

Effect of Baking Treatment and Materials Composition on the Properties of Bulky PMMA–Silica Hybrid Sol–Gel Materials with Low Volume Shrinkage

Jui-Ming Yeh, Chang-Jian Weng, Kuan-Yeh Huang, Chun-Che Lin

Department of Chemistry and Center for Nanotechnology, Chung Yuan Christian University, Chung Li 32023, Taiwan, Republic of China

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ABSTRACT: A series of bulky PMMA–silica hybrid sol-gel materials had been successfully prepared through the conventional HCl-catalyzed sol-gel approach with 2-hydroxyethyl methyl methacrylate (HEMA) as coupling agent under pumping pretreatment (i.e., exhaustive vacuum evacuation). In this work, the hydroxyl groups of HEMA monomers were first cohydrolyzed with various contents of tetraethyl orthosilicate (TEOS) to afford chemical bonding for the forming silica networks by removal of solvent and by-product of sol-gel reactions through pumping pretreatment before gelation reactions. Subsequently, the resultant viscous solution was then copolymerized with methyl methacrylate (MMA) monomers at specific feeding ratios by using benzoyl peroxide (BPO) as free-radical initiator. Eventually, transparent bulky organic–inorganic hybrid sol-gel materials loaded with different silica content were always achieved. The obtained bulky hybrid sol-gel materials were

found to be transparent, crack-free, and of relatively low volume shrinkages even in high silica content. The as-prepared bulky hybrid sol-gel materials were then characterized through silicon element mapping studies of energy-dispersive X-ray (EDX) and transmission electron microscopy (TEM). Effect of heating process at 150°C for 5 h after polymerization and material composition on the thermal properties, mechanical strength, and optical clarity of a series of bulky PMMA–silica hybrid sol-gel materials was investigated and compared by thermogravimetric analysis (TGA), thermomechanical analysis (TMA), hardness test, dynamic mechanical analysis (DMA), and UV–vis transmission spectroscopy, respectively. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1151–1159, 2006

Key words: thermal properties; nanocomposites; copolymerization; silica

INTRODUCTION

In the past two decades, organic–inorganic hybrid materials have evoked intensive academic and industrial research activities, and therefore, has become a fascinating field in materials science.^{1–19} Generally, these materials prepared through the sol-gel pathway create homogeneous ceramic, glasses, and composites with wide range of composition and properties at low temperatures.^{20,21} Despite of many great advantages of the sol-gel process, there were several severe—some times detrimental—drawbacks in this process, which have limited its technological application. One of the inherent problems in the conventional sol-gel process is that it demonstrates exceedingly large volume shrinkages, which result from the removal of a large amount of solvent and small molecular byproduct of hydrolysis and polycondensation reactions, such as water and alcohol. The volume shrinkage of materials can easily reach up to 75% or more, and

thus, the preparation of monolithic sol-gel materials with predictable and controllable shape and dimension becomes very difficult because of the high internal stress induced by the volume shrinkage.

Wei et al.^{22,23} and Novak²⁴ have demonstrated that the synthesis of vinyl polymers–silica hybrid sol-gel materials in which the organic polymer chain were uniformly distributed in and covalently bonded to the inorganic matrix and the transparent, monolithic products have been obtained by drying the hybrid gels at a very slow rate for up to 2 months of drying time. Recently, an elegant synthetic route for the preparation of polyacrylate–silica composites by sol-gel reactions without significant volume shrinkage have been reported by Novak et al.^{7,25} The sol-gel reactions of $\text{Si}(\text{OR})_4$ proceed simultaneously with a free-radical polymerization of the acrylate sol-gel byproduct so that no small ROH molecules will be released from the system and volume shrinkage was reduced significantly.²⁵

In this article, we prepared a series of bulky PMMA–silica hybrid sol-gel materials with low volume shrinkage, revealing chemical bond formation between PMMA and the silica network, by using 2-hy-

Correspondence to: J.-M. Yeh (juiming@cycu.edu.tw).

TABLE I
Composition and Volume Shrinkage Ratio of a Series of PMMA–Silica Hybrid Sol–Gel Materials with HEMA as Coupling Agent

Code number ^a	Feed composition (molar ratio)			Volume shrinkage		
	HEMA	MMA	TEOS	Molding volume, V_o (mL)	Product volume, V_s (mL)	Shrinkage ratio ^b , $V_o - V_s/V_o$ (%)
HM	0.3	0.3	—	6	5.97	0.57
HMT0701	0.7	0.7	0.1	6	5.65	5.80
HMT0301	0.3	0.3	0.1	6	5.53	7.89
HMT0302	0.3	0.3	0.2	6	5.34	11.03

^a For HMT 0302, HM = poly(HEMA-*co*-MMA), T = TEOS, 0302 = feeding molar ratio of HEMA/TEOS.

^b The volume shrinkage ratio was measured on baked sample.

droxyethyl methyl methacrylate (HEMA) as coupling agent. By removal of solvent and byproduct of sol–gel reactions by pumping pretreatment (i.e., exhaustive vacuum evacuation) before gelation reactions, a series of densely bulky PMMA–silica hybrid sol–gel materials were obtained. Effects of baking treatment and material composition on the thermal stability, mechanical properties, and optical clarity of a series of bulky PMMA–silica hybrid sol–gel materials were studied by thermogravimetric analysis (TGA), thermomechanical analysis (TMA), hardness test, dynamic mechanical analysis (DMA), and UV–vis transmission spectroscopy, respectively.

EXPERIMENTAL SECTION

Materials and instrumentations

Tetraethyl orthosilicate (TEOS), methyl methacrylate (MMA), 2-hydroxyethyl methyl methacrylate (HEMA) were all purchased from Aldrich and purified through distillation under reduced pressure prior to use. Benzoyl peroxide (BPO) (Aldrich) was recrystallized in chloroform and methanol. Tetrahydrofuran (THF, Aldrich) was used as-received. Transmission electron microscopy (TEM JEOL-2000FX), applying an acceleration voltage of 200 kV, was used to study the morphology of as-prepared materials. Energy-dispersive X-ray (EDX) spectroscopy image of silicon element mapping was recorded on a HITACHI-S-4100 microscopy. TGA scans were performed under nitrogen flow, using a TA Q50 at a heating rate 10°C/min. TMA scans were performed under nitrogen flow, using a TA Q-400 at a heating rate 10°C/min. DMA scans were carried out on a TA Q800. The programmed heating rate is 3°C/min and a fixed frequency of 20 Hz was used. The UV–vis transmission spectra of the bulky PMMA–silica hybrid sol–gel materials were recorded on a Hitachi U-2000 UV–vis spectrometer with monitoring wavelengths ranging from 200 to 800 nm at room temperature. The surface hardness testing of the bulky PMMA–silica hybrid sol–gel materials was done by TECLOCK, GS-706N (Type D).

Preparation of bulky PMMA-SiO₂ hybrid sol–gel materials with low volume shrinkage

A series of bulky PMMA–silica hybrid sol–gel materials were prepared by the acid-catalyzed sol–gel reactions in conjunction with the BPO-initiated free-radical polymerization. In general, TEOS, HEMA, distilled water, HCl, and THF at various compositions were first mixed to give a two-phase mixture at room temperature under nitrogen. After stirring for about 15 min, the phase separation disappeared and a homogeneous solution was obtained. The solution was heated up to about 60°C for 3 h. Upon cooling the solution down to room temperature, BPO (typically 0.01 molar ratio with respect to HEMA) was dissolved into the solution and then connected to a vacuum pump to remove the solvent (i.e., THF) and other small molecular byproducts of the sol–gel reactions (i.e., ethanol and water). The system was pumped at about 10 mmHg at room temperature for 1 h till no more gas bubbles evolved from the highly viscous solution. At this stage, a second vinyl monomer, MMA could be added with stirring to yield a homogeneous solution. The solution was then cast into the molds of desirable shape and volume, which were heated to 80°C to initiate the free-radical polymerization of HEMA and MMA (if the latter was added) and to continue the sol–gel reactions. This process is referred as thermal curing or solidification. After heating for 12 h, the PMMA–silica hybrid sol–gel materials were obtained as monolithic and transparent films, discs, or objects of other shapes. Volume shrinkage from the casting solutions to the final hybrid sol–gel materials was significantly lower in comparison with that in the conventional sol–gel process. The compositions of the monomer mixture by molar ratio for preparing hybrid sol–gel materials were listed in Table I.

As a typical procedure for the preparation of the hybrid sol–gel materials, HMT 0301 (the molar ratio of HEMA : MMA : TEOS = 3 : 3 : 1), 31.55 g of TEOS, and 13.01 g of HEMA were dissolved in 20.00 g of THF at room temperature in a 250-mL three-necked round-bottomed flask, which was equipped with a thermom-

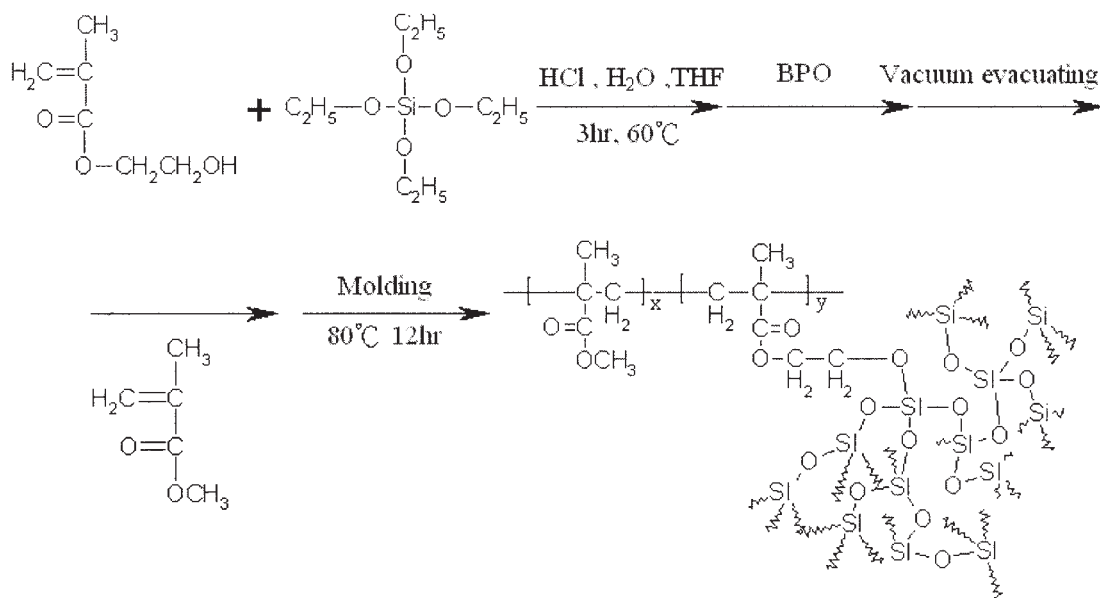


Figure 1 Flow chart for the preparation of bulky PMMA-silica hybrid sol-gel materials with HEMA as coupling agent.

eter, a condenser, and a gas inlet/outlet. To this solution was added 3.75 g of 2.00M HCl_(aq) to yield a two-phase liquid mixture. The mixture was stirred magnetically at room temperature under nitrogen for about 15 min until the phase separation disappeared and the content became clear and homogeneous. The reaction mixture was heated to 60°C with stirring, in a water bath. After heating for about 3 h, the reaction mixture was cooled down to room temperature. About 0.03 g of the initiator, BPO, was added to and dissolved in the system. The thermometer and the condenser were then replaced with rubber stoppers and the flask was connected to a vacuum line through an acetone-dry ice trap. The magnetic stirring was maintained while the system was pumped at room temperature. The viscosity of the solution increased visibly, as the volatile molecules were stripped away. About 1 h later, the solution became highly viscous and the evolution of gas bubbles from the solution slowed down to a negligible level. The vinyl monomer MMA was added into solution and stirred for 10 min to get a homogeneous solution. This viscous, transparent, colorless, and homogeneous solution was poured into polytetrafluoroethylene (PTFE) vials, which served as the molds. These vials were then placed in a water bath at 60°C to allow the free-radical polymerization of the vinyl monomer MMA and further sol-gel reactions. After heating at 60°C for ~1 h, the contents solidified and transparent hybrid materials were obtained. To ensure the high conversion of the free-radical polymerization and sol-gel reactions, the materials were heated in an oven at 80–90°C for 12 h. The typical flowchart for the preparation of bulky PMMA-silica hybrid sol-gel materials was given in Figure 1.

Synthesis of P(MMA-co-HEMA) copolymer

As a control experiment, copolymer P(MMA-co-HEMA) was also prepared for comparison. A typical procedure to prepare the copolymer P(MMA-co-HEMA) containing 0.07 mol of MMA and 0.07 mol of HEMA units by weight is as follows: 7.00 g of MMA and 9.10 g of HEMA monomers, 0.32 g of BPO, and 40.00 mL of dry THF were put in a 250-mL three-necked round-bottomed flask connected with a condenser, a thermometer, and a nitrogen gas inlet/outlet. Nitrogen gas was bubbled into the flask throughout the reaction. Under magnetic stirring, the solution was heated to 70–75°C and refluxed for 3 h. This viscous, transparent, colorless, and homogeneous solution was poured into PTFE vials, which served as the molds. After heating at 80°C for ~12 h, the contents solidified and transparent materials were obtained.²⁶

RESULTS AND DISCUSSION

Characterizations

The morphological images of the bulky PMMA-silica hybrid sol-gel materials (e.g., HMT0701) can be observed by the TEM studies. Clearly, we found a relatively uniform dispersion of nanoscaled silica particles in PMMA matrix (scale bar = 200 nm), as shown in Figure 2(a). At higher magnification (scale bar = 100 nm), we found that the average diameter of silica particles dispersed in PMMA matrix of sample HMT0701 is ~20–50 nm, as shown in Figure 2(b).

We also studied the Fourier-transform infrared (FTIR) spectroscopy of all as-prepared hybrid sol-gel

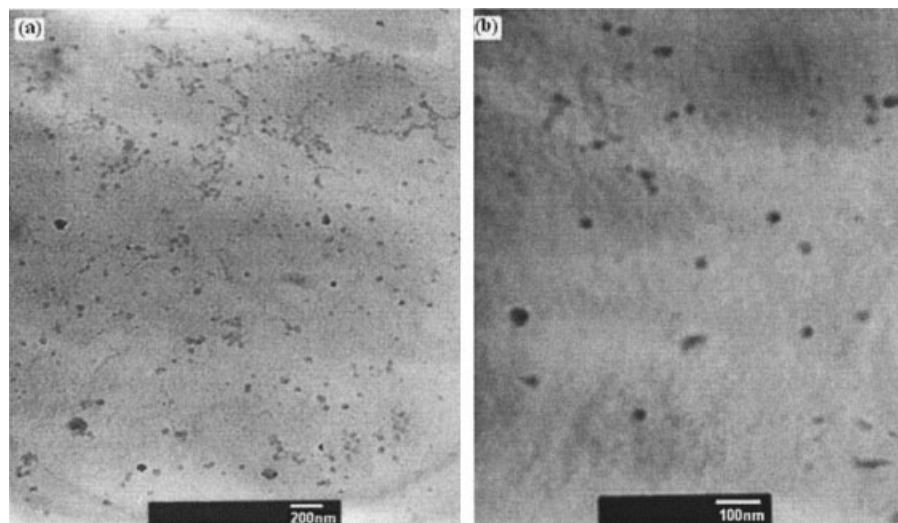


Figure 2 TEM image of as-prepared bulky hybrid sol-gel material HMT0701 (after baking) at various magnifications (a) $\times 20,000$ and (b) $\times 50,000$.

materials. However, observable absorption bands of Si—O—Si and Si—OH located at the position around ~ 1090 and 935 cm^{-1} , respectively.^{27,28} Therefore, silicon element-mapping studies of EDX on bulky PMMA-silica hybrid sol-gel materials were used to observe the distribution of silicon element existed in the polymer matrix. For example, Figure 3(a) shows the Si-mapping image of EDX on bulky hybrid sol-gel material at low silica content (e.g., HMT0701), showing lots of white spots (i.e., silicon element) dispersed uniformly in black background (i.e., polymer matrix) at $\times 3000$ magnification (scale bar = $10\ \mu\text{m}$). At higher silica content (e.g., HMT0301), the number of white spots was found to be significantly increased with clear resolution for each spot, indicating that the increase of silica loading revealed a densely and uniformly dispersed state in PMMA matrix, as shown in Figure 3(b).

Volume shrinkage of bulky PMMA-silica hybrid sol-gel materials

The characteristics of the baked hybrid sol-gel materials with pumping pretreatment was that they have very low volume shrinkage [$V\% = (V_o - V_s)/V_o \times 100$],²⁹ which may be achieved from the molding stage (volume; V_o) where the system was still a fluid and processable after the vacuum evacuated to the final product after baking at 150°C for 5 h. The relationship between bulk shrinkage and the composition of the hybrid sol-gel materials is shown in Table I. The volume shrinkage appeared to increase as the silica content was further increased, but smaller than the sol-gel of the inorganic precursor TEOS (about 55%) after solvent and byproduct were removed.²⁹ In this sol-gel process, the TEOS monomers were mostly hydrolyzed to silanols and polycondensated to certain extents to afford oligo-

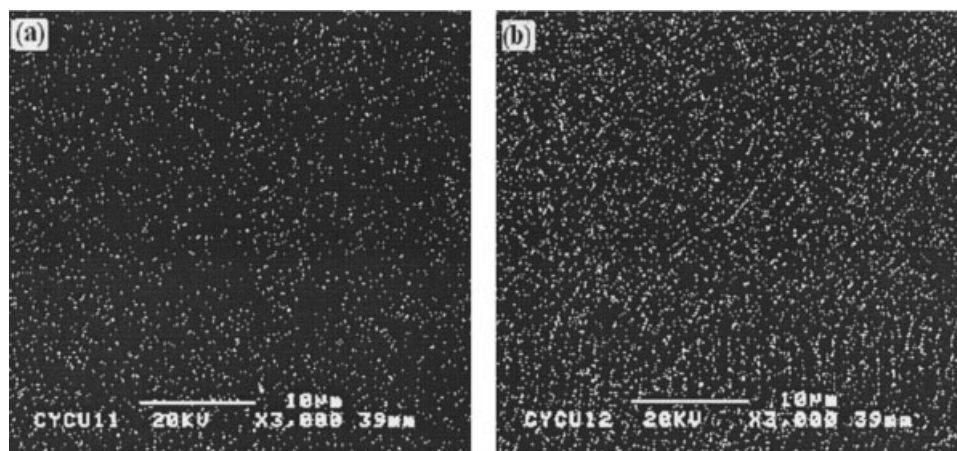


Figure 3 Si-mapping image studies of EDX on bulky PMMA-silica hybrid sol-gel materials (after baking). (a) HMT0701 and (b) HMT0301.

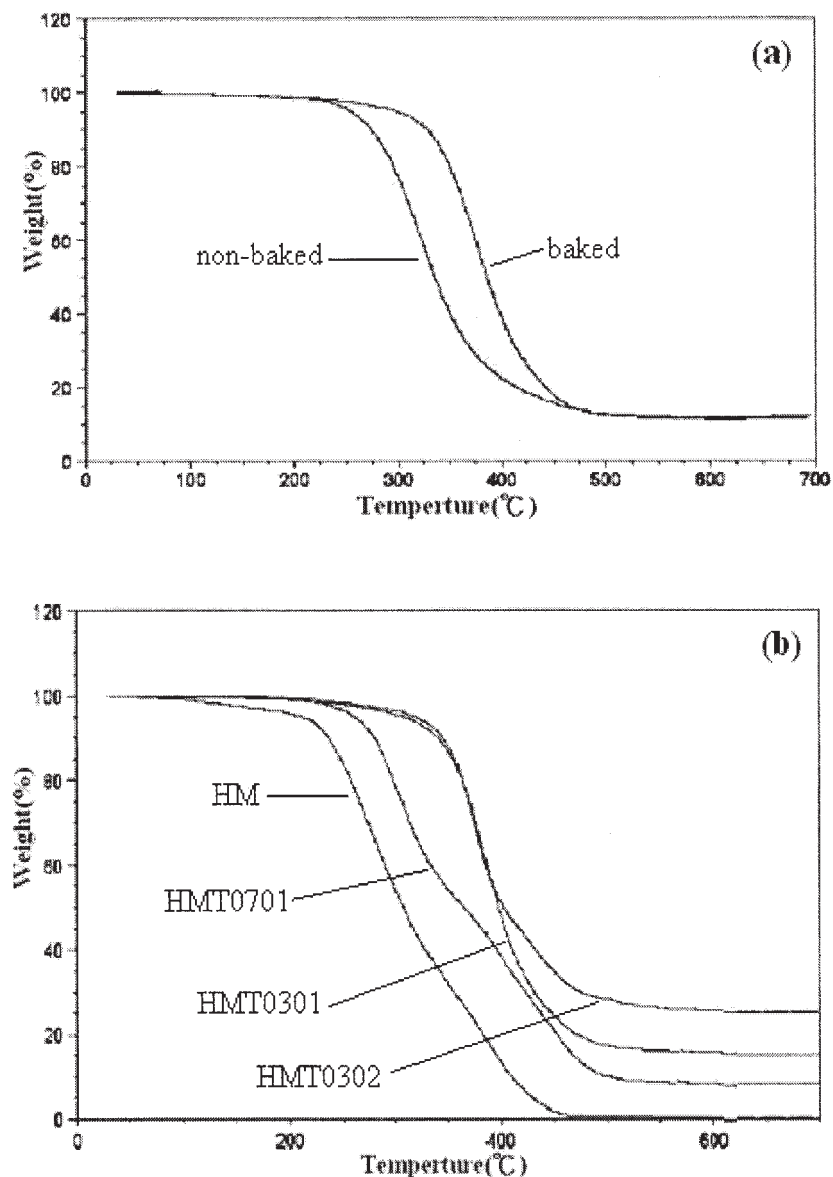


Figure 4 TGA curves of bulky PMMA-silica hybrid sol-gel materials. (a) Baked and nonbaked sample HMT0302. (b) Baked bulky hybrid sol-gel materials at different silica concentrations.

meric or polymeric silicate chains, thus the significant portion volume shrinkage were almost already.

Thermal properties of bulky PMMA-silica hybrid sol-gel materials

Figure 4 illustrates the TGA thermograms of weight loss as a function of temperature for the as-synthesized bulky hybrid sol-gel materials, as measured at a heating rate of 20°C/min under nitrogen flow. In general, there appeared to be one stage of weight loss starting at 200°C and ending at 500°C, which may correspond to the structural decomposition of the polymers. Furthermore, the baking effect (e.g., 150°C for 5 h) on the thermal stability of bulky hybrid sol-

gel materials (e.g., HMT0302) was enhanced remarkably due to the more dense microstructures formed, which may be resulted from the completeness of sol-gel reactions. For example, the thermal decomposition temperature (T_d) of bulky hybrid sol-gel materials (e.g., HMT0302) was shifted from 217.7 to 318.6°C after the baking treatment, as shown in Figure 4(a) and Table II, indicating that the baking treatment on sample led to an significant enhancement of T_d up to ~100°C. On the other hand, the increase of silica content in all the baking-treated hybrid sol-gel materials was also found to shift the thermal stability of as-prepared bulky materials to a higher temperature range, as shown in Figure 4(b) and Table II. The black color of the char residue after the TGA running also

TABLE II
Thermal Properties of the Bulky PMMA–Silica Hybrid Sol–Gel Materials as Measured by TGA, TMA, and DMA

Code number	T_d^a (°C)		CTE ^b ($\mu\text{m}/\text{m}^\circ\text{C}$)	Tan δ^c (°C)		Char yield (wt %)	
	Nonbaked	Baked		Nonbaked	Baked	Calculated value	Experimental value
HM	—	221.40	260.60	—	106.96	0	0
HMT0701	—	260.60	213.81	—	108.87	11.44	10.00
HMT0301	257.7	308.20	191.71	89.75	112.45	23.516	18.18
HMT0302	—	318.60	162.23	—	114.12	37.61	29.12

^a As determined by TGA measurements under nitrogen (5 wt % weight loss).

^b As determined from TMA measurements.

^c As determined from DMA measurements.

proves that the organic chains have been trapped in the inorganic silica matrix.

The coefficient of thermal expansion (CTE) of baked neat copolymer and all bulky hybrid sol–gel materials was determined by TMA as listed in Table II. The

value of α_f was the average CTE value, which showed the thermal expansion behavior above T_g . The neat copolymer was found to have CTE value of $260.6 \mu\text{m}/\text{m}^\circ\text{C}$ (α_f). However, the bulky hybrid sol–gel material (e.g., HMT0302) has CTE value of $162.2 \mu\text{m}/$

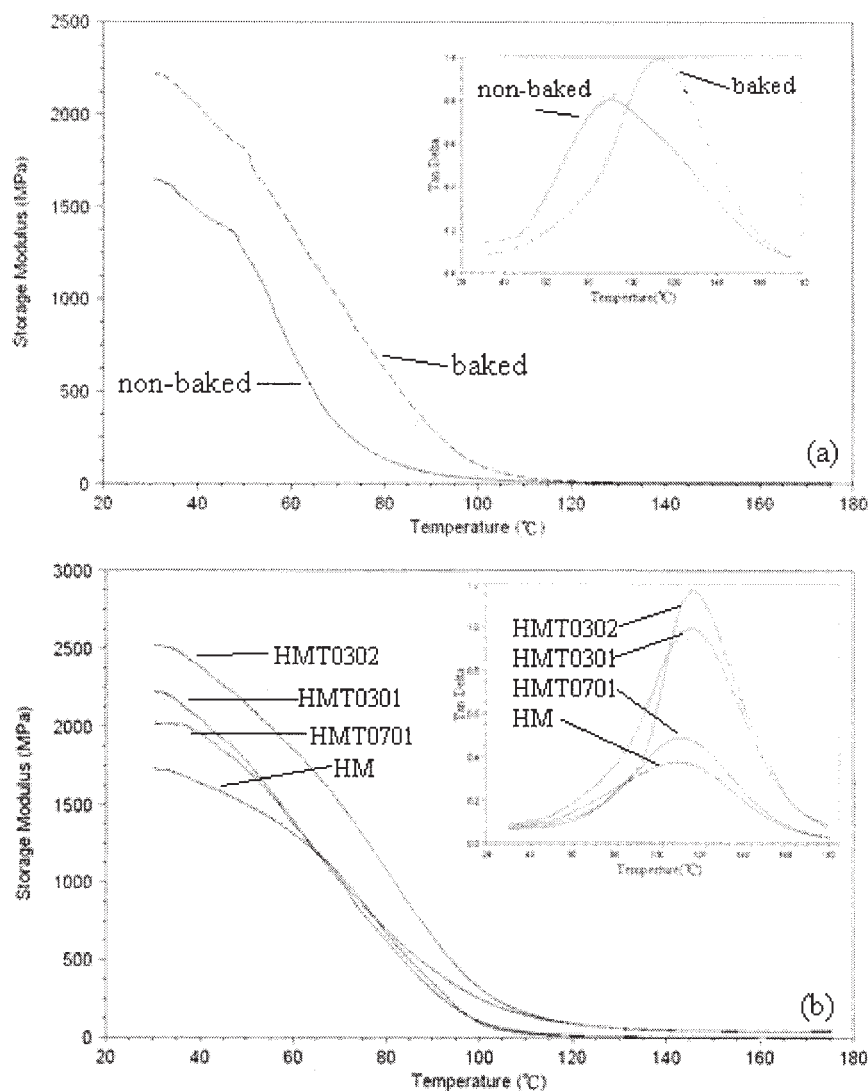


Figure 5 DMA curves of bulky PMMA–silica hybrid sol–gel materials. (a) Storage modulus and tan δ of baked bulky hybrid sol–gel materials at different silica concentrations.

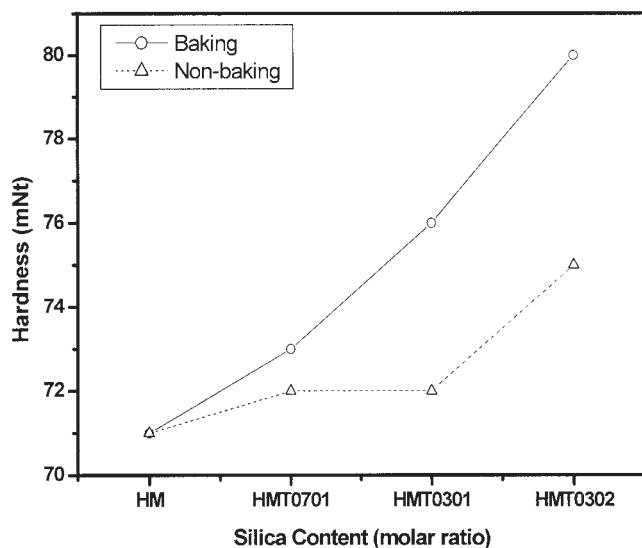


Figure 6 The hardness of baked and nonbaked bulky PMMA–silica hybrid sol–gel materials at different silica concentrations.

m°C (α_f), which is significantly lower than that of neat copolymer. As the silica content increases, the values of α_f decrease gradually, indicating that silica nanoparticles could be used to increase the dimensional stability of neat copolymer. Decrease in CTE value of bulky hybrid sol–gel materials clearly resulted from the low CTE of silica and the existence of strong interaction between polymer and the possible interpenetrated structure, which makes the silica particles act as the crosslink points.²⁶

Mechanical strength of bulky PMMA–silica hybrid sol–gel materials

In this study, mechanical strength of neat copolymer and bulky hybrid sol–gel materials was determined by the storage modulus value of DMA measured at 30°C. In addition to thermal property studies, baking treatment on bulky hybrid sol–gel materials also show remarkable enhancement of mechanical strength, as

shown in Figure 5(a). For example, the storage modulus of the baked bulky hybrid sol–gel material (e.g., HMT0302) is 2221 MPa, which is significantly higher than that of the nonbaked counterpart (storage modulus = 1650 MPa). Moreover, the baked bulky hybrid sol–gel materials exhibited a significant increase in storage modulus with the increase of the silica content in the entire temperature range. Since the polymer chain in the hybrid sol–gel materials are covalently bonded (or crosslinked) to the inorganic network, the thermal stability and mechanical properties of the polymer component should be improved.^{30,31}

On the other hand, $\tan \delta$ value (defined by the ratio of storage modulus/loss modulus) has been measured and can be employed as an index of glass-transition temperature (T_g).³² For example, T_g of baked bulky hybrid sol–gel materials (e.g., HMT0301) has the value of 112.45°C based on the measurement of $\tan \delta$, which was significantly higher than the nonbaked bulky hybrid sol–gel materials ($T_g = 89.75^\circ\text{C}$), as shown in Figure 5(a), indicating that the baking treatment shifted the T_g of as-prepared bulky hybrid sol–gel materials to the higher temperature up to $\sim 20^\circ\text{C}$. Furthermore, the increase of silica content in the baked bulky hybrid sol–gel materials also showed significant improvement on the T_g of as-prepared hybrid sol–gel materials, as shown in Figure 5(b) and Table II.

In addition to the studies of storage modulus, mechanical strength can also be evaluated by the surface hardness of materials. The hardness tests were all performed on the surface of neat copolymer and a series of baked and nonbaked bulky hybrid sol–gel materials, as demonstrated in Figure 6 and Table III. For example, the baked bulky hybrid sol–gel materials (e.g., HMT0302) exhibited a hardness value of 80 mNt (Shore D), which was obviously higher than that of the corresponding counterpart (i.e., 75 mNt). On the other hand, the increase of silica concentration in baked bulky hybrid sol–gel materials corresponded to an increase of surface hardness. For example, the hardness of baked bulky hybrid sol–gel material at high silica concentration (e.g., HMT0301, hardness = 76)

TABLE III
Mechanical Strength of the Bulky PMMA–Silica Hybrid Sol–Gel Materials as Measured by DMA, Hardness Testing, and Impact Toughness

Code number	Storage modulus ^a (MPa)		Hardness ^b (mNt)		Impact strength ^c (J/m)	
	Nonbaked	Baked	Nonbaked	Baked	Nonbaked	Baked
HM	—	1380	71	71	63.33	63.33
HMT0701	—	2020	72	73	16.26	10.11
HMT0301	1650	2220	72	76	15.27	9.5
HMT0302	—	2500	75	80	—	—

^a As determined by DMA.

^b As determined from TECLOCK, GS-706N (Type D) measurements.

^c As determined from ASTM D256.

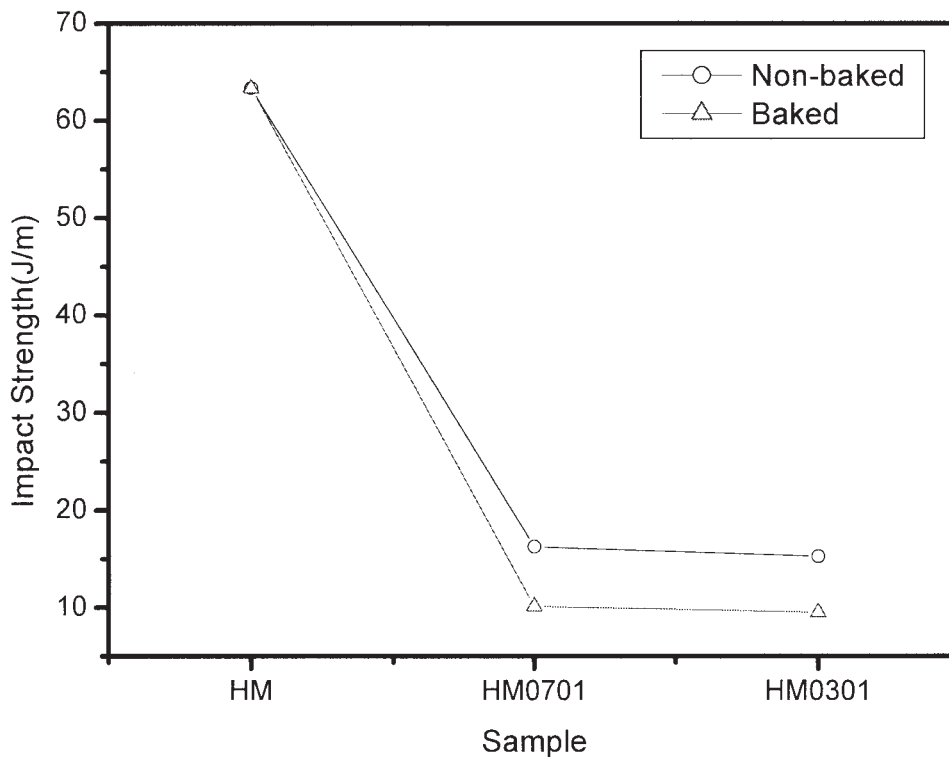


Figure 7 The impact strength of nonbaked and baked bulky PMMA-silica hybrid sol-gel materials.

was found to be higher than that of hybrid sol-gel materials at low silica concentration (e.g., HMT0701, hardness = 73). The impact strength of baked and nonbaked hybrid materials was also compared, as shown in Figure 7. As expected, the baked materials all showed a decrease in impact strength. On the other hand, the incorporation of silica into PMMA also exhibited a decrease in impact strength.

Optical clarity of PMMA-silica hybrid sol-gel materials

Figure 7 showed the UV-vis transmission spectra of the bulky hybrid sol-gel materials (~7–11 mm in thickness) at different silica concentrations. The appearance of copolymer at thickness of ~7 mm exhibited a relatively higher transparency as compared to the bulky hybrid sol-gel materials. When the concentration of silica in hybrid sol-gel materials was increased (e.g., HMT0302), the transparency of the nonbaked bulky hybrid sol-gel materials at thickness of ~11 mm is slightly affected by the introduction of silica content. However, nonbaked bulky hybrid sol-gel materials at high silica concentration led to an obvious decrease in optical transparency, as shown in Figure 8. Furthermore, the optical clarity of baked bulky hybrid sol-gel materials was significantly decreased as compared to the

nonbaked counterpart, as shown in curve (d) of Figure 8.

CONCLUSIONS

In this study, a series of PMMA-silica bulky hybrid sol-gel materials have successfully been prepared by using sol-gel process under pumping treatment (i.e.,

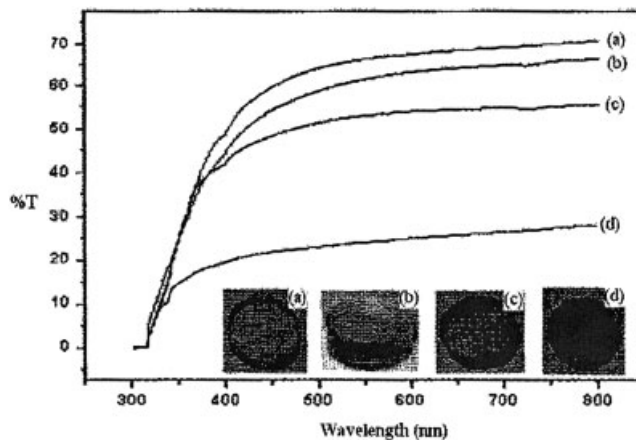


Figure 8 The UV-visible transmission spectra of bulky PMMA-silica hybrid sol-gel materials. (a) Nonbaked HM, (b) nonbaked HMT0301, (c) nonbaked HMT0302, (d) baked HMT0302.

exhaustive vacuum evacuation). In this work, HEMA was first cohydrolyzed with various content of TEOS to afford chemical bonds to the forming silica networks by removal of solvent and byproduct of sol-gel reactions by pumping treatment. Subsequently, the as-prepared copolymer was then copolymerized with MMA monomer at specific feeding ratio by using BPO as free-radical initiator. The bulky hybrid sol-gel materials with different concentrations of SiO₂ were always achieved.

For the material property studies, baking treatment and silica concentration were the two variables showing significant effect on the thermal property, mechanical strength, and optical clarity. In conclusion, the baking treatment (150°C for 5 h) on the bulky hybrid sol-gel materials was found to enhance the decomposition temperature, glass-transition temperature, and hardness of as-prepared materials based on the TGA, DMA, and hardness tests. Moreover, the baking treatment decreased the CTE and optical clarity of as-prepared materials, as can be seen from the TMA and UV-vis transmission spectra. On the other hand, the material composition (i.e., silica concentration in bulky hybrid sol-gel materials) also affected the properties of as-prepared materials significantly. For example, the increase of silica concentration in bulky hybrid sol-gel materials was correspondent to an increase of T_d , T_g , storage modulus and hardness and a decrease of CTE and optical clarity of as-prepared materials.

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