

Structure–Property Behavior of UV-Curable Polyepoxy–Acrylate Hybrid Materials Prepared via Sol–Gel Process

Ling Zhang, Zhaohua Zeng, Jianwen Yang, Yonglie Chen

Institute of Polymer Science, School of Chemistry and Chemical Engineering, Zhongshan University, Guangzhou 510275, People's Republic of China

Received 11 January 2002; accepted 5 June 2002

ABSTRACT: UV-curable, hard, transparent organic/inorganic hybrid material with an improved mechanical property was prepared by the sol–gel process, based on a commonly used epoxy acrylate (EA) oligomeric resin. Systematic experiments were carried out to study the effect of the inorganic content, the acid content, and the content of a silane coupling agent on the property behavior of the hybrid materials. The structure of the hybrids were characterized

by IR spectra and SEM observation. Results from thermogravimetric analysis (TGA) and mechanical measurement show that the properties of the hybrids differ with the changes of these variables. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1654–1659, 2003

Key words: nanocomposites; photopolymerization; microstructure

INTRODUCTION

In recent years, the sol–gel reaction has been extensively studied to improve or modify the process of making organic/inorganic hybrid materials.^{1–6} The hybrid materials obtained show some properties of the inorganic glass matrix, such as higher abrasion resistance and higher modules, as well as some characteristics of the incorporated oligomeric components.

For a sol–gel process of making inorganic glasses through the hydrolysis of a metal alkoxide, the acidity and the water content of the system have been proven to display a critical effect on the structure of the final products.^{7,8} However, some additional factors become important due to the addition of the oligomeric component, for example, the amount of the oligomer added, the difference between the solubility parameters of the oligomer and the glassy component, as well as the solvent(s) used and the reaction temperature employed. All these variables may affect the miscibility of the system during a reaction and, therefore, the structure and properties of the final products.

In this article, we describe the synthesis, characterization, and investigation of the morphological features of an organic/inorganic hybrid network material based on a UV-curable epoxy acrylate resin. The effects of acid content, inorganic content, and coupling agent content are discussed.

EXPERIMENTAL

Materials

Tetraethoxysilane (TEOS) and 3-(trimethoxysilyl)propyl methacrylate (TMSPM) were of analytical grade and were used without purification. Epoxy acrylate (EA; Ebecryl 600) from the UCB Corp. (Belgium) was a bisphenol A epoxy diacrylate resin (M_w 500, Höppler viscosity 3000 mPa s at 60°C). 1-Methyl-1-hydroxyacetophenone (Darocur 1173) was obtained from Ciba (Switzerland). All other reagents were of analytical grade and were used without further treatment.

Preparation of the silica sol

The hydrolysis and condensation of TEOS was performed using HCl as a catalyst. The mol ratio of TEOS: H₂O:ethanol:HCl was 1:6:6:*a* (*a* denotes mol number of HCl, which was varied). First, a part of ethanol and TEOS was charged into an Erlenmeyer flask, and then a mixture of ethanol and water, which had been acidified with HCl, was slowly dropped into the flask under stirring at room temperature; after the addition, the whole mixture was kept 12 h under stirring to obtain a stable silica sol A.

Synthesis of the hybrid systems

Into the silica sol A, TMSPM was dropped under stirring at room temperature and the mixture was allowed to stand for 24 h to obtain modified silica sol B. The EA resin, reactive diluent [(hexanediol diacrylate (HDDA)], Darocur 1173, and Tween 80 were

Correspondence to: Y. L. Chen (cescyl@zsu.edu.cn).

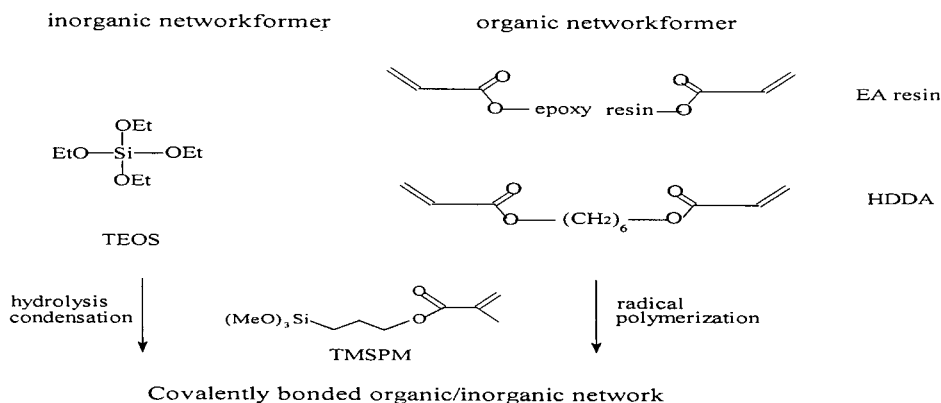


Figure 1 Schematic illustration of the formation of an organic/inorganic hybrid system.

charged into a three-neck flask and the mixture was vigorously stirred for 1 h to obtain solution C. Then, modified silica sol B was dropped into solution C (the ratio of modified sol B/sol C by weight is represented by *f*) under intense stirring until the system became transparent; the (EA-TMSPM)/SiO₂ hybrid system was thus obtained.

Photocuring of the hybrid systems

The obtained hybrid system was applied onto a polished substrate (steel or glass), and photocuring was carried out by passing through a UV-curing machine with an appropriate conveyor speed under a 2.4-kW medium-pressure mercury lamp.

Characterization of the cured material

IR spectra of the hybrid systems were recorded using a Nicolet-205 Fourier transform infrared (FTIR) spectrometer. A field-emission scanning electron micrograph was obtained on a JEOL JSM-6330F instrument using an accelerating voltage of 15 kV. The photocured film was etched with acid before the experiment. The glass transition temperature (T_g) was measured on a TA DSC 2910 instrument with a heating rate of 30°C/min. The thermal stability was measured on a SHIMADZU TGA-50 instrument from room temperature to 800°C in air with a purging rate of 45 mL/min under a heating rate of 20°C/min.

Mechanical properties were measured in accordance with the corresponding National Standard Testing Method (GB). These include the thickness (GB 1764-79), gloss (GB 1743-93), hardness (GB 2411-80), impact strength (GB 1732-93), and flexibility (GB 1731-93).

RESULTS AND DISCUSSION

Synthesis of the hybrid system

UV-curable, hard, and transparent organic/inorganic hybrid systems were prepared by the sol-gel method, using a commonly used EA oligomeric resin (Ebecryl 600), HDDA, as a reactive solvent, TMSPM as a coupling agent between the organic and inorganic phases, and a metal alkoxide, tetraethoxysilane (TEOS). By introducing the coupling agent into the hybrid system, all samples were transparent and did not display any sign of incompatibility between the components. Thus, the problem of macroscopic phase separation, arising from the difference between the solubility parameters of the oligomer and the glassy component, could be solved. A schematic representation of the formation of the (EA-TMSPM)/SiO₂ hybrid network with covalent links between the inorganic and organic network by the sol-gel method is given in Figure 1.

FTIR studies of the (EA-TMSPM)/SiO₂ hybrid system

For comparison, a system without the inorganic network and TMSPM was prepared and is termed EA/HDDA. FTIR spectra of the EA/HDDA and (EA-TMSPM)/SiO₂ hybrid photocured film are shown in Figure 2(a,b), respectively. According to the literature,⁹ broad bands at 1000–1100 cm⁻¹ are assigned to Si—O—Si antisymmetric stretching, while the band at 449 cm⁻¹ is assigned to Si—O—Si bending.

DSC analysis of the (EA-TMSPM)/SiO₂ hybrid materials

The glass transition behavior of the hybrid material is associated with cooperative motion of large-chain segments, which may be hindered by the inorganic metal

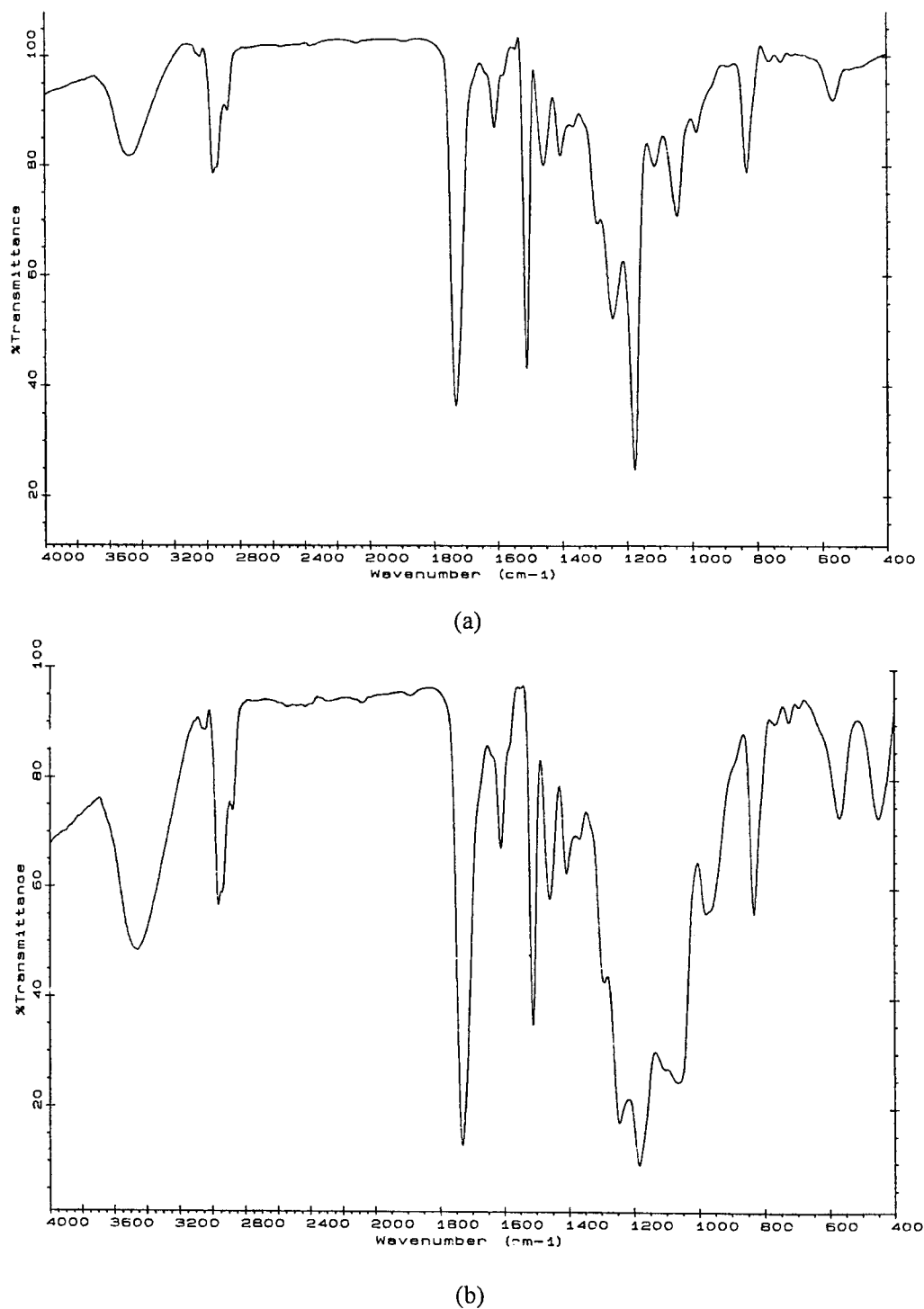


Figure 2 FTIR spectra of samples after photocuring: (a) EA/HDDA system; (b) (EA-TMSPM)/SiO₂ hybrid system.

oxide network. The effect of the inorganic content (f) or acid content (a) or TMSPM content on the DSC results of the (EA-TMSPM)/SiO₂ hybrid materials are listed in Table I-III, respectively. DSC analysis shows a detectable glass transition temperature (T_g) for (EA-TMSPM)/SiO₂ hybrid materials at 26–30°C, which is only slightly higher than that for the EA/HDDA sys-

tem. No obvious difference can be observed in the T_g of the (EA-TMSPM)/SiO₂ hybrids with an increasing inorganic content or acid content or TMSPM content. Apparently, although the polymer chains have been copolymerized with the silica network, their movement is not completely hindered. In these tables, the maximum peak temperatures of three distinct degra-

TABLE I
Effect of f on the Thermal Properties of Photocured Hybrid Materials

Sample	f	T_g (°C)	$T_{1\max}$ (°C)	$T_{2\max}$ (°C)	$T_{3\max}$ (°C)	Residue at 800°C (wt %)	SiO ₂ (wt %; calculated)
EA/HDDA	0	25.5	434	—	578	1.1	0
(EA-TMSPM)/SiO ₂	2/8	27.4	419	447	589	4.7	3.03
(EA-TMSPM)/SiO ₂	4/6	26.1	420	460	636	8.9	6.07
(EA-TMSPM)/SiO ₂	6/4	27.8	425	476	659	12.2	9.10

$a = 0.06$; TMSPM/TEOS = 1/2 (w/w).

TABLE II
Effect of HCl on Thermal Properties of Photocured Hybrid Materials

Sample	a	T_g (°C)	$T_{1\max}$ (°C)	$T_{3\max}$ (°C)	Residue at 800°C (wt %)	SiO ₂ (wt %; calculated)
EA/HDDA	0	25.5	434	578	1.1	0
(EA-TMSPM)/SiO ₂	0.06	26.2	415	621	12.3	7.59
(EA-TMSPM)/SiO ₂	0.12	26.2	416	630	12.1	7.57
(EA-TMSPM)/SiO ₂	0.48	26.7	417	643	12.1	7.50

TMSPM/TEOS = 1/2 (w/w); $f = 5/5$.

TABLE III
Effect of TMSPM on Thermal Properties of Photocured Hybrid Materials

Sample	TMSPM/TEOS (w/w)	T_g (°C)	$T_{1\max}$ (°C)	$T_{2\max}$ (°C)	$T_{3\max}$ (°C)	Residue at 800°C (wt %)	SiO ₂ (wt %; calculated)
EA/HDDA	—	25.5	434	—	578	1.1	0
(EA-TMSPM)/SiO ₂	1/16	30.0	427	465	655	13.1	6.88
(EA-TMSPM)/SiO ₂	1/4	28.6	431	469	661	13.5	8.03
(EA-TMSPM)/SiO ₂	1/2	27.8	425	476	659	14.0	9.10
(EA-TMSPM)/SiO ₂	3/4	27.3	418	485	646	14.8	9.88

$a = 0.06$; $f = 6/4$.

dation stages ($T_{1\max}$, $T_{2\max}$, and $T_{3\max}$) during TGA measurements are also listed.

Thermal stability of the (EA-TMSPM)/SiO₂ hybrid materials

The thermogravimetric behavior of the hybrids with increasing silica content (f) is shown in Figure 3. We can see that all samples have the same rate of weight loss over the temperature range from 20 to 300°C, indicating the condensation of the unreacted Si—OH. The subsequent rates of weight loss above 300°C decreases with an increase of the SiO₂ content in the systems. This is probably because the inorganic network prevents the degradation of the molecules. Thermogravimetric analysis showed (see Table I) that, with continuous increasing of the silica content, $T_{2\max}$ and $T_{3\max}$ shifted obviously to higher temperatures, showing that the connection of the organic molecules with the inorganic network by chemical bonds can improve the heat resistance. No significant difference was found in the $T_{1\max}$ among the (EA-TMSPM)/SiO₂ hybrids.

Morphology of the (EA-TMSPM)/SiO₂ hybrid materials

The etched surface of the hybrid materials with 40 and 60 wt% inorganic content were observed by scanning

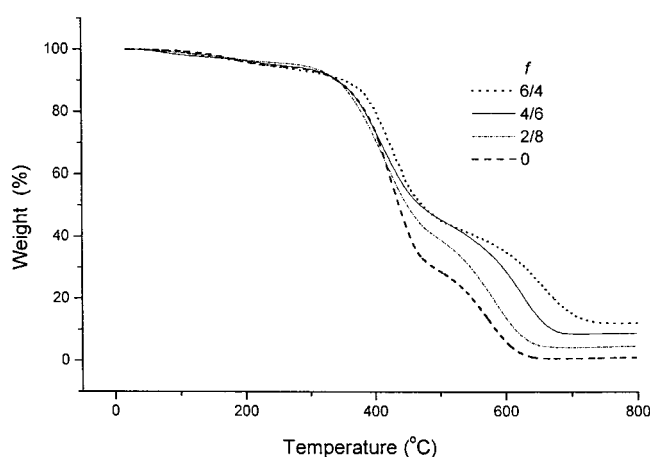
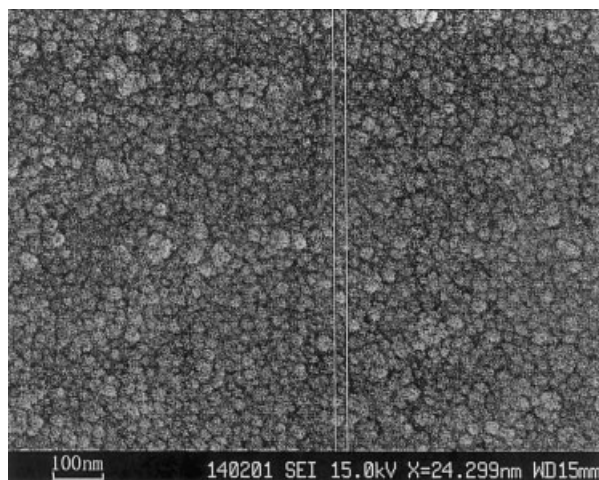
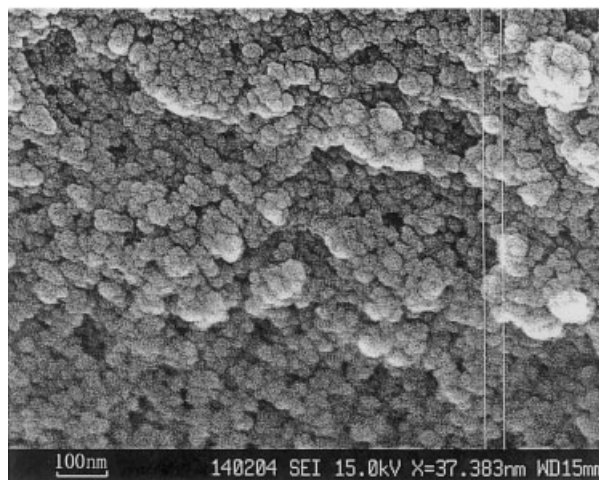


Figure 3 TGA curves of (EA-TMSPM)/SiO₂-photocured hybrid materials with different f values.



(a)



(b)

Figure 4 Field-emission SEM micrographs of (EA-TMSPM)/SiO₂ systems with different f , $a = 0.06$, and TMSPM/TEOS = 1/2 (w/w), f : (a) 4/6; (b) 6/4.

TABLE IV
Effect of f on the SiO₂ Particle Size of Photocured Hybrid Materials

Sample	f	SiO ₂ (wt %; calculated)	Particle size (nm)
(EA-TMSPM)/SiO ₂	4/6	6.07	24.3
(EA-TMSPM)/SiO ₂	6/4	9.10	37.4

$a = 0.06$; TMSPM/TEOS = 1/2 (w/w).

electronic microscopy (SEM), and the results are shown in Figure 4(a,b), respectively. It can be observed that the silica particles are evenly dispersed in the polymer matrix. The particle size increases with increasing silica content, as shown in Table IV. The picture shows that the size and number of the particles increases with an increasing silica content. As a result, the hybrid material with good optical transparency would be obtained with a typical average particle size of 20–40 nanometers.

Physical properties of the (EA-TMSPM)/SiO₂ hybrid materials

Mechanical tests were first carried out on this series to determine any differences in the macroscopic properties. The effect of different contents of SiO₂, acid, and TMSPM on some physical properties of hybrid films are compiled in Table V–VII, respectively. It can be seen that the hardness and impact strength for all hybrid materials are higher than are the corresponding values found in EA/HDDA, and these values increase with an increasing silica content and acid content as shown in Tables V and VI, respectively. From Table VII, we can see that impact strength of the hybrid decreases with an increasing TMSPM content.

TABLE V
Effect of f on the Properties of Photocured Hybrid Materials

Sample	f	SiO ₂ (wt %; calculated)	Thickness (μ m)	Lustre (%)	Pencil hardness	Impact strength (kg cm)	Flexibility (mm axis)
EA/HDDA	0	0	22	166.6	2H	21	10
(EA-TMSPM)/SiO ₂	2/8	3.03	15	165.9	3H	28	5
(EA-TMSPM)/SiO ₂	4/6	6.07	21	180.8	4H	30	5
(EA-TMSPM)/SiO ₂	6/4	9.10	16	182.4	4H	33	4

$a = 0.06$; TMSPM/TEOS = 1/2 (w/w).

TABLE VI
Effect of HCl on the Properties of Photocured Hybrid Materials

Sample	a	SiO ₂ (wt %; calculated)	Thickness (μ m)	Lustre (%)	Pencil hardness	Impact strength (kg cm)	Flexibility (mm axis)
(EA-TMSPM)/SiO ₂	0.06	7.59	21	180.8	4H	30	5
(EA-TMSPM)/SiO ₂	0.12	7.57	15	>200	5H	36	5

TMSPM/TEOS = 1/2 (w/w); $f = 5/5$.

TABLE VII
Effect of TMSPM on the Properties of Photocured Hybrid Materials

Sample	TMSPM/TEOS (w/w)	SiO ₂ (wt %; calculated)	Thickness (μm)	Lustre (%)	Pencil hardness	Impact strength (kg cm)	Flexibility (mm axis)
EA/HDDA	—	0	22	166.6	2H	21	10
(EA-TMSPM)/SiO ₂	1/16	6.88	12	198.7	5H	45	1
(EA-TMSPM)/SiO ₂	1/8	7.30	10	183.2	6H	34	1
(EA-TMSPM)/SiO ₂	1/2	9.10	16	182.4	5H	33	4

$a = 0.06; f = 6/4.$

Compared with the EA/HDDA system, the flexibility of all hybrids can be improved greatly.

CONCLUSIONS

Using EA resin as a basic polymer, (EA-TMSPM)/SiO₂ hybrid materials were obtained by incorporating TEOS with TMSPM via a sol-gel process. The results from SEM observation indicate that the inorganic content can influence the size and number of SiO₂ particles and, consequently, the properties of the final hybrid products. It is found that the thermal stability of the hybrids can be improved with an increasing silica content. The products show enhanced hardness, flexibility, and impact strength over an EA/HDDA pure organic system.

References

- Noell, J. L. W.; Wilkes, G. L.; Mohanty, D. K. *J Appl Polym Sci* 1990, 40, 1177.
- Landry, C. J. T.; Coltrain, B. K.; Wesson, J. A.; Zumbulyadis, N.; Lippert, J. L. *Polymer* 1992, 33, 1496.
- Huang, Z. H.; Qiu, K. Y. *Polym Bull* 1995, 35, 607.
- Makote, R.; Collinson, M. M. *Chem Mater* 1998, 10, 2440.
- Frings, S.; van Nostrum, C. F.; van der Linde, R. *J Coat Tech* 2000, 72(901), 83.
- Oh, I. S.; Park, N. H.; Suh, K. D. *J Appl Polym Sci* 2000, 75, 968.
- Zerda, T. W.; Artaki, L.; Jonas, J. *J Non-Cryst Solids* 1986, 81, 365.
- Strawbridg, L.; Craievich, A. F.; James, P. F. *J Non-Cryst Solids* 1985, 72, 139.
- Ting, X. X.; Chong, G. Z.; Sheng, Y. F.; Xin, Q. W. *J Appl Polym Sci* 2000, 75, 379.