

Reducing Volume Shrinkage by Low-Temperature Photopolymerization

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ABSTRACT: Low-volume-shrinkage poly(triethylene glycol dimethacrylate) was made by photopolymerization at a low temperature. The final double-bond conversion and dynamic mechanical analysis indicated the optimal cure temperature to be -40°C , at which a cured sample had

less volume shrinkage than samples cured at room temperature but similar mechanical properties. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1126–1130, 2007

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INTRODUCTION

Photopolymerization, a newly developed technology, has been used widely in a variety of fields such as coatings, adhesion, microlithography, and dental restoration because of advantages such as low energy consumption and fast polymerization speeds.^{1–5} However, one of the big drawbacks of free-radical photopolymerization is volume shrinkage during the fast formation of high-density networks, which has been attributed to changes in the interatomic interactions from van der Waals forces to covalent bonds.^{6,7} The volume shrinkage results in some failure of performance. For example, in dental restoratives, volume shrinkage causes the formation of a contraction gap between the restoration and the cavity walls and then leads to recurrent caries if cariogenic bacteria subsequently invade the gap.^{8,9} In industry coating applications, volume shrinkage causes a reduction of adhesion between coating layers and substrates. Thus, to solve this problem, a lot of research has been undertaken in recent years, such as the synthesis of expandable monomers, ring-opening polymerization, and cationic polymerization.^{10–12} For these polymerizable systems, the volume expands during polymerization because the release of ring strain through ring opening can compensate the volume shrinkage, which occurs because the distance between the monomer

molecules becomes close from the van der Waal distance to the covalent distance.¹³

Usually, photopolymerization is carried out at room temperature. Little attention has been paid to the influence of low temperatures on volume shrinkage. Research has indicated that the quantum yields of photoinitiators increase with increasing cure temperature (T_{cure}).¹⁴ The double-bond conversion is reduced at low temperatures, and then the shrinkage due to the polymerization reaction is lower. Recently, research results in our group¹⁵ indicated that the double-bond conversion was reduced for a system photopolymerized at a low temperature because of the vitrification of the polymer network at a very early stage of the polymerization. The free radical was trapped within the network, then the double bond could not move to approach the free radical, and the polymerization ceased at a very low double-bond conversion; however, the final conversion after the postcure was almost the same as that of a system polymerized at room temperature because the trapped free radical could continue to induce polymerization when the temperature changed from a low temperature to room temperature. The mechanical properties of the polymer film polymerized at a low temperature were almost the same as those of the film polymerized at room temperature. When the temperature was increased to room temperature, the volume of the polymer film expanded, and this counteracted the shrinkage due to the polymerization reaction. Then, the volume shrinkage of the polymer film polymerized at a low temperature was lower than that of the film polymerized at room temperature.

In this study, triethylene glycol dimethacrylate (TEGDMA) was photopolymerized at different T_{cure} values (from -75 to 20°C), the double-bond conver-

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sion was measured by Fourier transform infrared (FTIR), the loss tangent ($\tan \delta$) and the glass-transition temperature (T_g) were recorded by dynamic mechanical analysis (DMA), and the volume shrinkage was measured by the pycnometric method.

EXPERIMENTAL

The monomer TEGDMA (SR205) was donated by Sartomer Co., Inc. (Warrington, PA). The photoinitiator 1-hydroxycyclohexyl phenyl ketone (HCPK) was supplied by High-Tech Insight Co., Ltd. (Beijing, China). These materials were used without further purification. The basic formulation of the photopolymerization system was the monomer and 0.5 wt % HCPK. After the addition of the photoinitiator, the photopolymerization system was stirred until HCPK was dissolved completely.

For the investigation of the double-bond conversion, the sample was injected into a mold of a uniform size ($76 \times 26 \times 0.5 \text{ mm}^3$) and isothermally cured under a UV-light source (model 100 UV, Rolence, Taiwan) for 400 s with a light intensity of 2735 mW/cm^2 (UV meter, Honle, Grafelfing, Germany). The isothermal photopolymerization (at temperatures ranging from -75 to 20°C) was performed with a PSL1800 cooler (Eyela, Tokyo, Japan; ethanol was used as the cooler medium). The double-bond conversion was monitored by near-infrared (Nicolet 5700 FTIR, Nicolet Instrument, Madison, WI); the change in the absorption area from 6207 to 6124 cm^{-1} was measured before and after UV irradiation. The initial conversion was calculated with eq. (1). For the postcure reaction, the samples were taken from the cooler and put into the FTIR apparatus at room temperature to measure the change in the absorption area from 6207 to 6124 cm^{-1} at different times. The postcure conversion was calculated with eq. (2). The final double-bond conversion was defined as the double-bond conversion after the postcure process was finished:

$$\text{Initial conversion (\%)} = (1 - S_2/S_1) \times 100 \quad (1)$$

$$\text{Postcure conversion (\%)} = (1 - S_n/S_1) \times 100 \quad (2)$$

where S_1 is the =CH peak area before UV irradiation, S_2 is the =CH peak area after UV irradiation, and S_n is the =CH peak area during the postcure.

For DMA, samples of a uniform size of $35 \times 7 \times 0.5 \text{ mm}^3$ were prepared, and the measurements were performed with a DMTA-V dynamic mechanical analyzer (Rheometric, Scientific Inc., Piscataway, NJ) in the range of -60 to 200°C with a ramping rate of 5°C/min with an extension mode. $\tan \delta$ was recorded as a function of temperature. T_g was taken to be the maximum of the $\tan \delta$ /temperature curve. For each

system, three repeat experiments were performed. The densities of the monomer and polymer were measured by the pycnometric method.

RESULTS AND DISCUSSION

Effect of T_{cure} on the double-bond conversion

The photopolymerization system of TEGDMA and 0.5 wt % HCPK was cured by UV radiation at different T_{cure} values ranging from -75 to 20°C ; the double-bond conversions are shown in Figure 1 and Table I. Figure 1 illustrates that the double-bond conversion decreased steadily with the drop in T_{cure} . When T_{cure} was -75°C , the initial double-bond conversion was 9%; when T_{cure} increased to 20°C , the initial double-bond conversion (81.7%) was 9 times higher than that of the sample cured at -75°C .

During the process of free-radical polymerization, a microgel was formed at very early stages of polymerization, thus reducing the mobility of the molecular segments of the reacting systems. Once T_g approached T_{cure} , the system vitrified, so polymerization ceased.¹⁶⁻¹⁹ The difference between T_{cure} and T_g had an important effect on the vitrification of the system. When the formulation was cured at a lower temperature, the difference between T_{cure} and T_g was less, and the formulation vitrified at an earlier stage, so the double-bond conversion at a lower T_{cure} was low.

Moreover, the viscosity of the formulation was also a crucial factor for the double-bond conversion. Scherzer and Decker²⁰ found that the double-bond conversion strongly increased with decreasing viscosity because of the rise of T_{cure} , which led to a strong increase in the molecular diffusion and reactivity. Thus, a drop in T_{cure} led to an increase in the

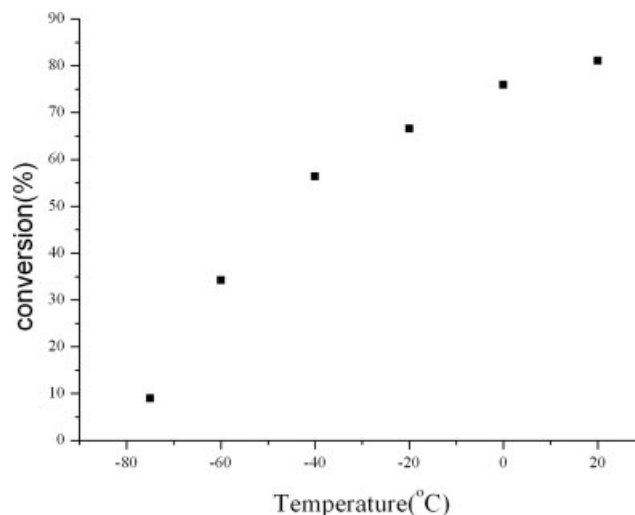


Figure 1 Double-bond conversion versus T_{cure} .

TABLE I
Data for the Samples Cured at Different Temperatures

	$T_{\text{cure}} (^{\circ}\text{C})$					
	20	0	-20	-40	-60	-75
Conversion after the photocuring (%)	81.7	75	66.8	56.6	34.4	9
Conversion after the dark reaction (%)	84.5	85.3	82.2	81.5	63.6	19.9
$T_g (^{\circ}\text{C})$	146	146	145	146	65	-1
Density of the monomer (g/mL)	1.08	1.11	1.15	1.18	1.22	1.24
Density of the polymer (g/mL)	1.24	1.25	1.26	1.24	1.25	1.22
Volume shrinkage (%)	12.9	11.2	8.7	4.8	2.4	-1.6

viscosity and hence a decrease in the double-bond conversion.

Influence of T_{cure} on the dark reaction

After being cured at different temperatures, the samples were put in the dark at room temperature to perform the dark reaction (Fig. 2 and Table I). Figure 2 illustrates that ascending trend of the postcure curves was much more striking for the sample cured at lower T_{cure} . As the temperature rose from a low temperature to room temperature, the trapped radical was released from physical crosslinking crystallinity, and the double bond was more moveable. Therefore, the double bond could approach the free radical, and the polymerization process occurred again. The double-bond conversion increased, and finally a highly crosslinked network formed; no more double bonds could approach any free radicals, and the polymerization process was finished.

Figure 2 also shows that, after 6 h of the dark reaction, the final conversions of the samples cured at different temperatures ranging from -40 to 20°C were almost the same (ca. 83%; Table I). This result agrees with the findings of Cook et al.¹⁷ and Ziaee

and Palmese,²¹ who demonstrated that the final conversion of vinyl double bonds after postcuring was the same in samples cured at temperatures ranging from -10 to 90°C . However, the final conversion of samples cured at -75 (19.9%) and -60°C (63.6%) was much less than that of samples cured at temperatures ranging from -40 to 20°C (Table I). This might be because the number of total free radicals generated, such as reactive fragments of the initiator and chain radicals, was very low at such low temperatures; on the other hand, the trapped free radical might gradually have lost its reactivity during the postcuring process, so the final conversion was lower.

DMA

After the postcure was completed, the mechanical properties of samples cured at different temperatures were measured with the DMTA-V. The effect of T_{cure} on $\tan \delta$ is shown in Figure 3, which illustrates that the $\tan \delta$ curves of these samples cured at -40 , -20 , 0 , and 20°C were very similar, but the profiles of $\tan \delta$ of those samples cured at -60 and -75°C were much lower than those of the samples cured at -40 , -20 , 0 , and 20°C . At the same time, the data in Table I indicate that the T_g values of the

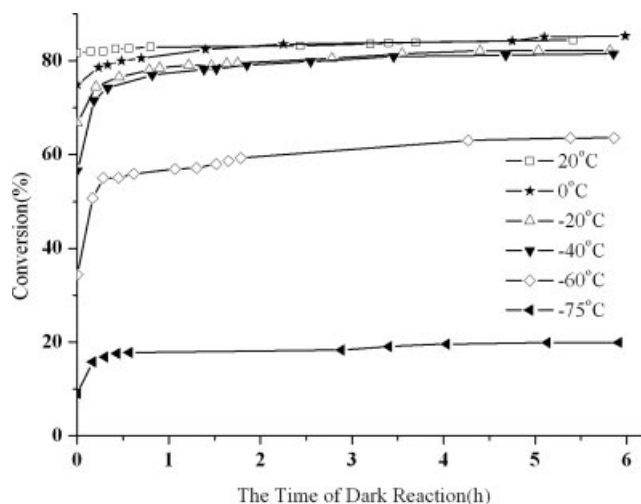


Figure 2 Postcure curves of TEGDMA cured at different temperatures.

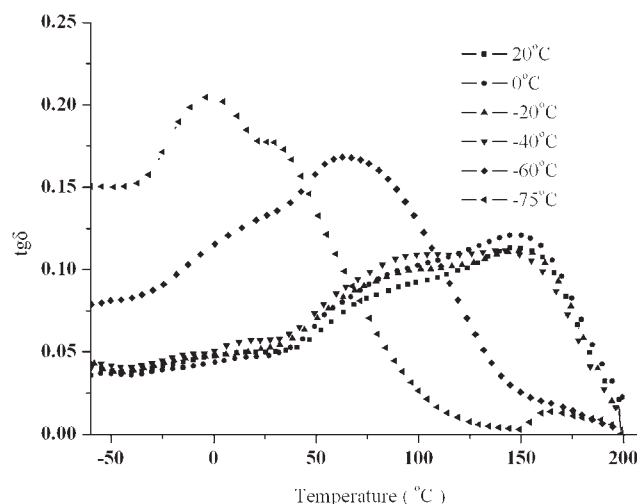


Figure 3 $\tan \delta$ /temperature curves of samples cured at different temperatures.

samples cured at -40 , -20 , 0 , and 20°C were almost the same (145°C) and much higher than those of the samples cured at -60 and -75°C . A number of studies have demonstrated that T_g of a photocured resin increases with the final conversion.^{16,17,23,24} These are comparable to previous results for double-bond conversion. The final double-bond conversions of samples cured at -40 , -20 , 0 , and 20°C were around 83% , which was higher than those of samples cured at -60 (63.6%) and -75°C (19.9%).

Volume shrinkage

Calculation of the density of TEGDMA at different temperatures

Because it was difficult to get credible experimental data for the density of TEGDMA at a low temperature, the specific density had to be calculated by some empirical equations. First, we estimated some thermodynamic critical constants with the Lydersen method revised by Joback,²⁵ which could calculate them accurately and is applied widely in some fields. The equations of the Lydersen method are as follows:

$$T_b = 198 + \sum \Delta T_b \quad (3)$$

$$T_c = \frac{T_b}{0.584 + 0.965 \sum \Delta t - (\sum \Delta t)^2} \quad (4)$$

$$p_c = \frac{0.1}{(0.113 + 0.0032N - \sum \Delta p)^2} \quad (5)$$

where T_b is the boiling temperature at the normal pressure; T_c is the critical temperature; p_c is the critical pressure; ΔT_b , Δt , and Δp are the parameters of the summation of the contributions of all groups; and N is the number of atoms of TEGDMA. These expressions could be used to estimate T_b [eq. (3)], T_c [eq. (4)], and p_c [eq. (5)].

Then, we estimated the densities of TEGDMA at different temperatures with the Rackett equations revised by Spencer and Danner,^{26,27} which were applied to estimate the density of the saturated liquid (ρ_s). The Rackett equations are shown as follows:

$$V_s = \frac{RT_c(Z_r)^k}{p_c} \quad (6)$$

$$k = 1 + (1 - T_r)^{2/7} \quad (7)$$

$$\rho_s = \frac{M}{V_s} \quad (8)$$

$$T_r = \frac{T}{T_c} \quad (9)$$

where V_s is the molar volume of the saturated liquid, Z_r is the characteristic constant of TEGDMA, k

is the index of Z_r , T_r is the ratio of the given temperature to T_c , R is the gas constant, and M is mass. The density of TEGDMA at 20°C was measured, and Z_r was calculated with these equations; then, the densities of TEGDMA at different temperatures could be calculated with the Rackett equations. The calculated values are shown in Table I.

Calculation of the volume shrinkage

All the samples for volume-shrinkage measurements were set at room temperature to complete the dark reaction after they were polymerized at different temperatures. Then, the volume shrinkage of the samples was calculated with the following expression:^{9,28}

$$\text{Shrinkage (\%)} = \left(1 - \frac{d_{\text{uncured}}}{d_{\text{cured}}}\right) \times 100 \quad (10)$$

where d_{uncured} is the density of the monomer at T_{cure} and d_{cured} is the density of the polymer at room temperature (measured by the pycnometric method).²⁶ The values of the volume shrinkage are shown in Table I and indicate that the volume shrinkage decreased with the drop in T_{cure} and became negative when T_{cure} was -75°C .

In eq. (10), the volume shrinkage is proportional to the value of d_{uncured} , which represents the numerator related to T_{cure} . When T_{cure} is lower, d_{uncured} becomes bigger, and so the volume shrinkage is less. This is a major reason for the results. Besides, the volume shrinkage is inversely proportional to the denominator, d_{cured} , which is measured at room temperature and is related to the final conversion of the completely postcured samples. The final conversions of the samples cured at different temperatures ranging from -40 to 20°C were almost the same and much higher than those of the samples cured at -60 and -75°C (Table I). Therefore, the lower final conversion was also a reason that the volume shrinkage decreased.

CONCLUSIONS

Near-infrared was used to investigate the double-bond conversion of TEGDMA cured at temperature ranging from -75 to 20°C . The double-bond conversion decreased steadily with the drop in T_{cure} ; however, the final conversion of a sample cured at a lower temperature increased much more dramatically after the postcure reaction.

Although the volume shrinkage decreased with decreasing T_{cure} , the mechanical properties of samples cured at -40 , -20 , 0 , and 20°C were much better than those of samples cured at -60 and -75°C .

The optimal T_{cure} value was found at -40°C , at which a cured sample had less volume shrinkage than a sample cured at room temperature but similar mechanical properties.

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