Polymeric materials for composite matrices in biological environments*

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Bifunctional monomers of new formulations have been synthesized and tested for potential use in dental composite filling materials. The monomers were designed to have lower viscosity than the standard basic monomer, thus requiring less dilution with low molecular weight monomer to achieve useful viscosities. It was hypothesized that the presence of the diluent is a main source of adverse effects on curing shrinkage and water sorption. The new materials were diluted to viscosities equivalent to commercial blends and tested for curing shrinkage, water sorption and wetting ability. Shrinkage was determined from the density differences between monomers and polymers, and polymer water sorption was determined gravimetrically. Wetting ability was measured by contact angle against human dentin and enamel as well as poly(methyl methacrylate) and glass. The newly synthesized monomers did exhibit reduced viscosity and required less dilution. They exihibited less curing shrinkage and water sorption. The contact angles showed little change from current materials.

(Keywords: composite matrix; monomers; polymeric materials)

INTRODUCTION

Composite materials based on crosslinked polymers are widely used as biomedical materials[1–4]. Among the most challenging applications is their use for the restoration of teeth[5,6]. Monomers for this use must be non-toxic and capable of rapid polymerization in the presence of oxygen and water, because the restorations are polymerized *in situ*. The products are expected to have optical and mechanical properties comparable to tooth enamel and dentin and to provide a service life of 10 years or more. Current 'dental composites' consist of three essential components: a crosslinked polymeric matrix, a high volume fraction of a particulate silicate filler, and a bonding agent to promote matrix–filler adhesion[7–9]. The most commonly used matrix component is 2,2-bis-(4-(2-hydroxy-3-methacryloxyprop-1-oxy)phenyl)propane (BIS-GMA), see *Figure 1a*. The filler is usually a combination of a finely divided crushed silicate glass and colloidal silica, while the bonding agent is a modified vinyl silane.

As long as bonding between the matrix and filler is adequate, and the quantity of the matrix is sufficient to fill the space between the filler particles, increased filler content tends to improve mechanical properties and to reduce curing shrinkage and the thermal expansion coefficient. Since the amount of filler which can be incorporated is limited by the viscosity of the resultant pastes, it is customary to dilute the highly viscous (~1200 Pa s) BIS-GMA with more fluid difunctional monomers[10,11]. The added diluent monomers tend to adversely affect the properties of the matrix material, increasing water sorption and curing shrinkage. As a result, it would be very beneficial to find less viscous substitutes for BIS-GMA which would reduce the need for diluents.

In this study, two potential substitute monomers were prepared, both of which were structural analogues of BIS-GMA (*Figure 1a*): CH_3 BIS-GMA (*Figure 1b*) and 3F BIS-GMA (*Figure 1c*). The effects of dilution of these base monomers (*Figures 1a* and *c*) with triethylene glycol dimethacrylate monomer (TEGDM) (*Figure 1d*) was evaluated. Properties of the base monomers, and of blends diluted to constant viscosity with TEGDM, were measured.

EXPERIMENTAL

Materials

The BIS-GMA and TEGDM monomers used in this study were obtained from Polysciences Inc. (Warrington, PA, USA) and were used as received.

Tetrahydrofuran (THF) (Fisher) was used as received for propoxylation reactions or distilled from a sodium dispersion for methacrylation. Bisphenols (bisphenol-A (Dow Chemical) and 3F-bisphenol[12]) were used as received. Propylene oxide (ARCO) and triethylamine (Fisher) were fractionally distilled from CaH_2 under an argon blanket

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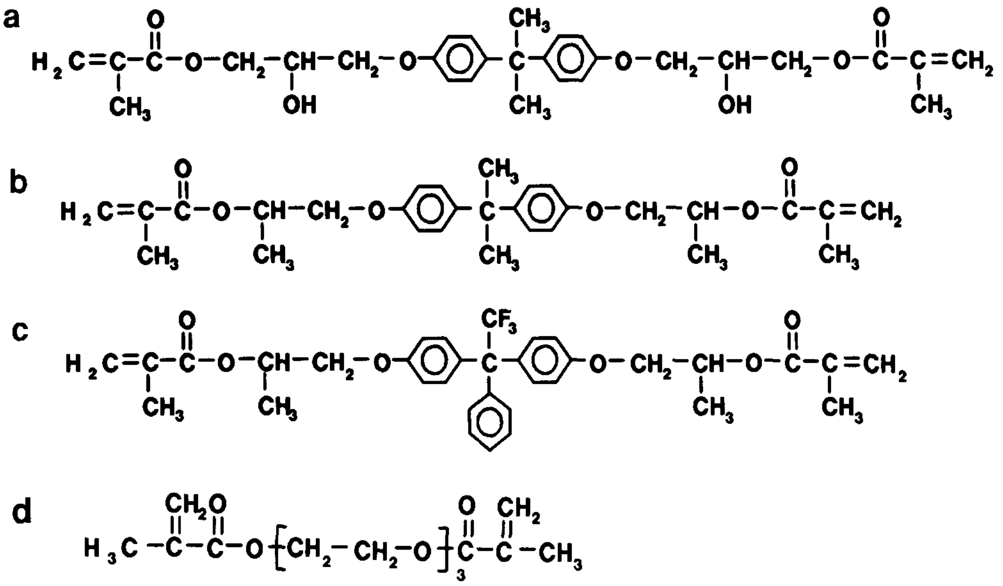

Figure 1 Structure of (a) 2,2-bis(4-(2-hydroxy-3-methacryloxyprop-1-oxy)phenyl)propane (BIS-GMA); (b) 2,2-bis(4-(2-methacryloxyprop-1-oxy)phenyl) propane (CH_3 BIS-GMA); (c) 1,1,1-trifluoro-2,2-bis(4-(2-methacryloxyprop-1-oxy)phenyl)-2-phenyl ethane (3F BIS-GMA); (d) triethylene glycol dimethacrylate (TEGDM)

prior to use. Methacryloyl chloride (Aldrich) was distilled under reduced pressure and stabilized with 150 ppm phenothiazine.

Characterization

^1H n.m.r. characterization was done on a Varian Unity 400 (400 MHz) in deuterochloroform solvent (~5% w/v). A 7.24 ppm chloroform chemical shift was used as the internal reference.

Propoxylated bisphenol-A(2,2-bis(4-(2-hydroxyprop-1-oxy)phenyl)propane)

To a clean, dry, one-necked 3 litre round-bottomed flask equipped with a magnetic stir bar was added 900 ml of THF and 250 ml of deionized water. Bisphenol-A (228.3 g, 1 mol) was then added followed by addition of sodium hydroxide (16 g, 0.4 mol). A septum was placed on the flask and the slurry was stirred under 55.16 kPa argon atmosphere until the contents of the reaction vessel were homogeneous. Propylene oxide (270 ml, 232 g, 4 mol) was added to the flask via syringe, and the reaction vessel was immersed in a water bath maintained at 40°C and stirred for 24 h. Quantitative conversion was evidenced by the complete disappearance of the aromatic resonances (AB) centred at 6.79 and 7.05 ppm and the appearance of the shifted pattern at 6.70 and 7.12 ppm in ^1H n.m.r.

The reaction mixture was then neutralized with concentrated HCl (48 ml, 0.48 mol). Upon neutralization, the contents of the vessel separated into two homogenous layers. The solvent was removed from the organic layer by rotary evaporation, and the crude product dissolved in diethyl ether. The aqueous layer was separated and extracted twice with ether. The combined ether layers were then extracted twice with water and twice with NaCl (aqueous, saturated), dried over $MgSO_4$ and the solvent stripped by rotary evaporation. The major side-product of the reaction, propylene glycol, was stripped in a Kugelrohr apparatus at 130°C and ~26.7 Pa pressure. The crystalline product (crystallized over a 2 week period, m.p. 98–99°C) was isolated in a 95% yield.

Propoxylated 3F-bisphenol (1,1,1-trifluoro-2,2-bis(4-(2-hydroxyprop-1-oxy)phenyl)-2-phenyl ethane)

To a clean, dry, three-necked 500 ml Morton flask with two necks septum sealed and equipped with a magnetic stir bar was added 250 ml of THF and 60 ml of deionized water. 3F-bisphenol (59.5 g, 0.173 mol) was then added followed by addition of sodium hydroxide (2.77 g, 0.069 mol). A septum was placed on the open neck and the slurry was stirred under 55.16 kPa argon atmosphere until the contents of the reaction vessel were homogenous. Propylene oxide (47 ml, 40.2 g, 0.69 mol) was added to the flask via syringe, and the reaction vessel was immersed in a water bath maintained at 40°C and stirred for 48 h. The shift of aromatic protons in ^1H n.m.r. was again used to indicate reaction completion.

The reaction mixture was then neutralized with concentrated HCl (8.3 ml, 0.083 mol). Upon neutralization, the contents of the vessel separated into two homogenous layers. The solvent was removed from the organic layer by rotary evaporation, and the crude product dissolved in diethyl ether. The aqueous layer was separated and extracted twice with ether. The combined ether layers were then extracted twice with water and twice with NaCl (aqueous, saturated), dried over $MgSO_4$ and the solvent stripped by rotary evaporation. The major side-product of the reaction, propylene glycol, was stripped in a Kugelrohr apparatus at 130°C and ~26.7 Pa pressure. The solid, amorphous product was isolated in a 90% yield.

Methacrylation of propoxylated bisphenol-A (2,2-bis(4-(2-methacryloxyprop-1-oxy)phenyl)propane)

To a clean, flame-dried, three-necked 3 litre round-bottomed flask fitted with overhead stirring, a water condenser, a pressure equilibrated addition funnel, thermometer and a dry argon atmosphere, was added 1700 ml of THF. Propoxylated bisphenol-A (344. g, 0.93 mol) was then dissolved in the THF. Triethylamine (263 ml, 226 g, 2.24 mol) was added through the addition funnel. A water/ice bath was placed around the reaction vessel and stirring was begun. Methacryloyl chloride (220 ml, 234 g, 2.24 mol) was added dropwise to the flask through the addition funnel at a rate such that the temperature of the reaction mixture was maintained at less than 50°C. After addition of all the acid chloride, the water/ice bath was removed and the contents of the reaction vessel were stirred for an additional 18 h. At this time the triethylamine hydrochloride salts were removed by filtration. The THF was then stripped by rotary evaporation under reduced pressure, and the crude product was purified by column chromatography (silica gel) using chloroform as eluent. Attempts at purification by crystallization, extraction and distillation were not successful.

Methacrylation of propoxylated 3F-bisphenol (1,1,1-trifluoro-2,2-bis(4-(2-methacryloxyprop-1-oxy)phenyl)-2-phenyl ethane)

To a clean, flame-dried, three-necked 500 ml Morton flask fitted with overhead stirring, a water condenser, a pressure equilibrated addition funnel, thermometer and a dry argon atmosphere, was added 350 ml of THF. Propoxylated 3F-bisphenol (71.5 g, 0.155 mol) was then dissolved in the THF. Triethylamine (44 ml, 37.7 g, 0.37 mol) was added through the addition funnel. Stirring was begun and methacryloyl chloride (36.4 ml, 39 g, 0.37 mol) was added to the flask at a rate such that the temperature of the reaction mixture was maintained at less than 50°C. After addition of all the acid chloride, the contents of the reaction vessel were stirred for an additional 18 h. At this time the triethylamine hydrochloride salts were removed by filtration. The THF was then stripped by rotary evaporation under reduced pressure, and the crude product was purified by column chromatography (silica gel) using a dichloromethane eluent.

Monomer viscosity adjustment

The viscosity of the matrix-forming monomers has a controlling effect on the amount of filler that can be mixed into a composite, and thus on the properties of the resultant material. Therefore the properties of BIS-GMA and the two experimental monomers were compared at equal viscosities.

A preliminary investigation indicated that the viscosity of the uncured matrix of commercial dental composites was in the range of 1–2 Pa s.

BIS-GMA and TEGDM were mixed in various proportions up to about 35 wt% of TEGDM (*Table 1*). Similarly, mixtures of 3F BIS-GMA and TEGDM, up to about 28%, were prepared (*Table 1*). The amounts of TEGDM required to produce useable viscosities of 1–2 Pa s were determined from viscosity *versus* dilution curves and are shown in *Table 1*. The viscosity of the CH_3 BIS-GMA monomer was less than 1 Pa s and thus no dilution was required.

Monomer characterization

Each base monomer and each base monomer–TEGDM blend was characterized for a series of properties. The properties measured were viscosity, density, curing shrinkage, water uptake and contact angle against dentin, enamel, glass and poly(methyl methacrylate) (PMMA). Each standard dilution was evaluated for curing shrinkage and wetting ability against surfaces encountered in use. Densities of the monomers were determined pycnometrically. Contact angle measurements were made for each of the monomers when applied to dentin, enamel, PMMA and glass surfaces. The method previously reported[13] used a Rome–Hart contact angle goniometer (model 100-00).

Polymerization

A 10 ml sample of each monomer and comonomer mixture was polymerized in a 15 ml test tube by 6 h exposure to a Cs γ-ray source (dose rate = 0.8 Mrad h^{-1}) at 35°C in a nitrogen atmosphere. Density of monomers was measured pycnometrically. Polymer density was measured by hydrostatic weighing. The density difference between the polymer and the monomer was used to determine the curing shrinkage. Water uptake by the polymers was determined gravimetrically. These procedures are described in detail in previous publications[6,13–15].

RESULTS AND DISCUSSION

Figure 2 shows the observed relationships of viscosity to TEGDM content for BIS-GMA and 3F BIS-GMA. These curves were used to select compositions with viscosity of 2 and 1 Pa s. The monomer formulations and viscosities are summarized in *Table 1*. As anticipated, replacement of the pendent–OH groups in BIS-GMA (*Figure 1a*) by $-CH_3$ groups resulted in less viscous monomers, and the CH_3 BIS-GMA (*Figure 1b*) with a smaller central group was less viscous than 3F BIS-GMA (*Figure 1c*). As the content of TEGDM increased, viscosities of the BIS-GMA and 3F BIS-GMA blends decreased (*Figure 2*). The amounts of TEGDM required to produce useable viscosities (2 and 1 Pa s) were relatively less (6.5 and 14.0%) for 3F BIS-GMA than for BIS-GMA (27.5 and 33.5%) (*Table 1* and *Figure 2*).

The monomer compositions and their contact angles on various surfaces are also shown in *Table 1*. Decreases in contact angle values were observed with increases in the proportion of TEGDM on all surfaces, suggesting an improved wetting ability. However, from these results it cannot be determined whether this is due to reduced viscosity alone or composition shifts resulting from the dilution. It is seen that at any given value of viscosity, all the monomers exhibited lower contact angles on dentin than on enamel and on PMMA than on glass.

Table 1 Monomer formulations and contact angles

Monomer	Viscosity (Pa s)	TEGDM (%)	Contact angle (deg)			
			Glass	PMMA	Enamel	Dentin
BIS-GMA	2	27.5	26	17	26	16
BIS-GMA	1	33.5	16	9	18	11
3F BIS-GMA	2	6.5	31	28	24	18
3F BIS-GMA	1	14.0	23	18	19	12
CH_3 BIS-GMA	0.321	–	19	14	16	11

These observations are not readily rationalized on the basis of hydrophilicity.

The final composite materials in use in dentistry are normally polymerized by the addition of a photosensitive initiation system such as camphoroquinone (0.19%) and dimethyl aminoethyl methacrylate (0.12%) as described in a previous study[14]. Such mixtures can be polymerized by exposure to intense, short wavelength visible light. This process is suitable for the polymerization of small clinical restorations, but not well suited to uniform initiation for some of the larger specimen designs required for mechanical testing. In anticipation of such testing as a logical future step and in the interest of consistent techniques, this investigation chose to conduct polymerization by a method suitable for the larger specimens.

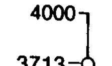

Figure 2 Variation of viscosities of BIS-GMA and 3F BIS-GMA with content of TEGDM. (Viscosity values are in centipoise; 1 cP = 10^{-3} Pa s)

Table 2 Some relevant properties of polymers

Material	Density at 25°C ($g\,cm^{-3}$) M	Density at 25°C ($g\,cm^{-3}$) P	Shrinkage (%)	Contact angle W/P (deg)	Water uptake (%)
BIS-GMA	1.1521	1.2308	6.39	88	3.05
3F BIS-GMA	1.1893	1.2585	5.35	64	0.91
CH_3 BIS-GMA	1.1047	1.1948	7.53	58	0.92

M, monomer; P, polymer; W, water

Densities of the undiluted base monomers (M) and their corresponding polymers (P) at 25°C, the calculated polymerization shrinkage, contact angle for water on polymer, and percentage water uptake by polymers are summarized in *Table 2*. Analysis of the data in *Table 2* reveals that pure CH_3 BIS-GMA and 3F BIS-GMA polymers sorbed relatively far less water (0.9%) than BIS-GMA (3.05%). This was anticipated from the incorporation of relatively hydrophobic $-CH_3$ and $-CF_3$ groups instead of hydrophilic –OH. These observations conform to the pattern of reduced water sorption with decreasing oxygen content previously observed[14].

The effect of dilution with TEGDM on the curing shrinkage of these monomers as well as the effect of the structural changes on both viscosity and shrinkage are shown in *Table 3*. As expected, replacement of the pendent OH group in BIS-GMA by $-CH_3$ resulted in less viscous monomers. This is consistent with the suggestion that the high viscosity of pure BIS-GMA is the result of intermolecular hydrogen bonding[13], rather than the result of oligomer formation[16].

The structure of the CH_3 BIS-GMA represents a single structural change from BIS-GMA but results in a viscosity so low that no dilution is required. At the same time the curing shrinkage exceeds that of BIS-GMA (7.5% *versus* 6.4%) but is still lower than that of the most viscous useable diluted composition (7.5% *versus* 8.2%).

The structure of the 3F monomer (*Figure 1c*) is a modification of CH_3 BIS-GMA (*Figure 1b*) with the substitution of $-CF_3$ and a phenyl ring for the central CH_3 groups. This bulkier structure is more viscous than CH_3 BIS-GMA but shrinks less. Because less dilution with TEGDM is required to reach the desired viscosity, this monomer has much lower shrinkage (5.8% *versus* 8.2%) than the BIS-GMA blends of the same viscosity. Adding TEGDM to either BIS-GMA or 3F BIS-GMA results in increased shrinkage (*Table 3*), as would be expected from the high inherent shrinkage of TEGDM[9,11]. To a first approximation, the shrinkage appears to be linearly related to the amount of diluent added.

CONCLUSIONS

1. The experimental CH_3 BIS-GMA and 3F BIS-GMA monomers did exhibit lower viscosity than BIS-GMA.

Table 3 Effect of TEGDM dilution on curing shrinkage

Monomer	Undiluted Viscosity (Pa s)	Undiluted Water sorption (%)	Undiluted Shrinkage (%)	Diluted to 2 Pa s TEGDM (%)	Diluted to 2 Pa s Shrinkage (%)	Diluted to 1 Pa s TEGDM (%)	Diluted to 1 Pa s Shrinkage (%)
BIS-GMA	1200	3.05	6.4	27.4	8.2	33.5	8.3
3F BIS-GMA	3.713	0.92	5.4	6.5	5.8	14.0	6.3
CH_3 BIS-GMA	0.321	0.91	7.5	–	–	–	–
TEGDM	0.011	6.0	11.9	–	–	–	–

2. The experimental polymers had lower contact angles for water and lower water sorption than BIS-GMA.
3. TEGDM reduced the viscosity of both BIS-GMA and the fluorine-containing analogue 3F BIS-GMA. The effect on the viscosity of CH_3 BIS-GMA was not evaluated due to its low initial viscosity.
4. Increasing TEGDM reduced the contact angle of the monomer blends on all surfaces. In general, contact angles of the monomers on the test surfaces increased in the sequence: dentin, PMMA, enamel, glass.
5. To a first approximation, the polymerization shrinkage varies monotonically with the amount of diluent (TEGDM) added (*Table 3*).

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REFERENCES

1 Phillips, R. W. 'Skinner's Science of Dental Materials', 9th Edn, Saunders, Philadelphia, 1982

2 Craig, R. G. (Ed.) 'Restorative Dental Materials', 6th Edn, C. V. Mosby Company, St. Louis, 1980

3 Greener, E. H., Harcourt, J. K. and Laurenschlager, E. P. 'Materials Science in Dentistry', Williams and Wilkins Company, Baltimore, 1972

4 Turner, D. T., Haque, Z. U., Kalachandra, S. and Wilson, T. W. in 'Cross-linked Polymers: Chemistry, Properties and, Applications', (Eds R. A. Dickie, S. S. Labana and R. S. Bauer), American Chemical Society Reprints Series 367, Washington, DC, 1988, pp. 427–438

5 Taylor, D. F. and Leinfelder, K. F. (Eds.) 'Posterior Composites: Proceedings of an International Symposium', University of North Carolina, Chapel Hill, 1982

6 Kalachandra, S. and Wilson, T. W. *Biomaterials* 1992, **13**, 105

7 Braem, M. Doctoral Thesis, University of Leuven, Belgium, 1985

8 American Dental Assoc. (CDMIE), *J. Am. Dental Assoc.* 1986, **112**, 707

9 Roulet, J. F. 'Degradation of Dental Polymers', Karger, Basel, 1987

10 Braden, M. *Oper. Dent.* 1978, **3**, 97

11 Davy, K. W. M. and Braden, M. *Biomaterials* 1991, **12**, 406

12 Grubbs, H. J. PhD Thesis, Virginia Polytechnic Institute and State University, 1992

13 Kalachandra, S. and Kusy, R. P. *Polymer* 1991, **32**, 2428

14 Kalachandra, S. and Turner, D. T. *J. Biomed. Mater. Res.* 1987, **21**, 329

15 Kalachandra, S. and Turner, D. T. *Polymer* 1987, **28**, 1749

16 Cowperthwaite, G. F., Kregg, C. R. and Higby, L. M. *J. Dent. Res.* 1991, **70**, 294