recharging behaviour of adhesives is caused by surface effects not chemical recharging (Gao and Smales, 2001) because fluoride uptake and rerelease is probably due to the processes of surface retention and matrix diffusion of fluoride (Cohen *et al.*, 2003; Preston *et al.*, 2003). All experimental materials were based on hydrophilic monomers HEMA and 4-META. These hydrophilic monomers readily absorb water in polymer form (Arima *et al.*, 1995; Van Landuyt *et al.*, 2007; Su *et al.*, 2010) with fluoride ions from the external fluoride source. This was likely to diffuse deeper rather than being on the samples' surface only. As water molecules binding via hydrogen bonding to the polar sites of HEMA

and 4-META contribute to water diffusion through polymer matrices (Yiu *et al.*, 2006). Thus, the fluoride that retained on the surface and on deeper layers re-released afterward. In addition to hydrophilicity of monomers, another factor might helped this water diffusion which is porosity of polymers of HEMA (Tay *et al.*, 2002a). It has been shown that presence of lots of porosities in GIC and RMGIC produce high fluoride recharging abilities (Xu and Burgess, 2003).

The second possible reason for this recharging is due to replacement of intrinsic fluoride and fluoride diffusion into porosities within the material (Xu and Burgess, 2003). The SEM images of aged specimens showed that the number of voids increased compared to fresh specimens, this was due to dissolution NaF particles. This might allow more fluoride ions from the external source to diffuse deeper into the samples, replacing the dissolved fluoride, resulting in a higher amount of re-release. The diffusion increases the entrapment of fluoride ions from the external source and re-releases it slowly into the local environment (Takahashi *et al.*, 1993; Yan *et al.*, 2007).

However, in case of Ketac-cement, the presence of a hydrogel matrix increases their permeability to water (Preston *et al.*, 2003) and their uptake/release of ions through the polyacrylic matrix (Takahashi *et al.*, 1993; Attin *et al.*, 1999). It has been proposed that the recharging ability of GICs is dependent on the glass component. In particular upon the structure of the hydrogel layer around glass filler particles, which is formed due to reactions between fluoridated glass particles and polyacrylic acids (Dionysopoulos *et al.*, 2013).

The results of the present study indicate that all the experimental acrylic resins possess fluoride recharging ability. Addition of 4-META did not increase fluoride recharge of the materials. The reason might be related to the water sorption of the materials that was not changed after 4-META addition consequently fluoride recharging was not increased. Therefore, the third hypothesis which was "4-META increase fluoride recharging ability of the material" was not accepted. From clinical point of view, the results of current study indicate that fluoridated acrylic resins could be used to act as reservoir for fluoride once internal fluoride has finished.

Further investigations may explain the recharge behaviour of the experimental materials by carrying out a longer pre- and post- recharge measurement. Evaluating the fluoride uptake/release of different fluoride sources may also be beneficial.

6.5.5 *SEM observation*

SEM was used to examine surface morphology of the disc shaped samples of the fluoride releasing samples. SEM is the most commonly used technique to analyze the morphology of the surface of the materials (Bootz *et al.*, 2004; Perevyazko *et al.*, 2010). It has been used to

analyze the changes of surfaces after exposure to storage environment (Markovic *et al.*, 2008). SEM can be used to record the surface appearance of specimens of differing thickness (Zhu *et al.*, 2010) depending on the imaging source of the focused electron beam (Giannuzzi and Stevie, 1999; Canovic *et al.*, 2008). An essential step in preparing specimens for SEM imaging is drying prior to gold coating which may cause deformation of biological samples (Pathan *et al.*, 2008). However, in the current study since dental material specimens were analysed, the drying effect was limited to formation of cracks on the materials surface (Zahroon, 2014).

The SEM images obtained in this study showed cracks in all groups of the fresh and aged specimens. These cracks could be formed during processing for SEM analysis by the dehydration of the samples. Similar cracks was found in previous studies on resin based materials and GIC (Bala *et al.*, 2012; Zahroon, 2014) which they referred to be formed during sample preparation for SEM images. The cracks were more predominant in the aged specimens compared to the fresh specimens. The reason behind that could be due to the prolonged storage in water leading to leaching out of elements during fluoride release.

In addition to cracks, voids were also found on the surface of specimens. These voids were thought to be produced due to elution of NaF particles during ion exchange process, releasing fluoride during 28 days in water, because these voids were not found in fresh specimens. The number of voids can be seen to be increasing with increasing NaF concentrations, supporting this theory. These voids were also observed in a previous study of acrylic resin adhesives (Zahroon, 2014). Some other voids might be produced during mixing and placing the specimens into moulds during specimen preparations, but these would be expected to be visible on both the fresh and aged specimens. Further investigation may be helpful in determining the morphology of these voids together with the morphology of NaF particles by using a different technique may be useful for future examination such as, using transmission electron microscope or perhaps using environmental SEM to avoid drying of specimens.

6.6 Summary

The results showed that 4-META addition had no detrimental effect on the DoC and fluoride releasing and recharging ability of the experimental materials. The results also showed that the developed materials had fluoride release in addition to recharging potential. Those groups with the highest fluoride content had high fluoride release ability and this resulted in greater solubility. The Group 9:1 demonstrated fluoride release, recharge ability and reasonable DoC and it was less soluble than the rest of the fluoride releasing groups therefore it was selected as the most suitable material for bond strength testing.

Chapter 7: **Investigating the shear bond strength of the developed materials**

7.1 Introduction

Previously the effect of adding 4-META to the experimental material was investigated, through the measurement of certain key handling properties and fluoride release. In this chapter the effect of 4-META on the SBS of the experimental materials was investigated. Two experimental groups (9:1 10%A and 9:1 10%A 5%M) were chosen based on previously measured properties such as DoC, fluoride release, recharge and water solubility. Another two experimental groups, without NaF, (10:0 10%A 0%M and 10:0 10%A 5%M) were taken as comparators, together with Transbond XT as a composite resin based commercial orthodontic adhesive.

7.2 Aims and hypothesis

7.2.1 *Aims*

To investigate the effect of 4-META on SBS of the developed material and compared with Transbond XT.

7.2.2 *Hypothesis*

4-META increases bond strength of the experimental materials

7.3 Materials and methods:

Based on previous experiments four groups were chosen for SBS testing see Table 7.1. For assessing SBS Transbond XT was used as a commercial comparator (see table 7.2). The experimental materials were mixed using the same method as described in chapter 4.

Table 7.1 Experimental groups used for SBS study.

Experimental materials	PMMA%	NaF%	Acetone%	4-META%	Other components
10:0 10%A 0%M	100	0	10	0	40% HEMA 60% MMA 1% CQ 1% DMAEMA
10:0 10%A 5%M	100	0	10	5	
9:1 10%A 0%M	90	1	10	0	
9:1 10%A 5%M	90	1	10	5	

7.3.1 *Sample selection and storage:*

A total of 200 fresh permanent bovine central incisors were extracted at a local slaughter house and stored in a solution of 0.1% wt Chloramine-T (Sigma-aldrich.Dorset.UK) at 4°C. The criteria for tooth selection were that it must have an intact facial surface with no obvious defects

(cracks or caries). The crowns were split into three sections, see figure 7.1 using a diamond disc (Skillbond direct Ltd., UK). The sections were then stored in Chloramine T until required. The storage solution was changed every week to preserve the integrity of the tooth structure.

7.3.2 *Roughness*

In order to compare the roughness variation between sections, 7 bovine teeth were randomly selected for investigation using profilometry. Each tooth was sectioned into three sections as previously described in section 1.3.1. Three measurements were recorded from the surface of each tooth specimen as illustrated in figures 7.1 and 7.2. A stylus profilometer (Mitutoyo Surftest SV-2000) and its associated software (Surfpak-SV Mitutoyo Corp V1.600) were used for sample profiling. Sections were mounted in the profilometer perpendicular to the stylus tip, using a spirit level. The stylus was a diamond cone tip with a 5 μm radius applying a force of 4 mN. The profilometer was calibrated at the start of each assessment day using a standard metal calibration block Ra 2.9 μm (Mitutoyo precision reference specimen, serial number 534298, Japan) to ensure that the results were within the normal range of reproducibility. The stylus was run with a speed of 1 mm/sec on an evaluation length of 4 mm. Three measurements were taken in each section, 1 mm apart. The Ra value, the arithmetic mean value of the profile, was obtained from the 3 lines of each section by the associated software. A final Ra average was then calculated for that specimen which was transferred to Microsoft Excel (Microsoft office 14) for analysis.

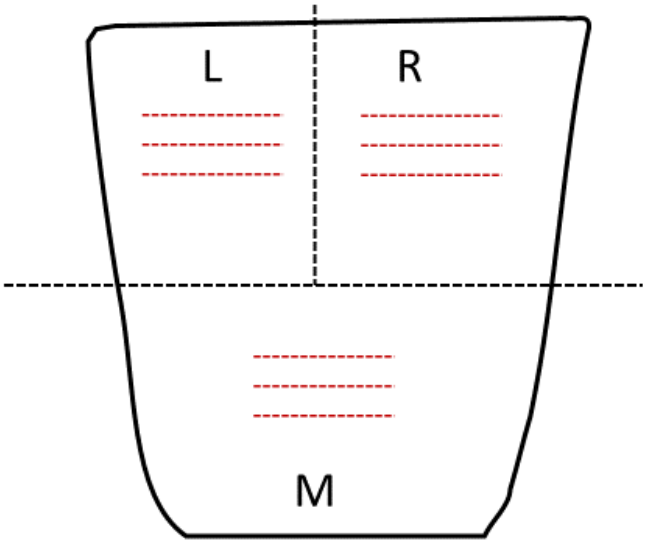


Figure 7.1 Schematic diagram showing bovine incisor teeth dissection in to three sections (black dot lines) including right section (R), left section (L) and middle section (M). The red lines indicate the surface profilometery taken on each section.

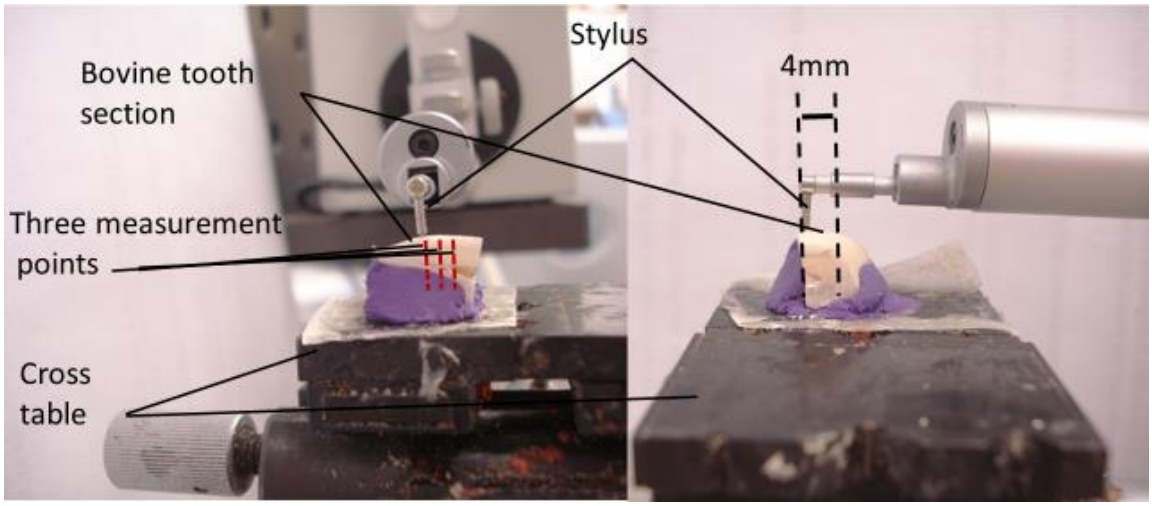


Figure 7.2 Stylus profilometry. Sample preparation

Epoxy resin (Bonda clear casting resin, UK) was used to embed the teeth, using plastic rings (Samplkups, 30mm diameter, Buheler, UK) of 30 mm diameter. Each specimen was encased in resin, but leaving the facial surface exposed. Each tooth was oriented so as that its labial surface would be parallel to the shearing force (see figure 7.3).

7.3.3 *Bracket*

Standard Edgewise central incisor orthodontic brackets (0.022-inch slot, Orthocare, UK) were used for bonding to bovine teeth. The average surface area of the bracket base was measured using digital Vernier callipers (Mitutoyo Digimatic, Japan) and it was 11 mm² (0.2) based on measuring width and length of the base of 10 brackets.

7.3.4 *Bonding procedure*

The teeth were polished for 10 seconds using fluoride/oil free prophy paste (Orapol polishing paste, S.S. White Group, UK) using a prophy cup (Junior Rubber Prophy Cups, UK) attached to a slow hand-piece see table 7.2. The teeth were washed and dried for 10 seconds using oil free compressed air. Acid etchant (36% conditioner, Dentsply, UK) was used to etch the enamel surface for 30 seconds before thorough rinsing and drying for another 30 seconds using compressed air until the enamel surface appeared chalky white. A thin coating of Heliobond (Ivoclar Vivadent, Uk) was used as a primer before applying the bracket, coated with the experimental material. The bonded interface was light cured for 20 seconds from each side (80 seconds in total) at a 3-5 mm distance at 45 degree angle using bluephase® 20i LCU emitting 1130 mW/cm^2 intensity (measured using Coltolux Intensity Meter, Germany). The cordless Bluephase LCUs were returned to their battery chargers after each specimen was cured. For the comparator group Transbond® XT primer (3M Unitek , UK) was used with Transbond® XT (Unitek, UK) adhesive according to the manufacturer's instructions and light cured as above.

21 samples were prepared for each group for each experiment. The first group (30 MINUTES) were tested after 30 minutes of water storage and the second group (30 DAYS) were stored in phosphate buffer saline (PBS) (phosphate buffer saline, Sigma Aldrich, UK) at 37 °C for 1 month. The storage solution was changed every week.

Table 7.2 Commercial materials used in this study.

Names	Type	Manufacture	Composition
Heliobond	Primer	Ivoclar Vivadent	BisGMA 60% TEGDMA 40%
DeTrey® Conditioner 36	Acid etchant	DENTSPLY DeTrey GmbH	Phosphoric acid 36%
Transbond ™ XT	Light cure orthodontic adhesive	3M Unitek	Silane treated quartz, BisGMA, Silane treated silica, Bisphenol A Bis(2-Hydroxyethy ether) Dimethacrylate ,Diphenylidonium, Hexafluorophosphate
Ketac™ Cem radiopaque	Glass ionomer luting cement	3M ESPE	Powder: Glass powder, Polycarboxylic acid Liquid: Water, Tartaric acid
Transbond XT Primer	Primer	3M Unitek	BisGMA, TEGDMA, Triphenylantimony, 4-(Dimethylamino)-benzene ethanol, Dl-camphorquinone, Hydroquinone.
Orapol Prophylaxis paste	Dental cleaning pastes	S.S. White Group, UK	-
Standard Edgewise Twin Bracket	Upper Central Incisor. Wide 0.022-inch slot	Orthocare, UK	

7.3.5 *Debonding and shear bond strength (SBS)*

All samples were mounted in a universal testing machine (Instron model 5567, Berks, UK) with the enamel surface parallel to the direction of the applied force. Shear bond strength was measured using the wire loop technique by threading a stainless steel orthodontic wire (0.6 mm) under the gingival wings of the bracket and then attaching this wire to a specially made holder in the machine at a cross head speed of 1mm/min see figure 7.3. The force required to debond the bracket was recorded in (N) using a 1KN load cell. The SBS was determined by dividing the debonding force over the surface area of the bracket using Equation 7.1. A typical force of 120 N for Transbond XT was measured see figure 7.4. The average surface area of the bracket base was measured using digital Vernier callipers (Mitutoyo Digimatic, Japan) and it was 11 mm² (0.2) based on measuring width and length of the base of 10 brackets.

Equation 7.1 $$\text{Shear force (MPa)} = \frac{\text{Debonding force (N)}}{\text{area (mm}^2\text{)}}$$

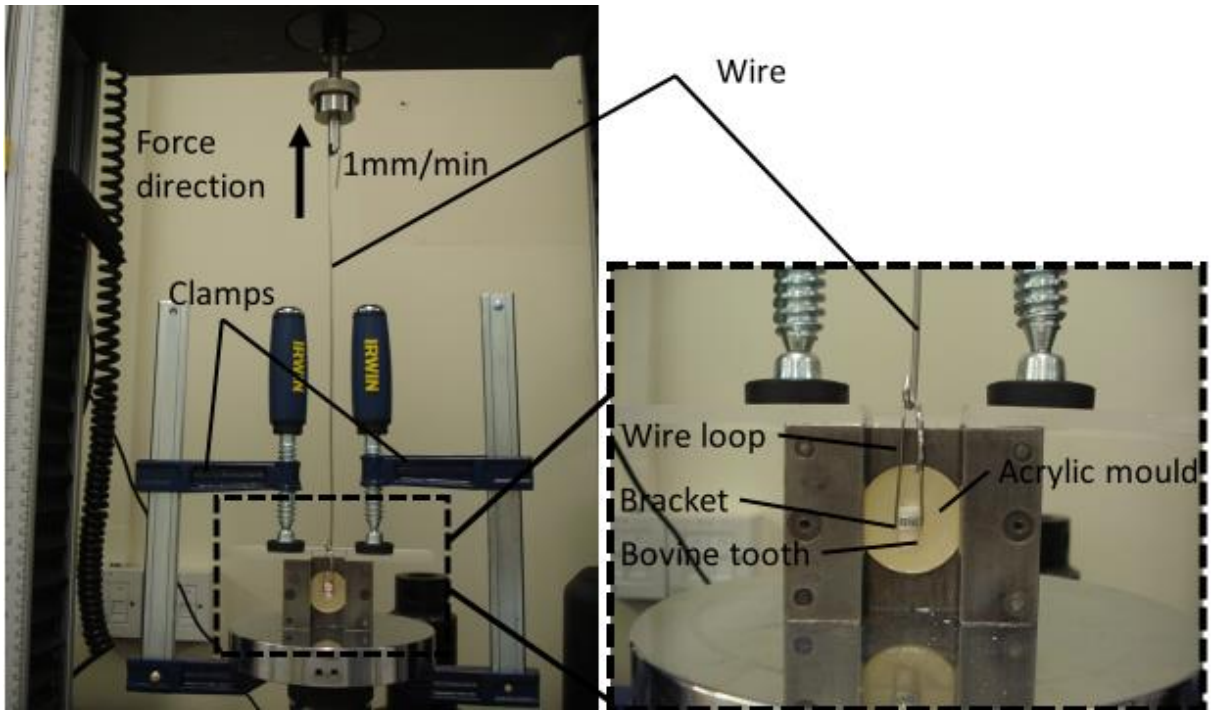


Figure 7.3 Shear bond strength testing setup.

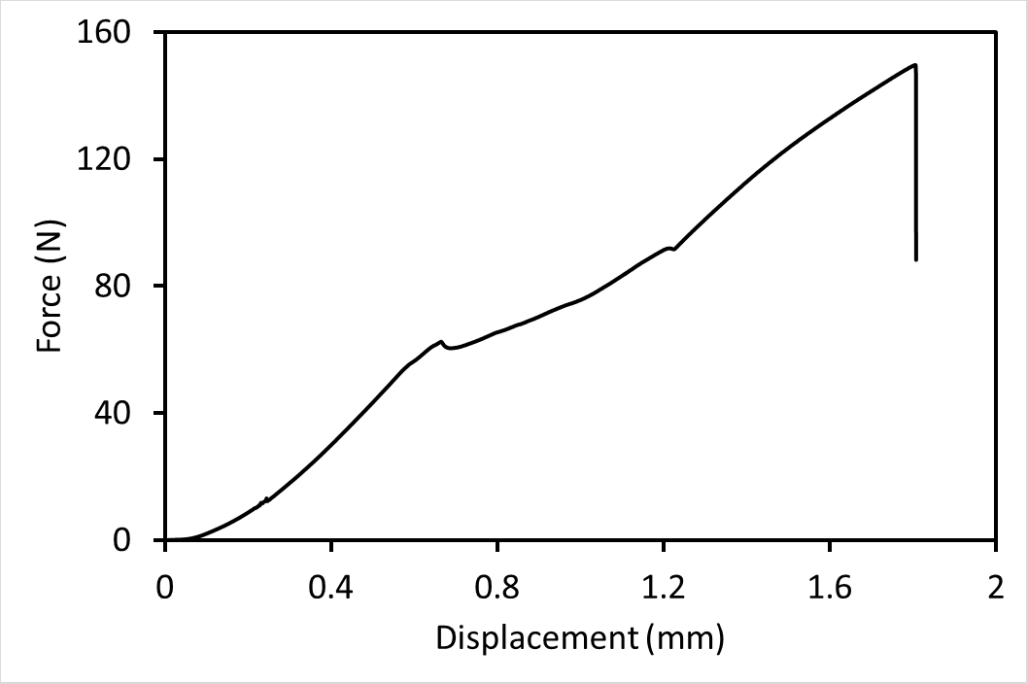


Figure 7.4 Representative force displacement of one sample of Transbond XT group at day 30.

7.3.6 *Adhesive Remnant Index*

The debonded samples were examined under a stereomicroscope, using 10X magnification to assess the mode of failure. The enamel surfaces were scored according to adhesive remnant index (ARI) (Artun and Bergland, 1984) score (0) no adhesive left on the tooth; score (1) less than half of the adhesive left on the tooth; score (2) more than half of the adhesive left on the tooth; and score (3) all adhesive left on the tooth with a distinct impression of the bracket mesh.

7.3.7 *Statistical analysis*

All data were analysed using statistical software (SPSS 19 for windows, IBM SPSS Inc., USA). The Shapiro-Wilk test was used to test normality of the data. The Roughness and SBS data were normally distributed. One-way ANOVA and post hoc Tukeys test were used to determine statistically significant differences between groups at the 5% level ($P<0.05$). Kruskal–Wallis and Mann–Whitney tests were used to determine significant differences in ARI scores between groups at $P<0.05$.

7.4 Results

7.4.1 *Roughness of bovine enamel sections*

Figures 7.4, 7.5 and 7.6 show similar mean profile roughness of the right left and middle sections. The Ra values are shown in table 7.3 there was no significant differences in Ra between sections (ANOVA, Tukeys test $P<0.05$).

Table 7.3 Mean Ra.

Bovine tooth sections	Mean Ra (µm) / (SD)
R	4.2 (1.4)
L	4.3 (1.6)
M	6.2 (1.3)

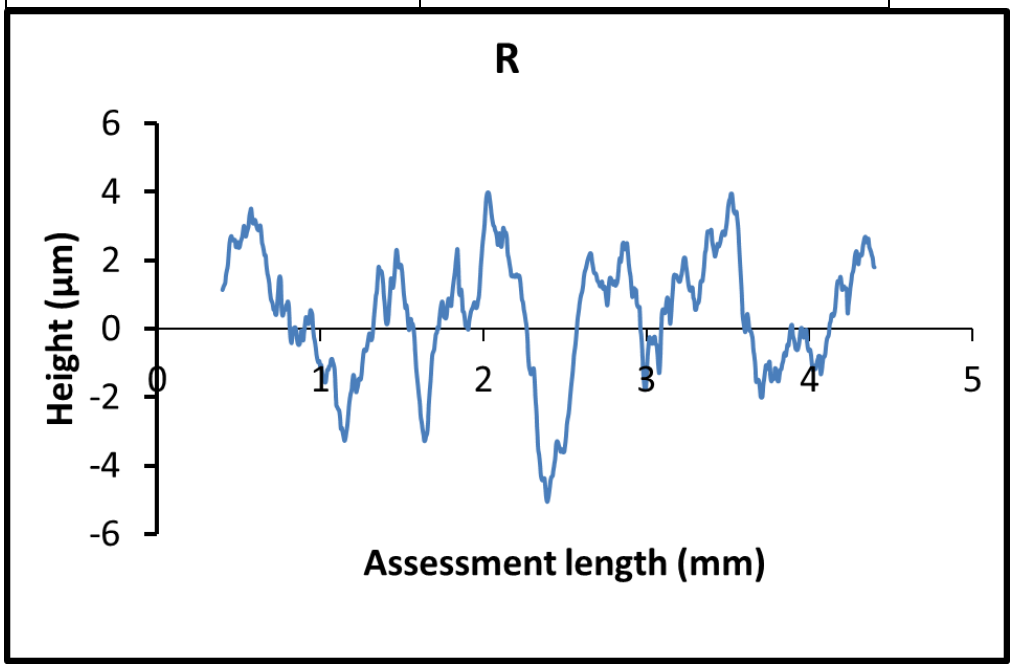


Figure 7.5 Typical stylus profilometry profile of the right section.

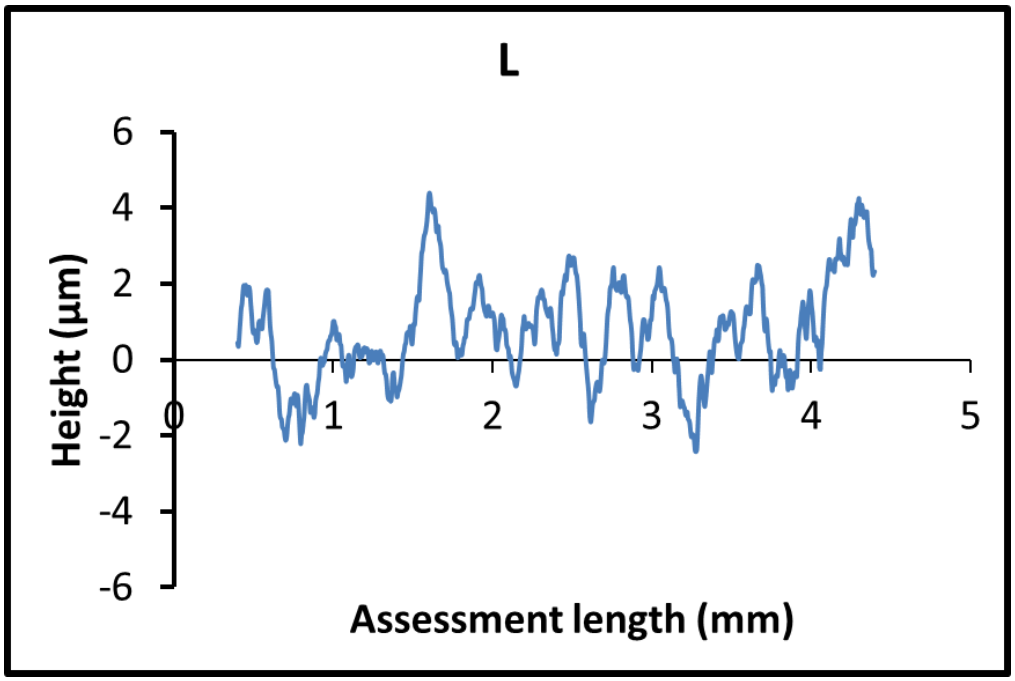


Figure 7.6 Typical stylus profilometry profile of the left section.

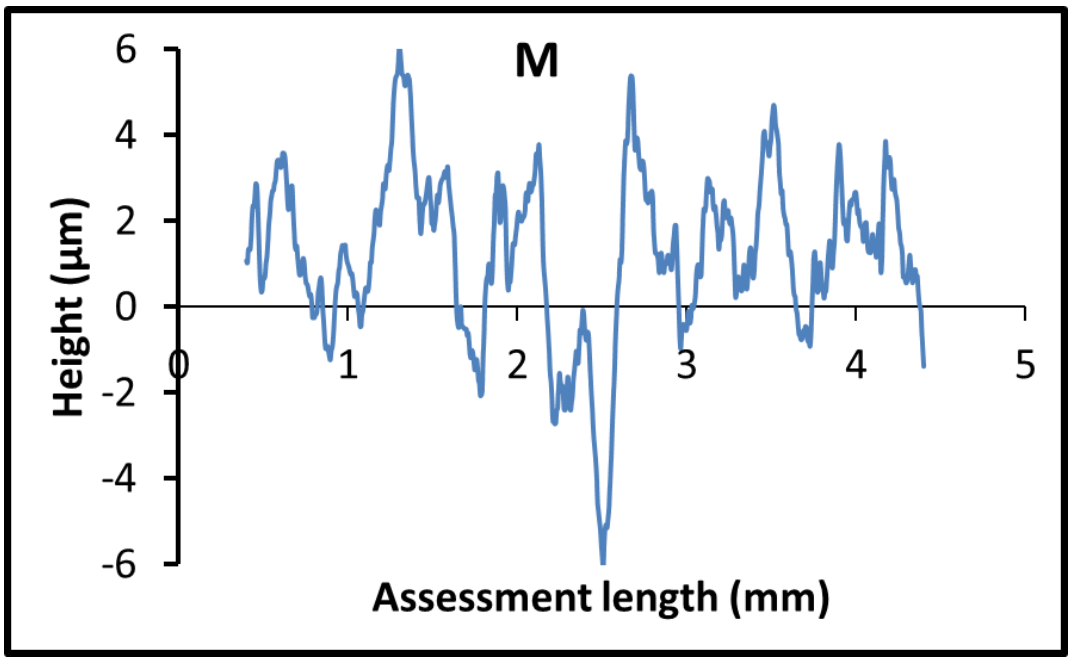


Figure 7.7 Typical stylus profilometry profile of middle part.

7.4.2 *Shear bond strength (SBS).*

Bond strengths of the experimental materials were significantly decreased at 30 days compared to 30 mins ($p<0.05$, one-way ANOVA) and were lower than Transbond XT ($p<0.05$). Neither the 4-META nor NaF affected the SBS of the material ($p<0.05$) see table 7.4 and figure 7.7.

Table 7.4 Mean SBS of all experimental groups and the comparator group.

Experimental groups	SBS Mean (SD)	
	30 mins	30 days
10:0 10%A 0%M	4.8 (1.1)[a]	1.7 (0.7)[b]
10:0 10%A 10%M	4.1 (1.8)[a]	1.6 (0.7)[b]
9:1 10%A 10%M	6.2 (1.4)[a]	2.3 (1)[b]
9:1 5%A 10%M	5.8 (1)[a]	2.7 (1)[b]
Transbond XT	12.8 (2)[c]	16.4 (4.6)[c]

Superscript letters indicate no significant differences between groups.

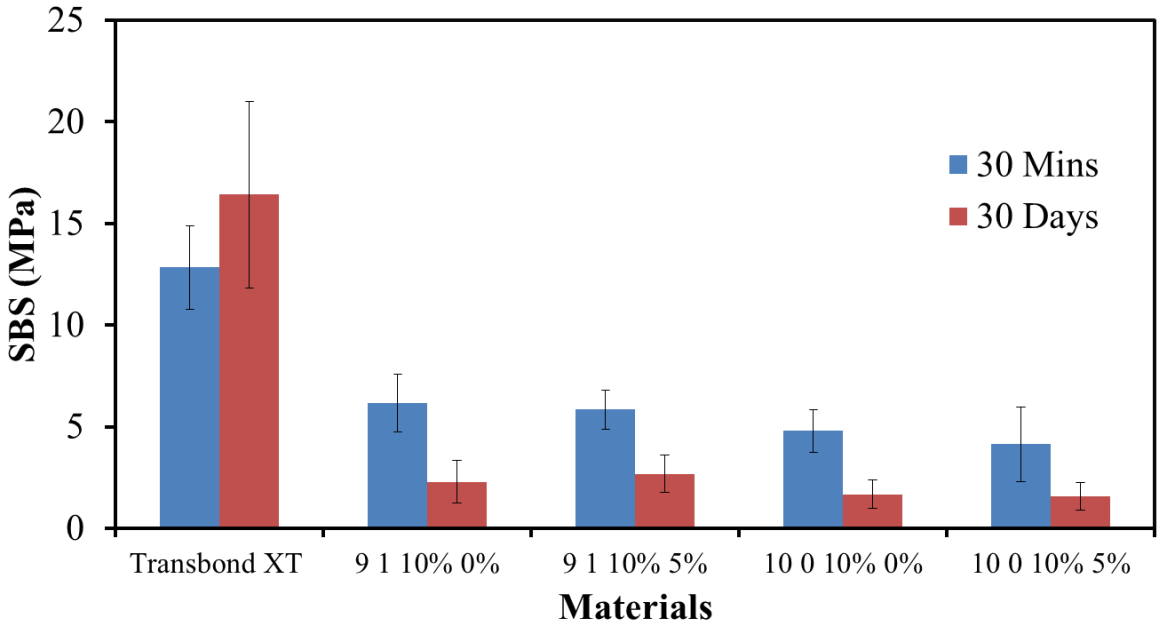


Figure 7.8 Mean SBS of all experimental groups and the comparator group

7.4.3 *Adhesive Remnant Index*

Kruskal-Wallis test showed highly significant differences at 30 minutes and 30 days ($P<0.05$). Mann-Whitney test showed that all experimental groups at 30 minutes had significantly lower ARI score than Transbond XT ($P<0.05$). At 30 days, the Mann-Whitney test revealed Transbond XT had significantly higher ARI score than groups 9:1 at ($P<0.05$) see Table 7.5.

Table 7.5 ARI of all experimental groups on bovine teeth.

Experimental groups	ARI			
	0	1	2	3
30 mins				
10:0 10%A 0%M	2	17	2	0
10:0 10%A 5%M	0	17	4	0
9:1 10%A 0%M	0	17	4	0
9:1 10%A 5%M	0	18	3	0
Transbond XT	0	1	8	12
30 days				
10:0 10%A 0%M	0	2	12	7
10:0 10%A 5%M	1	4	12	4
9:1 10%A 0%M	1	5	14	1
9:1 10%A 5%M	2	6	9	2
Transbond XT	0	3	10	8

7.5 Discussion

Bond strength is an important factor that determines success and efficacy of orthodontic treatment. In the current study some experimental groups (9:1) were chosen for SBS study to investigate the clinical performance (bond strength of the developed materials). Previous results had shown that the group 9:1 had fluoride release and recharge, together with reasonable DoC. In addition, the 9:1 groups were had a lower solubility than other experimental groups. To test the SBS of the materials bovine teeth were used to bond orthodontic brackets using experimental materials and then debonding them for measuring SBS.

Bovine teeth are not identical to human teeth in either chemistry or micro-structure (Yassen *et al.*, 2011), however, they have been suggested as a useful substitute to human teeth in orthodontic bonding tests (Oesterle *et al.*, 1998) and have been used before in many bond strength studies (Klocke and Kahl-Nieke, 2005; Yamamoto *et al.*, 2006; Parrish *et al.*, 2011). In the current study bovine central incisors were used, due to their relatively flat buccal surface allowing us to bond to intact surface. The bovine central incisors were large enough to be

dissected into three sections, giving sufficient samples for a meaningful sample size. It was decided to take 21 specimen per each group. It was based on previous studies which are mostly taken between 15 - 30 samples per group as mentioned in literature review see (Table 2.1) (Evans *et al.*, 2002; Swanson *et al.*, 2004; Klocke and Kahl-Nieke, 2005; Su *et al.*, 2010; Parrish *et al.*, 2011; Yoshida *et al.*, 2012; Vinagre *et al.*, 2014). Previously bovine teeth have been sectioned to remove the incisal edge and root prior to bond strength testing (Farret *et al.*, 2012). Human premolars have also been dissected into buccal and lingual sections in many studies (Parrish *et al.*, 2011). Even buccal surfaces of premolars dissected in to right and left to increase sample size (Chow *et al.*, 2011)

A study has shown that the topography of the adherent surface (bovine enamel and dentine) can affect bonding of a resin based adhesive system (Eick *et al.*, 1972). While others has been previously shown that there is no correlation between roughness and adhesive bond strength in a range of studies (Jung *et al.*, 1999; Barkmeier *et al.*, 2009; Sabatoski *et al.*, 2010). Therefore, in order to know if there is any effect due to roughness on bond strength, it was decided to measure the roughness of the specimen. The roughness of each section was investigated to determine if there was any difference in roughness between different sections. No significant differences were found between different sections of bovine teeth. Stylus profilometry was used to investigate the roughness profile of each sections of bovine teeth (Sabatoski *et al.*, 2010). In this study, stylus profilometry was used as it can measure samples with larger size and scale in comparison with atomic force microscopy.

While many studies have used both bovine and human enamel with an intact surface, some studies have used a ground enamel surface to obtain a flat substrate. This was to overcome the roughness variability of the substrate (Gibb and Katona, 2006). However, in the current study intact enamel surface was used for some reasons. Firstly there was no significant differences in the roughness between different sections. Secondly, the procedure of grinding of the outer most enamel surface is inappropriate if attempting to replicate clinical conditions (Eliades and Brantley, 2000), in addition, extra variability may arise in the roughness as well as in the thickness of the remaining enamel after grinding as this is difficult to control (Schneider *et al.*, 1981). In terms of the impact of grinding the tooth surface on bond strength, this is controversial in the literature. Some studies have shown increasing bond strength on ground surfaces compared to the intact enamel surface of (Hadad *et al.*, 2006), while others report no difference in the bond strengths (Perdigao and Geraldeli, 2003). In general using an intact enamel surface better replicates the clinical situation.

The enamel surfaces were prepared by polishing and etching. An enamel conditioner, which was composed of 36% phosphoric acid, was used to etch the enamel surface for 30 seconds.

This is has been used previously in studies using bovine teeth with etching for 30 seconds (Oesterle *et al.*, 1998; Shinchi *et al.*, 2000). 30 seconds of acid etching has been recommended for cleaning and producing a proper etch (Gardner and Hobson, 2001). No differences were found in the tensile bond strength of enamel to composite resin when bovine enamel surfaces were treated with phosphoric acid between 3% to 65% for 30 seconds (Shinchi *et al.*, 2000). After etching, the enamel surface was painted with a primer. A primer with a very simple structure compared to other available commercial primers, based on 40 wt% BisGMA and 60 wt% TEGDMA, was used to paint the enamel surface prior to application of the experimental material and brackets. The reason was to choose a primer that should be compatible with experimental materials. The data would suggest the primer and experimental resin were compatible as few failures were observed entirely at the tooth – experimental resin interface. In addition, there are some *in vitro* studies showing no significant difference in orthodontic bond strength between using a primer or without using it (Chalgren *et al.*, 2007). A randomized clinical trial has shown no significant difference in the failure rate between using primer (11.1%) and without primer (15.8%) for a period of 12 months using pre-coated brackets (Nandhra *et al.*, 2015). While, for the Transbond XT the Transbond XT primer was used as supplied with the adhesive by manufacturer.

During treatment and debonding, orthodontic brackets are exposed to combination of forces in many directions. Therefore, different modes of applying force have been used for testing orthodontic bond strength such as torsion, tensile and shear/peel loading. The most commonly used method is shear bond strength (SBS). Many methods have been used to apply shear such as wire loops and steel blades or rods (Rognvald and Peter, 2001; Lamper *et al.*, 2012; Shooter *et al.*, 2012; Vinagre *et al.*, 2014). As mentioned in the literature review, there are some advantages and disadvantages of each technique. In the current study the wire loop method was used as it is considered to more closely resemble the clinical situation compared to using a blade (Mojtahedzadeh *et al.*, 2006).

Debonding was undertaken at two time points at 30 minutes and 30 days after curing of the bonded interface. Most studies have measured bond strength 24 hours after a bracket has been bonded (Arnold *et al.*, 2002), which is different to the clinical scenario where load would be applied shortly after bracket placement, as most clinicians activate orthodontic appliances within 10-15 minutes of the appliance placement. Studies have demonstrated higher SBS at 24 hours compared to 30 minutes after bracket bonding using a range of filled and unfilled BisGMA, UDMA and TEGDMA based commercially available orthodontic adhesives (Bishara *et al.*, 1999; Yamamoto *et al.*, 2006; Su *et al.*, 2010; Yoshida *et al.*, 2012; Vinagre *et al.*, 2014). In the current study bond strength was taken after 30 minutes to more closely simulate the

clinical scenario. Another SBS measurement was taken after storage in PBS for 30 days, to investigate longer term performance of the materials. PBS was used because it has neutral pH in comparison to DW which is acidic and might demineralize the enamel surfaces and affect the SBS results.

The results showed no significant differences between different sections of the teeth. The initial bond strength (30 minutes) was nearly 5-6 MPa which was significantly lower than Transbond XT. However, this is near the range that considered to be acceptable clinically (6-8 MPa) (Reynolds, 1975). The low bond strength of the experimental materials compared to the Transbond XT was related to the fact that it was based on a linear co-polymer of HEMA and MMA which are both linear and less crosslinked compared to a highly crosslinked nature of BisGMA of the Transbond XT. Experimental materials form linear structure after polymerization (Imai and Ikeda, 1997; Tsuruoka *et al.*, 2007). This resulted in a more flexible polymer (Tay *et al.*, 2002a; Kim *et al.*, 2014). This may contribute in making debonding of the experimental materials easier and safer than Transbond XT (Kim *et al.*, 2014). One of the primary aims for the developing of the current experimental materials was to make it easier and safer at debonding compared to composite resin based orthodontic adhesives which can result in enamel loss during debonding and adhesive removal (Ireland *et al.*, 2005; Kim *et al.*, 2014). The results of the SBS test also showed that the SBS of the experimental materials decreased after being in PBS for 30 days, to an unacceptably low value (2 MPa). This is probably due to presence of 40% of HEMA in the material, which leads to high water absorption (Arima *et al.*, 1995; Van Landuyt *et al.*, 2007; Su *et al.*, 2010). The water absorbed by the materials reduces the frictional forces between polymer chains, plasticising them, negatively affecting the mechanical properties of the polymer (Sideridou *et al.*, 2007). This is supported by the data of water sorption in which the group 9:1 demonstrated high water sorption which was significantly higher than Transbond XT. Transbond XT showed a slight increase in SBS at 30 days compared to 30 minutes, which may be attributed to continued post curing polymerization of the resin during storage (Al-Ahdal *et al.*, 2015). The higher the DoC the higher mechanical properties of the material. However, these were not significantly different.

4-META has been widely used as an adhesion promoting monomer to increase the bond strength of adhesive resins to enamel, amalgam, gold alloy, metal alloys and porcelain (Ohno *et al.*, 1992; Björn *et al.*, 1995; Büyükyilmaz *et al.*, 1995; Zachrisson *et al.*, 1996; Minami *et al.*, 2013). It was shown that using 4-META at 5% with acetone as a primer increases bond strength of 4-META/methyl methacrylate (MMA)-tri-n-butyl borane adhesives resin to dentine (Nakabayashi and Hiranuma, 2000). It has been also shown that 4-META containing adhesives had higher SBS than composite resin based orthodontic adhesives like Transbond XT (Clark *et*

al., 2003). In the current study, the SBS of the experimental materials was lower than Transbond XT. In addition, no significant differences were found between groups with and without NaF and 4-META, therefore the hypothesis "4-META increases bond strength of the experimental materials" was rejected.

Previous work by Su *et al.* (2010) on a similar material showed bond strength results higher than those measured in our work. One possible reason for this difference could be due to different tooth structure, human teeth were used by Su *et al* (2010) compared to bovine teeth used in this study. A study has shown no significant differences in SBS values using bovine and human teeth in using a light cured composite resin (Fowler *et al.*, 1992), however, in this study only 10 samples were used per each group. In contrast, in most studies have shown higher SBS value in human teeth compared to bovine teeth (Oesterle *et al.*, 1998; Rüttermann *et al.*, 2013). This could be due to the differences in crystal configuration and more lattice defects than human enamel (Fonseca *et al.*, 2008; Tanaka *et al.*, 2008)

The ARI scores were used to determine the site of bond failure within each experimental and Transbond XT group. During debonding, the bond failure occurs either at bracket/adhesive and/or enamel/adhesive interface. The latter is more favourable since it contributes to minimise the time required and enamel loss after debonding (Fox *et al.*, 1994). At 30 minutes, significant differences in ARI scores were observed for all experimental groups compared with the Transbond XT control material. All experimental materials had a preponderance of score 1 (< 50% adhesive retained on the enamel surface). By contrast, Transbond XT was likely to leave adhesive on at least more than 50% of the bonded area of the tooth on half of the cases on the other half all adhesive left on the tooth surface (score 2). This would imply that there should be some differences in the materials when ease of clean up considered. Therefore, experimental materials may be more easily removed compared to Transbond XT. This might be due to the increased flexibility of the experimental materials which are MMA based resin in comparison to Transbond XT which is filled dimethacrylate-based resin. It has been shown that less enamel fracture occurs after debonding an experimental MMA based resin in comparison to conventional Transbond XT (Kim *et al.*, 2014). At 30 days there was significant differences between Transbond XT and experimental groups. However, as the experimental materials bond strength was quite low the mode of failure may be relatively meaningless. When the ARI score of Transbond XT at 30 minutes compared to 30 days there was no significant differences in ARI score. This might indicate that 30 days water storage did not affect ARI and SBS of Transbond XT.

For future work the bond strength of the experimental materials should be optimized. One suggestion may be decreasing the concentration of hydrophilic monomer HEMA to reduce

water sorption of the material, replacing part of the HEMA content with different monomers such as BisGMA or UDMA. As it has been shown that the mechanical properties of adhesive resins (such as compressive and flexural strength) can be improved by reducing hydrophilic monomers so as to reduce water sorption (Ling *et al.*, 2009) In addition it was found that SBS increased with decreasing TEGMA (hydrophilic) in a base monomer of UDMA as an orthodontic adhesive (Papakonstantinou *et al.*, 2013).

Another suggestion might be adding some inorganic fillers and bioglasses to the material to increase bond strength of the materials as some studies have shown that addition of inorganic fillers increase bond strength of the orthodontic adhesives. Orthodontic adhesives with higher filler content offer higher bond strength than lower filled or unfilled resins (Faltermeier *et al.*, 2007). There is correlation between mechanical properties of composite (hardness and diametrial tensile strength) and the volume fraction of filler content (Chung and Greener, 1990).

A final suggestion would be to consider replacing NaF with a more stable fluoride source such as CaF_2 as a soluble salt or fluoraluminosilicate glass. CaF_2 has a lower water solubility 0.016 g/L at 18 °C in comparison to NaF which is 42 g/L at 20°C. Therefore it results in less release of fluoride ions from CaF_2 in comparison to NaF in the first four weeks in a matrix of DU-DMA/HEMA, BisGMA/HEMA (Kodkeaw *et al.*, 2010). This resulted in releasing fluoride at a low sustained level for as long as 4 months in a polymer resin of UDMA/TEGMA at ratio 70:30 (Anusavice *et al.*, 2005). Transbond XT has a combination of hexafluorophosphate with silanated filler particles. Perhaps, mixing silanated filler particles with NaF may provide a way forward in developing fluoride releasing materials with better bond strengths. Or perhaps using fluoraluminosilicate glass as a filler, as fluoraluminosilicate glass has been use as a fluoride source in GICs, RMGICs and compomers and has been shown to release fluoride at low levels for a long time.

However, at each stage of further development of the materials care should be taken to monitor other properties of the material that are considered to be important, such as the fluoride release and setting characteristics of the material as well as bond strength of the material.

7.6 Summary

Whilst the experimental materials demonstrated lower bond strengths in comparison to commercially available orthodontic adhesive, particularly after water storage, the initial bond strength (after 30 minutes) was close to the range that is considered an acceptable bond strength for orthodontic adhesives at 6-8MPa. In addition to that, the developed materials had lower ARI score indicating less adhesive remains on the enamel surface after debonding, which may contribute to less enamel damage at debond by reducing the need for adhesive removal, which

is usually undertaken with a steel bur. So the experimental materials, whilst exhibiting lower bond strengths leave less adhesive remnant than commercially available orthodontic adhesives. However, the developed materials had lower bond strength after being in water for a month due to presence of HEMA in the materials which absorbed water, resulting in plasticization of the material by water. Therefore these materials need further development to be used as an orthodontic adhesive. Future work should aim to optimize the bond strength of the material with consideration to maintaining key important properties of the materials such as fluoride release and setting characteristics of the materials.

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Chapter 8: **General discussion**

8.1 Introduction

White spot lesions (WSL) are one of the most common problems during fixed orthodontic treatment, they compromise one of the primary aims of the treatment, which is to improve esthetics. Fluoride releasing orthodontic adhesives are potentially one of the methods to prevent WSL, with some evidence in the literature to support their use (Corry *et al.*, 2003; Gorton and Featherstone, 2003). A number of studies have focused on developing new fluoride releasing adhesives, the majority of which aimed at developing materials suitable for use as an orthodontic adhesive. Su *et al.* (2010) developed an MMA-based fluoride containing material, which showed potential for use as a fluoride releasing orthodontic adhesive. The present study was designed to further develop this material for use as an orthodontic adhesive. During this development the ideal properties of orthodontic adhesives were used as a focus for the experimental work.

The ideal properties of an orthodontic adhesive were explored in detail in the literature review and the following characteristics were identified. Firstly, the adhesive should possess good handling characteristics, in particular viscosity and setting characteristics of the materials. Secondly, the materials should have fluoride release to help prevent WSL. Thirdly, the materials should have an adequate bond strength to minimize debonding during treatment, but be easily removed at the end of treatment (Mandall *et al.*, 2003). Therefore during developing the materials the focus was on keeping and improving these key important properties of the materials without deteriorating by further development.

8.2 Methodological considerations

Four experimental groups were prepared in this study based on fluoride content including group 10:0, that contained no fluoride representing a control group, group 9:1 with 10% fluoride, 8:2 with 20% fluoride and 7:3 with 30% fluoride (Su *et al.*, 2010; Zahroon, 2014; Al-Sammarraie, 2015). Sodium fluoride (NaF) was used as a source of fluoride in this study as NaF is a very soluble salt that easily dissolves to free Na and F ions in an aqueous environment (Nakajo *et al.*, 2009). NaF has been used before as a source of fluoride in orthodontic adhesives and in fissure sealants (Shen *et al.*, 2007; Zahroon, 2014). To make the materials absorb water more easily, HEMA was incorporated due to its hydrophilic nature which facilitates water sorption into the material. (Yiu *et al.*, 2006; Kodkeaw *et al.*, 2010). HEMA was used with MMA at 40:60wt% as it has previously been shown to be the best ratio to provide fluoride release after NaF addition (Su et al., 2010). To make bracket debonding easier and safer, MMA was chosen as a linear monomer as it is easily polymerized and has successfully been used in a commercial

orthodontic adhesive with PMMA and 4-META (Super-Bond, MCP Bond®). PMMA powder was used as an organic filler as it is compatible with MMA. PMMA is a linear polymer with low density chains (Ferracane *et al.*, 1998; Ferracane, 2006) which results in a softer, more flexible and potentially weaker material (Gorelick et al., 1978). Therefore, less enamel loss and fracture is seen after debonding a MMA-based orthodontic adhesive in comparison to a conventional BisGMA/TEGMA based composite resin (Brown and Way, 1978; Su *et al.*, 2010; Kim *et al.*, 2014).

In this work the experimental materials were developed by adding acetone, to decrease viscosity, then different photoinitiators were investigated and finally, 4-META was added to potentially increase the adhesion between the materials and a stainless steel bracket.

8.3 The "Ideal" orthodontic adhesive

8.3.1 *Handling properties*

To improve the handling properties of the experimental material, acetone was added at five concentrations, namely 0%A, 10%A, 20%A, 30%A and 40%A, to decrease viscosity of the materials. With increasing acetone concentrations the injectability of the materials increased, indicating that the viscosity of the materials was decreased, creating a material with handling properties more suitable for clinical use. However, the addition of acetone may affect setting characteristics and fluoride release of the materials. Measurement of DoC and heat release at different acetone concentrations indicated that the effect was not detrimental at low concentrations up to 20%A. The materials still continued to release fluoride after acetone addition for as long as 160 days, comparable to a commercial GIC. Therefore the first hypothesis "The addition of acetone will result in decreased viscosity of the material without deteriorating DoC, heat release, fluoride release of the material" was accepted, as acetone up to 20% can be used to decrease viscosity of the materials without deteriorating setting characteristics and fluoride release of the materials. Thus all experimental materials at 0%A, 10%A and 20%A were taken for further development, investigating different photoinitiators to reduce curing time to a clinically acceptable level.

Different photo-initiators were investigated at different concentrations in order to obtain maximum DoC at shorter exposure time. For this CQ, with either DMAEMA or EDAB as activator, and Lucirin TPO were used, the former as a most commonly used photo-initiator in dental adhesives and the latter as a relatively new photo-initiator. The DoC was taken as it has effect on mechanical and physical properties of the materials. The higher the DoC the greater the mechanical and physical properties of the materials (Ferracane and Greener, 1986; Calheiros *et al.*, 2008; Price *et al.*, 2011). The results showed that the DoC increased with

increasing CQ concentrations. In addition, the results also showed that DoC of CQ with 1% DMAEMA was higher than with 1% EDAB activator. Therefore, the second hypothesis, which is "The degree of conversion (DoC) of the material will increase with increasing photo-initiator concentrations" was accepted. The results also showed that all experimental groups with Lucirin TPO polymerize faster and with a highest DoC than groups with CQ. However, CQ was taken for further developing of the materials as CQ is still the most commonly used photo-initiator, and secondly, Lucirin TPO has a low depth of cure according to literature (Leprince *et al.*, 2011; Miletic and Santini, 2012a; Schneider *et al.*, 2012). This low depth of cure might be an issue for adhesion of orthodontic adhesives as they are light cured under metallic brackets which block light transmission. This may result in low DoC of the part of adhesive far from the LCU tip consequently results in low mechanical properties of the adhesive and low bond strength. Therefore, CQ at 1% with 1% DMAEMA was taken for further development of the materials. However, experimental groups containing 20%A acetone were omitted from further experiments as at 40 seconds of light curing (considered an acceptable curing time for orthodontic bonding) some of the experimental groups (group 7:3) excluded low DoC (below 40%).

8.3.2 *Fluoride release*

Fluoride release of the experimental materials was one of the focuses of this study. Therefore, at each stage of development the fluoride release of the materials was measured to make sure that changes made do not significantly deteriorate the fluoride release of the experimental materials. In this study NaF was used as a source of fluoride as it is a very soluble salt and it is easily dissolves to free Na^+ and F^- ions (Nakajo *et al.*, 2009). HEMA was used as a hydrophilic monomer to facilitate water diffusion and consequently fluoride release. HEMA makes the materials absorb water more easily as HEMA is hydrophilic and facilitates water sorption and diffusion into the material and consequently releasing fluoride (Arima *et al.*, 1995; Yiu *et al.*, 2006; Van Landuyt *et al.*, 2007; Kodkeaw *et al.*, 2010; Su *et al.*, 2010). Therefore, HEMA was used with MMA at 40:60wt% as it has previously been shown to be the best ratio to provide fluoride release after addition of NaF (Su *et al.*, 2010). All experimental materials had released fluoride up to 160 days of water storage. Interestingly, the fluoride release level up to 160 days was within the range that considered to be effective for prevention of enamel demineralisation which is daily fluoride release of about 0.63 to 1.3 μg/cm² is (McNeill *et al.*, 2001). More interestingly all experimental materials had recharged and subsequently released fluoride after being exposed to 1000 ppm NaF solution.

Water sorption and solubility were also measured to better understand the fluoride releasing ability of the materials. The water sorption of the experimental materials is attributed to the HEMA monomer. Acetone addition to the experimental materials seems to increase water sorption and fluoride releasing ability of the materials (Malacarne-Zanon *et al.*, 2009). This was due to increasing porosity within the materials after acetone evaporation. The solubility of the experimental materials increased with increasing NaF concentrations, with higher fluoride content correlating with greater solubility.

The presence of NaF provides high levels of fluoride release of the experimental materials. One of the disadvantages of using water soluble salts like NaF, KF, CaF_2 and SnF_2 is that once the fluoride has leached out it leaves porosity in the resin. This was seen in SEM images the higher the fluoride content the higher number of voids. It has been shown previously that leaching out soluble salts like NaF and CaF_2 from a resin based material will affect mechanical properties of the material (Arends *et al.*, 1995). Therefore, one of the recommendations for further study might be testing other less soluble sources of fluoride like fluoride releasing glasses.

8.3.3 ***Bond strength***

4-META was added as an adhesion promoting monomer with the aim of increasing the bond strength of the materials to enamel. However, this addition should not be to the detriment of DoC and the fluoride release of the materials. The results showed that all experimental groups still had acceptable DoC, fluoride release and fluoride recharge after 4-META addition. Group 9:1 demonstrated good fluoride release and recharge and reasonable DoC and it also had lower solubility than the other of the fluoride releasing groups, therefore, it was selected as the "best" material for bond strength testing.

Measurement of the SBS indicated that 4-META addition did not increase the SBS of the materials. Also the SBS of all experimental groups decreased after being in water for 30 days. Therefore, the third hypothesis "The addition of 4-META will increase the bond strength of the material without deteriorating the DoC, fluoride release and recharging ability of the material" was partially accepted, as there was no detrimental effect of 4-META on these properties. However, the bond strength was not changed after 4-META addition. Perhaps increasing 4-META concentration for future is an option to increase bond strength. Or reducing the concentration of HEMA to improve the mechanical properties of the material. As it has been shown the mechanical properties of adhesive resins (such as compressive and flexural strength) can be improved by reducing hydrophilic monomers so as to reduce water sorption (Ling *et al.*, 2009). However, presence of a hydrophilic monomer is necessary to maintain the ability of the materials to release fluoride.

8.4 Is the experimental material an "Ideal Orthodontic Adhesive"?

The group 9:1 was considered the "best" fluoride containing experimental material and was therefore compared to commercially available materials. Transbond XT was taken as the gold standard commercial material to compare the bond strength, water sorption, solubility and DoC. To compare fluoride release and recharge a glass ionomer, Ketac-cement, was taken as a commercial comparator.

The developed materials, particularly group 9:1, have some potential for use as an orthodontic adhesive, although further development is required. The materials exhibited a DoC similar to Transbond XT. They also exhibited fluoride release and recharge levels similar to Ketac-cement. Therefore, the experimental materials have the potential to reduce decalcification and caries around orthodontic brackets, an advantage over many commercial adhesives. However, the developed materials had lower bond strengths in comparison to Transbond XT. Whilst the initial SBS was near the range that is generally considered to be acceptable clinically at 6-8MPa (Reynolds, 1975), after storage the bond strength was disappointingly low.

After water storage for 30 days the bond strength of the experimental materials had dramatically decreased compared to the initial bond strength. The most likely reason for this was due to the plasticizing effect of water on HEMA. The water absorbed by the materials reduce the frictional forces between polymer chains which can in turn negatively affected the mechanical properties (tensile and flexural strength) of the polymer (Sideridou *et al.*, 2007). The primary aim of using HEMA was to make the materials absorb water more easily and to facilitate water diffusion and fluoride release. The second reason is flexibility and porosity of HEMA polymers (Tay *et al.*, 2002a) which might allow easier debonding at finishing. More flexible resins have been shown to leave less enamel fracture and adhesive remnants compared to filled dimethacrylate-based resin (Kim *et al.*, 2014).

The developed materials had lower adhesive remnant index (ARI) scores compared with the Transbond XT indicating less adhesive remained on the enamel surface after removal. All experimental materials had a preponderance to score 1 (< 50% adhesive retained on the enamel surface). By contrast, Transbond XT was likely to leave adhesive on at least more than 50% of the bonded area of the tooth on half of the cases on the other half all adhesive left on the tooth surface (score 2). So the developed materials tend to detach from the enamel surface rather than the bracket surface. This could potentially reduce the need for aggressive removal of adhesive remnants after treatment reducing the likelihood of enamel damage. Therefore, the fourth hypothesis "the properties of the experimental materials would not differ significantly from those of the controls (GIC and Transbond XT)" was partially accepted, as the DoC and fluoride

release of the materials were comparable with the commercial comparators. However, the bond strength of the experimental materials is lower than Transbond XT and it was significantly reduced after being in water for 30 days. Therefore, the experimental materials have potential to use as an orthodontic adhesive, however, they require further development, particularly to improve their stability.

8.5 Conclusions and suggestions

Within the limitations of this work and based on the results found in this thesis, the developed materials have potential to use as an orthodontic adhesive however, they require further development.

The following recommendations may be made to improve the current developed material focusing on optimizing the bond strength of the materials. However, care should be taken during further development to monitor other properties of the material that are considered important for a fluoride releasing orthodontic adhesive, such as fluoride releasing and recharging, in addition to having optimal setting characteristics.

1- Reduce HEMA content and replace it with a more stable and less hydrophilic monomer. However, all hydrophilic component cannot be completely removed as this will have a significant impact on fluoride release. Different types of monomers such as UDMA should be trialed, together with monitoring the rheological properties of the materials.

2- The combined effect of HEMA and 4-META needs to be studied in order to obtain improved bond strength.

3- Improvement of the mechanical properties of the experimental acrylic resin could be investigated by adding other type of fillers. Probably adding some glass fillers to replace part or all of polymethylmethacrylate powder.

5- Different fluoride sources may be recommended. Replacing NaF with a more stable fluoride source such as fluoraluminosilicate glass. Fluoride investigation in this study was 28 days, a longer study is suggested to examine the fluoride release for longer than 28 days and compare it with commercially available GIC.

6- Using silanated filler particles with the NaF may provide a way forward in developing fluoride releasing materials with better bond strengths

7- Further investigation is required to improve handling characteristics of the experimental materials and to investigate orthodontist's preference in terms of viscosity of the orthodontic adhesive.

Chapter 9: **References**

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Chapter 10: **Appendices**

Appendix 1:

The current project was a continuation of previous work by Su et al., (2010). I will therefore summarize the previous findings of Su, and compare them with current findings. Su et al., (2010) developed a new experimental fluoride releasing acrylic resin for using as an orthodontic adhesive. The material was based on MMA and HEMA liquids with NaF and PMMA added as powder, to act as a filler and as a source of fluoride (see table 10.1 below). Varying concentrations of these materials were used. This material was chemically cured, the PMMA powder contained a BPO chemical initiator, with a long setting time of 3-4 minutes. This would potentially make it difficult to use clinically, even as an orthodontic adhesive. In the current project a ratio of 60:40 HEMA/MMA was chosen to make four experimental groups with varying concentrations of PMMA:NaF (see table 10.2). CQ and DMAEMA was used as a photo-initiator.

Su's materials demonstrated fluoride release over a period of at least 16 weeks as shown in figure 10.1. The current experimental materials also demonstrated fluoride release, which was measured for 4 weeks (figure 10.2). Su's materials and the current experimental materials demonstrated relatively similar heat release during polymerization (see table 10.3).

Shear bond strength measurements were taken for Su's materials and the current experimental materials. The primary difference in the two experiments, apart from varying materials constituents was the type of teeth, human teeth were used in the earlier work compared to bovine teeth in the current work (see table 10.3). The SBS of Su's materials was shown to be comparable to commercial orthodontic adhesives and was not significantly adversely affected by storage. In comparison the bond strength of the current experimental materials was lower than that of commercial materials and decreased after storage in water for 30 days (see table 10.3).

Findings from studying the ARI were similar between Su's materials and the current work, despite the fact that a different ARI scoring system was used (see tables 10.4 and 10.5). A modified adhesive remnant index (ARI) analysis was used by Su, including a score for enamel fracture.

Table 10.1 Experimental groups of Su *et al.*, (2010) study.

Experimental groups	PMMA	NaF	MMA%	HEMA%
Ex1	90	10	60	40
Ex2	95	5	60	40
Ex3	90	10	90	10
Control group 1	100	-	100	-
Control group 2 (GIC)	Ketac™ Fil Plus (3M ESPE, Germany), glass ionomer cement			
Control group 3 Transbond XT	Transbond XT (3M Unitek, USA), composite luting material			

Table 10.2 Experimental groups of the current project

Experimental Materials	PMMA%	NaF%	Acetone%	4-META%	Other components
10:0 0%A 0%M	100	0	0	0	Monomers: 40% HEMA 60% MMA Photo-initiator system: 1% CQ 1% DMAEMA
10:0 0%A 5%M	100	0	0	5	
10:0 10%A 0%M	100	0	10	0	
10:0 10%A 5%M	100	0	10	5	
9:1 0%A 0%M	90	1	0	0	
9:1 0%A 5%M	90	1	0	5	
9:1 10%A 0%M	90	1	10	0	
9:1 10%A 5%M	90	1	10	5	
8:2 0%A 5% M	80	2	0	0	
8:2 0%A 5%M	80	2	0	5	
8:2 10%A 0%M	80	2	10	0	
8:2 10%A 5%M	80	2	10	5	
7:3 0%A 0%M	70	3	0	0	
7:30%A 5%M	70	3	0	5	
7:3 10%A 0%M	70	3	10	0	
7:3 10%A 5%M	70	3	10	5	
Ketac-cement	Ketac-Cem (3M ESPE, Germany), glass ionomer cement				
Transbond XT	Transbond XT (3M Unitek, USA), composite luting material				

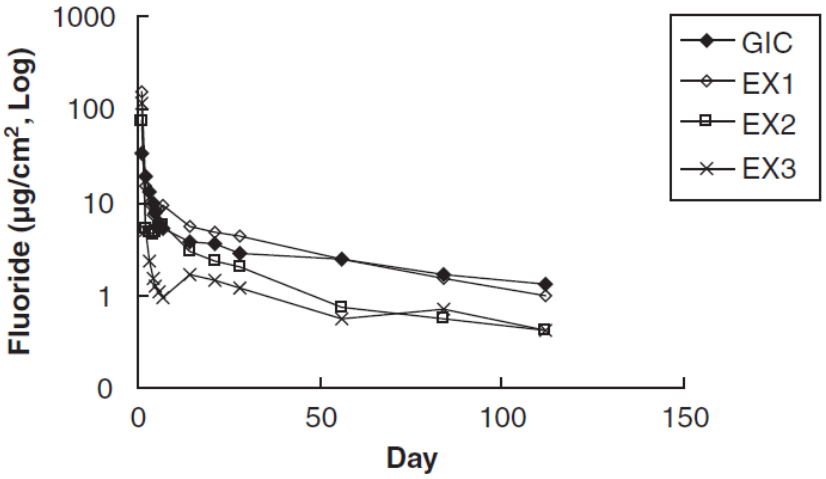

Figure 10.1 Mean daily flouride release of Su *et al.*, (2010) materials over a period of 16 weeks.

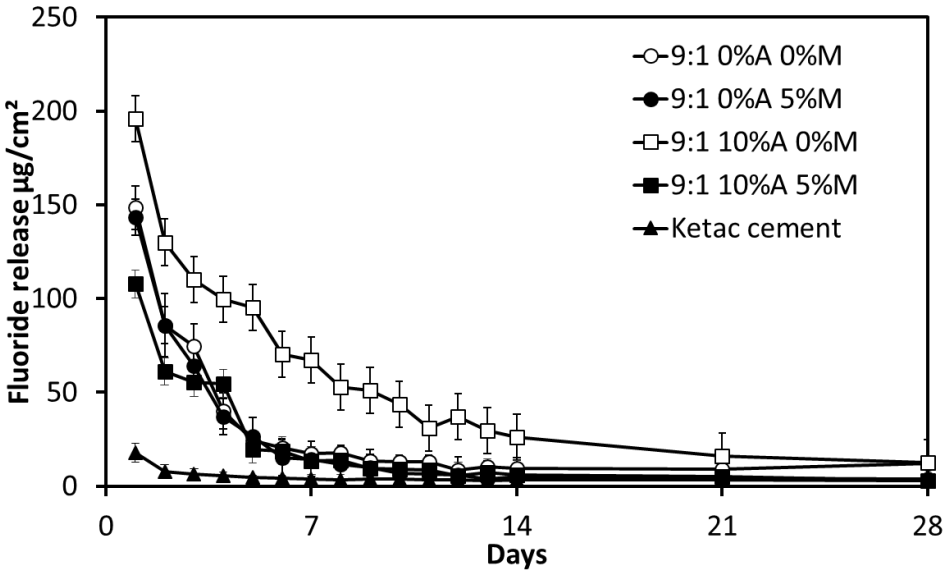

Figure 10.2 Mean daily fluoride release from the group 9:1 and Ketac cement over a period of 4 weeks.

Table 10.3 Comparison of SBS and heat release between current project and Su *et al.*, (2010) results:

	Groups	SBS MPa (SD)			Heat release
		at 30 min	at 30 days	Type of teeth used	
Su Li groups	Ex1	15.41 (2.92)	15.09 (3.19)	Human premolar	135.33 (6.5)
	Ex2	17.11 (3.46)	14.85 (2.89)		141.33 (12.1)
	Ex3	17.12 (2.80)	19.78 (3.93)		134.67 (4)
	Control 3	13.26 (3.79)	25.81 (5.62)		-
Current experimental groups	9:1 10%A 0%M	6.2 (1.4)	2.3 (1)	Bovine teeth	122(10)
	9:1 10%A 5%A	5.8 (1)	2.7 (1)		-
	Transbond XT	12.8 (2)	16.4 (4.6)		-

Table 10.4 ARI of the the Su *et al.*, (2010) experimental groups.

Experimental groups	ARI score					
	1	2	3	4	5	10
30 mins						
Ex1	1	6	3	8	0	0
Ex2	1	5	6	6	0	0
Ex3	1	10	3	4	0	0
Transbond XT	0	4	5	9	0	0
30 days						
Ex1	2	10	2	3	1	0
Ex2	3	10	4	1	0	0
Ex3	4	7	4	3	0	0
Transbond XT	0	3	7	4	0	4

Score 1 is assigned when no adhesive remained on the enamel; 2, when 90% of the enamel base area is covered with adhesive; 3, when 10% – 90% of the surface was covered with residual adhesive; 4, when >90% of the enamel base area was covered with adhesive; and 5 when all adhesive remains on the enamel surface, along with a clear imprint of the brackets base. A score of 10 is recorded when enamel fracture has occurred.

Table 10.5 ARI of the current experimental groups on bovine teeth.

Experimental groups	ARI score			
	0	1	2	3
30 mins				
9:1 10%A 0%M	0	17	4	0
9:1 10%A 5%M	0	18	3	0
Transbond XT	0	1	8	12
30 days				
9:1 10%A 0%M	1	5	14	1
9:1 10%A 5%M	2	6	9	2
Transbond XT	0	3	10	8

Score 0 no adhesive left on the tooth; score 1, less than half of the adhesive left on the tooth; score 2, more than half of the adhesive left on the tooth; and score 3, all adhesive left on the tooth with a distinct impression of the bracket mesh

Appendix 2:

Table 10.6 Results of three way ANOVA of DoC untransformed data.

Tests of Between-Subjects Effects

Dependent Variable: DoC

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	326560.061[a]	239	1366.360	31.831	.000
Intercept	1567399.551	1	1567399.551	36514.352	.000
fluoride	5953.692	3	1984.564	46.233	.000
Acetone	61050.407	4	15262.602	355.560	.000
Time	189371.328	11	17215.575	401.056	.000
fluoride * Acetone	38812.392	12	3234.366	75.348	.000
fluoride * Time	1481.811	33	44.903	1.046	.398
Acetone * Time	19083.737	44	433.721	10.104	.000
fluoride * Acetone * Time	10311.602	132	78.118	1.820	.000
Error	41079.775	957	42.926		
Total	1933933.941	1197			
Corrected Total	367639.836	1196			

a. R Squared = .888 (Adjusted R Squared = .860)

Table 10.7 Table Results of three way ANOVA of DoC of the transformed data.

Tests of Between-Subjects Effects

Dependent Variable: Transformed DoC

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	844.323[a]	239	3.533	29.504	.000
Intercept	578473.468	1	578473.468	4831105.296	.000
fluoride	16.552	3	5.517	46.077	.000
Acetone	149.786	4	37.446	312.733	.000
Time	493.829	11	44.894	374.927	.000
fluoride * Acetone	100.075	12	8.340	69.648	.000
fluoride * Time	4.404	33	.133	1.114	.303
Acetone * Time	54.086	44	1.229	10.266	.000
fluoride * Acetone * Time	23.664	132	.179	1.497	.001
Error	114.471	956	.120		
Total	579822.817	1196			
Corrected Total	958.794	1195			

a. R Squared = .881 (Adjusted R Squared = .851)

Appendix 3: Conference Attendance

9 September 2013: British Society for Oral and Dental Research 2013, bath (Poster presentation)

Effect of acetone on novel fluoride releasing acrylic orthodontic adhesives

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Hadi M Ismail, S L Rolland, M J German
Centre for Oral Health Research, Newcastle University
email: h.m.ismail@ncl.ac.uk

Aim

The aim of this project is to optimise rheological properties of fluoride releasing acrylic resins for use as an orthodontic adhesive, through monitoring degree of conversion (DC%) and fluoride release (F^-) of the acrylic resin after addition of acetone.

Introduction

- In fixed appliance treatment, bonding systems are used to secure orthodontic brackets to teeth. 73% of patients experience decalcification around brackets during treatment [1].
- Fluoride releasing adhesives are effective in preventing or reducing demineralization around brackets because they provide a fluoride reservoir that does not require patient cooperation.
- A fluoridated acrylic resin is being developed as a potential orthodontic adhesive. To be effective in preventing demineralization, it should provide sustained slow release of fluoride for a long period of time.
- One of the key properties of the orthodontic adhesives is handling, which is dependant on the rheological properties of the adhesive. Acetone is a good solvent for adhesives and may be used to control viscosity.

Methods

- Nine experimental groups were prepared.

Groups	Powder		Liquid		Initiator system		Acetone was used as a solvent with different concentrations of 0%,10% ,and 20% acetone
	PMMA %	NaF%	MMA%	HEMA %	CQ%	DMAEMA%	
9:1	90	10	60	40	0.6%	0.8%	
8:2	80	20					
7:3	70	30					

- Ion selective electrode used to measure fluoride release for 70 days.
- ATR-FTIR was used to measure DC% of five samples of each group after 120 second light curing. Peak height of 1638 cm^{-1} (C=C) and 1715 cm^{-1} (C=O) were compared to monitor DC%.

$$DC\% = \left(1 - \frac{1638cm^{-1}/1715cm^{-1}\ cured}{1638cm^{-1}/1715cm^{-1}\ uncured}\right) \times 100$$

- Data were analysed by Mann-Whitney test ($p<0.05$).

Results

- Fluoride release at day 1 was greater with 20% acetone for all groups except 7:3 ($p<0.05$).
- All groups continued to release fluoride at day 70 , with 20% acetone groups releasing higher fluoride compared to those with 0% acetone ($p<0.05$).
- After 80 second light curing all groups with 20% acetone achieved significantly higher DC% than 0% acetone except 7:3 ($p<0.05$).
- All groups with 20% acetone achieved higher DC% than with 10% acetone after 120 second light curing ($p<0.05$).

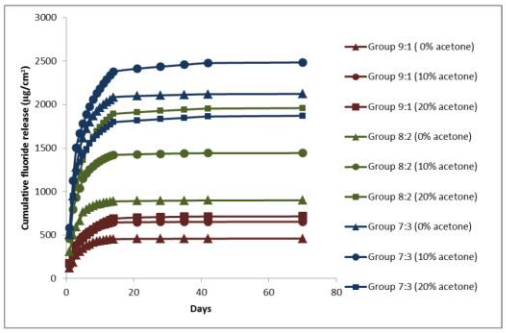

Figure 1: Cumulative fluoride release for all experimental groups (9:1,8:2,7:3) with different concentrations of acetone (0%,10% and 20%).

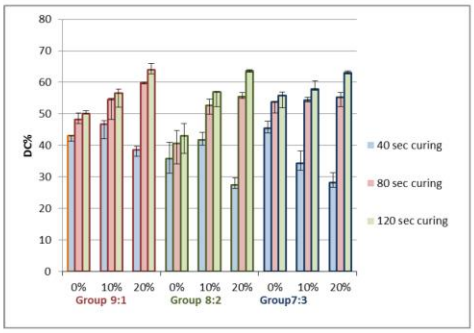

Figure 2: Median DC% for all experimental groups (9:1,8:2,7:3)with different concentrations of acetone (0%,10% and 20%).

Discussion

- The addition of acetone increased the degree of conversion of the experimental acrylic resin, potentially due to increased diffusion of free radicals and growth of polymer chains after acetone addition[2].
- Addition of acetone has increased fluoride release from the acrylic resin, which may be due to increased water sorption. This may result in accelerating diffusion of fluoride ions within absorbed aqueous medium within first 12 – 24 h. [3] In addition, inclusion of a solvent may influence on long term release of fluoride.
- Further study is needed to investigate the effect of acetone on viscosity of the material.

Conclusion

Acetone may be a suitable solvent to reduce the viscosity of the acrylic resin as it does not appear to have a detrimental effect on either degree of conversion or fluoride release. Therefore acetone will be used to optimise rheological and handling properties of the novel acrylic resin being developed for use as an orthodontic adhesive.

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Abbreviations: Polymethylmethacrylate (PMMA), sodium fluoride (NaF), methylmethacrylate (MMA), 2-hydroxyethyl methacrylate (HEMA), Camphorquinone (CQ), 2-(Dimethylamino) ethyl methacrylate (DMAEMA).

11 March 2015 International Association for Dental Research, 2015 General exhibition Boston, MASS., USA.

Effect of acetone and NaF on an orthodontic-adhesive's handling properties

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Hadi M Ismail, S L Rolland, M J German
Centre for Oral Health Research,
Newcastle University, Newcastle-upon-Tyne, United Kingdom
Email: h.m.ismail@ncl.ac.uk

Newcastle University

COHR Centre for Oral Health Research

Aims

- To optimise the handling properties of fluoride releasing acrylic resins for use as orthodontic adhesives, through monitoring the effect of NaF and acetone concentration on injectability, heat release and degree of conversion (DoC).

Introduction

- In fixed appliance treatment, bonding systems are used to secure orthodontic brackets to teeth. 73% of patients experience decalcification around brackets during treatment [1].
- Fluoride releasing adhesives are effective in preventing or reducing demineralization around brackets.
- A fluoridated acrylic resin is being developed in our lab as a potential orthodontic adhesive.
- One of the key properties of the orthodontic adhesives is handling, which is dependant on the rheological properties of the adhesive.

Methods

- Twelve experimental groups were prepared.

Groups	Powder		Liquid		Initiator system		Acetone was used as a solvent with different concentrations (0%,10% and 20%)
	PMMA %	NaF%	MMA%	HEMA %	CQ%	DMAEMA %	
10:0	100	0	60	40	0.6%	0.8%	
9:1	90	10					
8:2	80	20					
7:3	70	30					

- Heat release was measured using a differential scanning calorimeter after 60s illumination with a Heliomat QTH at 250mW/cm².
- Degree of conversion (DoC) was measured using ATR-FTIR by taking the ratio of unpolymerised and polymerised aliphatic and aromatic C=C bonds, polymerisation activated using a Coltolux® LED at 475mW/cm² for 60s.
- Injectability was measured using the force required to extrude 1 ml of unpolymerised material from a full 5 ml syringe using a universal test machine at 1mm/minute compression rate.

Results

- The addition of up to 20% acetone had no effect on the heat release until the concentration of NaF increased at least 20%, after which there was a significant decrease in heat release as the acetone concentration increased ($p < 0.05$).
- Up to 30% NaF the DoC for 0% acetone containing materials was significantly lower than other materials ($p<0.05$), no other significant DoC differences were found.
- Both NaF and acetone concentration significantly affected injectability, with an increase in the concentration of either resulting in a significant decrease in the force required to extrude the material ($p<0.05$).

Abbreviations: Polymethylmethacrylate (PMMA), sodium fluoride (NaF), methylmethacrylate (MMA), 2-hydroxyethyl methacrylate (HEMA), Camphorquinone (CQ), 2-(Dimethylamino) ethyl methacrylate (DMAEMA).

Results

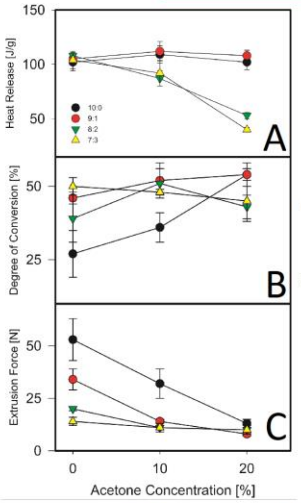

Figure 1:
A. Mean heat release
B. Mean DoC
C. Mean Extrusion force of all experimental groups with different acetone concentrations.

Discussion

- The heat released during polymerization is proportional to the percentage of the reacted monomers as the polymerization reaction is exothermic. Therefore with increasing acetone and NaF concentration, the possibility of physically separation of free radicals, photo-activation constituents and growing polymer chains from each other occur. This may lead to decreased monomer conversion, consequently decreased heat release by the material [2].
- The addition of acetone increased the degree of conversion of the experimental acrylic resin, potentially due to increased diffusion of free radicals and growth of polymer chains after acetone addition [2].However, above certain concentrations acetone may absorb the heat generated during exothermic reaction [3].
- Injection force decreased due to the effect of acetone as the solvent lowered resin viscosity. In addition, increasing NaF concentrations resulted in reduced injection force. This could be due to less PMMA powder which absorbs monomer up to 100% of its weight [4].

Conclusions

- The concentrations of NaF and acetone affect all of the parameters tested in this study. Further work is required to optimise their concentrations for use as an orthodontic adhesive.

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1- Richter AE, Arruda AO, Peters MC , Sohn W(2011). Incidence of caries lesions among patients treated with comprehensive orthodontics, *A J O D O*, 139:657-64.
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Fluoride uptake/ release from a new 4-META-acrylic-based orthodontic adhesive

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Hadi M Ismail, S L Rolland, M J German
Centre for Oral Health Research,
Newcastle University, Newcastle-upon-Tyne, United Kingdom
Email: h.m.ismail@ncl.ac.uk

Newcastle University

COHR Centre for Oral Health Research

Aims

- To investigate the effect of 4-META (adhesion promotor) and acetone (solvent) on the fluoride releasing and recharging characteristics of the developed material compared to a proprietary GIC-based cement.

Introduction

- In fixed appliance treatment, bonding systems are used to secure orthodontic brackets to teeth. 73% of patients experience decalcification around brackets during treatment [1].
- Fluoride releasing adhesives are effective in preventing or reducing demineralization around brackets. Fluoride recharging helps to maintain prolonged fluoride release.
- A fluoridated acrylic resin is being developed in our lab as a potential orthodontic adhesive.
- Orthodontic adhesives should provide sufficient bond strength to retain brackets throughout treatment.

Methods

- Four experimental groups were prepared at 2:1 Powder:Liquid ratio.

Experimental groups	Acetone (%)	4-META (%)	Powder (%)	Liquid (%)	Initiator (%)
9:1 0%A 0%M	0	0	10 NaF 90 PMMA	40 HEMA 60 MMA	1 CQ 1 DMAEMA
9:1 0%A 5%M	0	5			
9:1 10%A 0%M	10	0			
9:1 10%A 5%M	10	5			

- Fluoride release was measured using an ion selective electrode for 28 days.
- Next, specimens were exposed to 1000ppm NaF for 3 minutes every two weeks, then returned to distilled water at 37°C and fluoride release measured daily for a week. This procedure was repeated three times.
- Results were compared to those for the GIC Ketac Cem.

Results

- All experimental materials had significantly greater fluoride release than Ketac Cem at day 1 ($p<0.05$, one-way ANOVA), with the 10% acetone 0% 4-META group exhibiting the highest amount.
- By day 28, the 0% 4-META specimens had significantly higher daily fluoride release than the 5% 4-META and the Ketac Cem specimens ($p<0.05$).
- All of the developed materials showed similar recharge behaviour to the Ketac Cem specimens.

Abbreviations: Polymethylmethacrylate (PMMA), sodium fluoride (NaF), methylmethacrylate (MMA), 2-hydroxyethyl methacrylate (HEMA), Camphorquinone (CQ), 2-(Dimethylamino) ethyl methacrylate (DMAEMA).

Results

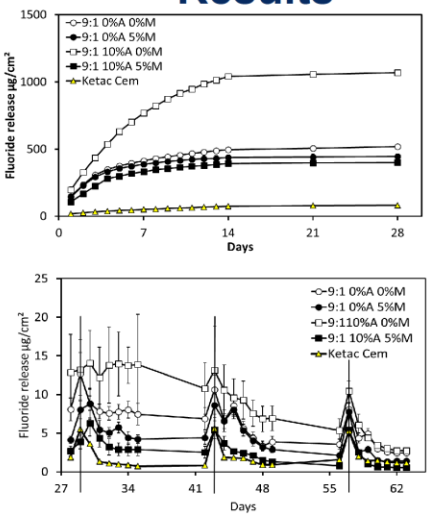

Figure (A) Cumulative fluoride release for the first 28 days (B) Mean fluoride recharging of experimental groups and Ketac Cem. The black lines indicate fluoride release the first day after recharging. The peaks represent an increase in the fluoride release levels 24 hours after exposure to the recharging solution.

Discussion

- The addition of acetone increased the fluoride release. The addition of solvents has been shown to increase water sorption in adhesives [2], which may result in accelerating diffusion of fluoride ions within absorbed aqueous medium within first 12 – 24 h.
- The addition of 4-META led to a reduction in fluoride release irrespective of whether acetone was present or not. While it is not clear what the reason for this is, the 4-META containing adhesives still exhibited significantly greater fluoride release than the GIC.
- All adhesives showed increased fluoride release 24 hours after recharging, suggesting that these materials can act as a fluoride reservoir in a similar manner to GICs.

Conclusions

- All the experimental resins have fluoride releasing and recharging ability comparable to a commercial GIC.

References

1- Richter AE, Arruda AO, Peters MC , Sohn W(2011). Incidence of caries lesions among patients treated with comprehensive orthodontics, *A J O D O*, 139:657-64.

2- Malacarne-Zanon J, Pashley DH, Agee KA, Foulger S, Alves MC, Breschi L, Cadenaro M, Garcia FP , Carrilho MR (2009). Effects of ethanol addition on the water sorption/solubility and percent conversion of comonomers in model dental adhesives, *Dent Mater*, 25: 1275-84.

14 September 2015 British Society for Oral and Dental Research 2015, Cardiff (Oral presentation, Voco prize)

Title: Optimizing photo-initiator system of new fluoride-releasing acrylic orthodontic adhesive

Objectives: White spot lesions are a common complication with orthodontic treatment. We are developing a photo-polymerizing fluoride-releasing orthodontic adhesive. This study aims to investigate the effect of different initiator systems on degree of conversion (DoC) of the developed material.

Methods: Sodium fluoride at 10wt% was added to 90wt% polymethylmethacrylate powder and mixed at a powder:liquid ratio of 2:1 with liquid 2-hydroxyethylemethacrylate and methylmethacrylate (40wt%:60wt%), alongside two concentrations of acetone (A-0wt% and 10wt%). Four groups of resin were prepared with varied photo-initiator systems: (1) 1wt% camphorquinone and 1wt% N,N-dimethylaminoethylmethacrylate (DMAEMA); (2) 1wt% camphorquinone and 1wt% Ethyl 4-(dimethyl-amino) benzoate (EDAB) activator; (3) 1wt% diphenyl (2, 4, 6-trimethylbenzoyl) phosphine oxide (Lucirin TPO) and (4) 1.5wt% Lucirin TPO (table 1). FTIR was used to measure DoC for all the materials at 10, 20, 30, 40 and 80s of light curing using Bluephase®20i at 1130mW/cm^2.

Results: The DoC of group CQ/DMAEMA at 10%Acetone are higher than CQ/EDAB at 30, 40 and 80s ($p<0.05$). The DC of all groups with Lucirin TPO was higher than groups with CQ initiator system ($p<0.05$, one-way ANOVA).

Conclusion: Lucirin TPO is an effective photo-initiator system which results in higher and faster polymerisation than the CQ system.

Time s / Acetone % / Photo-initiators %	DoC % Mean (SD)									
	10s		20s		30s		40s		80s	
	0%A	10%A	0%A	10%A	0%A	10%A	0%A	10%A	0%A	10%A
(1) 1CQ/1DMAEMA	24 (4)	11 (1)	34 (8)	23 (2)	39 (10)	38 (1)	42 (10)	48 (1)	46 (9)	59 (2)
(2) 1CQ/1EDAB	25 (12)	10 (6)	32 (13)	17 (6)	34 (13)	21 (6)	38(13)	24 (5)	41(10)	35 (6)
(3) 1 Lucirin	47 (3)	52 (1)	51 (3)	56 (1)	53 (3)	58 (2)	54 (3)	60 (1)	58 (3)	63 (2)
(4) 1.5 Lucirin	49 (2)	56 (3)	52 (1)	60 (1)	54 (1)	62 (2)	56 (1)	64 (1)	59 (1)	67 (2)