1.1 Introduction

Dental composites were developed over 40 years ago, and have been widely accepted by the profession, as one of the main direct restorative materials (Tian et al., 2007). Dental composites have also been used as replacement material for amalgam restorations (Wilson et al., 2002; Sunnegadh-Gronberg et al., 2009). The dental composites currently used consist of three main components: the polymeric matrix resin which includes resin monomer, initiator systems and inhibitors, a high volume fraction of particulate fillers, and a coupling agent to ensure matrix-filler adhesion (Bowen, 1962; Pereira et al., 2005).

Developments in filler technology and initiation systems have improved the physical properties of dental composites considerably and expanded their clinical applications (Braga and Ferracane, 2004). However, the composition of the polymeric matrix resin has remained principally unchanged since the introduction of Bis-GMA resin (Bisphenol A glycidyl methacrylate) by Bowen in the early 1960s (Bottenberg et al., 2007). The rigid phenolic groups in the backbone of the Bis-GMA structure impaired rotation about the bonds. The strong intermolecular interactions due to the hydroxyl groups resulted in a very viscous and stiff polymer material and its degree of conversion was found to be not higher than 42% (Sideridou et al., 2003; Floyd and Dickens, 2006).

In order to reduce the viscosity of Bis-GMA and to incorporate the reinforcing fillers, a diluent co-monomer, such as triethylene glycol dimethacrylate (TEGDMA) is commonly used in most commercially available dental composites. Increasing the content of TEGDMA in a BisGMA/TEGDMA polymeric matrix resin will increase its degree of conversion; however, the copolymerization may be compromised as

TEGDMA remains mobile and diffuses out of the matrix over time. Increasing the content Bis -GMA cause higher probability of copolymerization as it is not very mobile. However, incorporation of optimum amount of filler particles can be difficult. The water uptake will also be increased leading to inferior mechanical properties (Peutzfeldt, 1997; Sideridou et al., 2002; Atai et al., 2005; Ge et al., 2005; Vasudeva, 2009). Besides this, the relatively high hydrophilicity and penetrability to tissues of TEGDMA raises biocompatibility issues (Geurtsen and Leyhausen, 2001). Therefore, Bis-GMA analogue, such as ethoxylated bisphenol A dimethacrylate (EBPADMA or Bis-EMA) has been developed and has been suggested to be used as an alternative diluent for TEGDMA. Bis-EMA is a hydrophobic dimethacrylate monomer with lower water sorption and polymerization shrinkage relative to TEGDMA (Pereira et al., 2002; Sideridou et al, 2003). It has however been reported that Bis-EMA showed higher viscosity and lower degree of conversion and flexibility (Sideridou et al., 2002). All these shortcomings of Bis-GMA-based dental composites have stimulated constant interest in the development of new polymeric resin systems (Moszner and Salz 2001).

Peutzfeldt (1997) stated that there was a need for a new resin system with a high degree of conversion and strength to ensure durability of composite restorations and this has remained a major task for researchers (Vasudeva, 2009). The successful development of resin systems for use as dental biomaterials requires that they exhibit the fracture toughness of elastomer-modified resins, while maintaining their durability in the oral environment (Sterrett et al., 1987). The chemical composition of the dental monomer system and its degree of conversion are directly related to the final properties of a dental composite restorative material (Antonucci and Toth, 1983; Musanje and Ferracane, 2004). Urethane dimethacrylate-based monomers (UDMA) have been developed and used in the resin matrix of dental composites. It has been shown that the functionality offered by these groups adds toughness and flexibility to the monomer backbone chain, providing the possibility for enhanced conversion and durability (Peutzfeldt, 1997; and Rueggeberg, 2002). Abu Kasim (1995), in an in-*vitro* study reported that UDMA-based composites proved to be more fatigue resistant compared to Bis-GMA-based composites, while Söderholm et al. (2001) observed the same trend for wear resistance in their *in vivo* study.

The variety of possible structures of urethane dimethacrylate, allows synthetic flexibility in obtaining new urethane dimethacrylates with desirable properties that could enhance both the degree of conversion and its ultimate properties when combined with other monomers for commercial and biomedical applications (Assumption and Mathias, 2003). There has recently been renewed interest in the development of new UDMA-based monomers which could potentially be used as substitutes for Bis-GMA-based monomers (Atai et al., 2007; Chen et al., 2008; Moszner et al., 2008).

A new UDMA-based composite utilising a DX-511 molecule was introduced recently (Kalore, GC America, USA) based on a recent technology developed by DuPont. DX-511 is a monomer which has a long rigid molecular core and flexible arms in its structure and its molecular weight is twice than that of Bis-GMA and UDMA. The long rigid core prevents deformation and lowers polymerization shrinkage but results in a decrease in reactivity. The addition of the flexible arm increases the potential for reactivity (Terry et al., 2009; Kalore technical overview, GC America, 2009). Another type of dental composite, Filtek™ Silorane (3M ESPE, Germany) has also been introduced into the market recently, where the resin matrix is based on the combination of siloxanes and oxiranes chemistry. Apart from improved properties of the resultant composite, these two different chemical structures are known for their low shrinkage and Burgers et al., (2009) suggested that the increased hydrophobicity is likely to be responsible for the low adhesion of streptococci strains, thus may reduce the occurrence of secondary caries. The ring opening step in its polymerization process caused lower volumetric shrinkage, between 0.66 to 1% (Terry etal., 2009; Filtek Silorane technical profile, 3M ESPE, 2007). Although the polymerization shrinkage of dental composites has been successfully lowered, there are many other properties such as water sorption and hygroscopic expansion that have yet to be addressed for this new resin matrix. McCabe (2010) stated that even though Filtek™ Silorane showed the least water absorption compared to other conventional composites included in their study, the radial expansion was found to be the highest. This finding is a cause for concern. Another drawback for the clinical use of silorane-based composites is that it requires a dedicated adhesive system, as the current adhesives are based on methacrylate materials.

Although these two new resin technologies are very promising, further researches both *in vitro* and *in vivo* long term clinical trials need to be carried out to validate its durability as a restorative material. While, the conventional methacrylate-based dental composites are clinically well accepted with long term clinical data (Mair, 1998; 2002; Sunnegadh-Gronberg et al., 2009; Fagundes et al., 2009; Terry et al., 2009) exploration and search for new formulations of methacrylate-based monomers are still relevant. Gan (2004) patented several palm oil-based polyols and successfully produced polyurethane foam for industrial applications. He reported that the properties of this palm oil-based polyurethane were comparable to polyurethane produced from petrochemical-based polyols (Gan, 2004). These findings form the basis of this study where palm oil polyols will be used in the modification of the existing methacrylate-based monomers. The potential of this new formulation for application in dental composites will be investigated.

1.2 Aim of the study

The aim of this study is to synthesize the urethane acrylate macromer (UAM) using palm oil-based polyol and investigate the possibilities of its application in flowable dental composite.

1.3 Objectives of the study

The objectives of this study are:

1. To synthesize urethane acrylate macromer (UAM) and identify its chemical structure using FT-IR.

2. To determine the following properties of UAM resin and to compare it with Bis-GMA;

   a. Viscosity
   b. The degree of conversion and cross-linking density
   c. The volumetric polymerization shrinkage
   d. The water sorption and solubility.
   e. The flexural strength, modulus of elasticity and toughness.

3. To determine the following properties of UAM-based resin systems and compare them with the commonly used Bis-GMA/TEGDMA (BT) resin system. The UAM-based resin systems include: U/BT (blending of UAM and Bis-GMA/TEGDMA) , U/E(3/1) (blending of UAM and Bis-EMA with mass weight 3/1), U/E(1/1) (blending

of UAM and Bis-EMA with mass weight 1/1), and U/E/BT (blending of UAM, Bis-EMA and Bis-GMA/TEGDMA).

a. Viscosity.

b. The degree of conversion and cross-linking density

c. The volumetric polymerization shrinkage

d. The water sorption and solubility.

e. The flexural strength, modulus of elasticity and toughness.

4. To determine the following properties of experimental UAM-based flowable composite, and compare them to an experimental control flowable composite based on Bis-GMA-TEGDMA (FC-BT), and a commercially available flowable composite Esthet.X flow. The experimental UAM-based flowable composites include: flowable composite based on U/BT resin system (FC-U/BT), flowable composite based on U/E(1/1) resin system (FC-U/E), flowable composite based on U/E/BT resin system (FC-U/E/BT).

a. The volumetric polymerization shrinkage.

b. The volumetric change

c. The water sorption and solubility.

d. The flexural strength, modulus of elastucity and toughness.

5. To assess the cytotoxicity, via percentage of cell viability, of experimental UAM-based flowable composites and to compare with FC-BT and commercially available Esthet.X flow.

1.4 Null hypothesis of the study

In order to investigate the possibilities of UAM to be used as resin for dental composite, the null hypotheses are:

1- There is no difference in the degree of conversion, volumetric polymerization shrinkage, water sorption, water solubility, flexural strength, modulus of elasticity and toughness between UAM resin and Bis-GMA resin.

2- There is no difference in the degree of conversion, volumetric polymerization shrinkage, water sorption, water solubility, flexural strength, modulus of elasticity and toughness between UAM-based resin systems and Bis-GMA-based resin system.

3- There is no difference in the percentage of volumetric polymerization shrinkage, percentage volumetric change, water sorption, water solubility, flexural strength, modulus of elasticity, toughness, and percentage of viable cell between UAM-based experimental flowable composite and commercial flowable composites Esthet.X flow.