



## Low-shrinkage visible-light-curable urethane-modified epoxy acrylate/SiO<sub>2</sub> composites as dental restorative materials

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### ABSTRACT

In this study, low-shrinkage high-strength dental restorative materials were prepared and their properties were investigated. Epoxy acrylates modified with various stoichiometric amounts of urethane acrylates were used as the resin matrix and 3-(trimethoxysilyl)propyl methacrylate (MSMA)-modified monodisperse nano-sized SiO<sub>2</sub> particles were synthesized and used as the inorganic reinforcing filler. Polymer composites suitable for using as dental restorative materials were formed by curing the resin matrices containing MSMA-SiO<sub>2</sub> with visible-light. The viscosities of the obtained resin matrices, their polymerization shrinkages, hardness, flexural strengths, and flexural moduli of the obtained polymer composites were investigated. Compared with bisphenol-A/glycidyl dimethacrylate (Bis-GMA)-based dental restorative materials, the polymer composites obtained in this study exhibited greatly reduced degrees of shrinkage and better mechanical and physical properties.

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### 1. Introduction

Dental restorative materials often consist of base monomers, diluent monomers, and inorganic fillers in high loadings. High molecular weight dimethacrylate monomers are often used as the matrices of dental restorative composites because they provide high-strength and low polymerization shrinkage [1]. Although 2,2-bis[4-(20-hydroxy-30-methacryloyloxypropoxy)phenyl]propane (Bis-GMA) is the base monomer most commonly used in restorative materials, its very high viscosity ( $>10^3$  Pa s) results in limited loadings of reinforcing fillers and low final conversions of homopolymerized Bis-GMA [2]. Therefore, a reactive diluent, such as triethylene glycol dimethacrylate (TEGDMA), is often added to reduce the viscosity and improve both the reactivity and the final conversion [2]. However, its use results in polymerization shrinkage which may lead to secondary caries [3].

Shrinkage occurring during polymerization of the matrix monomers of restorative materials remains one of the common causes of failure during dental composite restoration. Such polymerization shrinkage is the result of contraction due to the conversion of van der Waals distances to covalent bonds and the expansion

due to the conversion of double bonds to single bonds after polymerization [3,4].

Several approaches for reducing the degree of curing shrinkage of dental composites have been reported. For example, the shrinkage can be reduced significantly by increasing the amount of the filler [5]. Although this method is generally simple, problems can arise in mixing the fillers with organic resins when the filler content becomes too high. An alternative approach is to synthesize monomers that undergo a lower degree of polymerization shrinkage. For example, dental composites containing hyperbranched or dendritic methacrylates exhibit low curing shrinkage [6]. The high molecular volume and multiple functionality of a trimethacrylate system has been shown to reduce the amount of shrinkage [7,8]. Moreover, techniques such as substituting the methoxyl groups for hydroxyl groups in Bis-GMA have also led to a decrease in curing shrinkage [9]. Although the use of branched methacrylates helps to reduce the degree of reaction shrinkage, the mechanical properties of the resulting polymer may deteriorate over time [10].

We focused our attention on synthesizing urethane-modified epoxy acrylates and reacting them with functionalized nano-sized silica particles to form low-shrinking composites possessing excellent mechanical properties that would be suitable for use in dental restorative materials. These composites are featured as tooth-like properties and designed to be used easily by the dentist as they easily penetrate into the cavity and harden quickly under the radiation of visible-light. The novel monomers were synthesized by reacting toluene 2,4-diisocyanate (TDI), 2-hydroxyethyl

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methacrylate (HEMA), and epoxy acrylate in various stoichiometric ratios. It was expected that the polymer composites based on the urethane-modified epoxy acrylate would exhibit low degrees of polymerization shrinkage because of their relatively high molecular weight and cohesive energy density resulting from the presence of the urethane group. In addition, it was also expected that the polymer composites would have excellent mechanical properties because of their high crosslinking densities.

## 2. Experimental

### 2.1. Preparation of multifunctional methacrylates

Toluene 2,4-diisocyanate TDI (2 equivalent) was placed into a reaction kettle. Dry nitrogen gas was continuously purged through the reaction kettle to remove oxygen and moisture. 2-Hydroxyethyl methacrylate (HEMA; 1 equivalent) (ACROS Chemical Co., Geel, Belgium) was then added into the kettle drop wise. The reaction temperature was maintained at 30 °C while the mixture was agitated vigorously. An FT-IR spectrometer (Bio-Rad Laboratories, Hercules, CA) at a resolution of 4 cm<sup>-1</sup>, scanning 16 times over the range from 4000 to 850 cm<sup>-1</sup> was used to monitor the changes in the intensity of the signal of the isocyanate group (NCO, 2270 cm<sup>-1</sup>) at regular intervals. When this peak intensity reached half of its original value, indicated that the hydroxyl groups (OH) on the side chains of HEMA had reacted completely with the NCO groups of TDI. At this stage, a certain amount (1, 2 or 3 equivalents) of Epoxy Acrylate (EA) (Agi Co., Taipei, Taiwan) dissolved in pure acetone was added into the reaction mixture and the temperature was maintained at 40 °C under the nitrogen atmosphere. Again, the signal for the NCO groups was monitored at 2270 cm<sup>-1</sup>. When its peak intensity disappeared, all of the NCO groups were deemed to have reacted completely with the OH groups of the EA moieties. No catalyst or inhibitor was used in this reaction. The obtained resin was purified under a reduced pressure to remove solvent and impurities.

### 2.2. Measurement of molecular weight and viscosity of urethane-modified epoxy acrylates

The obtained urethane-modified epoxy acrylates were then freed from solvent through rotary evaporation under reduced pressure. After the removal of solvent, the neat urethane-modified epoxy acrylates were dissolved into tetrahydrofuran (THF, ACROS Chemical Co., Geel, Belgium) at a concentration of 0.1 wt%. Gel permeation chromatography (GPC) (SUPER CO-150, Enshine, Taipei County, Taiwan) analysis was performed using Enshine super Co-150 columns with THF as the eluent. The retention times were then recorded and analyzed to confirm the molecular weights of the products. The viscosity of resins was measured using a DV-E viscometer (Brookfield Engineering Laboratories, Inc., Middleboro, MA) at 35 °C.

### 2.3. Preparation of monodisperse MSMA-silica colloids

Silica colloids were prepared according to the method reported by Stöber et al. [11]. Ammonium hydroxide, deionized water, and TEOS (SiO<sub>2</sub> colloid-tetraethoxysilane, ACROS Chemical Co., Geel, Belgium) were mixed in absolute ethanol at concentrations of 1.03 M, 8.80 M, and 0.40 M, respectively. After heating at 70 °C for 2 h with magnetic stirring at 500 rpm, the silica colloids were produced. After addition of MSMA (3-(trimethoxysilyl)propyl methacrylate, ACROS Chemical Co., Geel, Belgium) and heating at 70 °C for another 12 h, the MSMA-silica colloids were isolated by centrifugation (7500 rpm, 5 min), washed three times with abso-

lute ethanol (to remove any residual ammonium hydroxide), and then washed three times with acetone (to exchange the residual solvent). The silica and MSMA-silica colloids were characterized using dynamic light scattering (DLS) (Zeta-Sizer 3000, Malvern Instruments Ltd., Malvern, Worcestershire, UK) and field emission scanning electron microscopy (FE-SEM) (S-4200, Hitachi High Technologies Corporation, Tokyo, Japan).

### 2.4. Preparation of composite resin

The urethane-modified acrylate and the diluent monomer tripropylene glycol diacrylate (TPGDA) (Eternal Technology Co., Kaohsiung, Taiwan) were dissolved in acetone and then the well-dispersed MSMA-silica spheres in acetone were added. After stirring for 10 min, the initiator systems, ethyl 4-dimethylaminobenzoate (EDMAB) and DL-camphoroquinone (CQ), were added and then the mixture was stirred for another 12 h in a darkroom as an open system. The solvent was removed from the paste under vacuum at 30 °C for 24 h. This paste consisted of resin matrix, MSMA-SiO<sub>2</sub> spheres, CQ, and EDMAB at a weight ratio of 30:70:0.3:0.6.

### 2.5. Measurement of Vickers hardness

To determine their Vickers hardness, five specimens of each material were prepared by stuffing the composite resins in cylindrical poly(methyl methacrylate) molds having a diameter of 6 mm and a depth of 2 mm. To avoid an oxygen-inhibited superficial layer with lower hardness, the surfaces of the specimens were covered with a transparent PET film prior to light-curing for 30 s. The microhardness measurements on each specimen were performed using a Vickers indenter (HMV-2, Shimadzu Co. Ltd., Kyoto, Japan) with a load of 980.7 mN for 10 s. For the hardness measurement, five indentations were made on each specimen and the mean and standard deviations were also calculated.

### 2.6. Measurement of flexural strength and flexural modulus

For flexural strength studies, composite paste samples were photopolymerized in a stainless steel mold (specimen dimensions: 25 × 2 × 2 mm) using visible-light ( $\lambda = 400\text{--}520\text{ nm}$ ; 550 mW cm<sup>-2</sup> min<sup>-1</sup>) (Optilux 500, Kerr Corporation, Orange, CA) for 30 s on each side under ambient conditions. After polymerization, specimens of each material were stored in distilled water at 37 °C for 24 h. A three-point bending flexural test was performed using a span width of 20 mm and a crosshead speed of 1.0 mm min<sup>-1</sup> by a PT-1066 tensile strength tester (Perfect International Instruments Co., Chingshui Town, Taichung County, Taiwan). The flexural strength ( $\sigma$ ) and flexural modulus ( $E_f$ ) were calculated using the equations  $\sigma = (3Fl)/(2bh^2)$  and  $E_f = (F_1 l^3)/(4bh^3d)$ , respectively, where  $F$  is the peak load (in N),  $l$  is the span length (in mm),  $h$  is the specimen thickness (in mm),  $b$  is the width of the specimen (in mm) and  $d$  is the deflection (in mm) at load  $F_1$  (in N) during the straight line portion of the trace [12]. Ten specimens were prepared and tested for each sample and the mean and standard deviation were also calculated.

### 2.7. Measurement of polymerization shrinkage

The strain gauge method [2,13,14] was used to study the development of the linear post-gel polymerization shrinkage of composites. The composite was placed on a single axial strain gauge (EA-06-062AP-120, Vishay Intertechnology, Inc., Shelton, CT) in a rectangular poly(methyl methacrylate) mold (4 × 3 × 1 mm) in a darkroom. The polymerization data were collected using a Vishay System 5000 Stress Analysis Data System (Vishay Intertechnology,

Inc., Shelton, CT). The data analysis system was zeroed for the first 10 s and then the composite was cured using visible-light ( $\lambda = 400\text{--}520\text{ nm}$ , Optilux 500, Kerr Corporation, Orange, CA) for a total exposure time of 30 s. The shrinkage was measured and recorded continuously for 200 s after the radiation of visible-light.

### 2.8. Statistical analysis

One-way analysis of variance (ANOVA) and Duncan's multiple-range statistical tests ( $p < 0.05$ ) were conducted on all physical and mechanical test results.

## 3. Results and discussion

The urethane acrylate-modified epoxy acrylate samples T1, T2, and T3 were synthesized using a mixture of HEMA, TDI, and epoxy acrylate with molar ratios of 1:1:0.5, 1:1:1, and 1:1:1.5, respectively (Fig. 1). The reactions were monitored using FT-IR spectroscopy to characterize the changes in the appearance of the functional groups of the monomers (Fig. 2). The urethane-modified epoxy acrylate produced polymers having higher molecular weights than did the epoxy acrylate. By increasing the content of the modified epoxy acrylate, the resulting polymers (Fig. 3) had higher molecular weights and broader polydispersity indices (PDI).

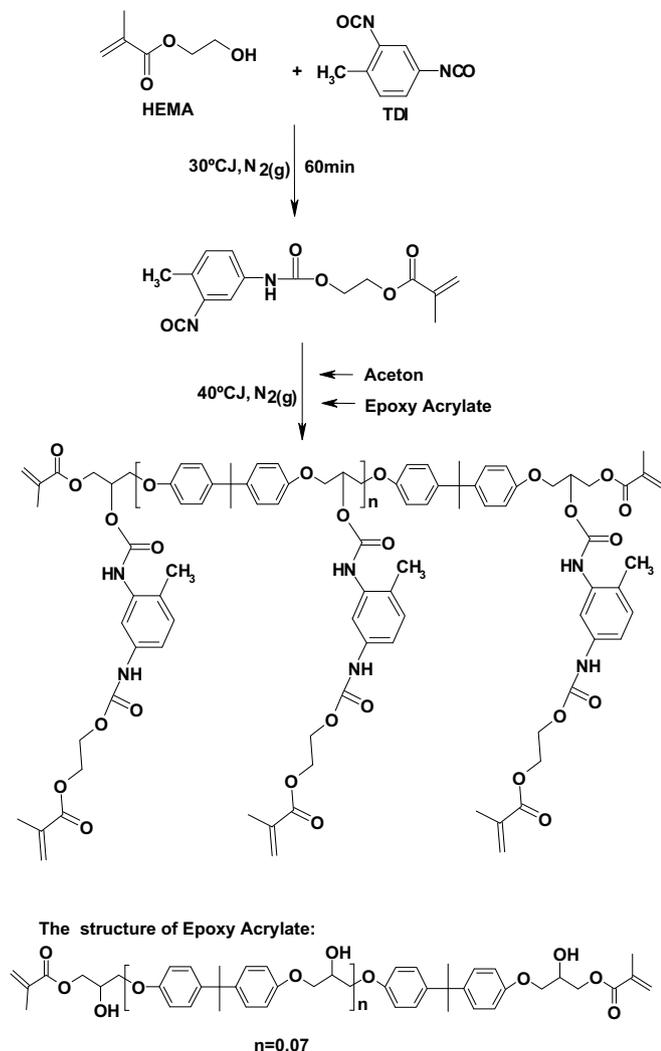


Fig. 1. Synthesis of the urethane acrylate-modified epoxy acrylate T1-0.

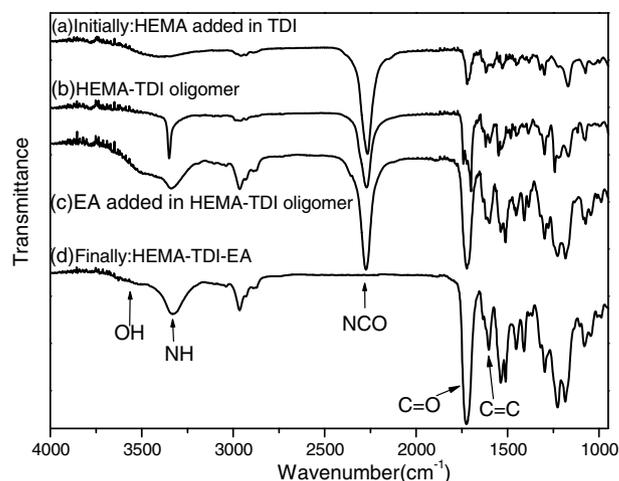


Fig. 2. FT-IR spectra recorded during the synthesis of the urethane acrylate-modified epoxy acrylate T1-0: (a) mixture of TDI and HEMA; (b) product obtained after reaction for 60 min; (c) mixture formed after adding EA in acetone; (d) product obtained after reaction for 180 min.

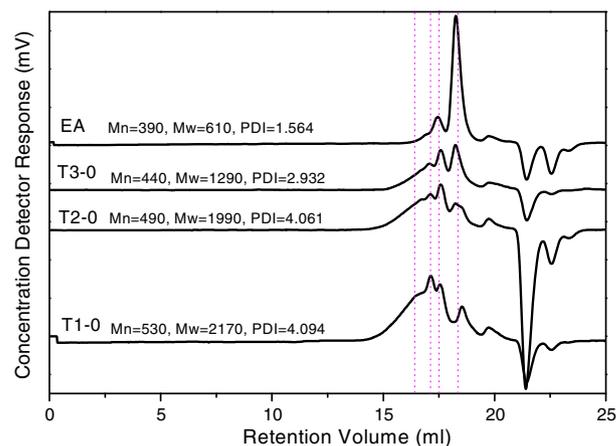


Fig. 3. Gel permeation chromatography (GPC) of T1-0, T2-0, T3-0, and EA.

The syntheses of the silica colloids and MSMA-silica colloids were carried out under basic conditions (Fig. 4). The average particle sizes of the silica and the MSMA-silica colloids were 431 and 452 nm (Fig. 5), respectively. The average size of the MSMA-silica colloids was larger than that of the silica colloids because their surfaces had been modified with the MSMA units. The appearance of the MSMA-silica spheres was examined by FE-SEM (Fig. 6). The surface functionalities of the silica and MSMA-silica spheres were characterized by FT-IR (Fig. 7).

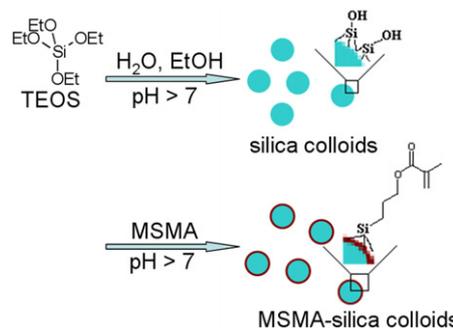


Fig. 4. Synthesis of the urethane acrylate-modified epoxy acrylate T1-0.

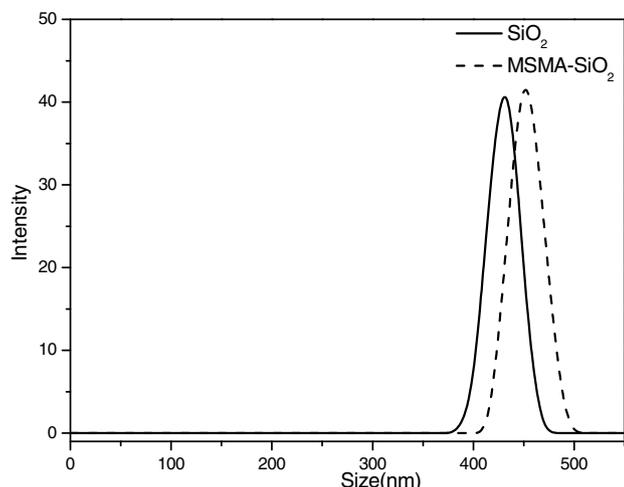


Fig. 5. Dynamic light scattering (DLS) analyses of silica spheres (—) and MSMA-silica spheres (---).

The samples T1, T2, and T3 all exhibited viscosities higher than that of pure epoxy acrylate with a higher degree of modification leading to a higher viscosity (Table 1). In contrast, the viscosities of the modified epoxy acrylates were greatly reduced upon adding the diluent TPGDA.

The oligomers obtained through the reaction of TDI and HEMA in a 1:1 molar ratio were reacted with epoxy acrylate in various stoichiometric ratios in order to control the functionality during the formation of the Bis-GMA analogues. The T3, T2, and T1 samples, which possessed increasing urethane functionality in that order, exhibited good solubility in the diluent TPGDA. The viscosities of the urethane acrylate-modified epoxy acrylates were higher than that of the epoxy acrylate because of their increasing molecular weight and the presence of hydrogen bonds between the urethane groups. As expected, the viscosities of the urethane-modified epoxy acrylates decreased upon adding TPGDA. Thus, there was no difficulty in loading the inorganic filler up to 70 wt% content.

The values of the Vickers hardness of the polymer composites were in the range of 37.0–62.1 (Table 1). The urethane-modified epoxy acrylate-based composites were found to be harder than

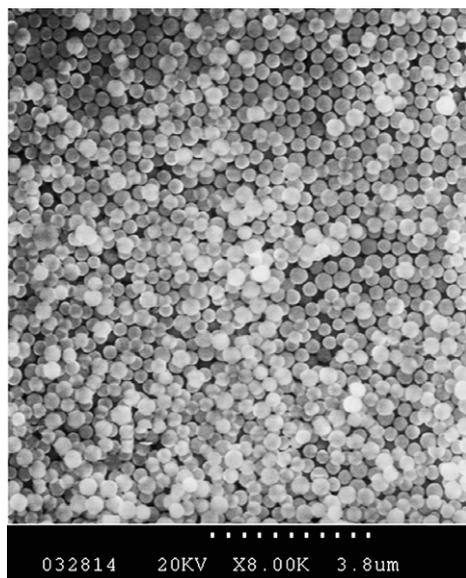


Fig. 6. The FE-SEM picture of the MSMA-silica spheres.

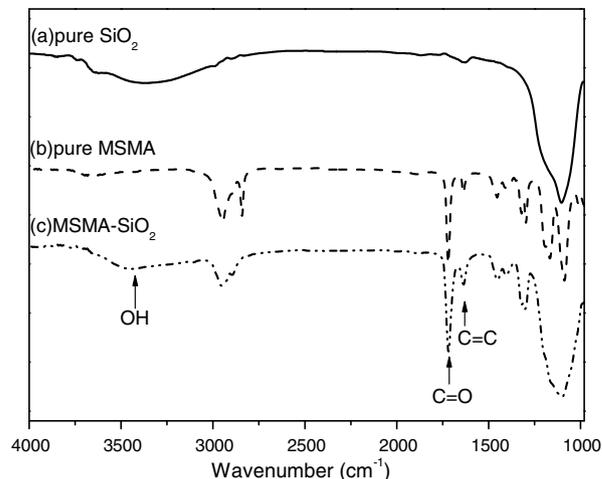


Fig. 7. FT-IR spectra recorded the modification of SiO<sub>2</sub> by MSMA: (a) SiO<sub>2</sub> sphere; (b) MSMA; (c) MSMA-modified SiO<sub>2</sub>.

those of the polymers based on epoxy acrylate (Fig. 8a). In addition, samples T1-40C ( $55.9 \pm 1.7$  Hv) and T2-40C ( $62.1 \pm 4.6$  Hv) were harder than Bis-30C ( $51.8 \pm 1.6$  Hv). For the T1 or T2 monomer-based materials, the highest hardness values were obtained by adding 40 wt% of the diluent TPGDA, whereas the hardness of the T3 monomer-based materials were independent of the amount of TPGDA added. It was concluded that for epoxy acrylate-based materials, the addition of TPGDA produced harder resultant materials.

The hardness of a solid material is determined by its resistance to local indentation [15]. A positive correlation had previously been established between the hardness of dental restorative composites and their inorganic filler content [16]. Moreover, the composition of the resin matrix, the nature of the interface between the organic monomers and inorganic fillers, and the particle size distribution of the inorganic fillers all influence the hardness of their resulting materials [15]. In this study, the hardness of the various polymer composites varied only slightly because they had the same inorganic filler contents but different resin matrices. The hardness of the urethane-modified epoxy acrylate monomer-based composites were higher than those of the epoxy acrylate-based materials because of the multiple functionalities in the urethane-modified epoxy acrylate. The addition of 40 wt% TPGDA to the T2 monomer resulted in the hardest polymer composites because the presence of TPGDA reduced the viscosity of the resin matrix to increase the mobility of its monomer units and, hence, the degree of conversion [17]. The same result was observed in the T1 system, but not in the T3 system because of its lower viscosity. The pure epoxy acrylate-based polymer composite, that is, the one prepared without the addition of TPGDA, had the lowest hardness of any of the materials examined in this study. A higher content of modified epoxy acrylate led to a higher viscosity and cohesive energy density. As a result, it was necessary to add more diluent to increase the mobility of the monomer units to obtain a harder material. Therefore, it is reasonable to conclude that the composite based on a suitable proportion of urethane-modified epoxy acrylate and TPGDA would be sufficiently hard to use in dental composite applications.

The maximum flexural strengths of the T1 monomer-based composites increased continuously upon adding the diluent TPGDA. The maximum flexural strengths of the T2 and T3 monomer-based materials occurred when 30 wt% of the diluent was added (Table 1 and Fig. 8b). The flexural strengths of T1-40C, T2-30C, T2-40C, T3-20C, T3-30C, and T3-40C were all higher than those of the corresponding epoxy acrylate-based materials and

**Table 1**Viscosities of monomers and Vickers hardness, flexural strengths, and flexural moduli of composites (means  $\pm$  standard deviation)

Monomer	TPGDA content (wt%)	Unfilled resin		Composite			
		Code	Viscosity (Pa s)	Code	Hardness (Hv) <sup>b</sup>	Flexural strength (MPa) <sup>b</sup>	Flexural modulus (GPa) <sup>b</sup>
T1	0	T1-0	— <sup>a</sup>	T1-0C	—	—	—
	20	T1-20	1100.00	T1-20C	50.1 $\pm$ 3.5 <sup>a</sup>	20.0 $\pm$ 3.5 <sup>a</sup>	6.1 $\pm$ 0.23 <sup>a</sup>
	30	T1-30	340.00	T1-30C	47.4 $\pm$ 1.7 <sup>b</sup>	43.3 $\pm$ 1.4 <sup>b</sup>	9.5 $\pm$ 0.31 <sup>b</sup>
	40	T1-40	14.00	T1-40C	55.9 $\pm$ 1.7 <sup>c</sup>	87.2 $\pm$ 7.8 <sup>c</sup>	9.6 $\pm$ 0.78 <sup>b</sup>
	0	T2-0	2700.00	T2-0C	—	—	—
T2	20	T2-20	940.00	T2-20C	44.2 $\pm$ 1.9 <sup>a</sup>	48.8 $\pm$ 4.2 <sup>a</sup>	5.1 $\pm$ 0.23 <sup>a</sup>
	30	T2-30	10.00	T2-30C	48.7 $\pm$ 1.3 <sup>b</sup>	75.7 $\pm$ 8.1 <sup>b</sup>	9.3 $\pm$ 0.50 <sup>b</sup>
	40	T2-40	0.79	T2-40C	62.1 $\pm$ 4.6 <sup>c</sup>	75.9 $\pm$ 6.7 <sup>b</sup>	6.1 $\pm$ 0.57 <sup>c</sup>
	0	T3-0	520.00	T3-0C	—	—	—
	20	T3-20	43.00	T3-20C	50.9 $\pm$ 0.4 <sup>a</sup>	71.0 $\pm$ 6.7 <sup>a</sup>	7.9 $\pm$ 0.87 <sup>a</sup>
T3	30	T3-30	5.20	T3-30C	47.1 $\pm$ 1.1 <sup>b</sup>	90.2 $\pm$ 8.7 <sup>b</sup>	9.3 $\pm$ 0.24 <sup>b</sup>
	40	T3-40	0.72	T3-40C	47.7 $\pm$ 2.5 <sup>b</sup>	90.9 $\pm$ 8.8 <sup>b</sup>	8.3 $\pm$ 0.56 <sup>c</sup>
	0	EA-0	410.00	EA-0C	37.0 $\pm$ 1.9 <sup>a</sup>	25.1 $\pm$ 2.1 <sup>a</sup>	2.2 $\pm$ 0.40 <sup>a</sup>
	20	EA-20	10.00	EA-20C	44.4 $\pm$ 1.5 <sup>b</sup>	48.5 $\pm$ 5.4 <sup>b</sup>	3.6 $\pm$ 0.59 <sup>b</sup>
	30	EA-30	1.00	EA-30C	45.2 $\pm$ 1.2 <sup>b</sup>	51.2 $\pm$ 5.4 <sup>c</sup>	3.5 $\pm$ 0.39 <sup>b</sup>
Epoxy acrylate	40	EA-40	0.18	EA-40C	45.1 $\pm$ 2.0 <sup>b</sup>	49.2 $\pm$ 0.8 <sup>d</sup>	4.3 $\pm$ 0.51 <sup>c</sup>
	0	—	—	—	—	—	—
	30	—	—	Bis-30C	51.8 $\pm$ 1.6	61.3 $\pm$ 2.6	7.4 $\pm$ 0.25

T1: Molar ratio of HEMA, TDI, and epoxy acrylate was 1:1:0.5.

T2: Molar ratio of HEMA, TDI, and epoxy acrylate was 1:1:1.

T3: Molar ratio of HEMA, TDI, and epoxy acrylate was 1:1:1.5.

Duncan's method was used to determine whether the differences between samples were statistically significant with a 95% confidence coefficient. Means within one field without a common letter (<sup>a</sup>, <sup>b</sup>, <sup>c</sup>) are significantly different ( $\alpha < 0.05$ ).<sup>a</sup> Solid at 37 °C.

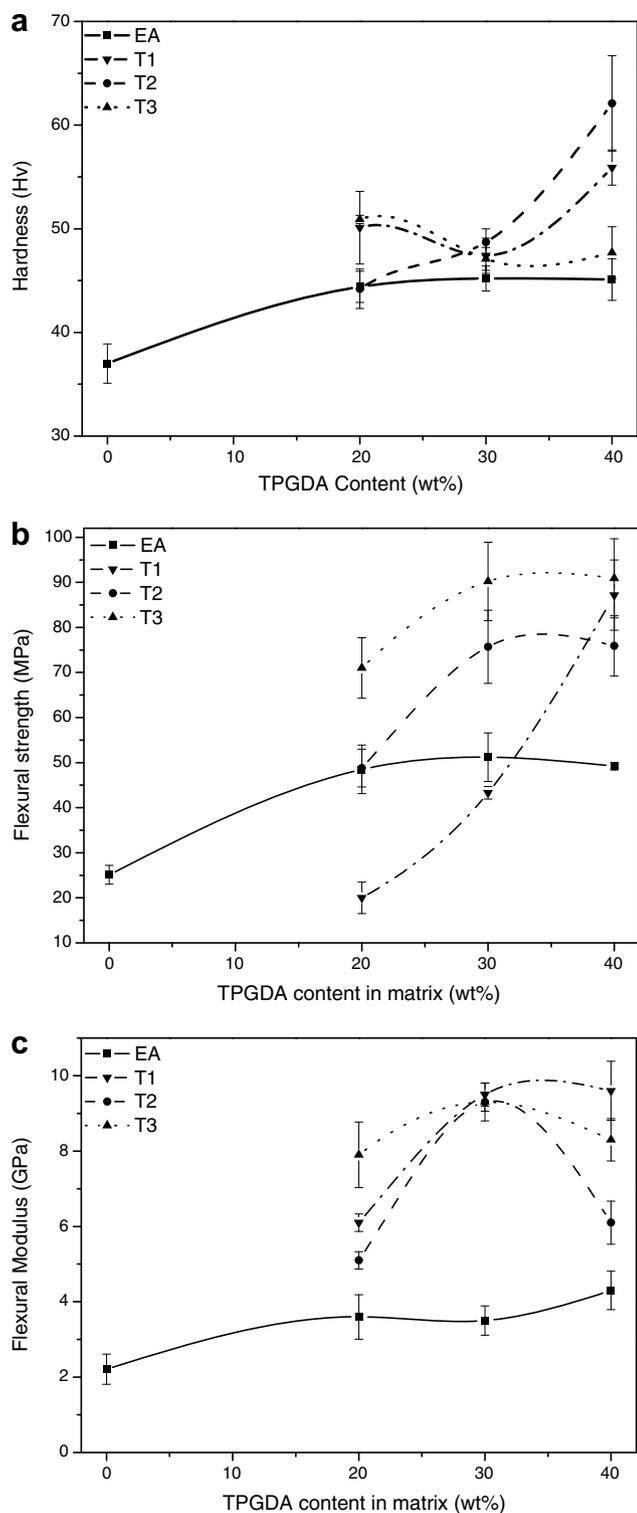
Bis-30C. The flexural moduli of the urethane-modified epoxy acrylate monomer-based polymer composites were all higher than those of the epoxy acrylate-based polymer composites.

Three-point bending flexural strength tests are employed routinely to examine the mechanical behavior of dental restorative materials because they combine the effects of compressive deformation (adjacent to the point of applied load) and tensile deformation (on the opposite side of the specimen) [18]. The flexural strength of the T1 monomer-based polymer composites increased upon increasing the TPGDA content (Fig. 8b) because the addition of TPGDA could increase the mobility of the monomer units and, hence, the degree of conversion [17]. For the T2 and T3 monomer-based polymer composites, the addition of more than 30 wt% of TPGDA resulted in their maximum flexural strengths. Because the viscosity of T1 was much higher than the viscosity of T2 and T3, a greater amount of diluent was required to increase the mobility of the T1 resin matrix. The T3-based polymer composites had higher flexural strength than did the T1- and T2-based systems because the T3 monomer had a lower viscosity. The flexural strengths of the T1, T2, and T3 monomer-based composites were all higher than those of the EA-based polymer composites because of their higher degrees of functionality and molecular weights. The lowest-flexural-strength material in this study was T1-20C, possibly as a result of phase separation occurring between the polymer and the inorganic filler due to the high viscosity of the resin. The flexural strengths of the polymer composites prepared from the T1, T2, and T3 monomers and their optimal TPGDA contents were much higher than those of the Bis-GMA-based materials.

For the T1, T2, and T3 monomer-based composites, the maximum flexural moduli were achieved after the addition of 30 wt% of the diluent (Fig. 8c). The flexural moduli of T1-30C, T2-30C, and T3-30C were all higher than what was found for Bis-30C. The flexural moduli of the T1 monomer-based polymer composites continued to increase after adding more than 30 wt% TPGDA. In contrast, for the T2 and T3 monomer-based polymer composites, the flexural moduli were maximized at 30 wt% TPGDA. Although the addition of the diluent TPGDA increased the degree of conversion, it also decreased the concentration of the functional groups in

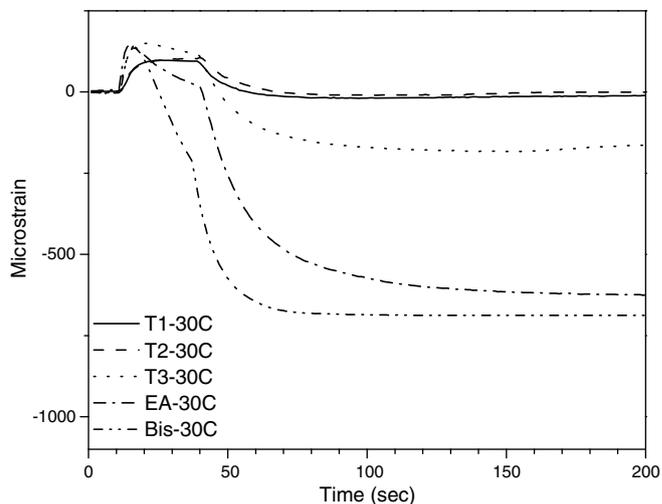
the resin matrix. This led to a lower crosslinking density which resulted in lower flexural moduli. For the T1 monomer-based polymer composites, because of the large viscosity difference between T1-0 and TPGDA, the addition of 40 wt% TPGDA greatly increased the mobility of the resin matrix molecules and thus, increased the flexural modulus. The polymer composites that consisted of the urethane-modified epoxy acrylate with TPGDA in the resin matrix provided materials of much higher flexural strength and flexural modulus than did those made of Bis-30C. Therefore, the urethane-modified epoxy acrylate monomers have great potential as dental restorative matrices.

As shown in Fig. 9, with the addition of 30 wt% TPGDA to the urethane-modified epoxy acrylate resin matrix, all the polymer composites T1-30C, T2-30C, and T3-30C shrank much lower than those made from the non-modified epoxy acrylate (EA-30C) or Bis-30C. This is evident that the increased functional acrylate group in the side chain of epoxy acrylate monomer can dramatically decrease the polymerization shrinkage of the polymer composites. The polymerization shrinkages of the T3 monomer-based materials, which has 4.07 functional acrylates in monomer unit, in this system were much lower than those found for Bis-30C and EA-30C as shown in Fig. 10. The polymerization shrinkages of the polymer composites that were formed from the T3 monomer and 40 wt% of the diluent, which reduced the acrylate group in the system, were larger than those obtained when adding 20 or 30 wt% of the diluent. Also, after the addition of 40 wt% TPGDA in the urethane-modified epoxy acrylate resin matrix, the polymer composites all shrank less than did those composed of EA-40C and Bis-40C as can be seen in Fig. 11. The polymerization shrinkages of the polymer composites formed from 30 wt% TPGDA and the T3 monomer were larger than those of the samples prepared from the T1 or T2 monomers at the same TPGDA content. Indeed, the resin materials made from the latter two monomers and 30 wt% TPGDA formed polymer composites that exhibited almost no polymerization shrinkage. The polymerization shrinkages of the composites prepared from 40 wt% TPGDA and 60 wt% T3 monomer were larger than those prepared from the TPGDA/T2 monomer (40:60 wt%), but less than those prepared from the TPGDA/T1 monomer (40:60 wt%).

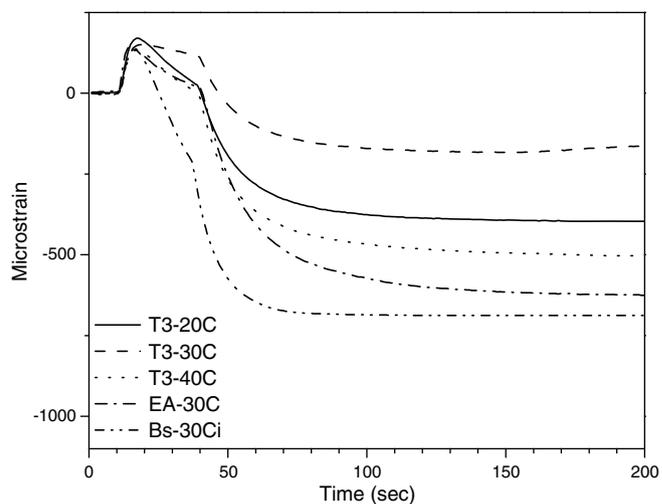


**Fig. 8.** The physical properties of the composite matrix with various amounts of TPGDA: (a) Vickers hardness; (b) flexural strengths; (c) flexural moduli; where T1(▼), T2(●), T3(▲), and EA (■) (error bar mean average standard deviations).

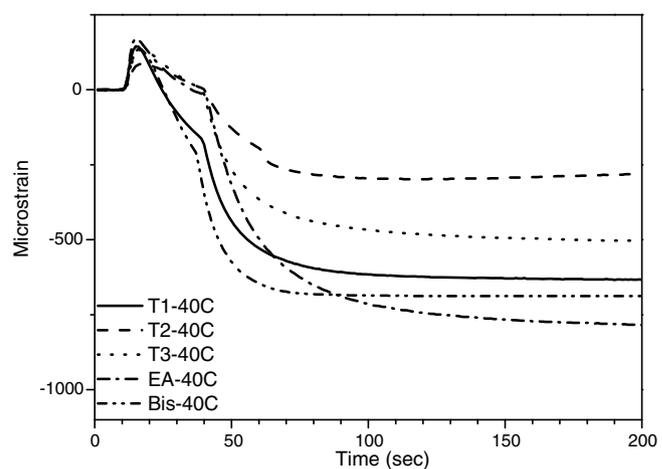
The degrees of shrinkage of the polymer composites prepared from resin matrices of urethane-modified epoxy acrylate monomers and TPGDA were all lower than those based on epoxy acrylate monomers or Bis-GMA. For the T3 monomer-based polymer composites, the addition of 30 wt% TPGDA provided the lowest shrinkage and highest flexural modulus as a result of high cross-linking densities and limited post-gel polymerization. The poly-



**Fig. 9.** Polymerization shrinkages of T1-30C (---), T2-30C (---), T3-30C (....), EA-30C (---), and Bis-30C (---).



**Fig. 10.** Polymerization shrinkages of T3-20C (---), T3-30C (---), T3-40C (....), EA-30C (---), and Bis-30C (---).



**Fig. 11.** Polymerization shrinkages of T1-40C (---), T2-40C (---), T3-40C (....), EA-40C (---), and Bis-40C (---).

merization shrinkage of T3 increased upon the addition of 40 wt% TPGDA, which has two functional acrylates in the mono-

mer unit, because of the lower average overall functional acrylate groups per monomer unit and the soft reactive chains on the TPGDA. The polymerization shrinkage of the composites is resulted from the difference between the contraction and expansion effects of the reaction system. The contraction effect is due to the conversion of van der Waals distances to covalent bonds. However, the expansion effect is attributed to thermal expansion as the reaction heat generated during the polymerization and the conversion of double bonds to single bonds after polymerization [3,4]. The small differences of these two effects were resulted in the low shrinkage of the system. Both the addition of 30 wt% TPGDA in the T1 and the T2 systems show the almost zero shrinkage of the polymer composites obtained from the same polymerization condition.

#### 4. Conclusion

In this study, low-shrinkage high-strength dental restorative materials were developed from urethane-modified epoxy acrylates containing MSMA-modified nano-sized silica spheres. The polymer composites prepared from suitable formulations of the urethane-modified epoxy acrylates T1, T2, and T3, provided low degrees of polymerization shrinkage and good mechanical properties. In some instances these improvements were better than those offered by Bis-GMA-based dental composites. The low degree of polymerization shrinkage of the multifunctional epoxy acrylate/SiO<sub>2</sub> composites leads to the better properties as the dental restorative materials.

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