PHYSICAL PROPERTY EVALUATIONS OF PERFLUOROTRIETHYLENE GLYCOL DIMETHACRYLATE AS A POTENTIAL REACTIVE DILUENT IN DENTAL COMPOSITE RESINS

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ABSTRACT

Perfluorotriethylene glycol dimethacrylate (FTEGDMA), a fluoro analog of triethylene glycol dimethacrylate (TEGDMA), was evaluated in dental composites. Curing, physical properties, and water sorption of FTEGDMA-ethoxylated bisphenol A dimethacrylate (BisEMA) and bisphenol A glycol dimethacrylate (BisGMA) - TEGDMA as well as TEGDMA - BisEMA blends were evaluated and compared. BisEMA and FTEGDMA viscosities were lower than BisGMA and TEGDMA. FTEGDMA has the lowest refractive index and contact angle on silanated or non-silanated glass. Polymerization studies showed that FTEGDMA did not significantly alter the decrease of C=C conversion of the various formulations. Further, the experimental FTEGDMA resins absorbed much less water than the control formulations.

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INTRODUCTION

BisGMA resin based dental composites have many advantages, such as good mechanical properties, satisfactory esthetic quality, and the ability to bond to acid-etched enamel surfaces. However, they are generally considered to have limited clinical use in posterior areas due to the material wear and degradation, water sorption, and recurrent caries [1]. The high water sorption, which is detrimental to many physical and mechanical properties of composites, is considered the major drawback of current composite materials [3]. Water in the oral cavity could cause filler-matrix debonding, thereby leading to a substantial decreasing of physical properties such as tensile and compressive strength, fracture toughness, and wear resistance [2, 3]. In addition, there is a decrease in the glass transition temperature (T_g), and an increase in the creep potential because of the plasticizer effect of the water molecules [4]. All these deleterious effects can reduce the long term durability of composite restorations.

Several studies have been undertaken to enhance the service performance of dental composite resins by changing the formulations of the materials. One effective approach has been the synthesis of the fluorinated analogs of currently used monomers for dental composites. Fluorinated epoxy resins have been successfully used to prepare materials for use in the US space activities and submarine optical fiber transmission systems [5, 6]. Several studies have investigated the use of a fluorinated analog of Bis-GMA in the processing of visible light cured dental composites. The BisGMA-F based composite resins generally retained a higher percentage of their initial properties than the conventional BisGMA composites when exposed to either water or thermal fatigue [7-9]. It has also been reported that the application of a fluorinated aromatic dimethacrylate to light-cured composite resins can improve the light transmittance resulting in an improved depth of cure for the material [10]. In one clinical study, a fluoropolymer was found to accumulate less plaque than metal on the tissue side of pontic surfaces [11]. Therefore, fluoropolymers are expected to produce novel composites with superior clinical characteristics.

Primarily, the fluoropolymer research in dental composites to date has focused on the oligomer phase of the resin. The diluent, however, makes up approximately 50 mol% of current resin formulations and has been found to be released from resin composite into the aqueous phase or diffuse through dentine because of its small molecular weight and hydrophilicity [12-14]. The goal of this

study was to investigate the potential use of perfluorotriethylene glycol dimethacrylate (FTEGDMA), which is the fluoro analog of the commonly used triethylene glycol dimethacrylate (TEGDMA), in dental composites.

FTEGDMA has a much higher fluorine content in its molecular structure when compared to those fluorinated oligomers previously studied [7-10]. It was anticipated to lead to higher hydrophobicity.

The objectives of this paper were to (1) investigate the basic physical properties of the FTEGDMA and compare it to the currently used monomers to predict its potential use in dentistry, (2) test its visible light polymerization by FT-IR, and (3) study its effect on the water sorption property of dental composite.

EXPERIMENTAL

Materials

Four monomers were used to formulate the resin phase of the experimental dental materials used in this study. These consisted of two oligomers: Bisphenol A glycol dimethacrylate (BisGMA) and Ethoxylated bisphenol A dimethacrylate (BisEMA), and two diluents: Triethylene glycol dimethacrylate (TEGDMA) and perfluorotriethylene glycol dimethacrylate (FTEGDMA). BisGMA (Cook Composite and Polymers, Port Washington, WI) and TEGDMA (Aldrich Chemical Company Inc., Milwaukee, WI), which are commonly used in commercial product formulations, were used as the control monomers in this study. Due to the limited miscibility of FTEGDMA (Exfluor Research Corporation, Austin, TX) with BisGMA, BisEMA (Esschem Inc., Essington, PA), which is also used in commercial dental resins, was chosen for use in the experimental formulations. The novel FTEGDMA was synthesized using direct fluorination technology.

Basic Physical Property Determination

The viscosity (h) of the above four monomers and 50/50 (mol%) comonomers of TEGDMA/BisGMA, TEGDMA/BisEMA and FTEGDMA/BisEMA were tested by a dynamic mechanical analyzer [Reometrics, Inc. (RDA II)] in a dynamic mode. A parallel plate geometry was utilized in all rheological tests. All experiments were conducted at 37°C, with shear rates ranging from 0.1 to 100 s^{-1}.

The refractive indices of the four monomers were examined at room temperature with an Abbe Refractometer. The instrument was calibrated with distilled water each time before testing.

The contact angles of the monomers (except BisGMA, which was too viscous to be tested) on silanated or non-silanated cover glass slides were studied with a model 100-00 Contact Angle Goniometer. The cover glass slide was made of a similar material to the silica fillers used in dental composite. The method of silanization was similar to that described elsewhere [15]. The glass slides were soaked in silanization solution (2% by volume of g-methacryloxy-propyltrimethoxy silane in cyclohexane solvents in the presence of 2% by volume of n-propylamine) for 2 hours at room temperature, then washing with acetone for 10 minutes and air-drying.

Determination of Degree of Conversion (DC)

The degree of polymerization of comonomers BisEMA (oligomer) with commonly used TEGDMA (diluent) and BisEMA with experimental FTEGDMA (new diluent) at different molar ratios (Table 1) were tested by Fourier Transformed Infrared (FT-IR) spectroscopy. Commonly used 50/50 (mol) BisGMA/TEGDMA was used as a control. Camphoroquinone (0.5 wt%) and 2-N,N-diethyllaminoethyl methacrylate (1.0 wt%) were added to comonomers to allow for photopolymerization.

The method similar to that described by Ferracane and Greener was used to evaluate DC for the monomer solutions [16]. The concentration of available $C=C$ double bonds in the monomer formulations was determined in the transmission mode by smearing a drop of the resin between NaCl crystals, placing the crystals into a cell holder, and obtaining a spectrum from 16 scans over the 800-4000 cm^{-1} range.

TABLE 1.   Codes and Formulations of the Materials Used in the Study

Code	Material	Molar Ratio
T5G5	TEGDMA/BisGMA	50/50
T1E9	TEGDMA/BisEMA	10/90
T5E5	TEGDMA/BisEMA	50/50
T3E7	TEGDMA/BisEMA	30/70
F1E9	FTEGDMA/BisEMA	10/90
F5E5	FTEGDMA/BisEMA	50/50
F3E7	FTEGDMA/BisEMA	30/70

The polymerized visible-light-cured specimens were obtained by pressing a drop of the mixed resin between two NaCl crystals and illuminating the thin resin film between the crystals with radiation from a visible light source for 5 minutes. The crystal-film-crystal sandwich was then placed into a cell holder within the spectrometer. The intensities of the C=C absorbance peak at 1637 cm^{-1} and the C...C reference peak at 1581 cm^{-1} were measured using a standard baseline technique. The C...C peak at 1581 cm^{-1} is the aromatic bonding in the BisEMA molecule, and its intensity remains unchanged during the polymer-ization reaction. The ratio of the absorbance intensities of C=C/C...C are deter-mined before and after polymerization. The percentage of unreacted carbon double bonds remaining (% C=C) can be calculated by the following equation:

$$\% \text{ C=C} = (\text{C=C} / \text{C...C})_{polymer} / (\text{C=C} / \text{C...C})_{monomer}$$

The degree of double bond conversion (DC) was obtained by subtracting the percent residual C=C from 100. Representative IR spectra of a typical monomer and polymer formulation are shown in Figure 1.

Water Sorption and Solubility Evaluation

The same monomer formulations (Table 1) which were used to study the DC were also used to evaluate water sorption, using tests similar to those
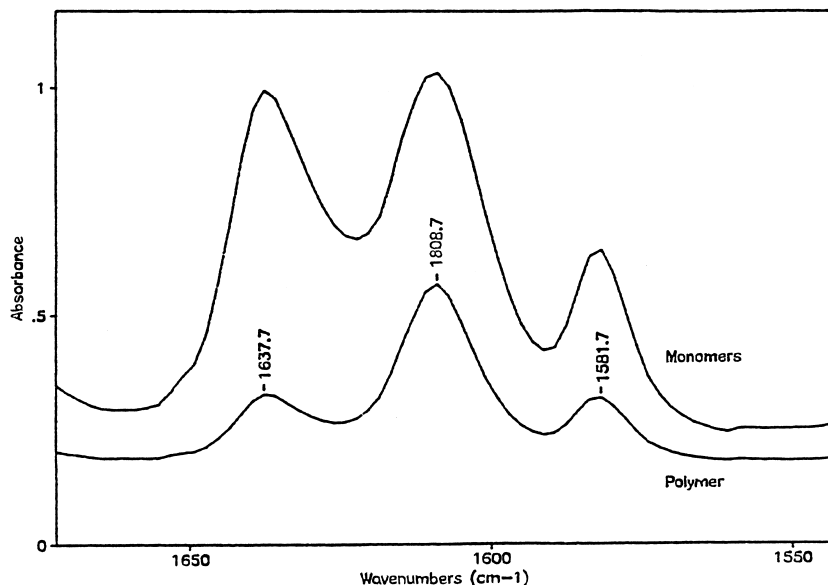

Figure 1. Representative graph from FT-IR.

described in ADA Specification No. 27 for Resin Based filling materials were used. Specimen discs 15 mm in diameter and 0.5 mm thick (1 mm thick for composite) were formed in a plastic mold between two glass slides and irradiated with visible light for 2 minutes on each side. Five specimen discs were prepared for each sample. Upon removal, the specimens were placed in a desiccator maintained at 37°C for 24 hours, then placed at room temperature for 1 hour. The specimens were later removed from the desiccator and weighed with a precision of 0.2 mg. This cycle was repeated until the mass remained constant over a 24 hour period. This mass was recorded as m_i. The discs were then immersed in distilled water at 37°C for time (t) weeks after which time the discs were removed, blotted dry and weighed (m_t). The specimens were reimmersed and subsequently measured at 1 week intervals up to 4 weeks. The specimens were then placed in a desiccator maintained at 37°C until constant weight (m_o) was achieved. The diameter and the thickness of the specimen were measured at five points and the volume (V) calculated in cubic mm. The values of water sorption (WS) were calculated in $\mu g/mm^3$ for each disc using the following formula:

$$WS = (m_t - m_i) / V$$

where t=1,2,3,4 weeks.

The values of one month water solubility were calculated in $\mu g/mm^3$ for each disc using the following formula:

$$Solubility = (m_i - m_o) / V$$

Statistical Analysis

One-way analysis of variance (ANOVA) with the *post hoc* Tukey-Kramer multiple range test, was used to determine the significant differences among the materials for the degree of conversion and water sorption tests. A rejection level of $p = 0.05$ was used for statistical significance.

RESULTS AND DISCUSSION

Figure 2 and Table 2 show the results of the basic physical properties, viscosity, refractive index and contact angle of the monomers and their comonomers.
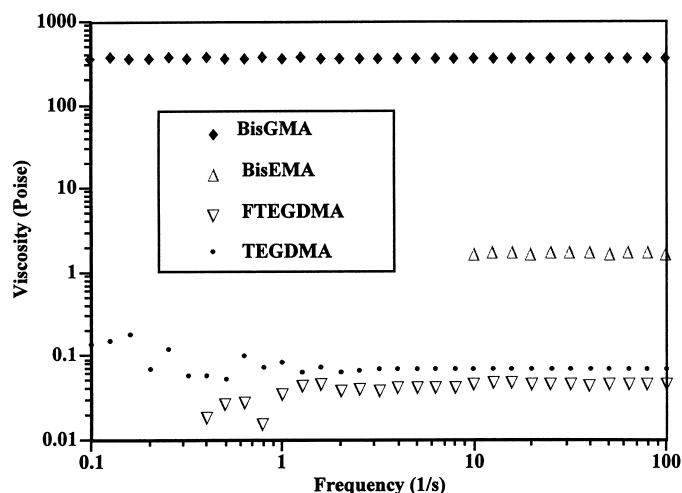
Figure 2. Viscosity of four monomers. The x-axis and y-axis represent testing frequency and viscosity of materials tested, respectively.

The viscosity of the BisEMA was much lower than that of the BisGMA, and the viscosity of the FTEGDMA was lower than that of TEGDMA. Based on the rule of mixtures and additive nature of viscosity, the following viscosity order of oligomer/diluent are observed: BisGMA/TEGDMA > BisEMA/TEGDMA > BisEMA/FTEGDMA. BisEMA/FTEGDMA comonomer should have the lowest viscosity among these three.

The rheologic properties of the monomer formulations will aid in assessing the filler/liquid ratio and processing methods which can be used with the new materials. Lower viscosities are more readily suited to higher filler/liquid ratio, injection processes and may be particularly of interest for cement applications while high viscosities are needed to be considered for direct placement processes. From the viscosity result, we know that the FTEGDMA and BisEMA have lower viscosity than the TEGDMA and BisGMA separately.

TABLE 2. Basic Physical Properties of the Monomers

Monomer	Refractive Index	Contact Angle (degree)	
		Silanated	Non-silanated
BisGMA	1.5497	--	--
BisEMA	1.5362	30 (1)	36 (1)
FTEGDMA	1.3823	2.33 (0.58)	5.17 (1.26)
TEGDMA	1.4604	11.67 (2.08)	13.67 (2.08)

This is likely to result in a lower viscosity of the FTEGDMA/BisEMA combination than that of the TEGDMA/BisGMA. Due to this lower viscosity it is possible to use higher filler/liquid ratios for new dental composite materials. Alternatively, it may also be possible to use less diluent in the system, hence reducing the polymerization shrinkage, which is a major problem in current dental composites.

The refractive indices of oligomers (BisEMA, BisGMA) were higher than that of diluents (TEGDMA, FTEGDMA). Among these, the FTEGDMA had the lowest refractive index. It is encouraging to find out that the FTEGDMA had the lowest refractive index among those monomers. By using the FTEGDMA as a diluent, it may be possible to decrease the refractive index of the polymer matrix and make it closer to that of fillers. This supports the concept discussed in the introduction that fluorinated monomer can improve the light transmittance of the composite resulting in an improved depth of cure. It is also important to understand that the polymer often has a different refractive index from its monomer precursors. Further investigations are needed to determine the refractive index of their corresponding polymers.

All the monomers exhibited smaller contact angles on silanized cover glass than on non-silanized cover glass. The FTEGDMA gave the smallest contact angle. During composite processing, Whether fillers can be wet well by monomers is very important to know, and this is tested by contact angle. All the monomers showed smaller contact angles on silanized cover glass than on non-silanized cover glass, which meant that the silanization method was effective. The FTEGDMA gave the smallest contact angle. This is very favorable when processing composite. If we use the FTEGDMA instead of the TEGDMA as diluent, filler particles should be wet better by the monomers. And this might improve the polymer-filler interphase compatibility. Compared to the basic physical properties of other monomers, the FTEGDMA is very suitable to be used as a novel diluent in the polymer phase of dental composites.

The means and standard deviations of the calculated DC of the two series of experimental neat resins and the BisGMA/TEGDMA, tested by FT-IR, are summarized in Figure 3. All of the experimental formulations had higher DC than the control BisGMA/TEGDMA. The statistical analysis suggests that the diluent type did not significantly affect the resulting DC values of the various monomer solutions. The DC values increased as the diluent concentrations increased.
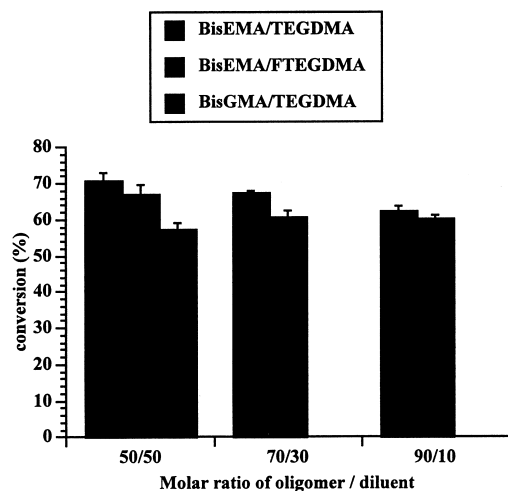
Figure 3. Conversion of resins with different monomer ratios. The x-axis and y-axis represent molar ratio of oligomer/diluent and degree of monomer conversion determined by FT-IR, respectively.

The degree of polymerization in crosslinked polymeric systems has a potential role in determining the ultimate physical and mechanical properties of the material. Residual methacrylate groups have been implicated in causing reduced hardness [17], wear resistance [18], strength [19], color stability [20], and accelerated degradation [21] in dental restorative resins. The significance of this work suggests that the perfluoro analog of the commonly used diluent TEGDMA could be substituted into the polymer phase of composites without significantly altering the reaction kinetics. This makes it possible to take advantages of the superior properties of the FTEGDMA. Given the acknowledgment that up to 30% by volume oxygen can be dissolved in fluorocarbons [6], it is very promising to know that the fluorinated diluent didn't decrease the degree of polymerization. Further work needs to be done to cure the system in a nitrogen atmosphere, which would allow for an increase in the degree of conversion.

In Table 3, the values of the calculated water sorption of the two series of unfilled resins (including the control) at different time periods are presented. The results showed that the experimental fluoro-containing resin absorbed significantly less water than the conventional formulations. The BisEMA system resulted in significantly lower water sorption than the more hydrophilic BisGMA system. Table 3 also shows that the water sorption reaches a maximum at 1 week and then shows a decreasing tendency. This can be explained as some

TABLE 3.   Water Sorption for Materials Used in the Study

Material	Water Sorption ($\mu m / mm^3$)			
	Week 1	Week 2	Week 3	Week 4
T5G5	50.6	49.6	48.9	47.3
T1E9	11.6	11.2	10.8	9.45
T5E5	16.5	15.1	14.0	12.9
T3E7	13.2	10.6	12.0	9.96
F1E9	8.75	8.23	10.07	9.65
F5E5	6.68	7.06	7.28	5.77
F3E7	8.67	7.08	7.05	7.27

dissolution of the materials. The results for one month water solubility of these materials showed that there were some degradation or leaching from these materials, based on the following data: 6.36 (T5G5), 5.95 (T1E9), 3.39 (T3E7), 6.25 (T5E5), 4.97 (F1E9), 6.98 (F5E5), and 3.54 mg/mm^3 (F3E7).

It is believed that water in the oral cavity could, with time, cause a composite filler-matrix debonding, thereby leading to a series of problems. It has been suggested that the surface layer of the filler is first attacked by stress corrosion. Water is absorbed preferentially into the resin component of composite and the filler particle-resin debond could happen because of the stress resulted from the swelling of the resin matrix. Second, if the filler is made of Sr or Ba glasses, leaking of these elements would cause the building up of hydroxyl ions at the filler interface. After reaching a certain concentration, these ions start breaking up the silica network. Also, an osmotic pressure could build up in pre-existing cavities inside the composite as a result of water accumulation and filler leakage, causing crack formation and growth along matrix-filler interfaces [2-4]. As a result of the long term contact with water, the physical properties of composites can decrease substantially. In the present study, we replace the conventional diluent TEGDMA with its fluorinated analog FTEGDMA and resulted in greatly enhanced hydrophobicity of the neat resin. As a result, we suspect that the long term properties of composites made with these hydrophobic monomers may be substantially improved over those commercial monomers.

CONCLUSION

FTEGDMA has lower viscosity and refractive index than the conventional dental composite diluent TEGDMA. FTEGDMA also showed smaller contact angle on both silanated and non-silanated surfaces than

ORDER   REPRINTS

TEGDMA. The combination of FTEGDMA and BisEMA demonstrated favorable physical properties, when compared to the conventional TEGDMA and BisGMA formulations.

Replacing TEGDMA with FTEGDMA did not adversely affect the reaction kinetics of the experimental dental unfilled resin formulations, which makes the application of FTEGDMA in dental composites possible. Incorporation of FTEGDMA in the polymer decreases the polymeric matrix water sorption.

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