Physicochemical properties of dimethacrylate resin composites with comonomer of Hexa/Tri-ethylene glycol bis(carbamate-isoproply-α-methylstyrene)

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Abstract

New photocurable "Phene" like monomers Hexaethylene glycol bis(carbamate-isoproply-α-methylstyrene) (HE-Phene) and Triethylene glycol bis(carbamate-isoproply-α-methylstyrene) (TE-Phene) were synthesized and incorporated into Bis-GMA/TEGDMA with the aim of reducing polymerization shrinkage without detriment to the physical and handling properties of the resin composites. Phene like monomers (HE/TE-Phene) were synthesized through a one-step reaction route, and their structures were confirmed by FT-IR and ^{1}H-NMR spectra. HE/TE-Phene were incorporated into Bis-GMA/TEGDMA (50/50,wt/wt) with a series of mass fraction (from 0 wt.% to 40 wt.%). Experimental resin composites were prepared by mixing 29 wt.% of resin matrix to 71 wt.% of particulate-fillers. Degree of conversion (DC) was determined by FT-IR analysis. The volumetric shrinkage (VS) was calculated as a buoyancy change in distilled water by means of the Archimedes principle. Polymerization shrinkage-stress (SS) was measured using the tensilometer technique. The flexural strength (FS), modulus (FM), and fracture toughness (FT) were measured using a three-point bending setup. Viscosity was analyzed with a rotating disk rheometer. Water sorption and solubility were also measured. ANOVA analysis showed that DC (after 40 s), VS, and SS were in a trend of decreasing with the increasing of HE/TE-Phene concentration. In general, the experimental resin composites had comparable FT, FS and FM (p>0.05) when the mass fraction of HE/TE-Phene in resin matrix was not more than 30 wt.%. The overall tested properties prove that including HE/TE-Phene up to 30 wt.% into Bis-GMA/TEGDMA resin could be potentially useful in the formulation of low-shrinkage resin composites.

Keywords: shrinkage stress, physical properties, volumetric shrinkage, degree of conversion.

1. Introduction

Resin composites used in restorative dentistry are materials created from a mixture of methacrylate monomers and silanized inorganic fillers. Bisphenol A glycidyl methacrylate (Bis-GMA), triethylene glycol dimethacrylate (TEGDMA) and urethane dimethacrylate (UDMA), are the most widely used monomers in dentistry [1-3]. The resin composites formulated with the above-mentioned monomers have characteristics that meet most of the demands for dental applications, such as high degree of monomer conversion and mechanical properties, low solubility and, good handling and esthetic features [1]. However, until now commercially available resin composites still have shortcomings that need to be addressed. Obviously, drawbacks related to polymerization shrinkage and polymerization-induced stress continue to be a clinical problem, contributing to premature failure in resin composite restorations [4,5]. Depending on their formulation, resin composites used in restorative dentistry exhibit volumetric shrinkage ranging from 1% up to 6% [6]. Generally, this property is greatly influenced by the chemical structure of the monomers used. Bis-GMA has a high viscosity that negatively interferes with the degree of monomer conversion [7], therefore, low molecular weight dimethacrylates such as TEGDMA or UDMA are incorporated. However, this methodology has been shown to increases water sorption and polymerization shrinkage [8]. Polymerization shrinkage behavior of resin composites has been determined to be dependent on several factors, such as rate and extent of the polymerization reaction, double-bond concentration, and the modulus of elasticity of the cured resin composites [6,9,10]. Low double-bond conversion and low double-bond concentration will lead to low volumetric shrinkage [11,12]. A reduced polymerization rate and stiffness of cured resin

composites, are a benefit for achieving lower shrinkage stress [12,13]. Development of a new polymeric system, differing from the traditional methacrylate systems, has been considered an alternative to produce resin composites with significant improvements. In our previous research, it was found that the reactivity of double bonds in α-methylstyryl group of a new monomer named Phene was lower than the double bond in a methacrylate group [14,15]. Thus, the polymerization rate of monomer containing α-methylstyryl groups was much slower than the monomer containing methacrylate group, which could delay the gel point during light irradiation and provide sufficient time to release the stress [8]. Therefore, using a α-methylstyryl structure containing monomer with a low double bond concentration was effective way to prepare low volumetric shrinkage and shrinkage stress resilient resin composites [15]. However, discoloration of cured Phene containing resin composite after storage was observed due to the tertiary amine structure in Phene, which could be oxidized and induce discoloration [16].

Based on this knowledge and with the goal of finding a new co-monomer that can markedly reduce the polymerization shrinkage behavior of Bis-GMA monomer without detriment to the physical, esthetic and handling properties of the resin composites, our research group has investigated the use of a novel Phene like monomers named "HE/TE-Phene" (Hexaethylene glycol bis(carbamate-isoproply-α-methylstyrene) (HE-Phene) and Triethylene glycol bis(carbamate-isoproply-α-methylstyrene) (TE-Phene)) with α-methylstyryl structures and with no tertiary amine structure for formulating experimental photo-polymerizable resin composites. Therefore, the purpose of the present study was to evaluate the polymerization shrinkage behavior (volumetric shrinkage and shrinkage stress), physical properties (degree of

conversion, water sorption/solubility, flexural strength and modulus and fracture toughness) and handling property (viscosity) of a novel experimental resin composite. The null hypotheses were: (1) experimental resin composites will have a similar degree of conversion and lower shrinkage behavior compared to conventional resin composite; (2) experimental resin composites will achieve similar material properties compared to conventional resin composite.

2. Materials and methods

2.1. Materials

Bis-GMA and TEGDMA were purchased from Esstech Inc. (Essington, PA, USA). Camphoroquinone (CQ), N,N'-dimethylaminoethyl methacrylate (DMAEMA), and 3-isopropenyl-α,α-dimethylbenzyl isocyanate (IDI) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Dibutyltin dilaurate (DBTDL), triethylene glycol (TEGOL), and hexaethylene glycol (HEGOL) were purchased from Sigma-Aldrich Co. All reagents were used without purification. Silaned $BaAlSiO_2$ filler particles (Ø 0.7µm) were received from Schott (UltraFine, Schott, Landshut, Germany).

2.2. Synthesis of "Phene like monomers" (Hexaethylene glycol bis(carbamate-isoproply-α-methylstyrene) (HE-Phene) and Triethylene glycol bis(carbamate-isoproply-α-methylstyrene) (TE-Phene))

Phene like monomers (HE/TE-Phene) were synthesized according to the route presented in Figure 1. A mixture of HEGOL or TEGOL (0.05 mol), IDI (0.10 mol), 100 mL of extra dry acetone, and 2 droplets of DBTDL as catalyst were stirred at 45℃. The reaction was continued until the reaction between IDI's isocyanate group and HEGOL/TEGOL's hydroxyl group was completed. The completion of the reaction was confirmed by FT-IR. The disappearance of the infrared absorbance peak of the -NCO group (2270 cm^{-1}) in the FT-IR spectra of the samples taken from the reaction medium revealed the end of reaction. After removing the acetone by distillation under vacuum, the product was washed with diethyl ether to remove the catalyst. Then the diethyl ether was evaporated from the colorless viscose liquid by drying it in vacuum at 35℃ for 24 h to obtain Phene like monomer (HE-Phene or TE-Phene). The correctness of the

chemical structure was confirmed by spectroscopic evaluations FT-IR (Figure 2) and ^{1}H-NMR (Figure 3).

2.3. Preparation of experimental dental resin composites

Resin matrices of resin composites were prepared according to the formulations shown in Table 1. All compounds were weighed and mixed under magnetic stirring. Experimental resin composites were prepared by mixing each resin matrix with fillers in a high-speed mixing machine (SpeedMixer, DAC150 FVZ-K, Hauschild, Germany) with a speed of 1900 rpm. The mass ratio between the resin's matrix and fillers was 2/5 (wt/wt).

2.4. Double bond conversion

Double bond conversion (DC%) during and after the photoinitiation of polymerization was monitored by Fourier transform infrared spectroscopy (FT-IR) (Spectrum One, Perkin-Elmer, Beaconsfield Bucks, UK) with an attenuated total reflectance (ATR) accessory. Resin composites were analyzed in a mold that was 1.5 mm thick and 4.5 mm in diameter. First, the spectrum of the unpolymerized sample was placed in the mold and measured. Then the sample was irradiated through an upper glass slide for 40 s with a visible light-curing unit (Elipar TM S10, 3M ESPE, Germany) producing an average irradiance of 1600 mW/cm^2 (Marc Resin Calibrator, BlueLight Analytics Inc., Canada). The sample was scanned for its FT-IR spectrum after being irradiated. The DC was calculated from the aliphatic C=C peak at 1636 cm^{-1} and normalized against the aromatic ring C=C peak at 1608 cm^{-1} according to the formula

$$DC = \frac{(A_{c=c}/A_{ph})_0 - (A_{c=c}/A_{ph})_t}{(A_{c=c}/A_{ph})_0} \times 100\%$$

where $A_{C=C}$ and A_{ph} were the absorbance peak area of methacrylate C=C at 1636 cm^1 and aromatic ring at 1608 cm^{-1}, respectively; $(A_{C=C}/A_{ph})_0$ and $(A_{C=C}/A_{ph})_t$ represented the

normalized absorbency of the functional group at the radiation time of 0 and t, respectively; DC is the conversion of methacrylate C=C at a given radiation time. For each resin composite, five trials were performed.

2.5. Volumetric shrinkage measurement

The specimens' densities (n=3) were measured to determine volume shrinkage according to Archimedes' principle with a commercial density determination kit of the analytical balance (XS105, Mettler Toledo, Greifensee, Switzerland). The mass of the specimen was weighed in air and water, and density was calculated according to the equation

$$D = \frac{M_1 \times D_w}{M_1 - M_2}$$

where D is the density of the sample, M_1 is the mass of the sample in air, M_2 is the mass of the sample in water, and D_w is the density of water at the measured temperature. Density of polymerized sample was measured 5 min later after being photo-cured for 40 s. For each composite, six trials were performed respectively to calculate the densities of polymerized and unpolymerized samples. The volumetric shrinkage (VS) was expressed in % and calculated from the densities according to the equation

$$VS = \frac{D_c - D_u}{D_c} \times 100\%$$

where D_u is the density of the unpolymerized sample and D_c is the density of the polymerized sample.

2.6. Shrinkage-stress measurement

Glass fiber-reinforced composite (FRC) rods 4 mm diameter and 4 cm in length, had one of their flat surfaces ground with 180 grit silicon carbide sand paper. Two FRC rods were attached

tightly to a universal testing machine (model LRX, Lloyd Instruments Ltd., Fareham, England) and resin composite was applied between the FRC rod surfaces. The height of the specimen was set at 1.5 mm. Two light units (Elipar TM S10, 3M ESPE, Germany) were used simultaneously for 20 s with the tips in close contact with the resin compsite specimen from both sides. Contraction forces were monitored for 5 min at room temperature (22°C). Shrinkage stress was calculated by dividing the shrinkage force by the cross-section area of the FRC rod. The maximum shrinkage stress (SS) value was taken from the plateau at the end of the shrinkage stress/time curve. Five specimens were tested for each experimental resin composite.

2.7. Mechanical tests

Three-point bending test specimens ($2 \times 2 \times 25$ mm^3) were made from each resin composite. Bar-shaped specimens (Figure 4) were made in half-split stainless steel molds between transparent Mylar sheets. Polymerization of the resin composites was done using a hand light-curing unit (Elipar TM S10, 3M ESPE, Germany) for 20 s in five separate overlapping portions from both sides of the metal mold. The wavelength of the light was between 430 and 480 nm and light intensity was 1600 mW/cm^2. The specimens from each resin composite (n=8) were stored dry (for one day) at 37°C before testing. The three-point bending test was conducted according to the ISO 4049 (test span: 20 mm, cross-head speed: 1 mm/min, indenter: 2 mm diameter). All specimens were loaded into a material testing machine (model LRX, Lloyd Instruments Ltd., Fareham, England) and the load-deflection curves were recorded with PC-computer software (Nexygen 4.0, Lloyd Instruments Ltd., Fareham, England).

Flexural strength (σ_f) and flexural modulus (E_f) were calculated from the following formula (ISO 1992):

$$\sigma_f = 3F_mL/(2bh^2) \qquad E_f = SL^3/(4bh^3)$$

Where F_m is the applied load (N) at the highest point of a load-deflection curve, L is the span length (20 mm), b is the width of test specimens and h is the thickness of test specimens. S is the stiffness (N/m). S=F/d and d represents the deflection corresponding to load F at a point in the straight-line portion of the trace.

Single-edge-notched-beam specimens (2.5 x 5 x 25 mm^3) according to an adapted ISO 20795-2 standard method (ASTM 2005), were prepared to determine fracture toughness (Figure 4). A custom-made stainless steel split mold was used, which enabled the specimen's removal without force. An accurately designed slot was fabricated centrally in the mold extending until its mid-height, which enabled the central location of the notch and optimization of the crack length (x) to be half of the specimen's height. The resin composite was inserted into the mold placed over a Mylar-strip-covered glass slide in one increment. Before polymerization a sharp and centrally located crack was produced by inserting a straight edged steel blade into the prefabricated slot. Polymerization of the resin composite was carried out for 20 s in five separate overlapping portions. The upper side of the mold was covered with a Mylar strip and a glass slide from both sides of the blade, before being exposed to the polymerization light. Upon the removal from the mold, each specimen was polymerized also on the opposite side. The specimens from each group (n=8) were stored dry at 37°C for 24 h before testing. The specimens were tested in three-point bending mode, in a universal material testing machine at a crosshead speed of 1.0 mm/min.

The fracture toughness (FT) was calculated using the Equation:

$$K_{max} = \left[\frac{P \cdot L}{B} \cdot W^{3/2} \right] \cdot f(x)$$

where:

f is a geometrical function dependent on x:

$$f(x) = 3x^{1/2} \left[1{,}99 - x(1-x)(2{,}15 - 3{,}93x + 2{,}7x^2) \right] \Big/ \left[2(1+2x)(1-x)^{3/2} \right]$$

Here P is the maximum load in kilonewtons (kN), L is the span length (2 cm), B is the specimen thickness in centimeters (cm), W is the specimen width (depth) in cm, x is a geometrical function dependent on a/W and a is the crack length in cm.

2.8. Viscosity measurement

Viscosity measurements were performed using a rotational rheometer (HAAKE RheoStress 300; Thermo Electron, Karlsruhe, Germany) applying shear stresses in dynamic oscillation mode with a parallel plate configuration (20 mm diameter). After resin composite was placed on the lower plate of the rheometer, the upper plate was moved downward to adjust the gap to a thickness of 0.5 mm. Excess resin composite present around the circumference of the plate was removed prior to the measurements. All measurements were performed at 25°C for 120 seconds and repeated for three times. Viscosity of each resin composite was calculated from the rheological measurement according to Equation:

$$\eta = \sigma / \dot{\gamma}$$

Here, η is apparent viscosity (Pa•s), σ is the shear stress (Pa), and $\dot{\gamma}$ is the shear rate (s^{-1}) with a value of 1.

2.9. Water sorption and solubility

Water sorption and solubility were measured, using eight specimens, each of them stored in 120 ml water for 30 days at 37°C. The dry weight (m_d) of the specimens was measured with a balance (Mettler A30, Mettler Instrument Co.,Highstone, NJ, USA), with an accuracy of 0.1 mg. During the water immersion, weight (m_w) of the specimens were measured at 1, 2, 3, 7, 14, 21, and 30 days. Solubility weight (m_h) was measured after the dehydration was stabilized at 60°C in air. Water sorption and solubility were calculated as follows:

$$\text{Water sorption \%} = (m_w - m_h)/m_d \times 100\%$$

$$\text{Water solubility\%} = (m_d - m_h)/m_d \times 100\%$$

2.10. Statistical analysis

The data were statistically analyzed with SPSS version 23 (SPSS, IBM Corp.) using analysis of variance (ANOVA) at the P<0.05 significance level followed by a Tukey HSD post hoc test to determine the differences between the groups.

3. Results

The values of DC, VS and SS of the experimental resin composites were listed in Table 2. The results showed that after 40 s of light curing, the control resin composite (Bis-GMA/TEGDMA) HE/TE-EC1, HE-EC2 and HE-EC3 had the highest DC value ($p<0.05$) among all of the resin composites (Figure 5). The rest of the experimental (HE/TE-Phene) resin composites had lower and comparable DC values ($p>0.05$). However, DC measurement after 5 min of light curing, showed more comparable values (Table 2). The data showed that by increasing the Phene like monomers (HE/TE-Phene) weight ratios, the VS and SS decreased ($p<0.05$). The VS (3.3%) and SS (0.4 MPa) of TE-EC4 was the lowest ($p<0.05$) among all experimental resin composites (Table 2 and Figures 6). The results of FS, FM and FT were presented in Table 3. All of the experimental resin composites had comparable FS and FM values ($p>0.05$) except for HE-EC4 and TE-EC2-4 which revealed lower flexural properties ($p<0.05$).

On the other hand, all of the experimental resin composites had comparable FT ($p>0.05$) except for HE-EC1 which revealed a lower value ($p<0.05$).

A marked increase in viscosity and water sorption/solubility were found for all resin composites by increasing the Phene like monomers (HE/TE-Phene) weight ratios (Figures 7 and 8).

4. Discussion

The structure and chemical properties of monomers have significant influences on the performance of resin composites, thus designing a specific monomer is an effective way to overcome the drawbacks that resin composites have faced. In this study, with the aim of decreasing volumetric shrinkage and shrinkage stress of resin composites, Phene like monomers were designed as high molecular weight monomers with a two α-methylstyryl structure.

Just as expected, volumetric shrinkage and shrinkage stress of resin composites were significantly decreased after incorporation of Phene like monomers (HE/TE-Phene). It is well known that volumetric shrinkage is influenced by DC and double bond concentration, lower DC and double bond concentration would lead to lower volumetric shrinkage [17,18]. After incorporating HE/TE-Phene into a Bis-GMA/TEGDMA resin system, double bond concentration of the resin system would be decreased, since the higher molecular weight of Phene like monomers (684.4 for HE-Phene, and 552.3 for TE-Phene) when compared with TEGDMA (286) and Bis-GMA (512). Therefore, with nearly the same level of DC, the reduction in volumetric shrinkage of HE/TE-Phene containing composites should be mainly attributed to their lower double bond concentration.

The magnitude of shrinkage stress has been determined to be dependent on the extent and rate of polymerization, volumetric shrinkage, and the modulus of the material. Higher DC and cross-linking density of composites may result in a higher modulus, which ultimately causes high shrinkage stress [19]. The slow polymerization rate could provide sufficient to release the stress by delaying gel point [20]. In this research, modulus of resin composite decreased with the increasing of concentration of HE/TE-Phene. Thus, lower modulus of HE/TE-Phene should

be one reason for lower shrinkage stress of HE/TE-Phene containing composites. Consistent with our previous finding [15], resin composites with more Phene like monomers had a lower polymerization rate, because the reactivity of double bonds in α-methylstyryl structure was much lower than the double bonds in the methacrylate group [21]. The lower reactivity of HE/TE-Phene might be attributed to its resonance structure which delocalizes the double bonds, thus inhibiting free radical addition reaction. It has been reported that polymerization of α-methylstyryl had an appreciable depropagation rate even at room temperature [22]. As the reverse reaction of propagation, depropagation could shorten the polymeric chain and broken the crosslinking point. Thus, a higher concentration of Phene like monomers in a resin matrix would lead to higher probability of depropagation and lower crosslinking density of a polymeric network. In addition to lower volumetric shrinkage, lower polymerization rate and crosslinking density were also a benefit for Phene like monomers-containing resin composites to exhibit lower shrinkage stress by delaying the vitrification state of the material [23,24].

In the structure of HE/TE-Phene, there are two benzene groups which can reinforce the physical and mechanical properties of resin composites [25-28]. However, HE-EC4 and TE-EC2-4 had lower flexural properties than the control resin composite when tested in dry conditions. Just as mentioned above, increasing Phene concentration in resin composites would lead to a reduction of crosslinking density, which is also an important factor for physical and mechanical properties of resin composites [25,29]. Therefore, when mass fraction of HE/TE-Phene in a resin matrix was not higher than 30 wt.%, the reinforcement effect of benzene groups was offset by a reduction in crosslinking density, leading to comparable mechanical properties as control group. However, when mass fraction of HE/TE-Phene in resin matrix was increased to 30 wt.%, the

effect of reduction of crosslinking density dominated, leading to lower mechanical properties than in the control. With the aim of keeping the physical and mechanical properties of resin composites, too much Phene like monomers should not be added, even though it has the ability to decrease volumetric shrinkage and shrinkage stress significantly. In this research, adding 20-30 wt.% of HE/TE-Phene to resin matrix of resin composites was the optimal concentration, in order to obtain resin composite with the best comprehensive properties.

As regards to flexural strength and modulus, there were no statistically significant differences between the HE/TE-EC1, HE-EC2 and HE-EC3 experimental resin composites and the control resin composite. In this study, for all experimental resin composites, the concentrations of filler and initiators were kept constant, so that the significant differences found were attributable mainly to the organic matrix. Several reasons could explain this behavior, especially, the chemical structure of HE/TE-Phene, which has two aromatic rings within its structure, thus a high mechanical resistance could be expected. Moreover, because rates of hydrolysis of carbamate esters were reported to be lower than that of carbonate esters [30], a high resistance to hydrolytic degradation of HE/TE-Phene could also be expected due to carbamate esters in the structure. However, because of the special polymerization mechanism of α-Methylstyrene [22], abundant HE/TE-Phene would lead to reduction of crosslinking density of the polymeric network. Therefore, resin composites with 30% and 40% Phene had lower flexural strength. On the contrary, all of the experimental resin composites had comparable FT values. Many studies in literature demonstrated that FT values of resin composites are dependent mainly on the reinforcing filler system and the adhesion of filler particles and matrix [31,32].

When the resin composites are exposed to or stored in water, two different mechanisms occur.

First there will be an uptake of water producing an increased weight (sorption) and leaching or dissolution of components from the material into the mouth (solubility) leading to a reduction in weight [33]. In the present study, control resin composite after 30 days showed a water sorption percentage of 1.3 wt.%, which was the highest in comparison to TE-Phene resin composites and lowest in comparison to HE-Phene resin composites (Figure 8). Water solubility was increased for all resin composites by increasing the HE/TE-Phene weight ratios. This should be attributed to the higher probability in depropagation of resin composites with large amount of HE/TE-Phene, which leaded to more unreacted monomers left in the composites. Moreover, residual monomers could be leached out more easily for the reduction of crosslinking density of composites with large amount of HE/TE-Phene.

The results of this study demonstrated that Phene like monomers (HE/TE-Phene) could be used to reduce volumetric shrinkage and shrinkage stress of resin composites, and similar mechanical properties could be achieved after optimizing the concentration. Because of the appreciable depropagation rate of α-methylstyryl during polymerization, the polymerization mechanism of HE/TE-Phene and how it influences the polymeric network should be investigated to guide further work. Moreover, the properties of HE/TE-Phene containing resin composites, such as wear, esthetic, prolonged water storage and biocompatibility should also be evaluated in the future to show whether Phene could be used as a potential resin matrix for resin composites in clinical settings.

5. Conclusion

The use of the Phene like monomers up to 30 wt% into Bis-GMA/TEGDMA based resin composite could led to materials with reduced volumetric shrinkage and shrinkage stress without detriment the physical properties of the resin composites. However, incorporation of abundant amounts of HE/TE-Phene would lead to lower double bond conversion and increase viscosity.

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Figure Captions

Figure 1. Synthesis route of HE/TE-Phene used in this study

Figure 2. FT-IR spectra of HE/TE-Phene

Figure 3. ^{1}H-NMR spectra of HE/TE-Phene

Figure 4. Schematic drawing of 3-point bending (A) and single-edge-notched-beam specimens (B)

Figure 5. Curves of double bond conversion versus irradiation time of experimental resin composites.

Figure 6. Curves of polymerization shrinkage stress versus time of experimental resin composites.

Figure 7. Viscosity of experimental resin composites using rotational rheometer at 25°C. Vertical lines represent standard deviation.

Figure 8. Water sorption and solubility of experimental resin composites during 30 days of storage in water at 37°C. Vertical lines represent standard deviation.