

Preparation of Silica-Filled Poly(2-hydroxymethyl methacrylate) Nanocomposites Cured by Photoirradiation during the Sol–Gel Process

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ABSTRACT: The sol–gel process was used to prepare a photosensitive inorganic–organic composite, silica/poly(2-hydroxymethyl methacrylate). Its nanoscale morphology was observed with field emission scanning electron microscopy at high magnifications (e.g., 160,000 \times). The size of the particles in the nanocomposite synthesized under various preparation conditions fell in the range of 20–50 nm. The effects of the pH, reactant composition, and solvent content in the reaction mixture on the thermal and mechanical prop-

erties of the nanocomposite were studied with thermogravimetric analysis, dynamic mechanical analysis, and thermomechanical analysis. The thermal stability of the synthesized nanocomposite could generally be improved by an increase in the molar ratio of the inorganic component, a reduction in the reaction pH, or an increase in the solvent content. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1927–1935, 2004

Key words: gels; nanocomposites; silicas

INTRODUCTION

Photosensitive polymeric materials have widely been used in the printed-circuit-board, semiconductor, and optical–electronic industries as a key component in applications such as plastic hard coatings, packaging, and photoresists. In many instances, for these applications, polymers with specific physical properties, such as high temperature stability, good mechanical strength, low thermal expansion, and low dielectric constants, are highly demanded. Unfortunately, conventional single-component polymers or polymer blends, being inherently organic in nature, are normally unable to fulfill these requirements. The incorporation of an inorganic component in the form of uniformly dispersed nanoparticles into a continuous polymer matrix has been demonstrated to be a promising route.^{1–12} As a result of excessive interfacial interactions between the organic and inorganic phases, the nanocomposite material manifests certain unique physical properties, which are not achievable with ordinary blends that often contain extensive large-scale phase domains. The sol–gel method, being a process that can be carried out at temperatures commonly used for polymer synthesis, is considered an important method for preparing organic–inorganic

nanocomposites that is comparable to the industrialized clay-intercalation method.^{13,14} Under the proper preparation conditions, the size of the particles in the formed composite can be reduced to approximately 10 nm.^{1–12} Therefore, the composite material possesses very good optical transparency, which is an important characteristic for a coating material.

Previously, a silica-modified photosensitive poly(2-hydroxymethyl methacrylate) [poly(HEMA)] was synthesized by the sol–gel method. We reported the chemical structure [as analyzed via Fourier transform infrared (FTIR) and solid ²⁹Si-NMR] and the nanoscale morphology [as observed with transmission electron microscopy (TEM) and field emission scanning electron microscopy (FESEM)] of this nanocomposite.¹⁵ Two of the major chemical reactions for this sol–gel process are (1) the hydrolysis and condensation of TEOS (tetraethoxysilane), which form the Si–O–Si network, and (2) the condensation between the hydroxyl groups of silanol and 2-hydroxymethyl methacrylate (HEMA) in the presence of acid. The feasibility of this reaction is discussed in the literature by, for example, Hajji et al.,² Novak et al.,³ and Bosch et al.¹² However, no solid conclusion has been reached yet. Although no direct evidence from ¹³C-NMR (shift ~ 60 ppm) was obtained by these authors, results from other techniques, such as ²⁹Si-NMR, FTIR, light scattering, and thermomechanical analysis (TMA), have indirectly supported the formation of the Si–O–C bond by condensation between silanol and HEMA. Another major chemical reaction is the UV curing of C=C in HEMA. In this article, the effects of some

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TABLE I
Compositions of the Reactants for the Preparation of the Nanocomposites

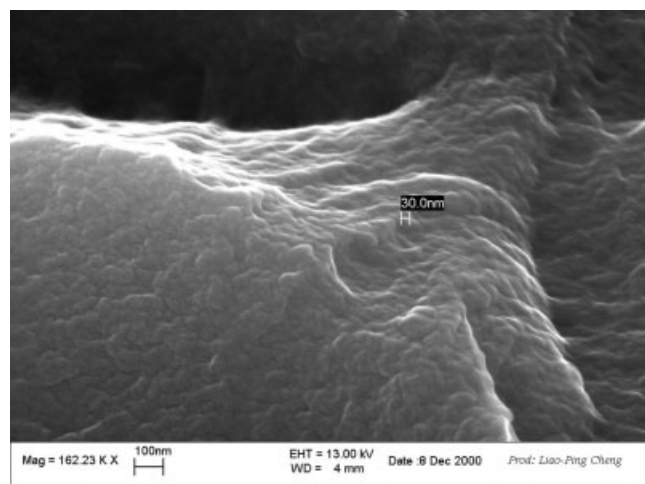
Sample code	TEOS/HEMA/IPA/CH ₃ COOH/H ₂ O (molar ratio)	pH
H2-2	1:2:1:0.2:2	2
H2-3	1:3:1:0.2:2	2
H2-4	1:4:1:0.2:2	2
H6-2	1:2:1:1:2	1.67
H6-3	1:3:1:1:2	1.67
H6-4	1:4:1:1:2	1.67
H6-4-2	1:4:0:1:2	1.67
H6-4-3	1:4:4:1:2	1.67
H6-4 (pH 4)	1:4:1: <i>x</i> :2	4
H6-4 (pH 12)	1:4:1: <i>y</i> (NaOH):2	12

$$x = 2.41 \times 10^{-5}; y = 3.6 \times 10^{-4}$$

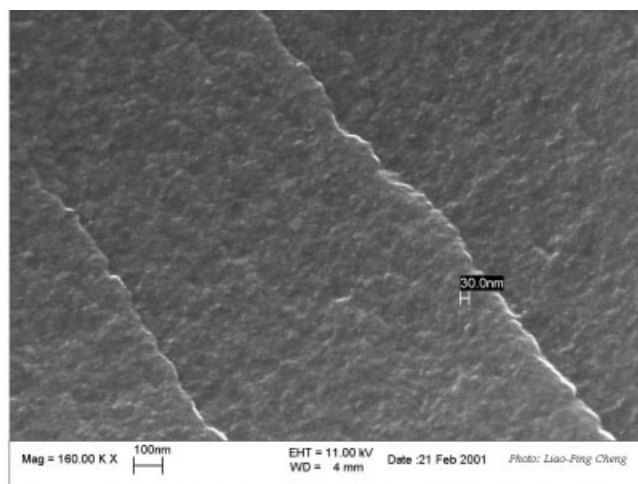
preparation parameters, such as the reaction pH, the concentrations of the reactants, and the solvent contents, on the morphologies and physical properties of the formed nanocomposites are reported.

EXPERIMENTAL

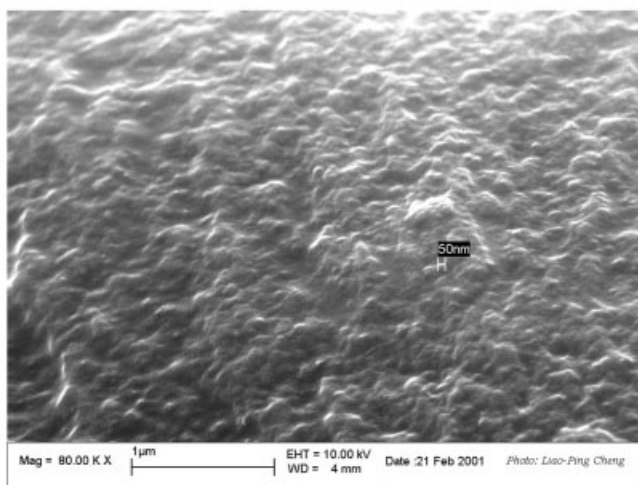
The composite material was prepared by the well-known sol-gel method. In brief, appropriate amounts of TEOS and HEMA were mixed with 2-propanol (in some cases, 2-propanol was not used) at room temperature to form a homogeneous solution. To this solution was added an acetic acid or NaOH aqueous solution of a known pH. The compositions of these species for various syntheses are summarized in Table I. The pH value in the third column represents the acidity of either the acetic acid or NaOH aqueous solution, with the given molar ratio in the second column rather than the pH of



(a)



(b)



(c)

Figure 1 SEM micrographs of nanocomposites prepared from solutions with different initial acidities: (a) H6-4, (b) H6-4 (pH 4), and (c) H6-4 (pH 12).

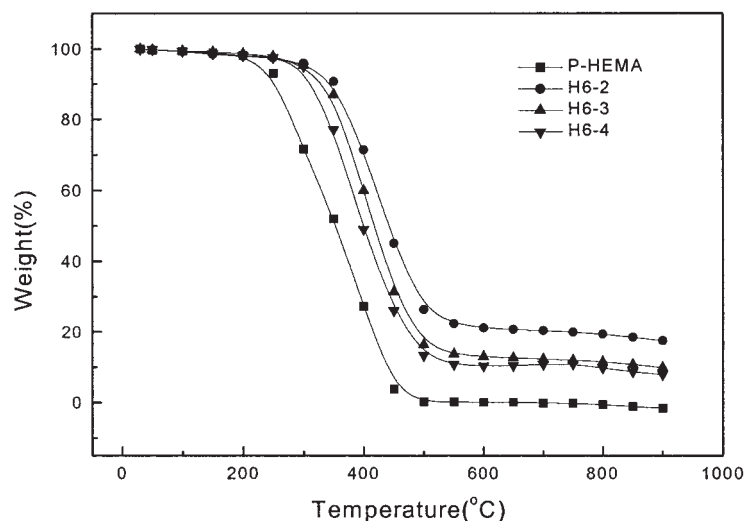


Figure 2 TGA thermograms of pure poly(HEMA) and nanocomposites prepared with different ratios of TEOS and HEMA.

the whole reaction mixture. For example, pH 1.67 in H6-2 is the pH value of the solution with the acetic acid/water molar ratio of 1:2. After the mixture was stirred for 6 h, a crosslinking agent (trimethylolpropane triacrylate, 5.26% of the total weight) and a photoinitiator (2,2-dimethoxy-1,2-diphenylethane-1-one, 5.26% of the total weight) were added directly under continuous agitation. This mixture was then spin-coated on a metal or polycarbonate substrate. Subsequently, it was placed in a thermostat kept at 70°C for 2 h to remove byproducts such as water and ethanol and some residual 2-propanol. Finally, the material was cured with UV irradiation (500 mJ/cm²) to yield a transparent film. The synthesized composites were characterized with the following methods.

Morphology

The nanoscale morphology of the composite was observed with FESEM. The samples were vacuum-dried

and then fractured in liquid nitrogen to expose the cross sections. The lateral sides of the samples were wrapped with conductive copper tape and clamped in a cross-section sample holder. They were then coated with a thin layer (ca. 1.0 nm) of a Pt-Pd alloy with a sputter coater equipped with a quartz crystal microbalance thickness controller. They were then imaged at high magnifications (e.g., 160,000×) with a Leo 1530 field emission scanning electron microscope (Carl Zeiss, Oberkochen, Germany).

Thermomechanical properties

The thermal decomposition, glass transition, and thermal expansion behaviors of the composites were studied with thermogravimetric analysis (TGA; Hi-Res TGA 2950, TA Instrument), dynamic mechanical analysis (DMA; DMA2980, TA Instrument, Newcastle, USA), and TMA (TMA2940T, TA Instrument). The

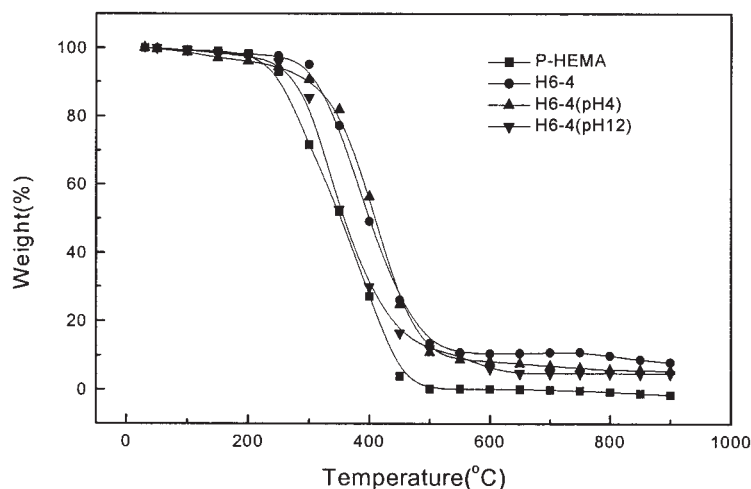


Figure 3 TGA thermograms of pure poly(HEMA) and nanocomposites prepared with different initial acidities.

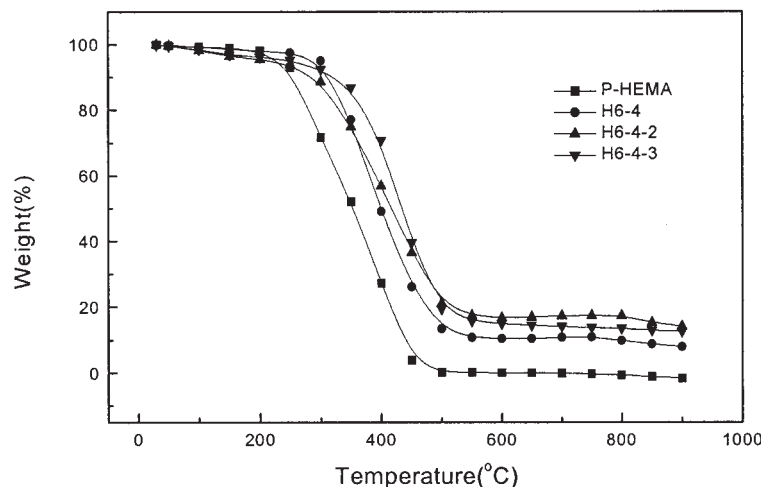


Figure 4 TGA thermograms of pure poly(HEMA) and nanocomposites prepared from solutions with different 2-propanol concentrations.

heating rates were 10°C/min for TGA and TMA and 3°C/min for DMA. The scanning ranged from 25 to 900, from -50 to 200°C, and from 25 to 180°C, respectively, for these instruments. The operating frequency for DMA was 1 Hz. All the experiments were carried out under a nitrogen environment.

Hardness and water and ethanol absorptions

The hardness of the nanocomposites was examined by the industrial pencil hardness test with pencils of different hardnesses.^{16,17} The water and ethanol absorptions of the formed composite material were measured by the immersion of the samples in pure water or ethanol for 2 weeks and by drying *in vacuo* at an elevated temperature to a constant weight. The absorption amounts were calculated.

RESULTS AND DISCUSSION

Effect of the acidity on the morphology of the nanocomposites

Generally, the pH of a reaction has a strong effect on the size of the nanoparticles in the composite formed via a

TABLE II
T_d and Char Yield of Poly(HEMA) and the Nanocomposites Determined by TGA

	<i>T_d</i> (°C)	Char yield (%)
Poly(HEMA)	240	0
H2-2	295	18.4
H2-3	284	12.72
H2-4	270	7.22
H6-2	313	17.52
H6-3	303	9.95
H6-4	299	7.96
H6-4-2	259	14.09
H6-4-3	301	12.51
H6-4 (pH 4)	264	5.54
H6-4 (pH 12)	252	4.63

sol-gel process. This was observed in the system under study. Figure 1(a-c) shows SEM photomicrographs of silica/poly(HEMA) nanocomposites prepared under both acidic and basic conditions. For the acid-catalyzed reactions, Figures 1(a) (pH 1.67) and 1(b) (pH 4) indicate that the nanocomposites consisted of irregularly shaped particulate entities whose sizes fell mainly in the range of 20–25 nm. This size was of the same order as that of the phase domains of the inorganic component reported in the literature and determined by SEM, TEM, and SAXS.^{2,15} The difference in the particle size between Figure 1(a,b) is, however, not distinguishable by FESEM because of the limitation of the imaging resolution. The differences in the physical properties between these two nanocomposites are shown later with TGA, DMA, and TMA. As the sol-gel reaction was carried out in a strong basic solution, the size of the nanoparticles in the synthesized composite increased considerably. This is demonstrated in Figure 1(c) for the case of pH 12. The nanoparticles were much larger than those in Figure 1(a), the average size here being greater than 50 nm [note the difference in magnification between Fig. 1(a,c)]. The reason that a base-catalyzed sol-gel reaction yields large particles has been discussed in the literature in terms of the relative rate of condensation (i.e., reaction A) and hydrolysis (i.e., reaction B).^{2,18,19} Under basic conditions, the condensation reaction is faster than the hydrolysis reaction, whereas under acidic conditions, the situation is reversed. As a result, more silica particles (with smaller sizes) tend to form in acid solutions than in basic solutions. In either case, the silica/poly(HEMA) particles were nano-size, and so the bulk material was visually transparent.

Thermal properties

TGA

The TGA results for various samples are given in Figures 2–4 and Table II. Figure 2 depicts the thermo-

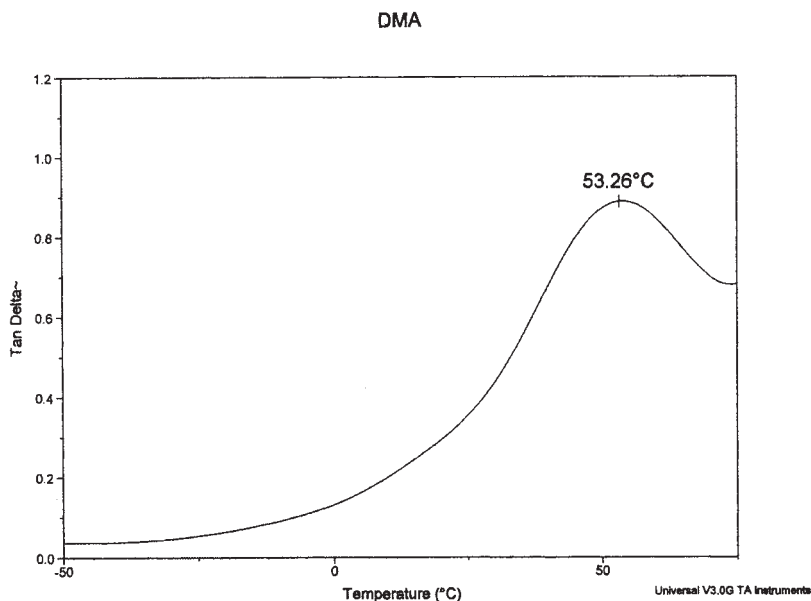


Figure 5 Tan δ of synthesized poly(HEMA) measured by DMA.

grams of pure poly(HEMA) and nanocomposites prepared with different molar ratios of the organic (HEMA) and inorganic (TEOS) components. The thermal decomposition temperature (T_d) of pure poly(HEMA) was about 240°C, and the char yield was nearly zero. The viscosity-average molecular weight of this polymer was measured to be 420,000. As TEOS was introduced, Figure 2 indicates that T_d of the formed nanocomposite increased considerably. For example, with the TEOS/HEMA molar ratio of 1:4, Table II shows that T_d of sample H6-4 was 59° higher than that of pure poly(HEMA). T_d was also found to increase with increasing inorganic content in the reac-

tant (cf. H2-2, H2-3, and H2-4 and H6-2, H6-3, and H6-4). The highest T_d for the nanocomposites in this study was 313°C for sample H6-2. Obviously, the silica nanoparticles within the continuous poly(HEMA) matrix made the composite material more stable against thermal decomposition, and the effect was stronger with higher silica contents. Figure 2 also shows that all the composites exhibited a one-step thermal decomposition profile. This suggested good homogeneity in these materials due to nanoscale mixing.

The effect of the reaction pH on the thermal decomposition behavior of the nanocomposites is illustrated in Figure 3 and Table II. T_d was higher for samples

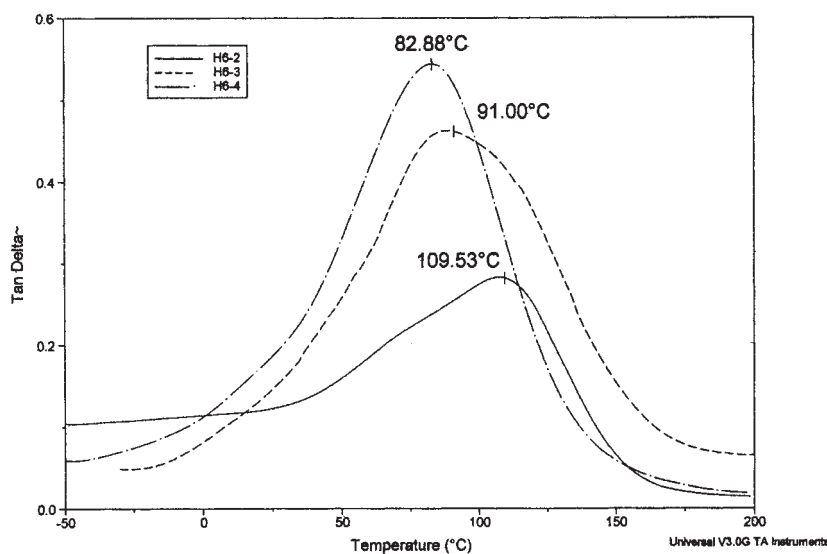


Figure 6 Tan δ of nanocomposites prepared with different ratios of TEOS and HEMA.

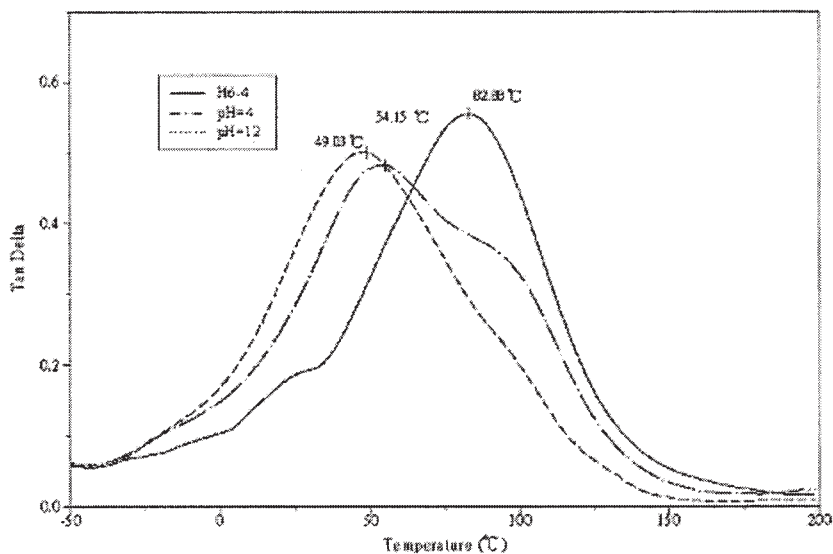


Figure 7 Tan δ of nanocomposites prepared with different initial acidities.

obtained at a lower reaction pH, and the char yield followed the same trend, but the difference was not as evident. This can be attributed to the size of the silica particles in the nanocomposites. For reactions carried out at lower pHs, the silica particles in the composite were generally smaller. This resulted in more interfacial contact, and so the total interaction between the organic and inorganic phases was stronger, leading to a higher T_d . Furthermore, even for H6-4 (pH 12), with the lowest T_d of the nanocomposites in this study, T_d was still 12° higher than that of pure poly(HEMA).

Figure 4 presents the TGA results, which reflect the effect of solvent usage on T_d of the nanocomposites. In most sol-gel processes, a solvent is used to obtain a

good dispersion of the organic and inorganic reactants. As TEOS is nonpolar, it is customarily required to use a polar organic solvent to enhance its miscibility with the aqueous phase.³ Although, for this system, TEOS could react directly with HEMA without the use of an external solvent, in some examples, 2-propanol was used to determine its effects on the properties of the formed nanocomposites. Figure 4 indicates that as the amount of 2-propanol was increased, T_d of the nanocomposite also increased. This suggests that with the aid of 2-propanol, the reaction mixture became more uniform and that the polymerization of HEMA could progress to a more complete extent in a dilute solution. The use of the solvent also has the benefit of

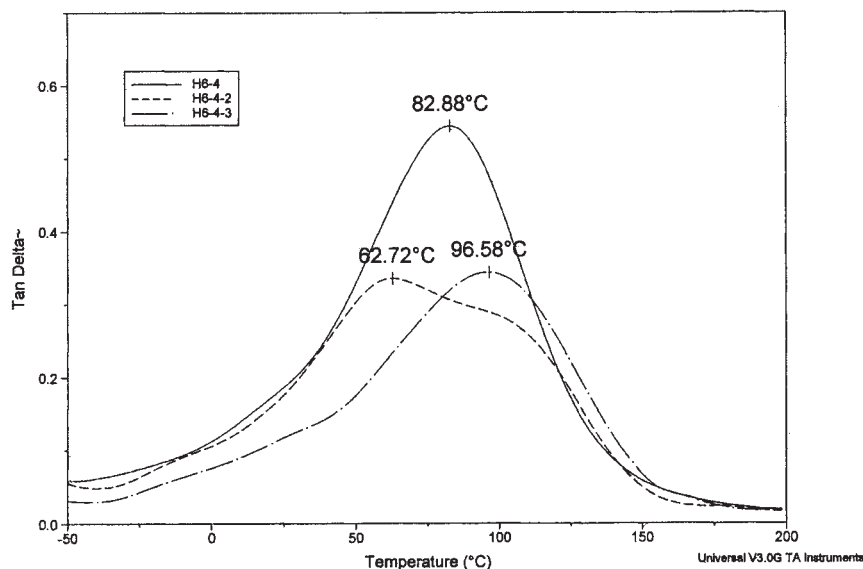


Figure 8 Tan δ of nanocomposites prepared from solutions with different 2-propanol concentrations.

TABLE III
Thermal Expansion Coefficients of Poly(HEMA) and the Nanocomposites as Determined by TMA

Sample	α_1 ($\mu\text{m}/\text{m } ^\circ\text{C}$)	α_2 ($\mu\text{m}/\text{m } ^\circ\text{C}$)	T_g ($^\circ\text{C}$)	
			TMA	DMA
Poly(HEMA)	234	643	55.39	53.26
H2-2	141	594	100.01	101.60
H2-3	79	854	92.63	87.21
H2-4	95.8	172	86.10	80.99
H6-2	64.5	180	107.46	109.53
H6-3	63.5	165	91.39	91.00
H6-4	47.5	148	82.58	82.88
H6-4-2	152	132	62.30	62.72
H6-4-3	148	243	88.03	96.58
H6-4 (pH 4)	53.2	269	71.16	54.15
H6-4 (pH 12)	109	195	58.04	49.03

prolonging the shelf life of HEMA–silica samples not yet UV-cured. However, care must be taken with respect to the amount of solvent usage because it can cause serious shrinkage of the coating during the drying procedure, and this sometimes leads to cracks in the composites.

DMA

The glass-transition temperatures (T_g 's) of pure poly(HEMA) and various composites were measured with DMA. As shown in Figure 5, T_g of pure poly(HEMA) was 53.26 $^\circ\text{C}$ [a DSC test of the sample produced a value of 63 $^\circ\text{C}$]. This was smaller than the data reported in the literature (ca. 80–100 $^\circ\text{C}$), possibly because of a smaller molecular weight.^{20–22} As a rigid and inflexible material, silica possesses a very high T_g . By the incorporation of silica into the polymer matrix in the form of nanoparticles, it was expected that the rigidity of the composite material would be significantly improved through extensive interfacial interactions between the organic and inorganic phases. As the motions of the polymer chains were hindered by silica, T_g was increased considerably. The measured results are given in Figures 6–8 and Table III. In Figure 6, the DMA thermograms for composites of different silica contents are shown. T_g increased with an increasing silica content in the composite. For 1:2 TEOS/HEMA in the reaction mixture (i.e., H6-2), T_g reached 109.5 $^\circ\text{C}$, which was 56 $^\circ\text{C}$ higher than that of pure poly(HEMA). The peak-broadening phenomenon common to composites was also evident here.²³ The effect of the reaction pH on T_g of the formed nanocomposite is shown in Figure 7. At the high pH value of 12, the measured T_g value was close to that of pure poly(HEMA), whereas at the low pH of 1.67, T_g was much higher. This is consistent with results shown earlier: the particle size of the nanocomposite obtained from a reaction at a high pH was much larger than that from a low pH. For a reaction carried out at

pH 4, the composite exhibited a very broad peak; the highest $\tan \delta$ value occurred at 54 $^\circ\text{C}$, and a shoulder could be observed at about 83 $^\circ\text{C}$. A possible reason for this behavior was that the composite had a wide range of particle size distributions. Figure 8 shows the effects of the solvent (2-propanol) contents in the initial reaction mixture on T_g of the formed nanocomposite. T_g generally increased with increasing 2-propanol contents. Just like the T_d results shown earlier, the homogeneity of the reaction mixture played the key role. Hence, the same reasoning for the T_d data is applicable here as well.

TMA

The linear thermal expansion coefficients of various nanocomposites were measured with TMA. In Figure 9, two typical results [i.e., for pure poly(HEMA) and H6-4] are shown in terms of the linear dimensional change versus the temperature. For pure poly(HEMA), Figure 9(a) indicates that the thermal expansion coefficients before (α_I) and after (α_{II}) the glass transition were 234 and 643 $\mu\text{m}/\text{m } ^\circ\text{C}$, respectively. T_g of the sample, as determined from the intersection of the two straight lines above and below the transition, was 55.4 $^\circ\text{C}$, close to the data measured by DMA in Figure 5. The thermal expansions of polymers are normally very high, and this limits their industrial applications as coating materials. In this research, we found that the level of thermal expansion could be tremendously reduced by the action of silica in the nanocomposites. Figure 9(b) shows the result of a typical case, H6-4. α_I and α_{II} were as small as 47.5 and 148 $\mu\text{m}/\text{m } ^\circ\text{C}$, respectively. Other measured data are summarized in Table III. Clearly, for all the synthesized nanocomposites, there were significant improvements in the thermal dimensional stability over a wide temperature range. However, unlike the TGA and DMA measurements, the effects of the silica contents, pH, and solvent contents did not follow a regular trend: α_1 (H6-4-2) > α_1 (H6-4-3) > α_1 (H6-4) and α_1 (H2-2) > α_1 (H2-4)

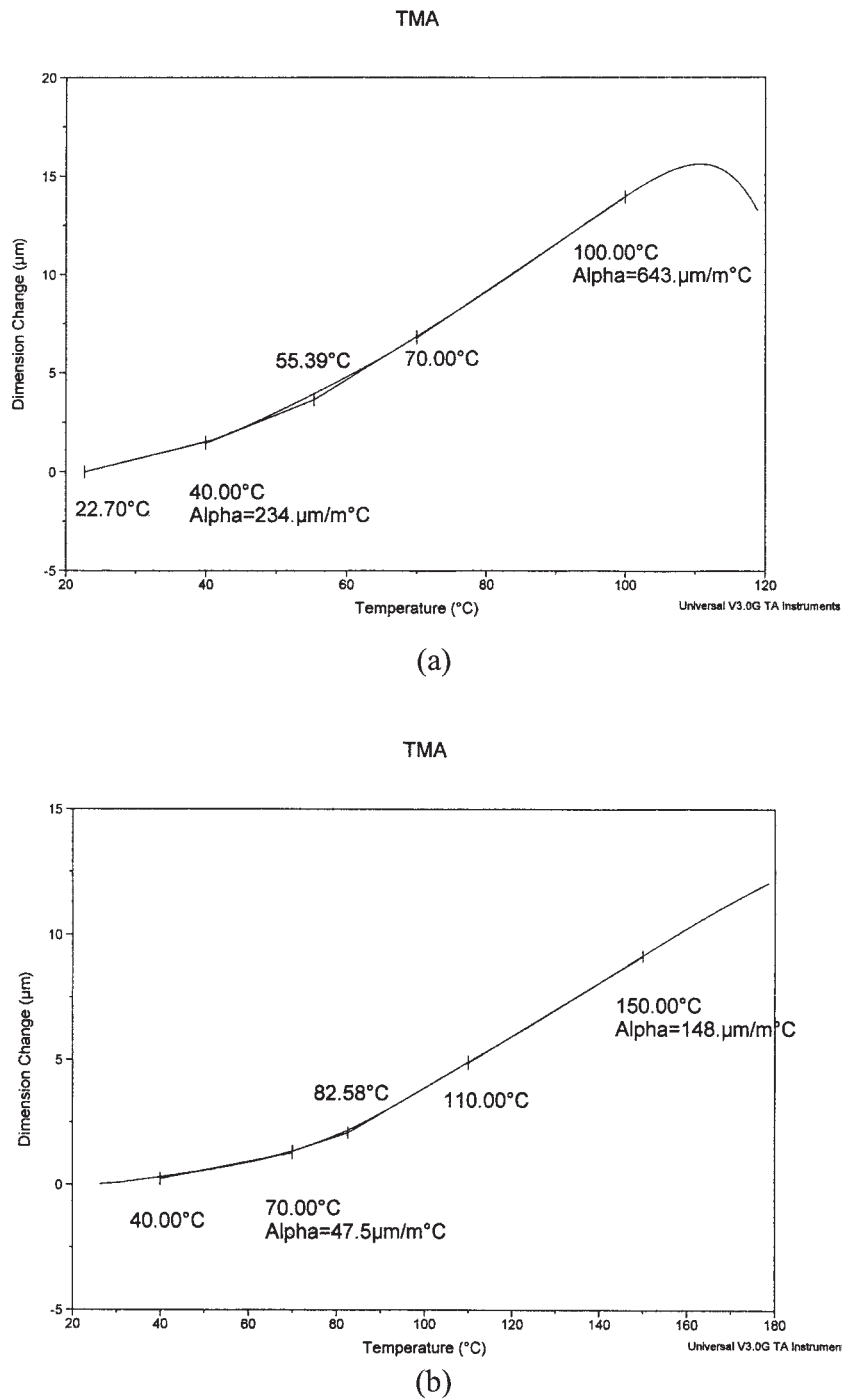


Figure 9 TMA thermograms of (a) pure poly(HEMA) and (b) nanocomposite H6-4.

$> \alpha_1$ (H2-3). The size, distribution, quantity, and uniformity of the silica phase in the composite were all considered to have contributed to this result. Also, possible errors involved in obtaining the slopes of the TMA thermogram could not be omitted.

Hardness and water and ethanol absorption

The hardness of the samples were examined with the pencil test widely used in the industry.^{16,17} Nanocom-

posites coated on different substrates, including polycarbonate, copper sheets, and aluminum sheets, were tested. The thickness of the coating layer was about 10 μm . Table IV lists the measured data for various cases with and without the crosslinking agent, TMPTA (trimethylolpropane triacrylate), in the sol-gel process. All the coated layers exhibited hardness higher than that of the substrate material, and this was true even for nanocomposites free of TMPTA. In other words, the nanocomposite material could effectively serve as

a protective coating for the substrate. The effects of the silica content, pH, and solvent usage are, however, not obvious from Table IV, and this is due to the fact that the accuracy of the pencil test was only 1 H.

As poly(HEMA) is both polar and hydrophilic, it takes up water and ethanol significantly upon immersion in these liquids. Table V shows the water and ethanol absorptions for several nanocomposites. The immersion time was 2 weeks for all the samples. The synthesized pure poly(HEMA) absorbed 54 and 76% water and ethanol, respectively. By contrast, the nanocomposite materials absorbed much less of these liquids. Also, the amounts of absorption decreased with increasing silica contents. This is consistent with the fact that silica is less hydrophilic than poly(HEMA) and that it is nonswellable. However, these absorption amounts are still too high for the electronics industry, which requires a value of less than 1% for different applications.

CONCLUSIONS

Photosensitive silica/poly(HEMA) nanocomposites were prepared by the sol-gel method. Depending on the preparation conditions, the size of the particles in the formed composites underwent significant changes. The smallest size attainable was about 20 nm. Several preparation parameters were investigated, including the ratio of the organic and inorganic reactants, the reaction pH, and the solvent content in the reaction mixture. By increasing the amount of the inorganic component, decreasing the reaction pH, or increasing the solvent content, we improved considerably the thermal stability of the synthesized nanocomposites. The highest T_g and T_d values of the nanocomposites

TABLE IV
Pencil Hardness of the Nanocomposites in Different Substrates

	PC-0	PC-1	Cu-0	Cu-1	Al-0	Al-1
H2-2	3 H	3 H	6 H	>6 H	5 H	5 H
H2-3	3 H	3 H	6 H	>6 H	5 H	5 H
H2-4	3 H	3 H	6 H	>6 H	5 H	5 H
H6-2	3 H	3 H	6 H	>6 H	6 H	6 H
H6-3	3 H	3 H	6 H	>6 H	5 H	5 H
H6-4	3 H	3 H	6 H	>6 H	5 H	5 H
H6-4-2	3 H	3 H	6 H	>6 H	5 H	5 H
H6-4-3	3 H	3 H	6 H	>6 H	5 H	5 H
H6-4 (pH 4)	3 H	3 H	6 H	>6 H	5 H	5 H
H6-4 (pH 12)	3 H	3 H	6 H	>6 H	5 H	5 H

-0-no TMPTA added; -1-TMPTA/HEMA = 1:10 (w/w); >6H-larger than 6H but less than 7H.

TABLE V
Water and Ethanol Absorption of Poly(HEMA) and the Nanocomposites

Absorption (%)	Poly(HEMA)	H6-4	H6-3	H6-2
Water	53.47	21.13	17.36	13.27
Ethanol	75.66	27.62	25.71	23.93

were 110 and 313°C, respectively, that is, 50 and 70°C higher than those of pure poly(HEMA). The thermal expansivity of the nanocomposites was also much lower than that of pure poly(HEMA), with the best being 34.3 (α_I) and 134 $\mu\text{m}/\text{m}^\circ\text{C}$ (α_{II}).

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