

New Epoxy/Silica-Titania Hybrid Materials Prepared by the Sol–Gel Process

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ABSTRACT: A new type of inorganic-polymer hybrid materials of epoxy/silica-titania had been prepared by incorporating grafted epoxy, which had been synthesized by epoxy and tetraethoxysilane (TEOS), with highly reactive TEOS and tetrabutyltitanate (TBT) by using the *in situ* sol-gel process. The grafted epoxy was confirmed by Fourier transform infrared spectroscopy (FT-IR) and ¹H-NMR spectroscopic technique. Results of FT-IR spectroscopy and atomic force microscopy (AFM) demonstrated that epoxy chains have been covalently bonded to the surface of the SiO₂-TiO₂ particles. The particles size of SiO₂-TiO₂ are about 20–50 nm, as characterized by AFM. The experi-

mental results showed that the glass-transition temperatures and the modulus of the modified systems were higher than that of the unmodified system, and the impact strength was enhanced by two to three times compared with that of the neat epoxy. The morphological structure of impact fracture surface and the surface of the hybrid materials were observed by scanning electron microscopy and AFM, respectively. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1075–1081, 2006

Key words: hybrid materials; epoxy/silica-titania; grafted; sol-gel process

INTRODUCTION

Organic–inorganic hybrid materials have been extensively studied recently.^{1–3} The properties of the hybrid materials could be tuned through the functionality or segment size of each component, including thermal, electronic, optical, and optoelectronic properties. Such a hybrid system was synthesized by the sol–gel process *in situ* formation of an inorganic structure with an organic polymer matrix.^{4,5} This interest relies upon the unique opportunity of combining in a controlled way the most remarkable properties of inorganic glasses, for instance, flexibility of synthetic polymers and high modulus, high thermal stability, and good optical properties of inorganic glasses. The main physical, mechanical, and optical properties of these composite materials, known as creamers, are strongly dependent on phase continuity, average phase size, molecular mixing at the phase boundaries, and intrinsic properties of the constitutive components.

Some works have already investigated the synthesis of new polymer/inorganic hybrid materials. Schmidt has reported several types of organic modification by the sol–gel process. One example is the coupling of oligomeric species terminated with functional groups, which can react with the metal hydroxide. The sol–gel condensation of tetraethoxysilane (TEOS) in the presence of poly(dimethylsiloxane) (PDMS) with silanol terminal groups can give a PDMS/silicate hybrid materials.⁶ These materials showed good optical transparency and very different mechanical properties compared to the neat PDMS system. Other types of the hybrid materials also have been synthesized, for example, polymers such as polyamides,⁷ poly(ether ketone),⁸ poly(ϵ -caprolactone),⁹ poly(vinyl acetate),¹⁰ etc. have been successfully incorporated into SiO₂ or TiO₂ inorganic networks by sol–gel process.

Nanocomposite technology using pores silica or organophilic layered silicates as *in situ* route to nanoreinforcement offers new opportunities for the modification of thermoset micromechanics. Large improvements of mechanical and physical properties, including modulus,¹¹ barrier properties,¹² flammability resistance,¹³ and ablation performance,¹⁴ have been reported for this type of material at low silica content. In principle, it should be possible to compensate matrix flexibilization via matrix reinforcement using silica.

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Epoxy resin as organic matrix has excellent heat, moisture, and chemical resistance and good adhesion to many substrates. They are mostly applied in the field of coating, adhesives, casting, potting, composites, laminates, and encapsulation of semiconductor devices.^{15,16} If epoxy resin could be covalently combined with an inorganic glass such as SiO₂ or TiO₂ at the molecular level by the sol-gel process, the new hybrid materials that would have tailored combinations of the hardness of the inorganic glass and the toughness of the polymer would be obtained. Sung-tack Kang et al.¹⁷ studied the nano-SiO₂ particles prepared via sol-gel process. Then, the surfaces of the nano-SiO₂ particles were modified by substituting silanol groups into other functional groups through changing the degree of substitution. These surface-tailored nano-SiO₂ were filled into epoxy resin and the obtained EP/SiO₂ hybrid materials showed superior thermal property and a decrease in damping and high glass-transition temperature (T_g) with the filler content.

This article describes the preparation of the EP/SiO₂-TiO₂ hybrid materials by incorporating TEOS and tetrabutyltitanate (TBT) via the sol-gel process, using epoxy-siloxane copolymer. In this article, epoxy-grafted copolymer was first prepared by epoxy resin and TEOS, using tetraisopropyl titanate (TPT) as the catalyst, and was then condensed with excess TEOS to give epoxy-siloxane copolymer. Finally, the epoxy-siloxane polymeric chain covalently bond with the inorganic network after sol-gel processing. The thermal, dynamic mechanical, and morphological properties of these materials were examined and discussed.

EXPERIMENTAL

Materials and measurement

Epoxy resin (diglycidyl ether of bisphenol A; DGEBA (E-51)), Wep = 196, purchased from Yueyang Chemical Plant, China, was used without further purification. 4,4'-Diaminodiphenylsulphone (DDS; from Shanghai Chemical Reagent Company, China) had a molecular mass of 248.31 and purity > 96%. TEOS and TBT (both of chemical-reagent grade) were ordered from Xilong Chemical Factory, Guangdong, China. TPT was obtained from Dupont Co. Distilled water was used to induce the hydrolysis of the alkoxysilane or TBT components, using HCl as the catalyst.

Fourier transform infrared spectroscopy (FTIR) was recorded between 4000 and 400 cm⁻¹ on a Perkin-Elmer 1710 instrument (KBr pellets) for organic polymer samples. The crystal behavior of the EP and EP/SiO₂-TiO₂ material were analyzed by X-ray diffraction (XRD; D/max-RB, Japan). ¹H-NMR spectra were recorded on a Bruker NMR 400 spectrometer operating at 400Mz; deuterated chloroform was used

as the solvent, and tetramethylsilane (TMS) was used as the internal standard.

The impact strength was measured on a tester of type XJJ-5, with no notch in the specimen. The flexural strength and tensile strength were examined on an electron omnipotency tester RGT-5, at a flexural rate of 2 mm/min⁻¹. All the presented results are average of five specimens. Thermogravimetric analyses (TGA) were carried out using Shimadzu TG-40 (Japan) from 10°C to 700°C at a heating rate of 10°C/min under nitrogen. Differential scanning calorimetry (DSC) was carried out using NETZSCH DSC 204 from 50°C to 270°C at a heating rate of 30 K/min under nitrogen. Dynamic mechanical analysis (DMA) was made with a TA Instruments (902-50010 Dynamic Mechanical Analyzer) under a frequency of 1 Hz from -120°C to 250°C at a heating rate of 5°C/min. The rectangular bending mode was chosen and the dimensions of the specimen were 48 × 5 × 2.5 mm³. Atomic force microscopy (AFM) was carried out using AJ-IIIa (Shanghai AJ Nano-Science Development Co. Ltd). The scan rate was 2.00061 Hz, scan size was 5.00061, and number of samples were 256.

Preparation of EP/SiO₂-TiO₂ hybrid materials precursor

About 100 g of epoxy resin, 0.35 g of 0.5 wt % TPT and the desired amount of TEOS were added to a 250-mL three-necked, round-bottom flask equipped with a reflux condenser and a Teflon-coated magnetic stirring bar. The mixing was carried out at 130°C for 2 h, followed by addition of distilled water. The molar ratio of water to TEOS was 2:1 in all formulations. Then, the reaction system was hydrolyzed and polymerized at 60–65°C for 3 h. After that, the solution was cooled to room temperature, an appropriate amount of TBT and distilled tetrahydrofuran (THF) were added by vigorous stirring for 1 h, to make the mixture homogeneous. Then, an appropriate amount of 1M HCl was added and the reaction mixture was stirred continually for 1 h. The solution was then transferred into a glass mold, which was partially covered with parafilm to avoid too rapid evaporation of the solvent during the hydrolysis and sol-gel reactions. The yellow viscous liquid was obtained after one week. The recipe for the EP/SiO₂-TiO₂ hybrid samples is given in Table I.

Curing procedure

A mixture of EP/SiO₂-TiO₂ materials precursors and a stoichiometric amount of DDS (30 g per 100 g of epoxy resin) were degassed in vacuum at 130°C for about 30 min. The resulting mixture was then cast into a preheated mold coated with silicone resin. All samples

TABLE I
Preparation Recipe for the EP/SiO₂-TiO₂ Hybrid Materials^a

Sample	EP (g)	Si(OC ₂ H ₅) ₄ (g)	Ti(OC ₄ H ₉) ₄ (g)	SiO ₂ -TiO ₂ ^b (wt %)
0	100	0	0	0
1	100	1.34	1.3	0.65
2	100	2.67	2.6	1.32
3	100	4.0	3.9	1.95
4	100	5.34	5.2	2.60
5	100	6.67	6.5	3.25

^a Preparation condition: [H₂O] + [Si(OC₂H₅)₄ + Ti(OC₄H₉)₄] = 1:1 and [HCl] + [Si(OC₂H₅)₄ + Ti(OC₄H₉)₄] = 0.05 (mol ratio).

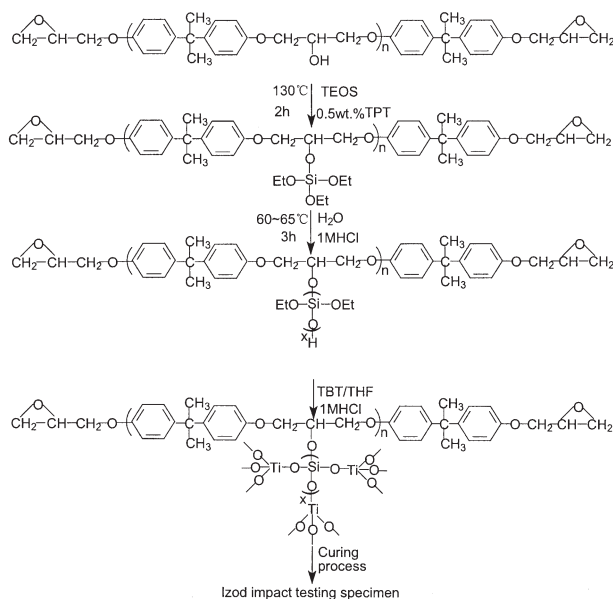
^b Silica and titania contents were calculated theoretically.

were cured at 130°C for 2 h, 170°C for 2 h, and 190°C for 2 h. Its chemical structure is shown in Scheme 1.

RESULTS AND DISCUSSIONS

Characterization

Figure 1 is the FTIR spectra of EP, TEOS-grafted EP, and EP/SiO₂-TiO₂ hybrid material. From Figure 1(a), we can see that the hydroxyl-stretching band of epoxy resin appears at 3507 cm⁻¹ and oxirane absorption at 915 cm⁻¹. When TEOS grafted epoxy resin, hydroxyl-absorption peak of epoxy disappeared [Fig. 1(b)]. In Figure 1(c), there is an absorption peak at 3402 cm⁻¹ (characteristic of —OH stretching, which is the unreactive Ti—OH or Si—OH groups in inorganic networks) and at 1108 cm⁻¹ (Si—O—C). There also was a broad absorption at lower wavenumber region, espe-



Scheme 1 Preparation and curing process of EP/SiO₂-TiO₂ hybrid materials.

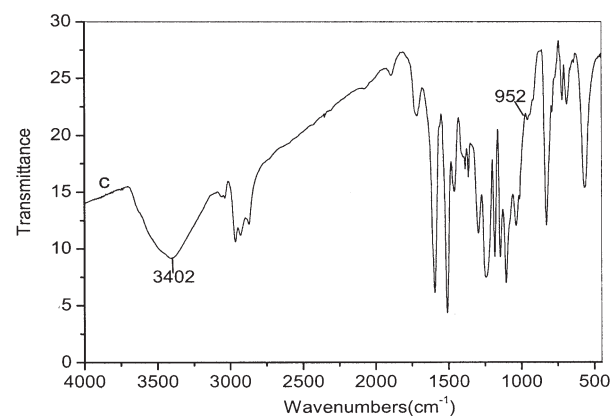
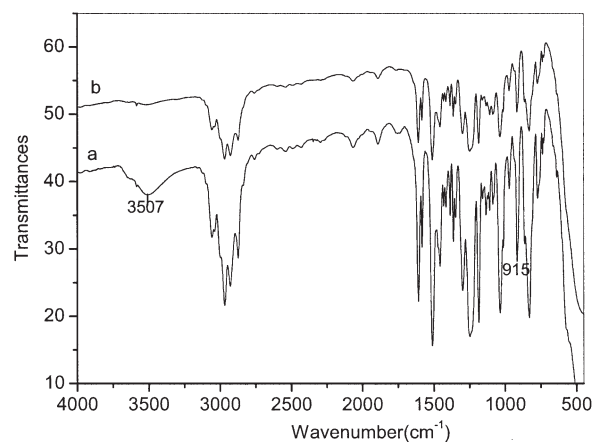


Figure 1 FTIR spectra of EP/SiO₂-TiO₂ hybrid material. (a) neat epoxy; (b) TEOS-grafted epoxy; (c) EP/SiO₂-TiO₂.

cially, at 1100–920 cm⁻¹ characteristic of Si—O—Si and Si—O—Ti networks and at 900–450 cm⁻¹ due to Ti—O—Ti linkage in the titania matrix.⁵ The bond at around 952 cm⁻¹ is attributed to Si—O—Ti bonds.¹⁸

EP- and TEOS-grafted EP copolymer was characterized through ¹H-NMR spectroscopy. Figure 2(a) shows the ¹H-NMR spectrum major chemical shifts (δ, in ppm from TMS = 0) at 7.1, 6.8 (C-phenyl-), 4.7

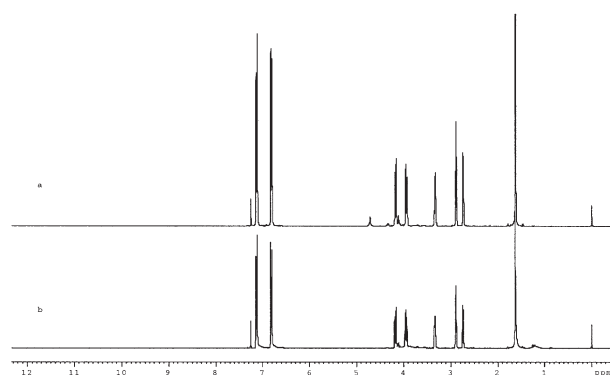


Figure 2 ¹H-NMR spectra of (a) neat epoxy and (b) TEOS-grafted epoxy.

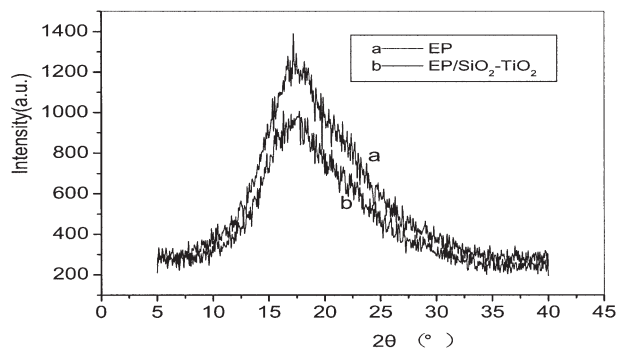


Figure 3 X-ray diffraction patterns of the EP and EP/SiO₂-TiO₂.

(—OH), 4.1, 3.9 [connected oxirane (CH₂)], 3.3 [oxirane (CH)], 2.9, 2.7 [oxirane (CH₂)], 1.6 [—C(CH₃)₂]. It can be seen from Figure 2(b) that epoxy rings did not open during the grafting between the OH group from epoxy resin and the methoxy terminal group of the TEOS, and the signals of OH group disappeared. Meanwhile, two signals that appeared at 3.8 and 1.3 ppm were assigned to —OCH₂C— and —C—CH₃ protons of the TEOS. The structure of TEOS-grafted EP copolymer has been indicated with the support from spectroscopic data of FTIR.

XRD analysis

Figure 3 shows the XRD patterns of the EP and EP/SiO₂-TiO₂. From the analysis of these patterns, it is possible to conclude that the curve of the EP and EP/SiO₂-TiO₂ are almost analogous. They have a broad amorphous peak, the contact angle of the peaks were around 2θ ranging between 10° and 30°, which shows that silica-titania networks and epoxy resins chain are incorporated through the covalent bond and hydrogen bond.

Mechanical properties and interfacial interaction

The most common approach used to enhance the toughness of epoxy resin is to add a softer second phase to epoxy resin.¹⁹ The dispersed rubber phase plays an important role in the toughness improvement of the material. Rubber particles acting as stress concentrators allow the matrix between the particles to undergo both shear and craze deformation. In this article, the rigid silica-titania acts as the dispersing phase, and the impact of epoxy/silica hybrid materials is shown in Figure 4.

Figure 4 shows the effect of SiO₂-TiO₂ content on impact resistance of the EP/SiO₂-TiO₂ hybrid materials. It can be seen that the impact resistance increased at first and then decreased with the SiO₂-TiO₂ content increasing. It reached the maximum when the SiO₂-

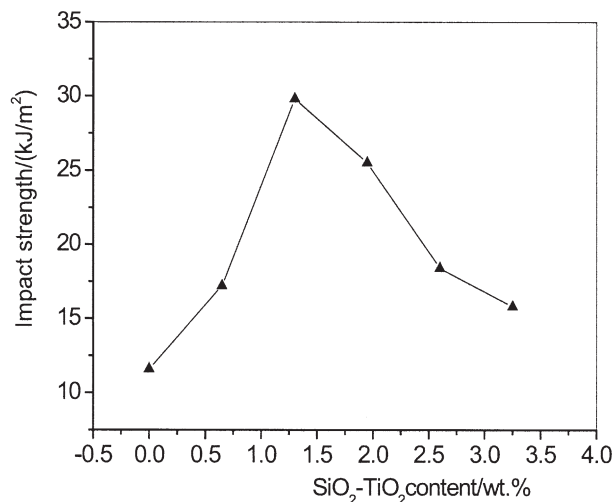


Figure 4 The relation between SiO₂-TiO₂ contents and impact strength.

TiO₂ content was about 1.32 wt %. Since impact strength reflects the energy consumed before fracture, when the material is subjected to an impact test, the EP/SiO₂-TiO₂ hybrid materials have generated micro-phase separation for introducing of the silica-titania particles, which may induce epoxy matrix yielding deformation and resistance to crack propagation. For this reason, the impact energy of the epoxy matrix is expected to decrease significantly as silica-titania particles are introduced, and resulted in enhanced toughening of the EP/SiO₂-TiO₂ hybrid materials.

The flexural strength of microparticle-filled composites is known to be reduced with rising filler content for the bonding between the filler particles and the matrix is poor.^{20,21} If the bonding between fillers and matrix is instead strong enough, the flexural strength of a particulate composite can be higher than that of the matrix polymer.²² From Figure 5, it can be seen that both flexural strength and modulus increase with SiO₂-TiO₂ content increasing. This means that the in-

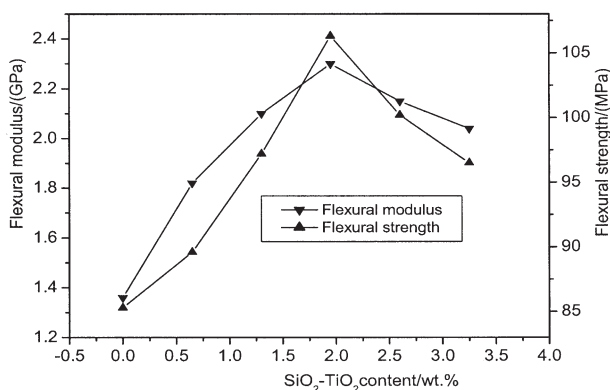


Figure 5 The relation between SiO₂-TiO₂ contents, flexural strengths, and flexural modulus.

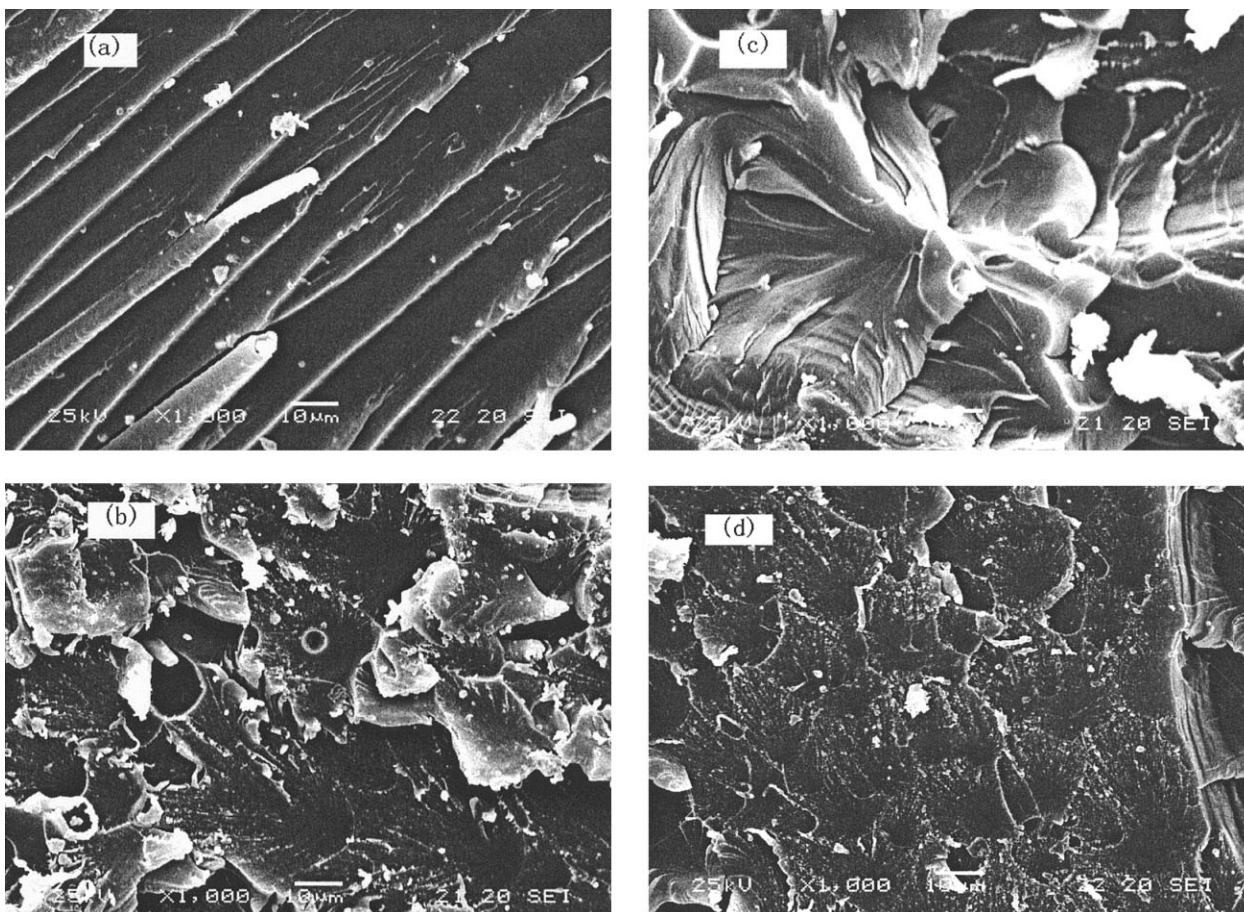


Figure 6 SEM of the fracture surfaces of the impact specimens for the curing system: (a) neat epoxy; (b) EP/SiO₂-TiO₂ (1.32 wt %); (c) EP/SiO₂-TiO₂ (1.95 wt %); (d) EP/SiO₂-TiO₂ (2.60 wt %).

teraction between nanoparticles SiO₂-TiO₂ and epoxy matrix are so strong that the nanoparticles are able to carry the applied load. The results of experiment indicated that, when the SiO₂-TiO₂ content is 1.95 wt %, the flexural strength and modulus of the hybrid materials were 76.4% (1.36 GPa) and 20.8% (85.3 MPa) higher than that of the epoxy resin, respectively.

Visual examinations on the fracture surfaces of EP/SiO₂-TiO₂ hybrid materials by scanning electron microscopy can often reflect detailed information on the cause and location of failure. Some representative specimens were chosen to study the acting deformation mechanisms responsible for the reinforcement. Resulting pictures can be seen in Figure 6(a–d). Figure 6(a) shows a fracture surface for neat epoxy matrix, which is very smooth and has uniform crack direction, and reveals the characteristic of brittle fracture. As for the EP/SiO₂-TiO₂ hybrid materials [Fig. 6(b–d)], the fracture surfaces present rough and irregular appearance, and many holes or indentations can be seen from the micrograph, and fracture stripes divert to different directions, which can disperse stress, indicating the characteristic of toughening fracture. The above results unambiguously support that the micromecha-

nism of shear yielding is the principal toughening mechanism and responsible for the enhancement of toughness. This is in very good agreement with the impact resistance experimental data.

Thermal properties

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-oxide network. The DSC traces of the EP/SiO₂-TiO₂ hybrid materials are shown in Figure 7. It can be observed that the glass-transition temperatures (T_g 's) progressively shift to higher values and the breadth of the transition and the decrease in ΔC_p , with SiO₂-TiO₂ content increasing. The T_g of EP/SiO₂-TiO₂ samples is 194°C, which is higher than that of pure epoxy resin (157°C) when SiO₂-TiO₂ content is 3.25 wt %. The result indicates that T_g reflects an increasing interaction between the SiO₂-TiO₂ phase and the epoxy resin chain in terms of the formation of EP-Si—O—Ti crosslinks.

TGA can be used not only to study the thermal decomposition and the stability of materials, but also

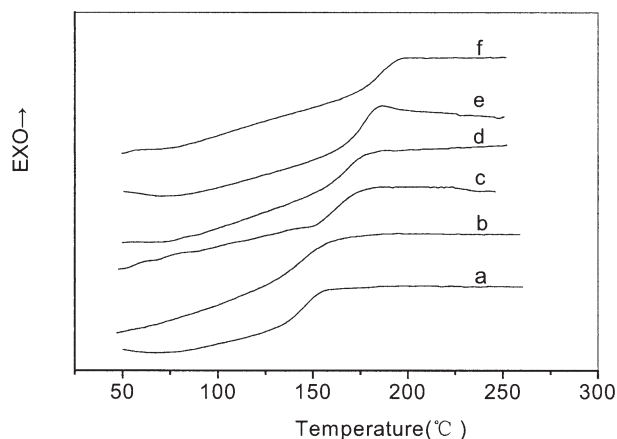


Figure 7 The DSC curves of (a) neat epoxy; (b) EP/SiO₂-TiO₂ (0.65 wt %); (c) EP/SiO₂-TiO₂ (1.32 wt %); (d) EP/SiO₂-TiO₂ (1.95 wt %); (e) EP/SiO₂-TiO₂ (2.60 wt %); (f) EP/SiO₂-TiO₂ (3.25 wt %).

to give important structural information. Figure 8 shows the results of the thermal decomposition of the pure epoxy resin and the hybrid materials. It is obvious that the initial thermal decomposition temperature of the EP/SiO₂-TiO₂ is higher than that of the pure epoxy resin, which is 379°C while the EP/SiO₂-TiO₂ is 391°C when SiO₂-TiO₂ content is 3.25 wt %. The results indicate that the hybrid system would become highly crosslinked with increasing the content of TBT and TEOS, and the thermal weight loss of the hybrid materials decrease with increasing the SiO₂-TiO₂ content. At the temperature of 700°C, the char yield of neat epoxy is 7.81 wt % and that of the EP/SiO₂-TiO₂ 3.25 wt % is 20.88 wt %. Consequently, the thermal stability of EP/SiO₂-TiO₂ hybrid materials is higher than that of neat epoxy at high temperature.

Dynamic mechanical behavior

The storage modulus data (E') of the modified system and unmodified system are shown in Figure 9(a). It

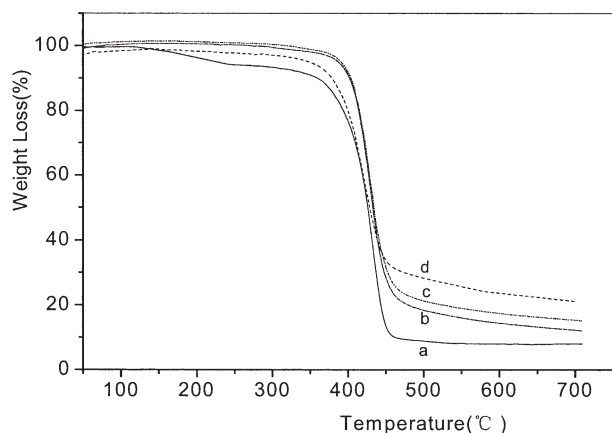


Figure 8 The TGA curves of (a) neat epoxy; (b) EP/SiO₂-TiO₂ (1.32 wt %); (c) EP/SiO₂-TiO₂ (1.95 wt %); (d) EP/SiO₂-TiO₂ (3.25 wt %).

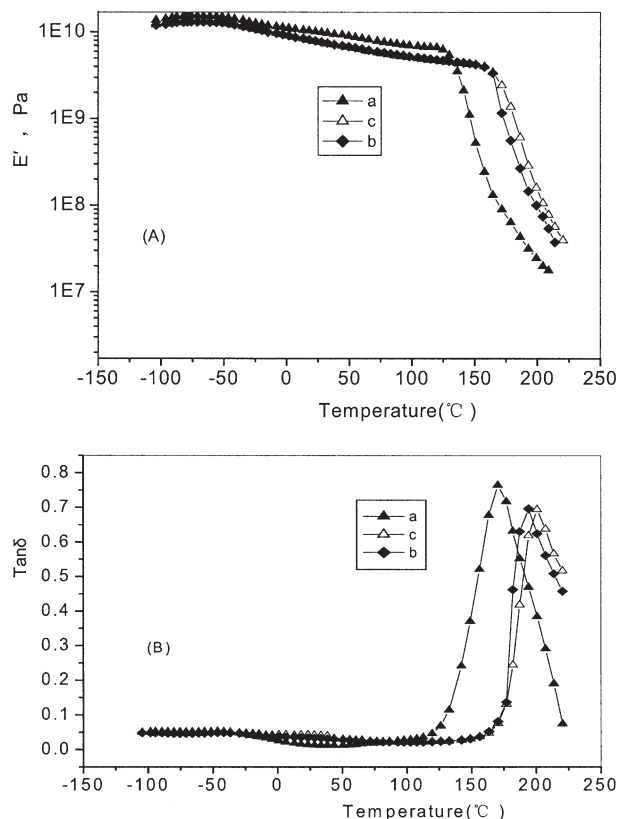


Figure 9 Temperature dependence of the E' of (a) neat epoxy; (b) EP/SiO₂-TiO₂ (1.32 wt %); (c) EP/SiO₂-TiO₂ (2.60 wt %).

can be seen that below 110°C, the storage modulus of the modified curing system is approximate to that of the controlled sample. With the temperature increasing, the storage modulus of the modified system appears much higher than that of the unmodified system. This indicates that the motion of epoxy matrix chains is strongly restricted by the SiO₂-TiO₂ inorganic networks.

The loss tangent data of the hybrids are shown in Figure 9(b). It can be seen that all spectra of the cured systems exhibit α - and β -relaxation peak. The peak $\tan \delta$ values for modified system appears to be slightly decreased with SiO₂-TiO₂ content increasing. The $\tan \delta$ peak temperature for the modified systems is considerably higher than that of the unmodified system. The addition of SiO₂-TiO₂ in matrix made it difficult to move the polymer chain. Therefore, the peak $\tan \delta$ values decreased and glass-transition temperatures (T_g 's) were shifted to higher temperature. The reason for this may be attributed to a loss in the mobility of the chain segments of epoxy resin, resulting from the SiO₂-TiO₂ nanoparticle/matrix interaction. The particle surface-to-surface distance should be relatively small and chain segment movement may be restricted.

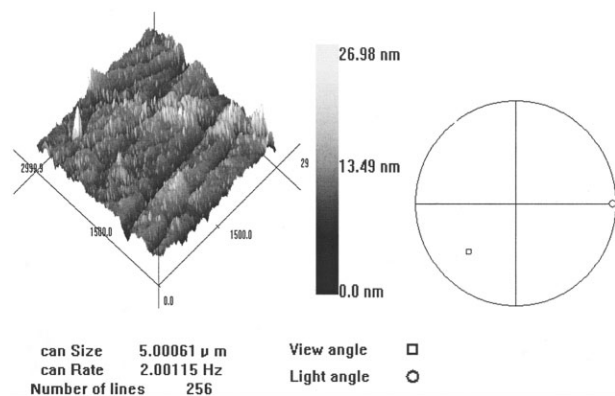


Figure 10 AFM surface images of the SiO₂-TiO₂ composite specimen. The scan area is 3 μm × 3 μm.

AFM surface image of hybrid material

The surface topography structure of the hybrid film (1.32 wt % SiO₂-TiO₂) is characterized by AFM (Fig. 10). The film thickness was about 27 nm, and the scan area was 3 μm × 3 μm. From the micrograph, it can be seen that the SiO₂-TiO₂ particle size is about 30–70 nm. This indicates that SiO₂-TiO₂ composite particles are homogeneous and well dispersed in the hybrid material matrix.

CONCLUSIONS

A novel epoxy resin containing silicon and titanium hybrid materials was prepared successfully via a sol-gel method. The hybrid materials have a network structure and inorganic phases have a size of less than 100 nm. The hybrids were nanocomposites. The sol-gel technique was used to incorporate silicon and titanium into the networks of hybrids increasing the mechanical strength, and the dynamic modulus is markedly improved and tan δ peak intensity decreases. The tan δ peak position shifts towards higher temperatures perhaps due to the presence of silica,

and titania particles are strongly bonded with the epoxy matrix. The thermal stability of EP/SiO₂-TiO₂ hybrid materials is higher than that of the neat epoxy resin at high temperature.

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