5.1 Experimental urethane acrylate macromer

The durability of restorations determines its success or failure, and this is highly dependent on the physical, mechanical and biological properties of the restorative materials employed (McCabe and Walls 1998). The literature reveals that fracture is one of the most common reasons of failure for composite restoration and merits further investigations (Qvist et al., 1990; Collins et al., 1998; Brunthaler et al., 2003; Sarrett, 2005). The properties of dental composites depend on several factors, related to the resin matrix, the filler particles, and the coupling between filler and resin matrix (Asmussen and Peutzfeldt, 1998). The resin matrix of current dental composites, are commonly composed of Bis-GMA. The presence of phenolic groups in the Bis-GMA backbone impairs rotation about the bonds and the strong intermolecular interactions by hydroxyl groups, results in a very viscous material causing the DC of Bis-GMA to be not being higher than 42% (Floyd and Dickens, 2006). In addition to water susceptibility, the Bis-GMA's proneness to brittle fracture and wear, have stimulated the development of Bis-GMA substitutes (Moszner and Salz, 2001).

Mastication process and thermal changes induced by many cycles of stress during the life of a restoration cause fatigue failure, which can be manifested as fracture or wear (Abu Kasim et al., 2006; and Papadogiannis et al., 2007). Increased filler loads in dental composites do not necessarily improve its fatigue resistance (Htang et al., 1995). The change in resin system however, has been shown to cause improvement of mechanical properties of dental composites, such as the incorporation of urethane dimethacrylate (Asmussen and Peutzfeldt, 1998). Urethane dimethacrylate (UDMA) monomers were introduced for dental composite formulation in the 1970s. The functionality offered by urethane groups adds toughness and flexibility to the monomer backbone chain, providing the possibility for enhanced conversion and durability (Peutzfeldt, 1997; Rueggeberg, 2002). UDMA-based composites such as Heliomolar (Vivadent, Liechtenstein) are more fatigue resistant when compared to a Bis-GMA-based composite such as P50 (3M, USA) and Silux Plus (3M, USA) in an *in vitro* study as illustrated in Figure 5.1 (Abu Kasim, 1995). The graph of mean depth (µm) against a number of cycles for composites tested after 24 hours under dry conditions showed that the 5 µm depth as marked by the dotted line indicated that Heliomolar was more fatigue resistant when compared to all the other materials following a rolling ball contact test.

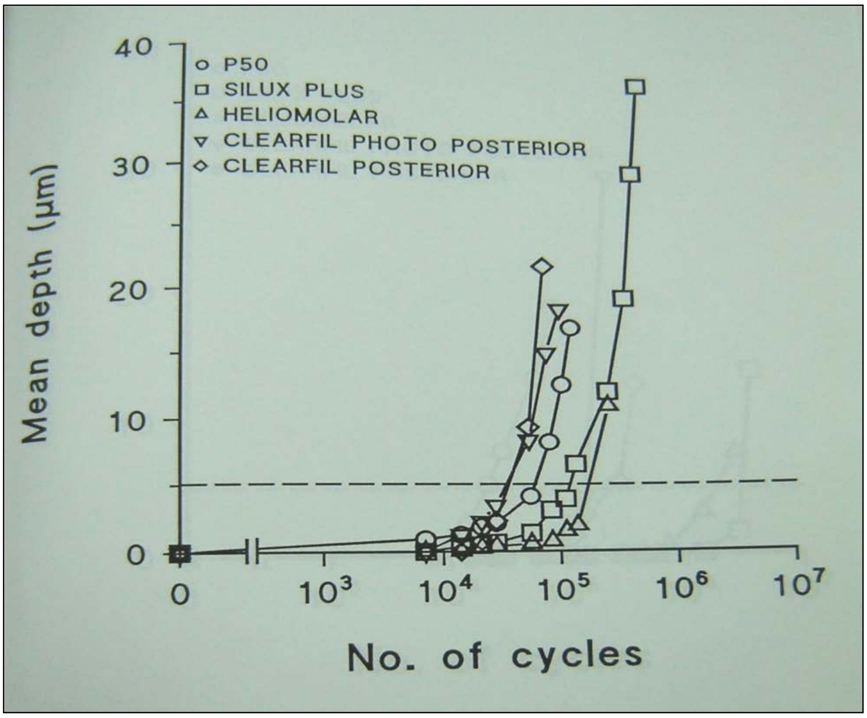

Figure 5.1 Comparison of materials tested in dry conditions after 24 hours following rolling ball contact test (Abu Kasim, 1995)

The same trend was observed by Söderholm et al (2001) in an *in vivo* study. Their 3 year data showed UDMA-based composites performed significantly better in terms of wear resistance when compared with BisGMA-based composites.

It has been suggested that toughness may be one of the key mechanical properties for clinical predictions of material performance (Bayne et al., 1998). Toughness is the resistance of material to fracture, which is an indication of the amount of energy required to cause fracture (Craig and Powers, 2002). Toughness can be correlated with both wear and fracture resistance (Bayne et al., 1998). Flexural strength has also been suggested as a criterion of durability and longevity of composites (Gladys et al., 1997). An increase in flexural strength and fracture toughness in a composite is likely to lengthen its service life in the oral cavity (Shenoy, 2008). On the other hand, the enhanced wear resistance found in some studies on heat-processed composite inlays is thought to be related to their higher degree of polymerization (O'Brien, 2002). A relatively high degree of conversion (DC) is preferred to produce a material with good mechanical properties and minimal unreacted leachable components which will enhance its biocompatibility (Geurtsen et al., 1998; Musanje and Ferracane, 2004). All these factors form the basis of a multitude of researches, including this current study, which was aimed at developing a new monomer with high DC, strength and toughness.

The significant aim of a high DC and high strength resin system does not mean that polymerization shrinkage is not important. Polymerization shrinkage produces stress, which tends to develop at the tissue/composite interface, weakening the bond and eventually producing a gap at the restoration margins (Anusavice, 2003; Ferracane, 2005). There is however, a lack of evidence that indicates polymerization shrinkage is the primary cause of secondary caries (Sarrett, 2005). Polymerization shrinkage should not be the only parameter to be considered for predicting composite behavior regarding stress development. The high inorganic filler content of composites present a high elastic modulus, which may also result in increased stress (Condon and Ferracane, 2000; Braga et al., 2005). In the past few years, several restorative techniques have been introduced to minimize the development of stresses, for example the multiple increment technique and the sandwich technique (Koenigsberg, 1989; Lindberg et al., 2000; Shenoy, 2008). The length of time a restoration will last is also dependent on the individual’s dental hygiene, home care, diet, and masticatory habits.

Various urethane dimethacrylate monomers (UDMA) have been produced, and based on the literature, UDMA has been synthesized from reaction of HEMA with isocyanate or polyols with isocyanate and HEMA (Sterrett et al., 1987; Matsukawa, 1994; Antonucci et al., 2006; Atai et al., 2007). When the polyol reacts with diisocyanate the urethane polymer is produced, however, extra amount of diisocyanate has to be reacts with polyol in order to produce urethane prepolymer. When this urethane prepolymer reacted with HEMA the urethane macromer is produced, and this composed of different monomer units (Alger, 1997; Koprululu et al., 2008). However, in dentistry the term monomer has been widely used for all uncured liquid, Bis-GMA for example is an oligomer, not a monomer, since it is composed of two different monomer units.

The polyols used for urethane production, such as polyethylene glycol and polyester, are usually derived from petroleum-based feed stock and urethane has widespread applications in the making of foams, resins, composites, and adhesives. Alternatively, there are other polyols derived from natural renewable resources, such as soya bean oil which can be reacted with isocyanate to form urethane products (Dwanisa et al., 2004). The use of renewable resources to substitute petrochemicals in many applications has gained considerable attention of late due to the supply, cost of these raw materials and the awareness in environmental issues. The polymer industry, especially in the manufacturing of polyurethane, has shown particular interest in this, and there have been several attempts to produce the raw materials, such as polyol and isocyanate, from natural oils instead of petroleum. In Malaysia, the cheap and abundant supply of palm oil begs for its use in the production of polyurethane foam (Shaari et al., 2004). In addition, the polyurethane foam produced for industry, derived from palm oil-based polyol has shown comparable properties when compared to polyurethane produced from petrochemical-based polyol (Gan, 2004).

The rationale of this study was to use palm oil-based polyol to act as a soft segment in urethane dimethacrylate monomers where the functionality of more than 2. The soft segment polyol provides higher flexibility and access of the (macro) radicals to the methacrylate C=C bonds during the polymerization process, resulting in a higher degree of conversion (Atai et al., 2007). Monomers with a higher degree of functionality, e.g higher number of double bond terminations per molecule, had higher reaction rates and higher cross-link density (Ogliaria et al., 2008). It has been theorized that dimethacrylates with “hard” segments and “soft” segments in the same molecule will result in polymers with increased toughness (Matsukawa et al., 1994). The structure and functionality of the polyol have a direct effect on the toughness and mechanical properties of the resultant resin (Sterrett et al., 1987). Thus, the palm oil-based polyol used in this study is likely to act as a soft segment and is expected to enhance the flexibility and functionality, resulting in a polymer with high DC, flexural strength and toughness.

Dimethacrylates with aromatic groups have been reported to produce rigid polymers, while dimethacrylates with aliphatic groups produce flexible polymers (Kawaguchi et al., 1984). The rigid phenyl aromatic diisocyanate (MDI) was used in this study for the synthesis of UAM instead of flexible aliphatic diisocyanate. Furthermore there has been recent interest in improving the rigidity of urethane dimethacryalte by utilizing aromatic (phenyl) groups (Moszner et al., 2008; and Chen et al., 2008).

During the synthesis of experimental urethane acrylate macromer (UAM) in this study, the diisocyanate (MDI) was highly reactive to moisture. This was overcomed through the cleaning and drying of all glassware used for the reaction set. A well-sealed reaction vessel, under a blanket of nitrogen also ensured that there was no leakage during the reaction, thus, avoiding the formation of any byproduct or gel formation (Atai, 2008).

During the synthesis of experimental UAM, 2-hydroxyethyl methacrylate (HEMA) was used in extra amounts, approximately ~ 3.6%. This was based on theory, to ensure that all the isocyanate will be reacted with HEMA. The addition of monomers such as HEMA to composites is of particular interest for the development of self-adhesive composites (Moszner and Salz, 2001; Mendes et al., 2005).

Fourier Transform Infrared Spectroscope (FT-IR) was used to monitor the chemical reaction and identify the chemical structure of the newly developed experimental monomer. FT-IR spectroscopy can illustrate the presence or absence of reaction chemical groups (Nie et al., 2001; Khatri et al., 2003; Atai et al., 2005). In this study, the UAM was free of isocyanate. The spectrum revealed absence of any isocyanate peaks at 2273 cm^{-1}, indicating that all the isocyanate have reacted, while a urethane -N-H peak at 3365 cm^{-1} was produced.

Many researchers have developed monomers based on UDMA-based monomers to overcome the shortcoming of Bis-GMA. Matsukawa (1994) developed a UDMA-based monomer with a higher toughness than Bis-GMA, and Atai et al. (2007) developed another UDMA-based monomer with a lower polymerization shrinkage. However, the viscosity was as high as Bis-GMA, thus limiting the filler loading. In this study, the experimental UAM was synthesized aiming to have a high DC with high flexural strength and toughness. When compared to the most commonly used monomer in commercial dental composite, Bis-GMA, UAM ascertains its potential as an alternative monomer. The ability of this UAM to be a resin for flowable composite was investigated and compared to the experimental Bis-GMA/TEGDMA resin system and both experimentally and commercially available Bis-GMA/TEGDMA-based flowable composite.

The UDMA is a group of monomers which is commonly abbreviated as UDMA. However, its chemical structure may vary from one commercially available composite resin to another as was discussed in the literature review. Thus, the experimental UAM was not compared to commercially available UDMA monomers, making it difficult to identify its reactive components. Polydorou et al. (2009b) reported that UDMA is one of the monomers that are most often tested with regards to elution from and cytotoxicity of resin-based materials. Although each chemical name represents the chemical type, chemical structure, and molecular weight of a molecule, it does not seemed to be the same with UDMA. Moreover, in order to make valid comparison amongst various resin systems formulations, it was decided to omit the commercially available UDMA as a co-monomer in this study.

For all experimental light-curable materials prepared in this study, the same camphoroquinone (CQ) and ethyl 4-(dimethylamino) benzoate (4EDMAB) was used with a weight percentage of 0.2% and 0.8% respectively. The concentration of CQ should be as little as possible because of its inherently yellowish-brown color and cytotoxicity issue (Landuyt et al., 2007). Furthermore when used above 0.25%, no drastic improvement in diametral and compressive strength was observed (Krishnan and Yamuna, 1998). 4EDMAB is a very effective hydrogen donor, and has been widely used in combination with CQ in dental resins formulations (Schroeder and Vallo, 2007; Tian et al., 2007). This light-initiator system, CQ and 4EDMAB in the mass ratio stated above are commonly used (Stansbury and Dickens, 2001; Skrtic et al., 2003; Skrtic and Antonucci, 2003; Fong et al., 2005; Lin-Gibson et al., 2006; Tian et al., 2007). It has been suggested that considerable improvement in the rate of polymerization and final conversion were achieved as the ratio of CQ to 4EDMAB was changed from 1:1 to 1:2 to 1:3. Any further change will produce little added benefit (Stansbury, 2008).

The selection of appropriate monomers for the formulation of a dental composite will strongly influence the reactivity, viscosity, and polymerization shrinkage of the composite paste, and consequently the mechanical properties, and water uptake, of the cured composite (Shalaby and Salz, 2007). Thus, the following properties; determination of viscosity, DC and CLD, polymerization shrinkage, water sorption and solubility, flexural strength, modulus of elasticity and toughness, were considered appropriate to ascertain the suitability of the experimental UAM to be used as a monomer for dental composite.

The viscosity of the monomer plays an important role in resin formulation for dental composite. Low viscosity monomers permit higher filler loading resulting in predictable properties of dental composite. Besides this, a highly viscous monomer could create some difficulty due to its diffusion to the chain propagating centers and influence the chain growing, thus reducing the DC (Mendes et al., 2005).

The viscosity of monomer is dependent on its chemical structure. It is a measure of the resistance of molecules to flow, and a high viscosity value is indicative of the presence of intermolecular interactions (Sideridou et al., 2002). Chemically, the Bis-GMA structure has 2 methacrylate groups with Bis-phenol A nucleus and hydroxyl groups in the spacer, which induce intermolecular interaction (strong hydrogen bond) resulting in high viscosity (Braden, 1978; and Floyd and Dickens 2006). In this study, the viscosity value of Bis-GMA was 407,350 cp (±51905) at 25ºC, and this value approximates that reported by the manufacturer (484,000 cp) at 25ºC (Appendix IV). This value is much higher than that obtained for the experimental UAM (4,453 cp ±217). This is likely to be due to the absence of hydroxyl groups on the spacer of the UAM molecule structure. Although hydrogen bonds are formed between the urethane (–NH-) and carbonyl (-C=O) groups, the imino groups form weaker hydrogen bonds compared to hydroxyl groups (Sideridou et al., 2002).

Measuring the conversion of double bonds in a given resin system has generally been considered a good indicator for the prospective physical properties of such systems (Floyd and Dickens, 2006). Various methods have been used to determine the DC of resin-based dental composites (Yoon et al., 2002). Some studies, quantify the exothermic heat released during polymerization by means of differential scanning calorimetry (Antonucci and Toth, 1983; and Lovell et al., 2001). Others have used a softening test using ethanol to estimate the cross-linking density (Asmussen and Peutzfeldt, 2003). FT-IR is the most widely used instrument, because the C=C of uncured monomer and cured polymer can be calculated (Asmussen 1982; Sideridou et al., 2002; Imazato et al., 2001; Young et al., 2004; Atai et al., 2004; Musanje and Ferracane 2004). Therefore it was decided that the FT-IR is the most appropriate method as the DC of monomer as a measure of the degree to which carbon double bonds (C=C) are converted into carbon single bonds (C-C) during polymerization.

The DC of the resin composite depends on the relative mobility, the molecular weight and functionality of the monomers (Dewaelea et al., 2006), composition (monomers mass ratio), viscosity (Prakki et al., 2007; and Sideridou et al., 2002), and polymerization activation system (Ruyter, 1988). In the present study, the effect of polymerization activation system on the DC was not included in the discussion of the results as it has been standardized e.g light-initiator system (type, concentration, mass ratio) and the visible light cure unit in terms of the type, light intensity and distance between light and materials during specimens preparation.

The effects of chemical molecular structure and viscosity of monomer could explain why a lower DC was obtained for experimental resin based on Bis-GMA as compared to the UAM. The DC of Bis-GMA resin in this study was consistent with findings of Sideridou et al. (2002) and Floyd & Dickens (2006), where they reported that the DC was not higher than 42%. The low DC could be related to the strong hydrogen bonds of hydroxyl groups and the presence of phenol groups in its backbone, which impaired the rotation about the double bonds (C=C). These groups are responsible for high intermolecular interactions, which consequently cause a decrease in the mobility of monomer molecules during polymerization (Floyd and Dickens, 2006; Charton et al., 2007).

The chemical structure of the experimental UAM has urethane linkage and a soft segment of polyol with a functionality of more than 2 due to the slightly branched polyol. This chemical structure and its low viscosity could be the reason for the increase in the mobility of free radicals, hence the increase in DC. As mentioned in the literature review, for urethane dimethacrylate, the urethane linkages can cause chain transfer reactions, which increase the mobility of radical sites on the network during polymerization (Sideridou et al., 2002). The soft segment polyol provides higher flexibility and access of the (macro) radicals to the methacrylate C=C bonds during the polymerization process, resulting in a higher DC (Atai et al., 2007). The segmental mobility and the functionality (numbers of double bonds terminates per molecule) leads to an increase in DC and CLD (Nie et al., 1999; Ogliaria et al., 2008). In this study, the viscosity of UAM was much lower than that of Bis-GMA, where the strong intermolecular hydrogen bond in the latter can cause a decrease in the mobility of monomer molecules during polymerization, resulting in a decrease in flexibility of the corresponding polymeric network (Sideridou et al., 2002).

The CLD also increases with increasing number of functional groups in the monomer (Tanaka et al., 2001). In this study the CLD was calculated according to the equation developed by Barszczewska-Rybarek et al. (2000), as it was shown that CLD is directly proportional to DC. It has been suggested that in order to characterize the structure of a prepared polymer network from polymerization of dimethacrylate monomer, the CLD can be calculated and used as direct method (Barszczewska-Rybarek et al., 2000; Sideridou et al., 2003; Silva et al., 2008). However, the CLD equation could not be applied to Bis-GMA, since the DC was less than 50% (Sideridou et al., 2003). Based on the DC results of this study, the CLD of UAM was 0.42 (±0.07), however the CLD of Bis-GMA was not calculated, because the DC of Bis-GMA was less than 50% and the value of CLD will likely be negative as shown by Sideridou et al. (2003). Silva et al. (2008) assessed the cross-linking density of two dental composites which were based on the same polymeric matrix but different types of filler particles. They utilized an indirect method by measuring the softening effect of ethanol after storage using a micro-hardness testing machine. This method was considered inappropriate as it could not be related directly to the conversion of C=C, which is responsible for the cross-linking.

At this point in time there has been no documentation for the determination of polymerization shrinkage in ISO 4049:2000. The volumetric shrinkage can be evaluated using the density determination based on Archimedes' principle (Buoyancy method). Archimedes' principle states that a solid immersed in a liquid loses an amount of weight equal to the weight of the fluid it displaces. The Archimedes method revealed higher shrinkage values compared to the bonded disc method, however, it has been reported that both methods revealed the same ranking of shrinkage (Dede et al., 2004). The Archimedes method is a relatively simple, inexpensive, and commonly used method (Uhl et al., 2005; Lohbauer et al., 2009). These early researchers formed the basis of the selection of the Archimedes method to determine the volumetric polymerization shrinkage (VPS) in this study.

Polymerization shrinkage is directly related to both double bonds (reactive groups) concentration and conversion (Nie et al., 1999; Ge et al., 2005). Bis-GMA showed lower DC and double bond concentration than UDMA (Sideridou et al., 2002). In this present study the higher VPS of UAM experimental resin than that of Bis-GMA was an expected observation as the UAM showed higher DC. The mean percentage of VPS for experimental Bis-GMA resin in this study was 3.8 % and this was consistent with results obtained by Khatri et al. (2003) and Sideridou et al. (2002), who reported values of 3.4% and 3.9% respectively. Even though the low VPS of Bis-GMA is an advantage, it could not be used as a sole monomer in a dental composite formulation, due to its high viscosity which limits the filler loading. On the other hand, the lowered viscosity obtained with the addition of diluents monomer will bring about a higher DC, thus indirectly causing a further increase in polymerization shrinkage (Labella et al., 1998).

Water sorption measurement actually measured the net gain in weight of a specimen as a result of the ingress of water molecules and egress of monomers and other small molecules (Chai et al., 2004). Most studies including this study followed procedures in the ISO 4049:2000 specification, where water sorption and solubility was calculated after 7 days of immersion in water. Based on this ISO requirement the water sorption and solubility (μg/mm^3) requirement limits are 40 and 7.5 respectively.

Water enters the polymer network through porosity and intermolecular spaces (free volume). The diffused water may be leached out of the free un-reacted monomers and ions from the resin matrix, leading to loss of weight resulting in solubility or hygroscopic expansion (Ferracane, 2006; Martin et al., 2003). Thus, water sorption in resin depends on both its chemical and physical structure (Siderdou et al., 2004). Since hydroxyl groups of Bis-GMA are more hydrophilic than urethane groups of UDMA, the later showed lower water sorption than Bis-GMA (Sideridou et al., 2003). In contrary to expectations, the result of this study recorded that water sorption and solubility of UAM was significantly higher than Bis-GMA. In order to explain the reasons of this unexpected result, the effect of chemical and physical network structures of the UAM on water sorption and solubility are considered.

Chemically, each Bis-GMA molecule has two hydroxyl groups, which is more hydrophilic than urethane groups. The experimental UAM synthesized in this study has more than 2 urethane groups, due to its polyol functionality (> 2). Palm oil-based polyol was used for the synthesis of the experimental UAM without further purification. The palm oil-based polyol also may contain a small amount of un-reacted phthalic anhydride and oleic, which are hydrophilic in nature. The small amount of HEMA used during the synthesis of UAM, to ensure complete reaction of isocyanate, is also hydrophilic in nature.

Physically, the more polymer networks show a spatial heterogeneity, where some parts are densely cross-linked and some parts are loosely cross-linked. The more densely cross-linked the network, the more heterogeneous will be its structure (Elliott et al., 2001). In a more heterogeneous network, the space created between the polymer clusters (microporous) is larger and can accommodate a larger quantity of water (Sideridou et al., 2003). This explained why the highly converted and flexible monomer, TEGDMA showed higher water sorption than Bis-GMA despite the hydrophilic hydroxyl groups of Bis-GMA which are stronger than either groups of TEGDMA (Siderodou et al., 2002; and Sideridou et al., 2003). Consequently, in this study, since the experimental UAM showed a higher DC than Bis-GMA, the more heterogeneous network and spaces in experimental UAM could be responsible physically for the higher water sorption.

Water uptake is accordingly accompanied by a loss of unreacted components (Sideridou et al., 2003; and Ferracane 2006). The water solubility of a monomer in the water is partly determined by the polarity of the spacer (hydrophilic groups) (Landuyt et al., 2007). In this study the high water solubility of UAM could be related to its network structure which is microporous and its polarity due to the presence of hydrophilic groups.

Mechanical properties of composite resins are related to the polymer matrix, the filler, the coupling agent and the light-initiator system (Pereira et al., 2005). Both tension and compressive events can occur in a transverse bending test and the flexural stress developed can be used to represent the ability of a material to resist deformation or fracture (Ho et al., 2001). In this study the 3-point bending parameters and specimen fabrication was carried out following the ISO 4049:2000.

The mechanical properties of polymers depend on its chemical structure and DC (Dulik et al., 1981; Kalachandra. et al., 1997; Sideridou et al, 2002; Stansbury and Dickens 2001; Sideridou. et al., 2003). However, it was suggested that higher DC does not always result in a higher Young's modulus, because molecular and network structural parameters play major roles in the final physical-mechanical properties of the mixtures (Emami and Söderholm, 2009). The higher rigidity of Bis-GMA, due to the phenyl groups and strong hydrogen bond, when compared to UDMA can be explained by the higher Young's modulus of Bis-GMA compared to UDMA, despite the higher DC of the latter (Emami and Söderholm, 2009). This can explain the higher modulus of elasticity of experimental resin Bis-GMA than UAM in this study. This result was also consistent with the findings of both Sideridou et al. (2003) and Barszczewska-Rybarek (2009) where it was indicated that Bis-GMA exhibited higher modulus of elasticity than UDMA (Sideridou et al., 2003).

In this study, the flexural strength and toughness of experimental UAM resin were higher than Bis-GMA resin, which was consistent with observations by Matsukawa et al. (1994), Sideridou et al. (2003) and Barszczewska-Rybarek (2009). As described in the literature review, the reason for increased flexural strength and toughness of experimental UAM resin in this study is likely to be related to the flexibility of both urethane linkage and soft segment polyol combined with the rigidity of the phenyl group in aromatic MDI. Moreover, the polyol used in formulation of urethane toughen methacryalte resins and serves as both oligomer backbone and urethane soft segment, which tends to possess improved toughness (Sterrett et al., 1987).

5.2 Experimental resin systems

At this point in time, the ideal monomer with an optimal hydrophobic monomer with high molecular weight, low viscosity, high DC, high strength and toughness, and low polymerization shrinkage does not exist. Thus, the resin system of dental composites is usually composed of 2 or more monomers for example Bis-GMA which is commonly combined with diluents monomer such as TEGDMA. The 25% mass weight of TEGDMA to 75% mass weight of Bis-GMA used in this study is similar to that in commercial dental resin formulations (Lovell et al., 2003). Accordingly, the most common combination Bis-GMA/TEGDMA (BT) with a mass weight of 3/1 was used as the control group for the experimental resin systems in this study. If the ratio of TEGDMA to Bis-GMA is increased, this will lead to higher polymerization shrinkage and inferior mechanical and physical properties, owing to the TEGDMA molecular structure (Atai et al., 2005; Floyd and Dickens, 2006).

The experimental resin system in this study was formulated once the properties of experimental UAM were determined. UAM showed significantly higher DC, flexural strength and toughness when compared to the experimental resin based on the common monomer Bis-GMA. Although the polymerization shrinkage, water sorption and solubility of experimental UAM were high, this could be due to its high DC and hydrophilic nature. The experimental UAM (U) was blended with Bis-EMA (E) with mass weight ratio of U to E being 3/1 and 1/1 to form the resin systems U/E(3/1) and U/E(1/1) respectively. Both resin systems were formulated aiming at investigating its possibilities to be a substitute of the common Bis-GMA/TEGDMA resin system. The rationale behind using Bis-GMA analogue as diluent, instead of TEGDMA is because Bis-EMA is a hydrophobic dimethacrylate monomer with less water sorption and lower polymerization shrinkage (Pereira et al., 2002; Pereira et al., 2005). In addition, the relatively high hydrophilicity and tissue penetrability of TEGDMA raises concern for biocompatibility issues, and it has been suggested that TEGDMA should be replaced by larger, more hydrophobic and biocompatible monomers (Geurtsen and Leyhausen, 2001).

The experimental UAM was also blended with Bis-GMA/TEGDMA (U/BT experimental resin system) to investigate the possibilities of modifying the common resin system Bis-GMA/TEGDMA. It was shown that the replacement of Bis-GMA and

TEGDMA by UDMA causes an increase in both the tensile and flexural strengths of the composite's resin matrix (Asmussen and Peutzfeldt, 1998). Moreover, when the resin system of composite matrix includes urethane monomers, the increased strength obtained for these resin matrices is assumed to be due to the urethane linkage which increases the degree of cross-linking and having a positive effect on their mechanical properties (Chowdhury et al., 1997).

The resin system recently introduced by 3M ESPE in their Filtek™ Z250 composite consisted of three major components; Bis-GMA, UDMA, Bis-EMA and a small amount of TEGDMA. TEGDMA was a major component in their previous composite, Z100 restorative system (Filtek Z250 Technical product file, 3M ESPE). This is also one of the reasons for blending 66% mass weight of UAM/Bis-EMA with 33% mass weight of Bis-GMA/TEGDMA in one of the experimental resin system formulation in this study, the U/E/BT group.

TEGDMA is commonly used with Bis-GMA, as a diluent monomer to decrease the viscosity and optimize the DC. In this study, the viscosity value of the uncured experimental resin system BT was much lower compared to the experimental uncured resin Bis-GMA alone. The viscosity of the uncured resin system BT in this study was 2,787 cp. This is considered to be consistent with the values reported by Lee et al. (2006), where the viscosity of Bis-GMA/TEGDMA (80/20) and Bis-GMA/TEGDMA (70/30) were 5004 cp and 1280 cp respectively at 25ºC. The viscosity of the BT experimental resin system increased with the addition of the experimental UAM as is shown in the U/BT experimental resin system (3,381 cp ±84) in this study. This could logically relate to the high viscosity of the experimental UAM (4,453 cp ±217), which was higher compared to the viscosity of BT (2,787 cp ±13). The viscosity of experimental resin systems changes according to their composition, e.g mass weight of monomers and monomer viscosity. In this study, the viscosity of co-monomers TEGDMA and Bis-EMA used were (5/30 cp) and (836 cp) respectively (Appendix IV). This could be the likely explanation for the lower viscosity observed in U/E(3/1), U/E(1/1) and U/E/BT resin systems when compared to the BT. The BT experimental resin system contains a high mass weight of the highly viscous monomer Bis-GMA. At the same time the U/E(3/1), U/E(1/1) and U/E/BT experimental resin systems contains a high mass weight percentage of low viscosity diluent Bis-EMA. The lower viscosity value observed for experimental uncured resin system U/E(1/1) compared to U/E(3/1) was likely to be due to the presence of higher mass weight percentage of the low viscosity monomer, Bis-EMA.

Network formation occurs during polymer chain propagation and includes a mixture of linear, cross-linked, entangled, and interpenetrating chain segments, which determines the materials properties. Cross-linking density is associated with increased mechanical properties and stability (Daronch et al., 2005). In addition, further conversion of monomer to polymer, limits the number of unreacted monomers that may serve as plasticizers in the polymer matrix (Ferracane, 1995). The unreacted double bonds may either be present in free monomer or as pendant groups in the network. Only very flexible monomers with reactive methacrylate groups which are relatively far apart can be completely reacted at ambient temperature (Sideridou et al., 2002). In this study, the U/BT experimental resin system showed a higher DC and CLD than BT control resin system, although U/BT possessed higher viscosity. The DC, however is largely affected by the molecular structure, for example although Bis-EMA showed lower viscosity than UDMA, the DC of Bis-EMA is lower than UDMA (Sideridou et al., 2002). This result and a recent study by Emami & Söderholm (2009) confirmed that the differences in the values for DC were mostly justified by the differences in the molecular structures of the different monomers. The monomer mass ratio has been also shown to strongly affect the DC, while the Bis-GMA content increased, the DC decreased (Lin et al., 2007). In this study, the mass weight of Bis-GMA in the U/BT experimental resin system was 37.12%, while it was 74.25% in the BT experimental resin system. At the same time, U/BT also contained 49.5% of the mass weight of experimental UAM and this variation in both monomer structure and composition could explain the higher DC and CLD of the experimental U/BT.

The U/E/BT experimental resin system in this study contained a lower mass weight of TEGDMA and UAM compared to U/BT, this explained the lower DC and CLD of U/E/BT despite its lower viscosity. A low viscosity monomer such as TEGDMA has low molecular weight and high double bond concentration (6.99 mol/Kg) and DC (75.7%) (Sideridou et al., 2002). Consequently, increasing the amount of TEGDMA should favour an increase in DC (Lin et al., 2007; Emami and Söderholm, 2009).

The U/E(1/1) experimental resin system has shown a higher DC and CLD than BT (Cont) and U/E/BT. This could be due to the presence of Bis-GMA in the latter groups. Based on the DC results of experimental resin systems in this study, further studies are recommended before it is stated that the DC and CLD of the different resin systems mainly depend on the monomer structure and its mass weight. The viscosity was significantly effective for binary resin systems, where the monomer structure was similar. In this study the experimental resin system U/E(1/1) showed a higher DC and CLD than U/E(3/1), which resulted from the lower viscosity of the former rather than the latter. This lower viscosity may be enough to increase the mobility of monomers causing higher DC and CLD. This finding concurred with the results of Sideridou et al. (2002), which showed that the DC of the experimental resin systems of Bis-GMA/TEGDMA and Bis-GMA/Bis-EMA increased by increasing the TEGDMA and Bis-EMA respectively.

In this study, the incorporation of TEGDMA to the Bis-GMA in the BT experimental resin system resulted in a higher DC (64.56%) than that of the Bis-GMA alone. The % VPS was also higher at (6.81%). This findings, agreed with the findings of Chung et al. (2002), which found that the addition of TEGDMA showed an increase in polymerization shrinkage.

Due to the positive correlation between the DC and polymerization shrinkage, the VPS of U/BT experimental resin systems was higher than that of the BT experimental resin system, where the former had significantly higher DC than the latter. Besides this, the higher percentage of Bis-GMA in the BT experimental resin system than the U/BT could be a contributing factor. This is in agreement with the findings of Atai et al (2005), where it was found that the total shrinkage of the samples decreased as Bis-GMA percentages increased.

Maximizing the total number of double bonds that react will increase the volume shrinkage during polymerization of the monomer resin (Anseth et al., 1996). In this study the U/BT experimental resin system showed higher VPS than other UAM-based experimental resin systems including; U/B(3/1), U/E(1/1) and U/E/BT. This could be due to the high concentration of double bonds in the U/BT with higher mass weight of TEGDMA compared to other UAM-based resin. On the other hand, the UAM-based experimental resin systems contain Bis-EMA, which is a high molecular weight monomer which is low in both double bonds concentration (3.7 mol/Kg) and limited DC (52.2%) (Sideridou et al., 2002). The addition of Bis-EMA could minimize or eliminate the use of TEGDMA as a diluent comonomer, thus potentially reducing the polymerization shrinkage and stress due to the higher molecular weight and lower mobility of Bis-EMA molecules compared with TEGDMA (Moraes et al., 2008).

In this study, it was observed that the introduction of TEGDMA to Bis-GMA caused an increase in the water sorption and solubility of the experimental Bis-GMA. This result was in agreement with the findings of Sideridou et al. (2003). This could be related to the TEGDMA affinity to water because of the water compatible linkage structure within the molecule (Örtengren et al., 2001). The monomer with smaller molecules, such as TEGDMA, showed enhanced mobility and is expected to be eluted at a faster rate than larger, bulkier molecules such as Bis-GMA (Ferracane, 1994). This statement was confirmed by a high-performance liquid chromatography (HPLC) analysis of eluted components, which revealed that TEGDMA was the main monomer released (Örtengren et al., 2001). Another explanation for more rapid elution of TEGDMA is that more of it is truly free. There is a high probably of Bis-GMA having one end but not both ends polymerized. TEGDMA has more tendency to homo-polymerize rather than copolymerize and it exists as mobile totally un-reacted monomer. When it desorbs out, there is plenty of free space for water to absorb into the polymer (Bayne, 2010).

In this study, the experimental U/BT resin system showed higher water sorption than the BT control resin system. This could be due to the hydrophilic nature of the UAM as described earlier. The TEGDMA monomer consists of aliphatic small flexible molecules which is hydrophilic in nature. The Bis-EMA molecules on the other hand are large aromatics molecules which is hydrophobic in nature. Hence the suggestion that Bis-EMA can decrease water sorption and solubility was confirmed in this study. All U/E(1/1), and U/E/BT showed lower water sorption and solubility than U/BT. This could be related to the high mass weight of hydrophobic Bis-EMA monomers in the former and high mass weight of hydrophilic TEGDMA monomers in the latter. Since the Bis-EMA chemical structure showed missing hydroxyl groups compared to Bis-GMA, and not as flexible as TEGDMA, the water sorption of Bis-EMA was lower than Bis-GMA and TEGDMA (Sideridou et al., 2003).

It has been assumed that urethane linkages increase the degree of cross-linking and has a positive effect on mechanical properties (Chowdhury et al., 1997). The flexural strength and toughness of all UAM-based experimental resin systems include U/BT, and U/E. The U/E/BT was significantly higher than the control resin system BT. This result could be related to the presence of flexible and tougher UAM in the UAM-based experimental resin systems. There was also the presence of high mass weight % of the rigid Bis-GMA in the BT experimental resin system. This result was further confirmed by the comparison between U/E(1/1) and U/E/BT, where the flexural strength and toughness of the former was significantly higher than the latter. The U/E(1/1) showed a higher mass weight % of experimental UAM than the U/E/BT, and Bis-GMA was available in the U/E/BT only. These findings were in agreement with Asmussen & Peutzfeldts (1998) results, which showed that the substitution of BisGMA or TEGDMA by UEDMA have resulted in an increase in flexural strength.

For modulus of elasticity, the UAM-based experimental resin systems and BT control resin system was similar with one exception; the U/E/BT experimental resin system was higher than the BT. The similarities could be due to the presence of rigid aromatic groups and hydrogen bonds in both the UAM and the Bis-GMA structures. The exception could also be related to the presence of Bis-EMA in the U/E/BT. The mass weight % of TEGDMA was higher in BT compared to U/E/BT. The stiffness of the polymer network structure may be obtained from the replacement of the flexible monomer TEGDMA with the stiffer Bis-EMA (Moraes et al., 2008). Moreover, it has been reported by Sideridou et al. (2003) that the Young's modulus of TEGDMA polymer (0.744GPa) was lower than Bis-EMA (1.134 GPa).

5.3 Flowable composites

In this study, the experimental resin systems U/BT, U/E, and U/E/BT were selected as resins for the experimental flowable composites FC-U/BT, FC-U/E, and FC-U/E/BT respectively. The U/E experimental resin system, U/E(1/1) was selected instead of U/E(3/1) for the flowable composite formulation, because of the observed properties; lower viscosity, higher DC, lower water sorption and solubility. All the UAM-based experimental flowable composites were compared with experimental control (Exp-Cont) flowable composite, which contained the common Bis-GMA/TEGDMA resin (FC-BT). A commercially avialable flowable composite, Esthet.X flow was selected to be another control (Com-Cont) in this study since it was also based on Bis-GMA/TEGDMA. Esthet.X flow could provide insight into the suitability of these experimental flowable composites for future clinical application.

Standard mass weight and fillers, silanated barium borosilica glasses were used for all the experimental flowable composites, to avoid the effect of filler loading, type and size variations. This glass filler was chosen as it was convenient to mix when viscosity of resin systems were varied. The sizes of the used filler are 0.5 µm (10%) and 1.4 µm (90%). The fillers were water insoluble and silanated with 3-(methacryloyloxypropyl) trimethoxysilane (MPTMS), which contained methacrylate groups. The determination of DC for all flowable composites was not carried out in this study, since the presence of unreacted methacrylate from the silanated fillers could underestimate the percentage of DC (Halvorson et al., 2003). The fabrication of thin standard films for FT-IR analysis was also difficult compared to unfilled resin materials. In addition, the DC could also be estimated from polymerization shrinkage, since polymerization shrinkage is directly related to DC (Venhoven et al., 1993). Therefore, in this study experimental flowable composites with high polymerization shrinkage value can be considered to exhibit high DC.

The VPS of all experimental resin systems were reduced by 30%, when loaded with 60% of the silanated fillers by weight. This reduction is logical and it could be related to the 60% decrease of matrix resin being replaced by the fillers. The filler loading is also inversely proportional to the DC (Barron et al., 1992; and Halvorson et al., 2003) and limits the actual shrinkage (Razak and Harrison 1997; Ge et al., 2005).

Moszner & Salz (2001) reported that there is a correlation between the polymerization shrinkage, filler loading and the viscosity of the dental resin composite. In this study, all the experimental flowable composites had a constant filler loading; however, the viscosities of the resin system were varied. The high viscosity of monomers in the composites created some difficulty for macro radical diffusion to the chain propagating centers which influenced the chain growing, thus reducing the DC (Mendes et al., 2005). In this study the most viscous resin system was in the experimental flowable composite FC-U/BT and the VPS of FC-U/BT was lower when compared to FC-BT. The effect of viscosity on VPS concurred with the findings of Goncalves et al. (2010), where both their experimental UDMA-based composites and Bis-GMA/TEGDMA-based composites had lower volumetric shrinkage and DC as the viscosity of monomer increased.

The high VPS in the experimental flowable composites FC-U/E and FC-U/E/BT could be reduced by increasing their filler loading. This is possible as the viscosity of their respective resin systems were lower compared to FC-BT.

There is no statistical significant difference in VPS between Esthet.X flow and FC-BT, and this could be related to the same resin type Bis-GMA/TEGDMA. However, the incomplete information on Esthet.X flow, such as mass weight of monomers, initiator system types, and its concentration, created difficulty in discussing the results. The filler loading of Esthet.X flow is approximately 61%, with filler size in the range of 0.01 to 5.0 µm, which are barium fluoroboroaluminosilicate glass and silica nanofiller. Smaller filler particles (0.01 to 1 µm) are most likely to scatter light and reduce the penetration of light because those particle sizes are similar to the wavelengths emitted from composite curing lights (Caughman, et al., 1995). However, the mass weight of the different filler sizes of Esthet.X flow was also unknown. In general, the VPS of UAM-based flowable composite is within acceptable limits compared to commercial Esthet.X flow, since the VPS of FC-U/BT was lower and the FC-U/E/BT was higher than Esthet.X flow and FC-U/E showed no significant difference.

In order to simulate the oral condition, a slight modification to the ISO 4049:2000 was made when the water sorption and solubility of flowable composite were determined in this study. Specimen’s dimensions were changed from 15 mm in diameter and 1 mm in thickness to 8 mm by 2 mm. The 8 mm diameter allowed direct irradiation through the light curing unit tip, thus avoiding the need for overlapping irradiation. The 2 mm thickness could be considered as the maximum depth of cure for most light curing units. In addition, the preconditioning stage using silica gel was not performed since clinically all polymeric restorations do not undergo any desiccation process prior to contact with oral fluids (Gerdolle et al., 2008).

Despite the specimen’s dimensions and no preconditioning, the water sorption and solubility requirements of ISO 4049:2000 were fulfilled by all flowable composites. The reduction of water sorption and solubility was likely to be due to the decrease of the resin content and substitution of 60% silanated glass fillers. This is further supported by Skrtic & Antonucci (2003) as they also attributed the lower water sorption to the presence of a coupling agent between the filler and organic matrix. An inverse relationship between the filler content and water sorption/solubility values of composite restorative materials has also been reported (Oysaed and Ruyter, 1986; Razak, 1995).

Monomers with high water uptake resulted in composites with high water sorption (Atai et al., 2004). The polar nature of the hydrophilic groups of such a polymer matrix is of importance for water sorption of composite resin materials (Peutzfeldt 1997). It was expected that the experimental flowable composites in this study, the FC-U/BT would show higher water sorption and solubility when compared to the FC-BT (Exp-Cont) and other experimental flowable composites. The highest water sorption and solubility values recorded for U/BT experimental resin system, was due to its hydrophilic nature. As stated earlier U/BT experimental resin system exhibited the highest viscosity when compared to that of other experimental resin systems. During the preparation of the experimental flowable composites, it was observed that high viscosity monomer increases the chance of micro-voids formation. Voids trapped in the bulk polymer contain oxygen and it may inhibit polymerization and consequently promote solubility (Gerdolle et al., 2008). The high viscosity may also decrease molecular mobility, thus, decreasing the DC and increasing the water solubility (Sideridou et al., 2002; Charton et al., 2007).

In this study the water sorption and solubility of FC-U/E were lower than FC-BT. This result could be related to lower water sorption and solubility of the U/E experimental resin system itself and also probably due to the hydrophobic Bis-EMA monomer. The U/E experimental resin system also showed lower viscosity than that of BT which contains hydrophilic TEGDMA monomer. For similar reasons, the FC-U/E/BT showed lower water sorption than the FC-BT. This finding further explained the lower water sorption of Z250 compared to Z100 observed by Sideridou et al. (2003). The lower hydrophilicity of Bis-GMA/UDMA/Bis-EMA in Z250 resulted in lower water sorption compared to Z100 which composed of Bis-GMA/TEGDMA. Even though the process of water absorption is multi-factorial, the moisture uptake of a polymerized composite resin may be largely due to the hydrophilic nature of its monomer units (Sideridou et al., 2003; Ferracane 2006; Kerby et al., 2009).

There are still several factors that may influence the interpretation of water sorption and solubility values of composite materials. These include silanated or not silanated filler, surface area, type, volume of the filler particles, and filler solubility (Fan et al., 1985; Söderholm, 1984; Örtengren et al., 2001). Although, the glass fillers used in this study was non-absorbable (Appendix IV), further studies should be carried out to characterize it and different filler types and sizes should be used with different storage duration in order to optimize the experimental composites.

Esthet.X flow showed significantly lower water sorption compared to all experimental flowable composites. The lab-scale experimental flowable composites were not prepared under a well-controlled environment as that employed by Denstply Caulk, USA during the manufacture of Esthet.X flow. It is likely that these experimental composites contain a large amount of micro-voids. However, the water solubility of experimental FC-U/E was significantly lower than that of Esthet.X flow (Com-Cont). This is probably attributed to the resin system, Bis-GMA/TEGDMA and fluoride releasing nature of Esthet.X flow (Appendix XII).

It has been suggested that the water sorption of composites could be advantageous and can be used to compensate the polymerization shrinkage. Thus, this study was carried out to determine the volumetric change of the experimental flowable composites. The water absorption causes a hygroscopic expansion, which had been able to compensate for the effects of polymerization shrinkage and relieve stresses and thereby reduce marginal gaps to a certain extent (Bowen et al., 1982; Martin et al., 2003). This expansion results from water sorption, and can be a clinically desirable phenomenon if it fully counteracts the effects of shrinkage. However, a coefficient of expansion that exceeds the shrinkage value is not desirable, as further stresses may be introduced to the cavity wall (Momoi and McCabe, 1994).

Archimedes' principle has been proposed as a method for determining dimensional change of restorative materials (Attin et al., 1995; Watts et al., 2000; Chutinan et al., 2004; Ruttermann et al., 2007) and this method was utilized in this study to determine the volumetric change of flowable composites after 7 days of water storage.

The polar nature of such a polymer matrix is an important factor for water sorption and hygroscopic expansion of composite resin materials (Peutzfeldt, 1997). In this study, FC-U/BT showed significantly higher volumetric change when compared to other experimental flowable composites and Esthet.X flow, and this could be related to the high water sorption value, since water sorption and hygroscopic expansion are positively correlated (Ruttermann et al., 2007). Consequently, this positive correlation also explained the slightly lower volumetric change of Esthet.X flow compared to all other experimental flowable composites.

It has been also reported that there was also a positive correlation between storage time and the water sorption process (Razak et al., 1995). However, Ruttermann et al. (2007) showed that after 7 days storage there was no further increase in expansion of composite when stored up to 30 days. Thus, in this study, the volumetric change of flowable composite was determined after 7 days water storage only.

The highest volumetric change of 1.03% was observed for FC-U/BT after 7 days in water. This small volumetric change is considered inadequate to compensate the volumetric polymerization shrinkage of 4.51%. The result of this study concurred with the observation of Razak (1995). Thus, before it is stated in this study that the volumetric change may reduce the amount of volumetric polymerization shrinkage, further investigations are necessary to determine the influence of volumetric changes and water uptake on the marginal seal of restorative materials.

The flexural strength and modulus of elasticity of experimental resin showed an increase by an average of 27% and 67% respectively, when the 60% filler (by weight) was added. The toughness however, decreased by 58%. The flexural strength values of all experimental flowable composites met the requirement of ISO 4049:2000, which was more than 80 MPa.

Since the properties of dental composites depend on factors related to its composition, the parameter for all experimental flowable composites was standardized except for the resin system types. A wide range of data was observed for the flexural strength and modulus of elasticity, when the experimental resin systems were tested. Less variation was observed when standardized fillers were added and the resin reduced to 40%. Consequently, this can also explain the lack of significant difference in flexural strength and toughness observed between the UAM-based flowable composites against the control FC-BT. These findings were similar to that reported by Moszner et al. (2008). They showed that the flexural strength of experimental composites with the same filler content (60% by weight) and different contents of the resin system tend to be not statistically different.

The flexural strength and modulus of elasticity values of Esthet.X flow flowable composite obtained in this study were 114 MPa and 5.9 GPa, respectively. This is consistent with the data in the technical manual, where 112 MPa and 5.62 GPa were reported for flexural strength for modulus of elasticity respectively (Appendix XII). Generally, the flexural strength, modulus of elasticity and toughness of Esthet.X flow was lower than the experimental flowable composite. The 60% filler loading in all experimental FCs consist of 90% of 1.4 µm and 10% of 0.5 µm which could be considered as small particle flowable composites; however, Esthet.X flow is categorized as a micro-hybrid flowable composite, where the particles size ranged from 0.01 to 5 µm. It has been reported by Anusavice (2003) that the modulus of elasticity of small particle composite was higher than micro-hybrid composites. Moreover, the lower irradiation time of 20 seconds recommended by the manufacturer could also be another reason for lower mechanical properties. It has been shown that the degree of conversion was increased when the time of irradiation increased (Rueggeberg, et al., 1994; Davidson-Kaban, et al., 1997). Before increasing the irradiation time for Esthet.X flow from 20 seconds to 40, further studies were recommended to determine the relationship of filler size and mass weight with the time of irradiation. The basis of this suggestion can be related to the finding of Turssi et al. (2005). They reported the lowest DC was achieved in composites with particle size closest to the critical wavelength of the activating light (470 nm). Esthet.X flow has a mixture of micro and nano fillers but unfortunately the weight percentage of each size of filler is unknown.

Filler-matrix interactions also determine the fracture parameter of composite rather than the structure of organic matrix (Skrtic and Antonucci, 2003). However, the silane coupling agent information was unavailable from the Esthet.X flow technical manual. A scanning electron microscope (SEM) can be used to determine the mode of fracture whether cohesive at resin matrix or adhesive at filler-matrix interaction. This could be one of the limitations of this study and further studies are recommended.

In this study, the experimental flowable composite FC-U/E showed significantly lower modulus of elasticity than the FC-BT. This could be owing to the resin system structure and composition of FC-BT. The bulky aromatic rings of Bis-GMA and the hydrogen bonding between the molecules also hinders the mobility of monomer and polymer chains, thus enhancing a three dimensional microstructure of the composite and increasing its mechanical strength (Musanje and Ferracane, 2004). The higher the amount of TEGDMA, the more polar is the organic phase, and therefore better is the interaction with the inorganic fillers, increasing the diametral tensile strength (Moraes et al., 2008). However, the hydrogen bond of Bis-GMA is responsible for high viscosity, and low DC and filler loading. Thus, the FC-U/E resin system showed lower viscosity with higher DC than that of FC-BT, as the former can accept a higher filler load physically, and a higher filler load showed better mechanical properties (Kim et al., 2002).

In this study, the biocompatibility of flowable composites was carried out according to ISO 10993; Part 5 and 12 and ISO/DIS 7405. Screening of cytotoxicity using fibroblast L-929 and Cell Titer 96$^{®}$ A$_{queous}$ one solution cell proliferation assay was employed. There are a number of factors that determine the cytotoxicity of dental polymers and composites. The chemical-structure property relations of the monomers in the resin system are undoubtedly involved in determining cellular response. Furthermore, compositional differences involving polymers and light-initiator systems can be a significant contributor (Simon et al., 2005). In this study, all these parameters were standardized for all experimental flowable composites except that the resin system was varied.

The experimental control flowable composite FC-BT and commercial control Esthet.X flow caused a significant drop in the percentage of viability of L-929 cells when compared to the solvent, however, the UAM-based flowable composites were not. This experimental flowable composite and Esthet.X flow were composed of a common Bis-GMA/TEGDMA resin system. The compositional differences in the resin and light-initiator systems of dental composites can be a significant contributor to the cell response determination (Simon et al., 2005). The resins that undergo a greater DC would exhibit enhanced properties and contain far less leachable components, thus, significantly improve the biocompatibility of the dental restoration (Nie et al., 2001). This assumption is further supported by Simon et al. (2005) who stated that the leach of monomers is an important factor that influences the cytotoxic response of polymerized materials. Moreover, the leaching process is also affected by the molecules structure and size, where the small sized molecules are expected to be eluted fast (Ferracane, 1994). The TEGDMA molecules are smaller sized molecules compared to that of the Bis-GMA or Bis-EMA (Sideridou et al., 2003) or the experimental UAM.

For the Esthet.X flow, the lower curing time of 20 seconds based on the manufacturer’s recommendation could be also responsible for lower percentage of cell viability. The efficacy of polymerization may affect the amount of monomers leached (Polydoroua et al., 2007). Caughman et al. (1991) reported that the cellular toxicity decreased as the curing time and resultant monomer conversion increased for each composite sample in their study.

There is no significant difference in percentage of viable cells between the experimental UAM-based flowable composite and the solvent. This could be due to the main component of the resin system being UAM, which is characterized by macromolecules with a high degree of conversion and lower amount of TEGDMA monomer. It was assumed that the cytotoxicity of the materials could be related to the amount of TEGDMA that was leached from the flowable composites compared with their non-flowable traditional composite (Al-Hiyasat et al 2005). This work however, only screened the cytotoxicity using percentage of viable cells. Further studies are recommended to ascertain the complete biocompatibility status of UAM as a potential resin for dental composite restorative materials.

5.4 Limitations of the study

The synthesized experimental UAM was slightly yellowish in colour, due to the light yellow colour of the starting polyol, which could be overcome with purification. This can be considered as a limitation to this study and further studies need to be conducted in order to optimize the aesthetic requirements for these UAM to be used as a commercial for dental restorative materials. This study could be considered as a step towards improvement of resin matrix of dental composite and the experimental UAM has been combined with other monomers as shown by the results of the experimental composites. This type of composite is clinically indicated for pit and fissure sealant and as cavity liner for Class I, II and V restorations (Deliperi and Bardwell, 2002). This may be the limited possible application of these experimental flowable composites as colour matching is not of prime importance.

The using of only one commercial flowable composite based on Bis-GMA/TEGDMA in comparison with UAM-based flowable composites was considered as a limitation of this study. Thus, work on the up-scaling of the experimental UAM should be carried be carried to obtain larger amount of experimental composites so that comparison with different commercial composites, such as UDMA-based composites, Bis-GMA-based composite and oxirane-based composites can be done.

Another major limitation of the study was the utilization of only one type of filler particles. The single type fillers with a narrow range of particle size may not have reflected the actual effect of varying resin systems on the chosen mechanical properties. Different types of fillers with different loading percentage are recommended for further evaluation, as most commercially available composites contained a broad range of particle sizes and types such as the microhybrid composite.

In this study the properties characterization were incomplete, since thermal properties such as coefficient of thermal expansion and glass transition temperature (Tg) was needed for determination in the future. The chosen mechanical properties determinations including wear resistance must also be done under thermal and mechanical load cycles. Scanning electron microscopy can also aid in the detailed characterization of the experimental UAM-based composite to provide better understanding of its failure modes. It has been observed that moderate-to-good filler/matrix adhesion in dental composites which depends upon filler type. If optimal adhesion between filler and matrix is required in these materials to provide adequate strength, further increase in the fracture toughness of dental composites will more than likely be achieved through improvements in the toughness of the resin matrix itself.

The percentage of viable cell study was considered to be a primary screening for cytotoxicity assessment. Therefore "Phase 2" screening methods are recommended to test specific cellular functions with the relevant cell types, such as gingival cell (Caughman et al., 1991), and detection of elution materials have suggested using HPLC as suggested by Al-Hiyasat et al. (2005). Further, preclinical tests are also recommended for UAM-based restoration such as animal trials and microleakge tests using natural extracted teeth under thermal and load cycles.

Finally, this study was focused on the experimental UAM as a resin for flowable composites. Further studies are recommended to investigate the possible application of UAM as an adhesive material. The high DC, toughness and flexibility of the experimental UAM can be advantages for a dental adhesive as it may be able to absorb the stress during composite polymerization, thus reducing microgaps formation and microleakage.

5.5 Summary

In this study, an experimental UAM was synthesized by reacting palm oil-based polyol with MDI to produce urethane prepolymer which was then acrylated later by HEMA. The FT-IR spectrum confirmed the urethane group formation and grafting of acrylate group. UAM showed lower viscosity and modulus of elasticity but higher DC and CLD, flexural strength and toughness than Bis-GMA monomer. This could be attributed to the higher functionally and flexibility of urethane linkage and soft segment of palm oil-based polyol compared to the rigid Bis-GMA. The UAM exhibited higher water sorption and solubility than Bis-GMA. This is likely to be related to its chemical structure and the high cross-linking polymer network. Even though the VPS of experimental UAM was higher than Bis-GMA, this was expected, since polymerization shrinkage is directly related to the DC (Venhoven, et al 1993). When considering polymer stability, higher conversion appears to be more desirable even though it also leads to greater shrinkage and stress development (Stansbury et al., 2005).

The potential of the experimental UAM for modification of BT resin system was also investigated. The incorporation of experimental UAM into BT resin system showed significant increase of DC, CLD, flexural strength and toughness as illustrated in the U/BT resin system when compared to the BT resin system. However, the VPS and water sorption of U/BT was higher than BT resin system, which could be attributed to the high DC and hydrophilic nature of UAM.

The high water sorption of UAM and U/BT resin systems was then further optimized by copolymerization with a hydrophobic monomer, Bis-EMA in the experimental resin systems U/E(3/1), U/E(1/1) and U/E/BT. The potential of the U/E(1/1) resin system to be a substitute of BT was illustrated, where the resin system U/E(1/1) showed higher DC and CLD, flexural strength and toughness, and the water sorption and solubility were significantly lower than the BT resin system. The U/BT/E resin system also showed increased flexural strength, modulus of elasticity, and toughness with lower water sorption and solubility significantly when compared to BT resin system. This could be attributed to the flexibility and toughness of UAM combined with the hydrophobic nature of Bis-EMA.

The experimental UAM showed its potential when used as a part of a resin system for flowable composite, since the experimental UAM-based flowable composites satisfy the flexural strength, water sorption and solubility requirement of ISO 4049:2000. The experimental flowable composites proved to be non-cytotoxic after primary screening, and were comparable to Esthet.X flow flowable composite where no significant difference was found in the percentage of viable cells.

With the limitation of filler particle used, the addition of fillers (60% by weight) to resin systems resulted in a reduction of the polymerization shrinkage, toughness, water sorption and solubility. The experimental flexural strength, modulus of elasticity and toughness of UAM-based flowable composites FC-U/BT, FC-U/E and FC-U/E/BT was comparable to FC-BT, except the FC-U/E which exhibited lower modulus of elasticity. However, the water sorption and solubility of FC-U/E and FC-U/E/BT showed lower than FC-BT.

The VPS of FC-U/E and FC-U/E/BT was higher than FC-BT, confirming the earlier findings where the DC of UAM was higher that Bis-GMA. In addition, the viscosities of FC-U/E and FC-U/E/BT resin systems were lower than that of FC-BT. This property is important since there is a correlation between the polymerization shrinkage, filler loading and the viscosity of the dental resin composite (Moszner and Salz, 2001). Consequently, the composites with the highest filler loading will exhibit the highest flexural strength, flexural modulus and lowest shrinkage as reported by Razak & Harrison (1997) and Kim et al. (2002). As the viscosity of FC-U/E and FC-U/E/BT resin systems were lower compared to FC-BT, higher filler loading is possible and this is likely to improve the final properties of the dental composite. Thus, it is not presumptuous to state at this juncture that this experimental UAM could be used as a resin with other co-monomers to form the matrix in dental composites.