Synthesis of fluorinated Bis-GMA and its use with other fluorinated monomers to formulate hydrophobic composites

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SUMMARY Fluorinated Bis-GMA was synthesized and used with other commercially available fluorinated monomers and diluents to prepare hydrophobic composites. The composites were formulated as one-paste systems and were polymerized using blue light. Mechanical properties and water-related qualities were determined. Fluorination generally improved the hydrophobicity of the composites, but there was no clear-cut effect on mechanical properties.

Introduction

The majority of current dental composites are based on a Bis-GMA or urethanedimethacrylate system that are reinforced with up to 80% by weight of silanted inorganic fillers. These composites have been shown by numerous investigators to have substantially improved physical and mechanical properties compared to unfilled acrylic materials (Vanherle & Smith, 1985; Craig, 1993). However, even with enamel etching and the use of bonding agents, penetration of oral fluids at the margins and boundaries of composite restorations with tooth structure occurs (Douglas, Chen & Craig, 1980).

The use of highly hydrophobic composites was shown (Douglas, Craig & Chen, 1979) to inhibit capillary penetration of water at the tooth–composite interface. They used octafluoropentylmethacrylate with a Bis-methacrylate with no hydroxyl groups to formulate their hydrophobic composites, since fluorine-containing polymers have low surface energy and are highly hydrophobic. Fluorinated Bis-GMA was not used since it was not commercially available. Unfortunately, the low molecular weight and large amount of fluorinated monomer needed resulted in a larger than desired polymerization shrinkage.

The objective of this study was to synthesize fluorinated Bis-GMA in order to formulate highly hydrophobic restorative composites, and to evaluate their mechanical and water-related properties.

Materials and methods

Materials

Bis-GMA and triethyleneglycoldiacrylate were obtained from Esschem*, and zirconium silicate was supplied by 3M†. 2,2-Bis (4-hydroxyphenyl)-hexafluoropropane (Bis-phenol F) was purchased from PCR‡. Bis-phenol A diacrylate (Bis-DA), Bis-phenol A dimethacrylate (Bis-DMA), hexafluoro-Bis-phenol A diacrylate (HF Bis-DA), hexafluoro-Bis-phenol A dimethacrylate (HF-Bis-DMA), 1,6-hexamethylene-diol-1,6-diacrylate (HMDA), 1,6-hexamethylene-diol-1,6-dimethacrylate (HMDMA), 2,2,3,3,4,4,5,5-octafluorohexamethylenediol-1,6-diacrylate (OFHMDA), and 2,2,3,3,4,4,5,5-octafluorohexamethylenediol-1,6-dimethacrylate (OFHMDMA) were purchased from Monomer Polymer Laboratories§. Camphoroquinone (CQ), glycidyl methacrylate (GMA), tetrabutylammonium chloride (Bu₄N⁺Cl⁻) and 2-dimethylaminomethylmethacrylate

(DMAMA) were bought from Aldrich*. 3-methacryloxypropyltrimethoxysilane (MAOPTMS) was obtained from Hüls†.

Synthesis of Bis-F-GMA

Bis-phenol F (6·72 g or 20 mmol), GMA (5·68 g or 40 m mol), toluene (20 g) and $Bu_4N^+Cl^-$ (0·085 g) were placed in a 250 ml, 3-neck flask equipped with a mechanical stirrer, a condenser, a thermometer and a N_2 gas inlet. The flask was flushed with N_2 and heated slowly to 105°C (reflux temperature of toluene) and held at this temperature for 4 h. The solution became light brown in colour during the reaction. The product was precipitated from hexane and was vacuum evaporated at room temperature (24°C) for 2 days.

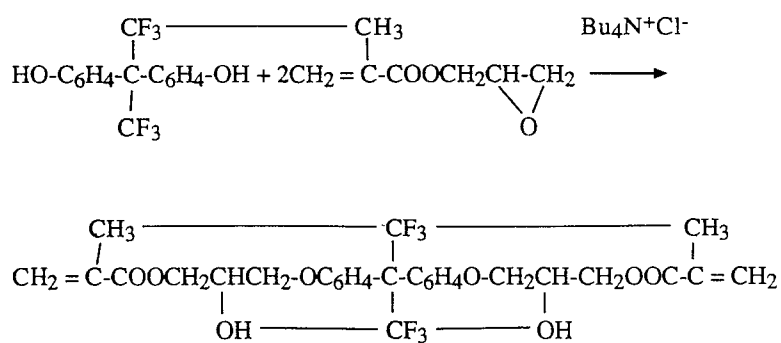The reaction of Bis-phenol F and GMA was as shown in Fig. 1.

Fig. 1. The reaction of Bis-pherol F and GMA.

Initially, the reaction was carried out in the presence of hydroquinone to prevent polymerization of the oligomer. However, this resulted in a dark coloured product and the hydroquinone residue was difficult to remove. When the reaction was run at the reflux temperature of toluene with no radical trappers present, the reaction proceeded smoothly with no polymerization of the oligomer.

The product showed only one peak by gas chromatography. Mass spectrometer results were as follows: $M^+(10) = 620$; M^+-GMA (35) = 478; M^+-2GMA (28) = 336; $M^+-2GMA-CF_3$ (50) = 267; $GMA^+ + 1$ (100) = 143. Nuclear magnetic resonance results were: $CH_2 = : 5·10$, 6·20; $CH_3 : 2·00$, $COOCH_2 : 4·35$, CH: 3·65, $CH_2OPh : 4·05$, $C_6H_4 : 6·90$, 7·40. Infra-red analysis showed: 1640 cm^{-1} (C = C), 1600 cm^{-1} (benzene), 1750 cm^{-1} (C = O), 3400 cm^{-1} (OH). Elemental analysis showed C = 55·68% (calc. 56·12%) and H = 4·86% (calc. 5·20%).

Specimen preparation and testing

Composites were formulated using oligomers, diluents, initiator system, and silanated ZrSi filler. Silanation of ZrSi was carried out with MAOPTMS in the presence of ethanol for 90 min using 3× the monolayer coverage (Mohsen & Craig, 1995). The oligomer to diluent ratio was 70/30 and the filler/organic ratio was 80/20. CQ/DMAMA was used as the initiating system with visible light curing (Douglas *et al.*, 1979).

The diametral tensile strength specimens were 0·6 cm diameter and 0·3 cm thick. The composites were polymerized in the mould with a clinical light for 90 s and then in a visible light box for 1 h. The replication number was five.

Specimens for water sorption, solubility and contact angle were made in 2·0 cm diameter × 0·2 cm thick molds and cured in the same way as the tensile strength specimens. No inorganic filler was used for the contact angle specimens. Tests were conducted according to American Dental Association Specification No. 27 (1989). The replication number was five.

Results

Composites containing Bis-F-GMA

Bis-F-GMA did not mix well with the various diluents and it was necessary to use it in combination with Bis-GMA at a ratio of 1/1. The formulations used of Bis-F-GMA and Bis-GMA and for Bis-GMA alone are listed in Table 1 along with their tensile strengths, and water sorptions and solubilities.

Sample 2 with the fluorine-containing oligomer and diluent had the lowest water sorption and solubility but with some sacrifice of tensile strength compared to the composite with Bis-GMA alone.

The contact angles of water for polymer samples without filler, but of the remaining composition similar to samples 1,2 and 3 were 60°, 65° and 50°, respectively, illustrating the effect of the presence of fluorine in both the oligomer and diluent.

Effect of fluorinated diluents on Bis-GMA composites

The compositions and properties of Bis-GMA-based composites formulated with two fluorinated and two non-fluorinated diluents in the ratio of Bis-GMA to diluent of 70/30 are listed in Table 2. The composites

Table 1. Formulations and properties of Bis-F-GMA and Bis-GMA composites

	Sample		
	1	2	3
Component, g			
Bis-F-GMA	0·693	0·693	0
Bis-GMA	0·693	0·693	1·386
ZrSi	8·0	8·0	8·0
TEGDMA	0·594	0·297	0·594
OFHDDA	0	0·297	0
CQ	0·152	0·152	0·152
DMAMA	0·01	0·01	0·01
Property			
Diametral tensile strength, kg/cm^2	369 (39)	449 (47)	515 (47)
Water sorption			
mg/cm^2	1·0	0·7	1·1
%	0·60 (0·02)	0·42 (0·02)	0·71 (0·03)
Water solubility			
mg/cm^2	0·03	0·05	0·10
%	0·02 (0·01)	0·03 (0·01)	0·06 (0·01)

Table 2. Compositions and properties of Bis-GMA composites containing fluorinated and non-fluorinated diluents

	Sample			
	4	5	6	7
Component, g				
Bis-GMA	2·772	2·772	2·772	2·772
HMDMA	1·088	0	0	0
HMDA	0	1·088	0	0
OFHMDMA	0	0	1·088	0
OFHMDA	0	0	0	1·088
ZrSi	16·0	16·0	16·0	16·0
CQ	0·03	0·03	0·03	0·03
DMAMA	0·015	0·015	0·015	0·015
Property				
Diametral tensile strength kg/cm^2	432 (27)	505 (41)	443 (33)	526 (38)
Water sorption				
mg/cm^2	0·83	0·76	0·69	0·69
%	0·53 (0·03)	0·50 (0·03)	0·43 (0·02)	0·43 (0·02)
Water solubility				
mg/cm^2	0·10	0·09	0·07	0·07
%	0·07 (0·02)	0·06 (0·02)	0·05 (0·02)	0·05 (0·02)

formulated with fluorinated diluents had lower water sorption and solubility than those non-fluorinated diluents, however, there was no trend with respect to tensile strength. Composites formulated with OFHMDA diluent had the highest tensile strength followed by those containing HMDA, OFHMDMA and HMDMA. These data suggest that the diacrylate diluents may be superior to the dimethacrylate diluents.

Effect of fluorinated comonomers on Bis-GMA composites

OF Bis-DA and OF Bis-DMA are solids at room temperature (24°C) and did not dissolve in diluents such as HMDA and TEGDA. Thus, they were used as comonomers with Bis-GMA (OF Bis-DMA/OF Bis-DA/Bis-GMA of 1/ 1/2). Their non-fluorinated analogues, Bis-DMA and Bis-DA were used in the same formulation ratio for

comparison. The composition and properties of composites formulated with these comonomers are listed in Table 3.

Sample 8 was formulated with non-fluorinated resins and diluents. Sample 9 had fluorinated diluents added, while sample 10 used fluorinated oligomers as part of the resin. Sample 11 was formulated with both fluorinated oligomers and diluents. The water sorption and solubility of samples (9 and 11) containing fluorinated compounds were lower than those without. The contact angle for sample 8 without filler was 65° compared to 80° for the formulations containing fluorinated diluent (sample 8) and to 70° for formulations containing fluorinated oligomers (samples 10 and 11). Samples containing fluorinated diluents (samples 9 and 11) had lower tensile strengths than those containing fluorinated oligomers (sample 10) or no fluorine compounds (sample 8).

Discussion

In general, incorporating organic compounds containing fluorine into composites increased their hydrophobicity based on water sorption and solubility and water contact angles. However, the use of fluorinated comonomers with Bis-GMA had the most pronounced effect compared to using fluorinated diluents or the synthesized oligomer Bis-F-GMA. Of the formulations containing fluorinated comonomers, composites containing HFHMDMA, HFHMDA, Bis-DMA, Bis-DA and Bis-GMA were the most hydrophobic, having the lowest water sorption and solubility and the highest water contact angle of 80°. However, based on the work of Douglas *et al.* (1980), a composite would need a contact angle of about 110° to prevent marginal penetration of fluid between it and tooth structure. Thus, it appears that the oligomer Bis-F-GMA will need to be more highly fluorinated by adding fluorine to the GMA or similar monomer and need to be used with fluorinated comonomers to produce materials with contact angles in the range of 110°.

It also appears that, in general, the use of fluorinated oligomers, diluents or comonomers results in a decrease in diametral tensile strength of 10–30%. Whether this reduction represents a serious problem with fluorinated composites remains to be determined based on other qualities such as abrasion resistance.

Table 3. Composition and properties of Bis-GMA composites containing fluorinated and non-fluorinated comonomers

	Sample			
	8	9	10	11
Component, g				
Bis-GMA	1·386	1·386	1·386	1·386
Bis-DMA	0·693	0·693	0	0
Bis-DA	0·693	0·693	0	0
OF Bis-DMA	0	0	0·693	0·693
OF Bis-DA	0	0	0·693	0·693
HMDMA	0·594	0	0·594	0
HMDA	0·594	0	0·594	0
HFHMDMA	0	0·594	0	0·594
HFHMDA	0	0·594	0	0·594
ZrSi	16·0	16·0	16·0	16·0
CQ	0·03	0·03	0·03	0·03
DMAMA	0·02	0·02	0·02	0·02
Property				
Diametral tensile strength kg/cm²	503 (43)	342 (37)	456 (49)	364 (38)
Water sorption				
mg/cm²	0·66	0·52	0·62	0·59
%	0·40 (0·04)	0·35 (0·03)	0·40 (0·03)	0·36 (0·02)
Water solubility				
mg/cm²	0·08	0·02	0·06	0·05
%	0·06 (0·03)	0·01 (0·02)	0·04 (0·02)	0·03 (0·01)
Water contact angle, Degrees	65 (2)	80 (3)	70 (3)	70 (2)

Acknowledgment

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