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METHACRYLOYL DERIVITIZED HYPERBRANCHED POLYESTER. 2. PHOTO-POLYMERIZATION AND PROPERTIES FOR DENTAL RESIN SYSTEMS

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ABSTRACT

The purpose of this research is to demonstrate the usefulness of the synthesized hyperbranched multi-methacrylates (H-MMAs) in dental applications. We synthesized three hyperbranched multi-methacrylate oligomers and evaluated them as modifiers for use in the dental resin system: bisphenol A glycidyl dimethacrylate (BisGMA)/tri(ethylene glycol) dimethacrylate (TEGDMA). Their photo-polymerization activities, viscosity, mechanical properties, such as compression, diametral tensile, and flexural strength, were evaluated. H-MMAs (10%) modified dental resins have lower polymerization shrinkage and about 15% increase in mechanical strength compared to the Bis-BisGMA control. For example, H30-MMA has compressive, diametral tensile, and flexural strength of 576, 47, and 85 MPa, compared with the BisGMA control having 497, 43, and 77 MPa. In addi-

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tion, hyperbranched polymer modified resins have higher glass transition temperature (T_g) and lower thermal expansion coefficient (α) than the control. This research is significant both for increasing our knowledge about hyperbranched multi-functional polymers as well as leading to new dental resin systems with better performance.

INTRODUCTION

Dental composites mainly contain an organic resin system, usually dimethacrylates, inorganic fillers such as glass, quartz or other metal oxides, coupling agent and an initiator system for free radical polymerization [1, 2]. Although each of the components contributes to the desirable properties of the curing process and to the final performance of dental composites, the resin system is the most critical element influencing the mechanical properties and the polymerization shrinkage. Hence, intensive research has been focused on developing new monomers or oligomers for the resin matrixes [3, 4].

BisGMA was the first dimethacrylate monomer used in dental composites in the late 1950s. Since then, many commercial BisGMA (2,2-bis[4-(2-hydroxy-3-methacryloyolxypropoxy) phenyl] propane) based composites have exhibited satisfactory clinical performance, especially for anterior restoratives. However, there are some deficiencies associated with using the BisGMA resin matrix, such as susceptibility to water sorption, incomplete conversion of double bonds, and high polymerization shrinkage. Over the past several decades, extensive efforts have been made to develop new resin systems. These new monomer systems include (1) BisGMA derivatives [5-7]; (2) Fluorides Dimethacrylates [8-10]; (3) Dimethacrylates with high molecular weight and rigid structure [11-13]; (4) Urethane dimethacrylate [14-16]; (5) Spiro-orthoester based monomers [17-20]. Each of these new monomers or oligomers can improve properties to some extent. The first four groups are based on dimethacrylates, which can be easily cured by the conventional chemical, thermal, and visible-light free-radical polymerization. Spiro-orthoester monomers can reduce the polymerization shrinkage up to 40%, but their polymerization should be under specific restricted conditions and the additives are generally toxic.

Among them, high molecular weight multi-methacrylates have been considered as one of the most promising resin systems to reduce the shrinkage and improve the mechanical strengths. However, using high molecular weight resin components could significantly increase the viscosity, which will have several negative influences on the manufacture or application of dental composites. Thus, a generation of high molecular weight multi-methacrylates without dramatically increasing the viscosity is a critical task in formulating new dental composites with improved properties. Recently, with the progress in polymer chemistry, new types of polymers such as dendritic and hyperbranched polymers have been synthesized. One of the eminent characteristics of these new polymers is that they have lower viscosity in either melting or solution conditions than their corresponding linear polymers [21-23], which is the property we are looking for. Several researchers have claimed that the aromatic or aliphatic hyperbranched polyesters could reduce the polymerization shrinkage [24-26].

In the previous study, we reported the syntheses, characterization, and copolymerization of methacrylated hyperbranched polyesters based on Boltorn polyols. The object of this study is to further evaluate these hyperbranched polyesters as modifiers in formulating dental neat resins. The properties of modified dental resin systems were evaluated, including photo-polymerization activities, polymerization shrinkage, thermal and mechanical properties such as glass transition temperature (T_g), compressive (CS) and diametral tensile (DTS) strength.

EXPERIMENTAL

Materials

Hyperbranched multi-methacrylates (H-MMAS), were synthesized and purified in our lab. BisGMA, Camphorquinone (CQ), 2-dimethylaminoethyl methacrylate (DMAEMA), and TEGDMA were used as received.

Measurement of Viscosity

The Brookfield CAP 2000 Viscometer (Brookfield Engineering Laboratories, Inc., Stoughton, MA) was used to measure the viscosity of each sample. Spindle #5 (Radius 0.953 cm, cone angle 1.8°) was used in the various runs. All samples were run five times at 25°C. The Bingham Plastic Math Model was then used to analyze the viscosity based on the linear regression of shear stress with the shear rate. The Bingham equation is:

$\tau = \tau_0 + \eta D$ where

τ: shear stress (Dynes/cm^2 or N/m^2);

τ_0: yield stress (shear stress at zero shear rate);

η: plastic viscosity (slope) (cP or mPa s); D: shear rate (1/s)

That is, the slope of the fitted straight line is the viscosity and the interception at zero shear rate is the yield stress.

Photopolymerization

The VLC characteristics of the experimental oligomer blends were evaluated by differential photocalorimetry (DPC). The VLC oligomer systems were formulated as follows: BisGMA/TEGDMA/H-MMA 45/45/10 g, CQ 0.5 g, and DMAEMA 1.0 g. The control was BisGMA/TEGDMA (50/50, wt./wt.) blends having the same levels of CQ/DMAEMA. The mixtures (about 5 mg) were weighed into a small aluminum pan and exposed to visible light (argon lamp, 80 W) for 1 minute under nitrogen gas at 25°C, using a TA Instruments 930 DPC unit (TA Company, Wilmington, DE). The heat of reaction (ΔH) was calculated by employing the TA data analysis DPC 4.1A program.

Characterization of Thermal Mechanical Properties

The thermal characteristics of the unfilled VLC resins were performed by employing a thermomechanical analyzer (TMA 2940, TA Instruments, Wilmington, DE), with an expansion probe from -30 to 150°C, at a heating rate of 10°C/min under N_2. The thermal expansion coefficient (α) and the glass transition temperature (T_g) were determined from the thermogram by using the TMA Standard Data Analysis V5.1 program. The disk samples (6 mm in diameter × 3.5 mm in thickness) were first visible light-cured by using a curing units having light density 320 mW/cm^2, for a total of five minutes. The samples were then conditioned in distilled water at 37°C for two weeks. For each VLC resin, three samples were tested.

Determination of Polymerization Shrinkage

The polymerization shrinkage was obtained by measuring the density differences between uncured and cured resin test specimens. The volumetric shrinkage was calculated using the following equation:

$$\text{Shrinkage\%} = (\text{dmon}/\text{dcured} - 1) \times 100\%$$

Monomer density was measured by weighing the liquid in a calibrated micro-graduate. The VLC-cured resins were made in cylindrical and disk shapes and cured for total of five minutes. Then the specimens were stored in 3°C oven for 2 or 3 days. Their densities were obtained by the calculation of weight divided by volume. For each sample, ten specimens were tested.

Mechanical Properties

The compressive (CS, 4 mm in diameter × 6 mm in thickness), diametral tensile (DTS, 6 × 3 mm), and flexural (FS, 25 × 2 × 2 mm) strength samples were visible-light cured for a total of five minutes. After removal from the mold, the sample surface was polished by using silicon carbide paper (FEPA P# 800). All specimens were conditioned in distilled water at 37°C for one week prior to property tests.

The CS, DTS, and FS tests were carried out using a screw-driven mechanical testing machine (Model 4204, Instron Corp., Canton, MA) at 25°C, with a constant crosshead speed of 0.5 mm/min. For each resin, five samples were tested.

RESULTS AND DISCUSSION

Boltorn H-MMAs were used as modifiers for the conventional BisGMA/TEGDMA dental resin systems. There are two ways to incorporate the H-MMAs into the systems. The first is using H-MMAs replacing BisGMA while keeping the same TEGDMA amount. Another is to simply add some percentages of H-MMAs into the BisGMA/TEGDMA mixture keeping the same BisGMA/TEGDMA ratio. For these two methods, viscosities of the final mixtures were tested.

Using 10% of H-MMAs to replace BisGMA, while keeping the same TEGDMA amount, the modified mixtures have lower viscosity than the corresponding BisGMA/TEGDMA control, as indicated in Table 1. The viscosities of pure BisGMA and H-MMAs are beyond our viscometer's test range. Thus, we formulated these mixtures to compare the relative viscosity of BisGMA with H-MMAs. Although the molecular weights of Boltorn H-MMAs are several times or even ten times higher than that of BisGMA, they gave lower viscosity when replacing BisGMA, possibly due to their highly branched molecular structures. This to some extent indicated that the molecular structure is an important factor for determining the viscosity.

If some portion of H-MMAs is directly mixed into BisGMA/TEGDMA (50/50, wt/wt), the viscosity only slightly increased (Table 2). For example, 10% of H30-MMA with BisGMA/TEGDMA 50/50 has a viscosity of 1.30, compared with the control of 1.04.

Visible-light (about 468 nm in wavelenght) is now used to cure dental composites at room or oral temperature. The photo-polymerization activity of

TABLE 1. Viscosity of BisGMA/TEGDMA with the Addition of Hyperbranched Multi-Methacrylates

Mixture	Viscosity (P)	Yield Stress (Dynes/cm2)
BisGMA/TEGDMA (40/50)	0.60 (0.14)	1576 (205)
BisGMA/TEGDMA (50/50)	1.04 (0.10)	1875 (338)
(BisGMA/H20-MMA) /TEGDMA [(40/10)/50]	0.99 (0.14)	1704 (141)
(BisGMA/H30-MMA) /TEGDMA [(40/10)/50]	0.91 (0.15)	1623 (236)
(BisGMA/H40-MMA) /TEGDMA [(40/10)/50]	0.86 (0.11)	1460 (278)
BisGMA/TEGDMA (60/30)	7.04 (0.54)	3847 (348)
BisGMA/TEGDMA (70/30)	10.35 (0.93)	5590 (665)
(BisGMA/H30-MMA) /TEGDMA [(60/10)/30]	7.24 (0.48)	3930 (307)

TABLE 2. Viscosity of BisGMA/TEGDMA (50:50, wt:wt) with the Addition of H-MMAs

Mixture	Viscosity (P)	Yield Stress (Dynes/cm2)
BisGMA/TEGDMA (50/50)	1.04 (0.10)	1875 (338)
10% H20-MMA	1.29 (0.10)	2057 (184)
10% H30-MMA	1.30 (0.21)	2388 (258)
10% H40-MMA	1.20 (0.16)	2260 (188)
5% H30-MMA	1.09 (0.12)	2428 (122)
15% H30-MMA	1.42 (0.15)	2600 (50)

dental neat resins is an important parameter in influencing conversion of polymerization, mechanical properties, amount of unreacted monomers, and toxicity. DPC is often used to measure the chemical reaction or polymerization heat released by samples when they are exposed to high-density ultraviolet or visible light. It records the changes of heat during the period of light shuttling on or off. After the curve is analyzed, it provides several parameters: enthalpy, peak maximum, reacted at peak, and induction time. Enthalpy (ΔH) is the calculated actual heat of polymerization of the sample. Peak time is the time shutter opens to the point where the curve reaches its maximum value and induction time is the segment of time from the shutter opening to the point where total conversion of 1% is reached.

The ΔH, from the DPC results for the BisGMA/TEGDMA with H-MMAs modifiers subjected to visible light-curing for 1 minute at 37°C, are shown in Table 3. The ΔH for the BisGMA/TEGDMA (50/50) control was not significantly different from that of each experimental oligomer system. The ΔH values of the experimental oligomers, with different molecular weights or branched generations, are also not significantly different after light-curing for 1 minute.

The photo-polymerization characteristics of BisGMA/TEGDMA (50/50, wt/wt) modified with different portions of H30-MMA were also studied. With the addition of 5% of H30-MMA, the system has the highest ΔH, which indicates the highest photo-polymerization activity. BisGMA/TEGDMA with 10% of H30-MMA has similar activity to the control, while incorporating 15% of H30-MMA causes the polymerization activity to significantly decrease.

TABLE 3. Photo-polymerization Characteristics of BisGMA/TEGDMA (50/50, wt/wt) modified by H-MMAs

Resin	Induction Time (s)	Peak Time (s)	Enthalpy (ΔH) (J/g)	Theoretic (ΔH_0) (J/g)	Degree of Cure (%)
BisGMA/TEGDMA (50/50:wt/wt)	14.0 (0.1)	36.3 (1.5)	83.3 (8.9)	299.7	27.8
10% H20-MMA	15.2 (1.1)	37.3 (2.5)	79.0 (5.6)	320.1	24.7
10% H30-MMA	14.9 (0.8)	41.0 (1.0)	78.5 (4.6)	318.6	24.6
10% H40-MMA	12.3 (0.6)	37.2 (2.3)	79.3 (5.6)	317.8	25.0
5% H30-MMA	15.1 (2.4)	37.3 (2.5)	96.9 (1.9)	309.2	31.3
15% H30-MMA	14.2 (0.9)	44.7 (5.1)	68.4 (4.8)	328.0	20.9

BisGMA/TEGDMA 50/50 (w/w) with 0.5 wt% initiator (CQ) and 1.0 wt% co-initiator (DMAEM). Each entry is the mean value (standard deviation) for a group of five specimens (N = 5).

H-MMAs as modifiers in BisGMA/TEGDMA systems have comparable photo-polymerization activities to the BisGMA/TEGDMA, a traditional dental resin system. This implies their possible applications in dental materials. Next, the polymerization shrinkage, thermal mechanical, and mechanical properties will be evaluated for the polymerized resins.

The polymerization shrinkage data of VLC cured resins are shown in Table 4. It can be seen that H-MMAs modified resins have lower polymerization shrinkage than the BisGMA/TEGDMA control. This is in good agreement with our initial hypothesis. For different dimensions of cured resins, the extent of shrinkage showed some difference, as indicated by others [27].

Thermal mechanical analysis (TMA) is a convenient and useful tool for determining the phase transition temperatures and many other thermal properties of various materials. With TMA, the slope of the dimension change with the temperature is defined as thermal expansion coefficient (α) and the temperature at which the slope changes is taken to be the glass transition temperature (T_g). In the present study, the α and T_g of the water saturated VLC experimental and BisGMA/TEGDMA unfilled resins were determined by TMA, with the results given in Table 5.

From Table 5, before and after the T_g, thermal expansion coefficients of the BisGMA/TEGDMA control are not significantly different from those of each experimental resin with 10% of H-MMA modifiers. However, the T_g of the modified resin systems are significantly higher than that of the BisGMA control. This is mainly due to the differences in monomer compositions and structure. The Boltorn H-MMA modifiers have unique starlike (or globular) shape with multi-methacrylate functional groups on their ends. Hence, they can form more rigid cross-linking structures and impose a strong stereo restriction on the segmental motion of the polymer chains. On the other hand, the Boltorn hyperbranched

TABLE 4. Polymerization Shrinkage of BisGMA/TEGDMA and Their H-MMA Modified Neat Resins

MMA Modified Neat Resins

Shrinkage (%)	BT *	BT with 10% H20-MMA	BT with 10% H30-MMA	BT with 10% H40-MMA
Disk (15 x 2 mm)	-9.67 (0.89)	-6.49 (0.59)	-4.98 (0.72)	-4.88 (0.40)
Cylinder (4 x 7 mm)	-13.9 (0.12)	-11.5 (0.07)	-9.95 (0.58)	-9.65 (0.82)

TABLE 5. The Thermal Expansion Coefficient (α) and Glass Transition Temperature (T_g) of the Water Saturated VLC BisGMA/TEGDMA (50/50, wt/wt) Modified by H-MMAs

	Tg (°C)**	Thermal expansion coefficient** (10^{-6}/°C)	
		< Tg	> Tg
BT control *	40.18 (3.2)	63.8 (8.9)	89.3 (3.2)
10% H20-MMA	48.2 (6.4)	60.0 (5.8)	93.9 (0.2)
10% H30-MMA	44.6 (1.1)	56.8 (0.9)	89.9 (4.7)
10% H40-MMA	42.1 (2.9)	55.0 (3.2)	88.0 (2.2)
5% H30-MMA	48.5 (3.2)	59.2 (1.3)	91.4 (3.4)
15% H30-MMA	45.1 (4.9)	54.9 (1.3)	85.7 (2.5)

*BT = BisGMA/TEGDMA 50/50 (wt/wt) with 0.5 wt% initiator (CQ) and 1.0 wt% co-initiator (DMAEMA), with 0, 5, 10, and 15% of H-MMAs.

** Resin specimens (6.0 mm in diameter × 3.5 mm in thickness) were conditioned in distilled water at 37°C for two weeks prior to characterization by TMA. Each entry is the mean value (standard deviation) for a group of four specimens (N = 4).

polymers have aliphatic polyester segments, which are known as soft molecular chains. As a result, the magnitude of the increase in T_g of the experimental resins is not as large as expected. With addition of 5% to 15% of H30-MMA into the BisGMA/TEGDMA (50/50) system, all of them have higher T_g than the BisGMA/TEGDMA control (Table 5).

Compressive (CS), diametral tensile (DTS), and flexural (FS) strengths are important properties for restorative dental materials. They are considered relevant because the restorative materials must withstand biting forces under *in vivo* condition. The measured values of CS for the water saturated or wet VLC experimental and BisGMA neat resins are shown in Tables 6, with the DTS and FS values shown in Table 7.

It can be seen from Table 6, H-MMAs modified BisGMA/TEGDMA neat resins have significantly higher CS than the control. They also have higher modulus and energy to break. Comparing the Boltorn types, H30-methacrylate shows the best results in modification of the BisGMA/TEGDMA control. This may partly be due to the suitable balance between the molecular weight and viscosity. For H40-MMA, its molecular weight is about 7300 and viscosity is relative higher. Hence it is not as good as H30-MMA.

The effect of modifying the BisGMA/TEGDMA neat resin with hyperbranched multi-methacrylate can be further studied by addition of different portions of H30-MMA (Table 6). The addition of only 5% of H30-MMA can increase the compressive strength, modulus, and energy to break, although these increases are not statistically significant. With the addition of 10% of H30-MMA, the compressive strength increases over 15% above the BisGMA/TEGDMA control. Adding H30-MMA at the level of 15% level fails to produce properties as good as the 10% addition, although the properties are still better than the control. It seems that the addition of 10% of H30-MMA is the appropriate portion to use.

Since dental resins fail by crack propagation, the material is generally much weaker in tension than in compression, which may contribute to failure of the material in service. Therefore, measurement of TS is considered necessary. For relatively brittle dental resins, the DTS is generally measured, rather than using the uniaxial tension test, because it is difficult to prepare samples and to obtain uniform results. However, if the specimen deforms before failure or fractures into more than two equal pieces, the data may not be valid. In this study, the neat resins failed with somewhat permanent deformation under the diametral compressive test. Hence, the DTS data were only used for relative comparison.

H-MMA modified resins have higher DTS than the BisGMA/TEGDMA (50/50, wt/wt) control (Table 7). H-MMA with higher molecular weight tends to have higher DTS, i.e., H40-MMA > H30-MMA > H20-MMA, BisGMA.

The DTS of BisGMA/TEGDMA (50/50) with different portion of Boltorn H30-MA is also shown in Table 7. The addition of only 5% of H30-MMA produces no changes. Adding 10% of H30-MMA to the control provides the highest DTS. Again, the data suggest that addition of 10% of H30-MMA is an appropriate ratio. This result agrees with the result from the CS testing.

Three-point bending was also used to test the FS of the neat resins. The modified resins containing 10% H20-MMA and H30-MMA showed higher FS than the BisGMA/TEGDMA control (Table 7).

For both the CS and FS tests, H-MMA modified resins showed less strain or deflection, further confirming they may form higher cross-linked resins.

TABLE 6. Compressive Strength of BisGMA/TEGDMA (50/50, wt/wt) modified by H-MMAs

	CS (MPa)**	Modulus (GPa)	Energy to Break (MPa)	Strain (%)
BT control *	497.1 (16.1)	3.16 (0.11)	5.90 (0.15)	15.6 (0.1)
10% H20-MMA	512.3 (41.7)	3.22 (0.27)	6.04 (0.43)	15.7 (0.2)
!0% H30-MMA	575.6 (67.7)	3.54 (0.40)	6.73 (0.63)	16.1 (0.1)
10% H40-MMA	552.1 (9.1)	3.37 (0.06)	6.59 (0.12)	16.2 (0.2)
5% H30-MMA	512.7 (64.8)	3.18 (0.37)	6.08 (0.70)	15.9 (0.2)
15% H30-MMA	522.7 (54.7)	3.20 (0.32)	6.15 (0.62)	16.2 (0.3)

*BT = BisGMA/TEGDMA 50/50 (w/w) with 0.5 wt% initiator (CQ) and 1.0 wt% co-initiator (DMAEM).

**Resin specimens (3.3 in diameter× 6.6 mm in thickness) were conditioned in distilled water at 37°C for one week prior to test. Each entry is the mean value (standard deviation) for a group of five specimens (N = 5).

TABLE 7. Diametral Tensile and Flexural Strength of BisGMA/TEGDMA (50/50, wt/wt) modified by H-MMAs

	DTS (MPa) **	Strain (%)	FS (MPa) **	Deflection (mm)
BT control *	43.4 (3.2)	47.3 (3.0)	76.9 (10.1)	1.8 (0.3)
10% H20-MMA	43.4 (3.3)	44.1 (4.1)	85.6 (7.1)	1.8 (0.3)
10% H30-MMA	46.5 (4.3)	46.2 (5.2)	84.5 (2.9)	1.7 (0.1)
10% H40-MMA	47.5 (1.4)	43.4 (1.9)	73.9 (10.0)	1.5 (0.3)
5% H30-MMA	43.5 (4.9)	44.2 (6.1)	----	---
15% H30-MMA	45.4 (3.4)	43.8 (11.4)	----	---

*BT = BisGMA/TEGDMA 50/50 (w/w) with 0.5 wt% initiator (CQ) and 1.0 wt.% co-initiator (DMAEM).

**Resin specimens, 6.0 mm in diameter× 3.0 mm in thickness for DTS and 25 x 2 x 2 mm for FS, were conditioned in distilled water at 37°C for one week prior to test. Each entry is the mean value (standard deviation) for a group of five specimens (N = 5).

CONCLUSION

The synthesized hyperbranched multi-methacrylates readily mix with monomers or dimethacrylates commonly used in dental composite formulations, such as the BisGMA/TEGDMA mixture, without significantly increasing the viscosity at the level of 10% percent. The modified VLC neat resins have comparable visible light-curing characteristics and lower polymerization shrinkage.

H-MMAs (10%) modified neat resins showed a 15% increase in mechanical strength including compressive, diametral, and flexural strengths, compared to the BisGMA/TEGDMA control. In addition, the modified resins have slightly higher glass transition temperatures.

Future studies will include water sorption, the amount of leachable ingredients, creep and biocompatibility tests. Moreover, the modified mixtures will be modified with suitable fillers to form composites and their properties will be tested.

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