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Preparation and characterization of epoxy-silica hybrid materials by the sol-gel process

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A transparent organic-inorganic epoxy/silica hybrid material was prepared by epoxy resin, functionalized-epoxy resin, which was partially functionalized by 3-aminopropyl triethoxylsilane(APTES), and highly reactive polysilcic acid (PSA), which was prepared through hydrolysis and condensation of metasilicate salt. The properties of hybrid materials such as impact strength, tensile strength, glass transition temperature (T_g), thermogravimetric temperature (TGA), and thermal effect of the hybrid materials were studied. The size of PSA particles in THF measured by dynamic light scattering technique, ranged from 10–28 nm. The results of experiment indicated that modified epoxy resin possed better roughness than that of the pure epoxy resin. The structure of the hybrid materials was characterized by FT-IR spectroscopy and ^{29}SiNMR spectroscopy.

1. Introduction

Epoxy resin is one of the most important thermosetting polymer materials. It has many excellent properties, such as high thermal stability, adhesion, mechanical and electrical properties. It is widely used in coating, adhesives, castings etc. However, it is well known that the commonly used epoxy resin is rather brittle due to its highly crosslinked structure, when cured with stoichiometric amount of common curing agents such as aliphatic or aromatic polyamides, dicarboxylic acids, anhydrides, boro- trifluoride, and tertiary amines.Therefore, the improvement of toughness for the cured epoxy resin is highly desirable to overcome their brittleness. One of the methods is by incorporating rigid, or reactive rubbery particles, or both of them [1, 2], However, modification by the addition of rubber is usually at the expense of T_g and modulus. Another way is by incorporating tough, such as polyethersulfones [3] and polyetherimide [4]. Liquid crystalline polymers as fillers are also used to improve the toughness recently [5]. All the approaches mentioned above have been achieved to improve toughness.

Organic-inorganic hybrid materials have been extensively studied recently because of their potential applicability to many industrial materials [6, 7]. One of the widely used organic-inorganic hybrid materials is the epoxy/silica system. Usually, silica particles are used for the reinforcement of epoxy matrix to decrease shrinkage on curing and thermal expansion coefficients, to improve thermal conductivity and meet mechanical requirement.

In general, sol-gel method is widely applied to prepare oxide particles of various properties, such as large porous gel spheres and small particles with high density. The preparation procedures of silica particles from silicon alkoxides in alcoholic solution were developed by Stober *et al.* and their resultant, particles are excellent in monodispersity [8]. The advantage of the sol-gel process over the traditional ceramic synthesis process is the abilities to form pure and homogeneous products at low temperature [9, 10]. However, the drawback of the traditional sol-gel process is the shrinkage of the xerogel by removing the cosolvent, excess water, and liberating alcohol during the drying process. Therefore, the mechanical properties of the hybrids were poorer than that of hybrids prepared via *in situ* sol-gel process. This is because that there is only little or no silanol groups in the fumed silica to create substantial hydrogen bonding between the organic and inorganic phases, like that of the hybrids prepared from the *in situ* process. This paper describes the preparation of hybrid materials incorporating polysilicic acid and epoxy resin by the sol-gel process. The sol-gel process produces a mixture of organic polymers and inorganic glasses, the compatibility of the two phases will affect the properties of the materials. Macro-phase separation can be Prevented by promoting reaction or the strong physical interaction between polymer chains and the inorganic network, either directly or via a "coupling agent" [11, 12]. In this article, trialkoxylsilyl-functionalized epoxy resin polymer was first prepared by epoxy groups and coupling agent via aminolysis reaction. Then added the nanoparticles of polysilicic acid (PSA), which contains a lot of silanol groups on the surface of the particle.The epoxy resin and trialkoxylsilyl-functionalized epoxy resin covalently bonded with the inorganic network after sol-gel process. The reactivity thermal, impact property and morphology for the curing systems were examined and discussed.

2. Experimental

2.1. Materials

Epoxy resin (diglycidyl ether of bisphenol A DGEBA(E-51), Wep = 196, purchased from Yueyang Chemical Plant, China, without further purification). 4,4′-diaminodiphenylsulphone (DDS), from Shanghai Chemical Reagent Company, China), with a molecular mass of 248. 31 and purity >96% according to the supplier. Sodium metasilicate was purchased from Guangzhou Chemical Reagent Company, China and was used without further purification. 3-aminopropyltrimethoxysilane (APTES) was received from Chemical Factory of wuhan University, China. Other reagents were purified by the conventional methods.

2.2. Synthesis and extraction of polysilicic acid

19.89 g (70 mmol) sodium metasilicate was dissolved in 70 ml water. The solution was added dropwise to 67 ml of 2.5 M HCl at 0°C with stirring for 2 h. The silicic acid was extracted into THF by addition of 30 g of sodium chloride and 100 ml of THF. The two-phase mixture was stirred vigorously for 2 h. The aqueous layer was removed and the THF solution was dried over 20 g of an hydrous sulfate to give an approximately 0.5 M silicic acid/THF solution (3.5 g of silicic acid, 89.1%SiO_2). The size and molecular weight of the nanoscaled PSA-THF solution thus prepared were investigated by dynamic light scattering measurement (DLS) and gel permeation chromatography (GPC), respectively.

2.3. Preparation of epoxy/silica hybrid materials precursor

In a 250 ml round-bottom flask, an appropriate amount of epoxy resin reacted with APTES coupling agent were reacted at 80°C for 3 h, Then the mixture were cooled to room temperature, and distilled to remove water. Hydrochloric acid and PSA/THF solution (with a stoichiometric amount of PSA) were introduced and stirred vigorously for 10 min. The mixture was transferred into a 150 ml beaker and covered with parafilm for 7days to allow the evaporation of small molecules. The epoxy/silica hybrid precursors were obtained according to recipe listed in Table I.

TABLE I Recipe of EP/SiO_2 hybrid materials

Sample code	$w(SiO_2)$/%	w(EP)/%	n (APTES)/ $n(SiO_2)$	n (HCl)/ n (APTES)
1#	0	100	0	0
2#	1	99	0.5	0.04
3#	2	98	1.0	0.08
4#	3	97	1.5	0.12
5#	4	96	2.0	0.16
6#	5	95	2.5	0.20

2.4. Curing procedure

A mixture of epoxy/silica hybrid precursor and a stoichiometric amount of DDS (30 g per 100 g of epoxy resin) was degassed in vacuum at 130°C for about 30 min. The obtaining mixture was then casted into a preheat mold coated with silicone resin. All samples were cured at 130°C for 2 h, 170°C for 2 h and 190°C for 2 h.

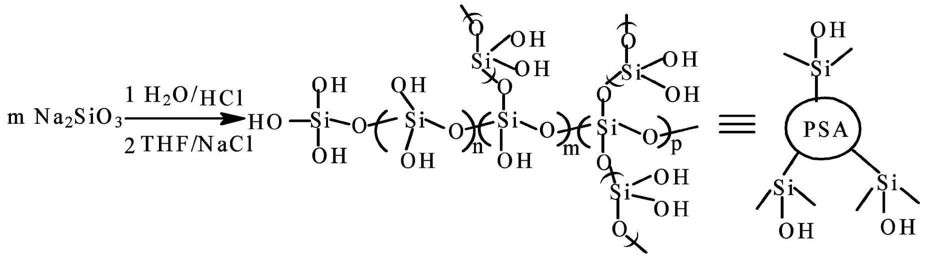
2.5. Measurement

The DLS measurement for the size of PSA particles was performed with a malvent series 4700 apparatus (Mslvemrn Instriments, Malvern VK). A 2 w argon-ion laser operation at a power of 100 mw with a wavelength of 514 nm used as the light Source, which was focused on the sample cell through a temperature controlled at 30°C, and with the scattering angle at 90°C, The solvent viscosity was chosen as 0.5 centiposes and the refractive index of the solvent was chosen as 1.10. Fourier transformed infrared spectroscopy (FT-IR) was recorded between 4000 and 400 cm^{-1} on a perlcin-Elmer 1710 instrument KBr pellets for organic polymer samples. The crystal phases of the silica and curing samples were analyzed by X-ray diffractometry (XRD: D/max -RB, Japan). ^{29}Si nuclear magnetic resonance spectroscopy (^{29}SiNMR)was recorded on a Bruker DSX-400WB. The sample was grounded into fine powder. Thermogravimetic analyses (TGA) was carried out using (shimadzu TG-40, Japan), analyzed from 10 to 650°C at a heating rate of 10°C/min under nitrogen. Differential Scanning Calorimetry (DSC) was carried out using NETZSCH DSC 204 from 50 to 300°C at a heating rate of 30 K/min under nitrogen. The morphology of the fracture surfaces was observed by a scanning electron microscope (SEM: JSM 5610LV), at an accelerating voltage of 25 KV. The samples were shadowed with gold and improved conductivity. Tensile measurements were carried out on specimens having a dimension of 10 mm wide and 2 mm thickness and 80 mm length using an RGT-5 (REGER instrument company, Shenzhen, China). The testing method according to china national Standard GB1040-92, with tensile rate of 10 mm/min. Bending strengths were carried out on specimens with a dimension of 10 mm wide and 4 mm thickness and 80 mm length using RGT-5.The testing method according to China national Standard GB1040-92, testing rate of 2 mm/min. The impact strength of the cured resins was determined by a charpy impact-testing machine (XJJ-50, chende, PRC) according to china national Standard GB1043-79. The specimen described in GB 1043-79 is with a thickness of 4.0 mm and width of 10 mm and length of 80 mm.

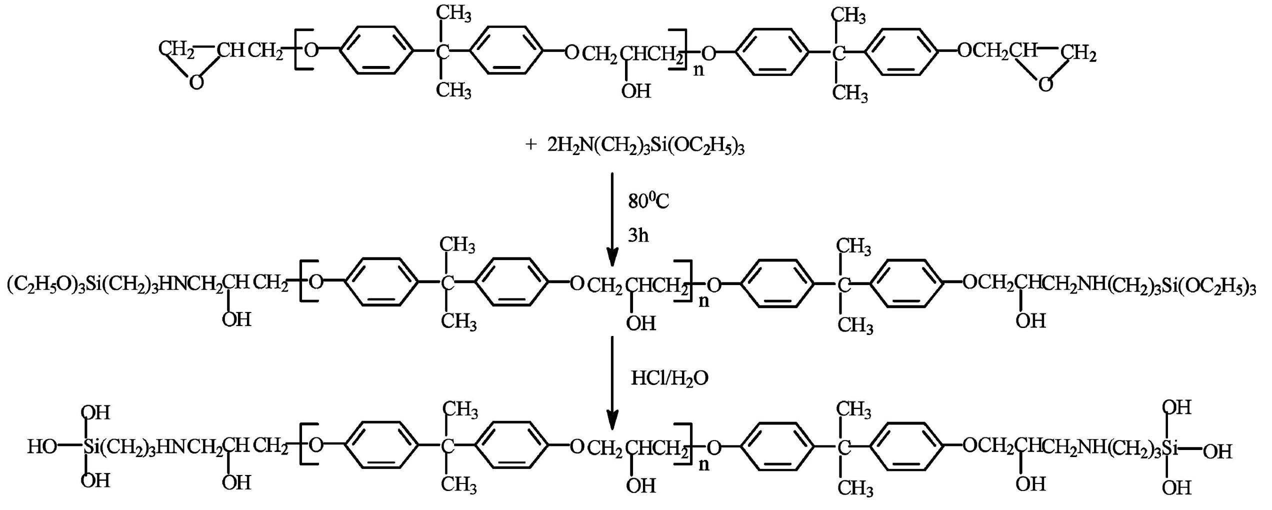
3. Results and discussions

3.1. Reaction scheme

This study showed that epoxy/silica hybrid material was obtained by a sol-gel method. The hybridization procedure between epoxy resin and PSA in this study is believed to be as follows. First polysilicic acid can be generated by the hydrolysis and condensation of sodium metasilicate (Na_2SiO_3) in acidic aqueous solution (2.5 M HCl) and extracted into organic solvent(THF) according to the following reaction.



Secondly, triethoxylsilyl-functionalized epoxy resin was prepared by partially epoxy groups and coupling agent (APTES) via aminolysis reaction. Then hydrolysise of trithoxysilane end-capped epoxy resin by the following reaction:



(Si-EP)

Finally, condensation reaction occurred between the hydrolyzed Si-EP and PSA particles, interpenetrating epoxy/silica network was formed as following scheme:

Silica network—epoxy—silica network

3.2. FI-IR analysis

FI-IR spectra of epoxy/silica and pure epoxy are shown in Fig. 1a. The hydroxyl-stretching band of epoxy resin appears a strong broad peak at 3501 cm^{-1}. Upon forming the hybrid with PSA, Fig. 1b the band appearing at 3471 and 1107 cm^{-1} was assigned to Si—O—Si asymmetric stretching modes [11]. From Fig. 1b the bands gradually shift toward the lower frequency and broaden with content of silica increasing. The band appears at 3445 cm^{-1} for the 1 wt%. silica and gradually shifts to 3424 cm^{-1} for the 5 wt% silica respectively. This is because the strong hetero-associated hydrogen bonding interaction between the hydroxyl groups of epoxy resin and triethoxylsilyl-functionalized epoxy resin and the silanol groups of PSA.

3.3. The size of PSA particles

The size of PSA particles (with a Mn is 7.1×10^3), which were prepared by the hydrolysis and condensation of sodium metasilicate in 2.5 M HCl solution for 2 h , was measured by the DLS measurement. The particle size distribution is shown in Fig. 2. The size of majority of particles is 10–28 nm. The PSA/THF solution containing the nanoscaled PSA particles was mixed with epoxy resin to form the homogeneous solution. After removing THF from the homogeneous solution, mixing system was cured by molecular level in modified epoxy nanocomposition. Finally, the transparent epoxy/silica hybrid materials were obtained.

3.4. ^{29}SiNMR spectrum

Fig. 3 shows the solid-state ^{29}SiNMR spectrum of the epoxy resin/silica hybrid material, Silicon atoms through mono- , di- , tri-, and tetra-substituted siloxane bonds are designated as Q^1, Q^2, Q^3, Q^4, respectively, Three types of chemical shifts (δ) at -91, -101, and -110 ppm respectively, are found in both hybrids due to Q^2, Q^3, and Q^4 groups, which are assigned as Q^n in $(HO)_{4-n}$ Si(—OSi≡)n with n equal to 2, 3, and 4, respectively. For 3-aminopropyl triethoxysilane (APTES), mono-, di-, tri-, tetra-substituted siloxane

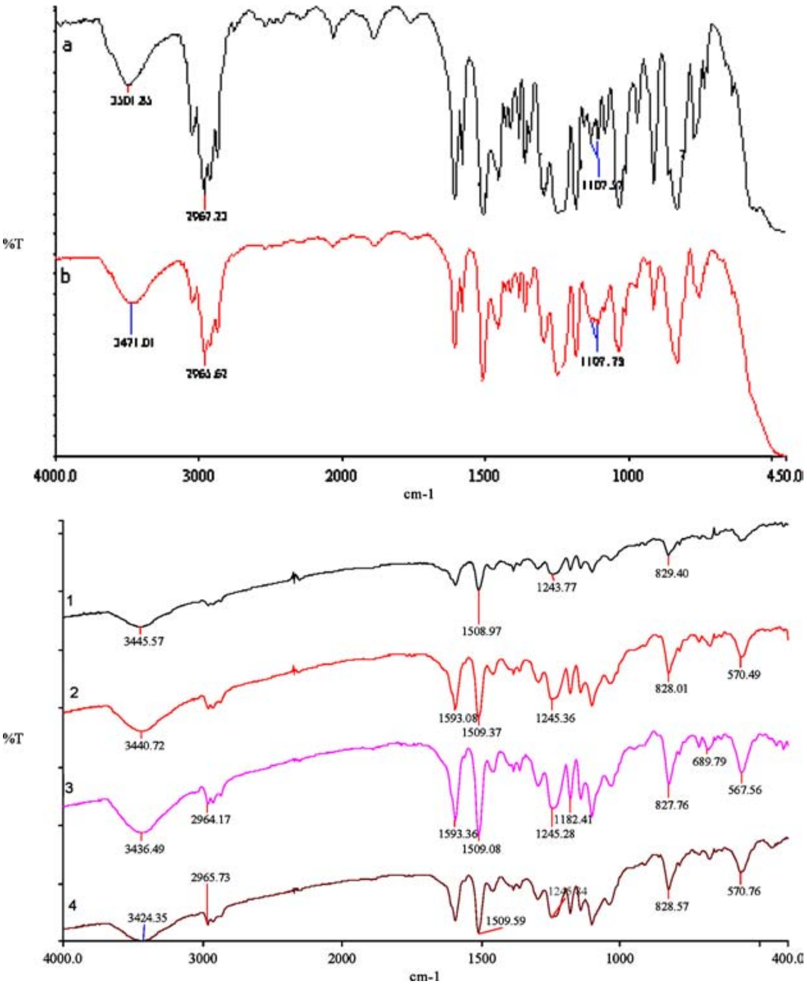


Figure 1 FTIR spectra of EP/SiO_2 hybrid material: (A) (a) FTIR spectra of pure EP and (b) FTIR spectrum of EP/SiO_2. (B) FTIR spectra of the different content of SiO_2: 1.1% SiO_2, 2.2%SiO_2, 3. 4% SiO_2 and 4. 5%SiO_2.

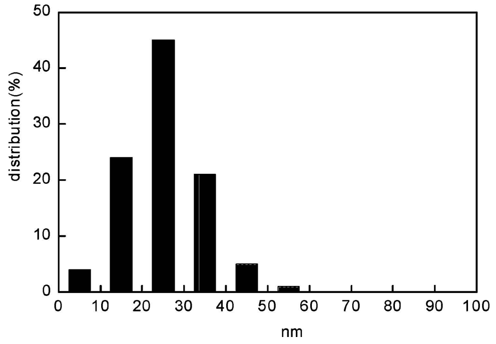


Figure 2 Distribution of PSA particle size in PSA-THF solution.

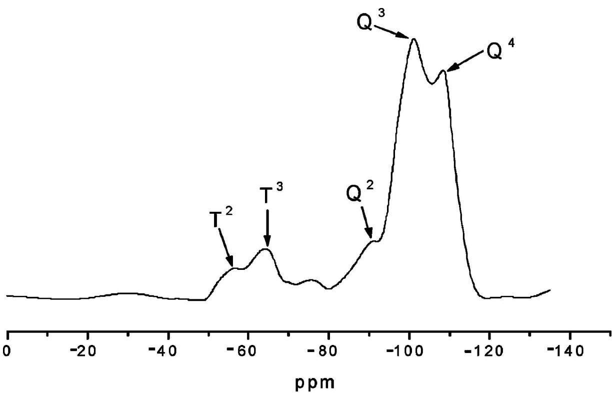


Figure 3 Solid-state ^{29}SiNMR spectrum of epoxy resin/silica.

bonds are designated as T^1, T^2, T^3, The chemical shifts of $T^2$and T^3 are −56.5 and −66 ppm respectively, and conformed to the literature [12]. Results reveal that Q^4, Q^3 and T^3 are the major microstructures forming the network structure.

3.5. XRD pattens

Fig. 4 shows the XRD pattens of reagent grade silica (a) and silica of PSA anhydration (b) and epoxy resin/silica hybrid material(c). Fig. 4a shows that the peaks are very sharp, which belongs to crystallite structure. Fig. 4b and c show a broad and low peak, respectively, which may be come from the amorphous silica phase. The contact angle of 4b and 4c were around 2θ ranging between 10° and 30°, which shows that silica networks and epoxy resins chain are incorporated through the covalent bond and hydrogen bond.

3.6. Mechanical properties of epoxy/silica hybrid materials

The most common approach used to enhance the toughness of epoxy resin is to add a softer second phase to epoxy resin [13]. The dispersed rubber phase plays an important role in the toughness improvement of the material. Rubber particles acting as stress concentrators,

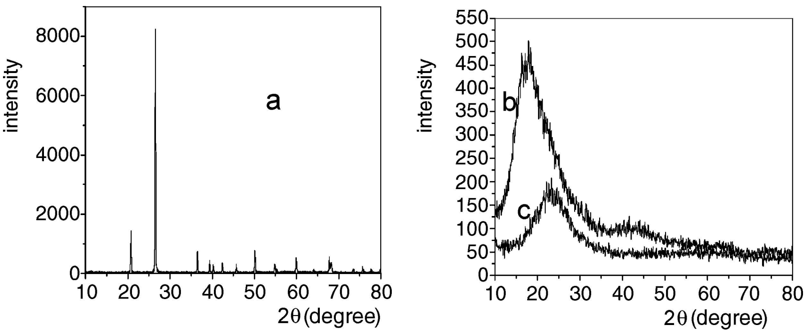


Figure 4 XRD patterns of EP/SiO$_2$ hybrid: (a) Reagent grade SiO$_2$, (b) polysilicic acid and (c) EP/SiO$_2$ hybrid material.

which allows the matrix between the particles to undergo both shear and craze deformation. In this article, the rigid silica acts as the dispersing phase, the impact and tensile properties of epoxy/silica hybrid materials are listed in Table II.

It is very clear that the addition of rigid silica particles can improve the toughness of the cured epoxy resin. When the silica content is up to 3 wt%, the impact strength and tensile strength are almost two times as much as that of the pure epoxy resin. This is because HO-terminated epoxy resin was successfully incorporated into the silica network by chemical bond. When the material is subjected to an impact test, the epoxy/silica hybrid materials have generated microphase separated for introducing of the silica particles [14], which may induce epoxy matrix yielding deformation and resistance to crack propagation [15]. For this reason, the impact energy of the epoxy matrix is expected to decrease significantly as silica particles are introduced, and resulted in toughening of the epoxy/silica hybrid materials enhancing.

3.7. DSC analysis of the 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 oxide network [16]. The DSC traces of the epoxy/silica hybrid materials are shown in Fig. 5, it can be observed that glass transition temperatures (T_g) progressively shifts to higher values and the breath of the transition and the decrease in ΔCp with silicon oxide content increasing [17]. The T_g of epoxy/silica samples is 21 and 31°C, which are higher than that of pure epoxy resin when silica content is 2 and 3%, respectively. The result indicates that T_g reflects an increasing interaction between the silicon oxide phase and the epoxy resin chain in terms of the formation of EP—Si—O—Si crosslinks.

TABLE II Mechanical properties of epoxy/silica hybrid materials

Silica content (wt%)	Impact strength (KJ/m^2)	Tensile strength (MPa)	Tensile modulus (GPa)	Bending strength (MPa)	Bending modulus (GPa)
0	11.58	34.7	0.96	85.28	1.36
1	15.72	50.1	1.4	89.30	1.87
2	18.29	59.62	1.56	98.24	2.14
3	21.48	67.59	1.68	105.42	2.18
4	19.81	62.24	1.62	102.37	2.24
5	17.35	52.0	1.08	94.65	2.17

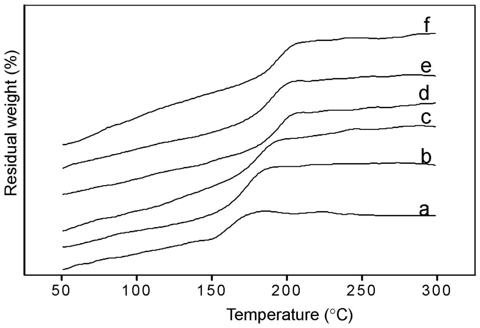


Figure 5 The curve DSC of EP/SiO$_2$ hybrid material. (a) 0%SiO$_2$, (b) 1%SiO$_2$, (c) 2%SiO$_2$, (d) 3%SiO$_2$, (e) 4%SiO$_2$, and (f) 5%SiO$_2$.

3.8. Thermogravimetric analysis

Thermogravimetric analysis (TGA) can be used not only to study the thermal decomposition and the stability of materials, but also to give important structural information. Fig. 6 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 epoxy resin/silica is higher than that of the pure epoxy resin,which is 351°C while the epoxy resin/silica is 361 and 372°C when silica content is 2 wt% and 5%, respectively. This is because the crosslinking density increased with the strongly hydrogen bonding between founctionalized-epoxy resin and PSA particle, reduced the chain mobility. Consequently, the thermal stability of epoxy/resin hybrid materials is enhanced.

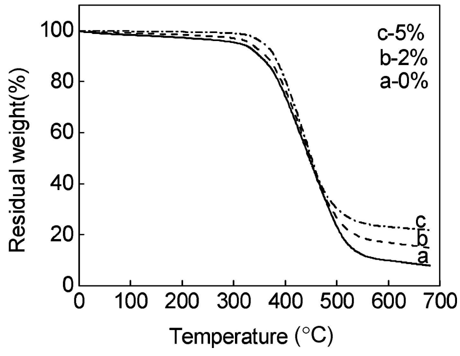


Figure 6 The curve TGA of EP/SiO$_2$ hybrid material. (a) 0%SiO$_2$, (b) 2%SiO$_2$, and (c) 5%SiO$_2$.

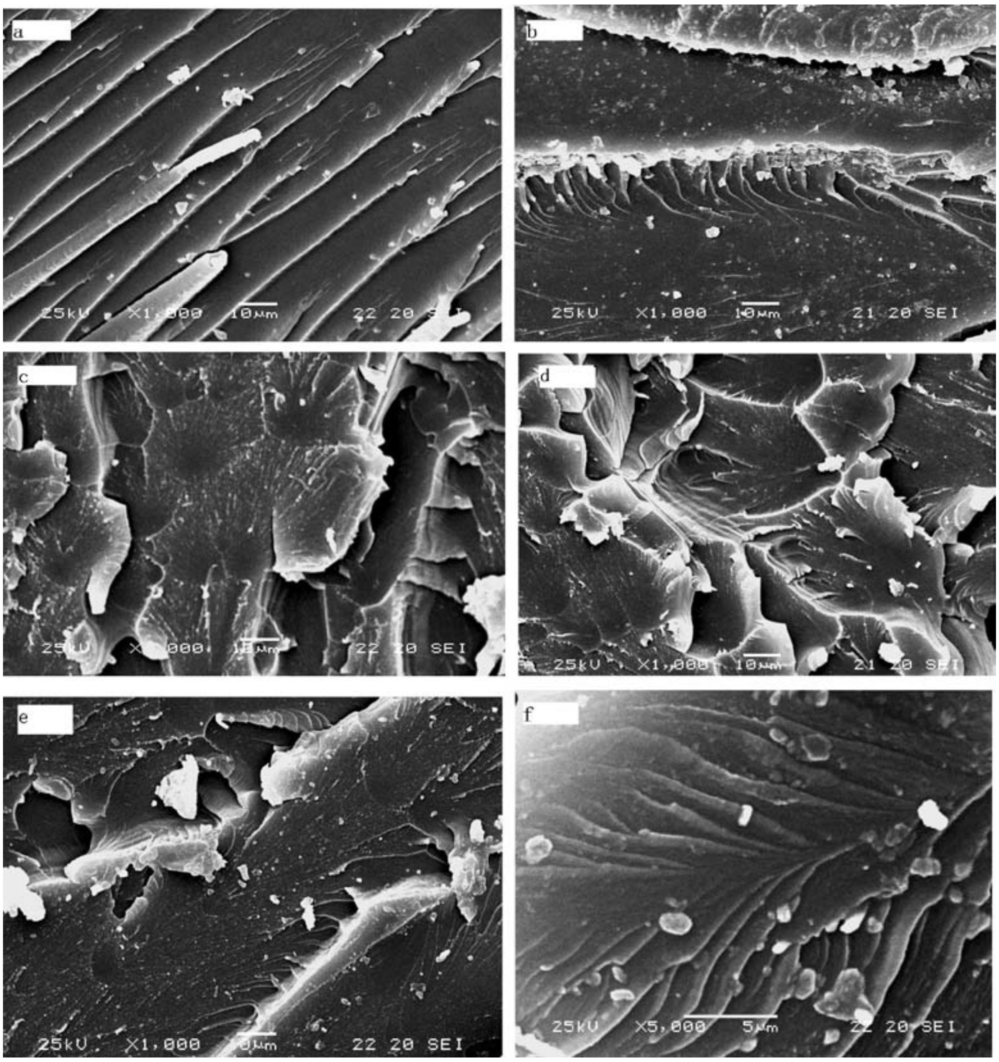


Figure 7 SEM graphs of materials with the different SiO_2 contents.

3.9. Morphology of the fracture surface

The impacting fracture surface of hybrid materials was observed by SEM, which can give important information about the morphology of the material samples. Fig. 7 is the SEM micrographs of the epoxy/silica hybrid materials. It can be seen clearly that the morphology of the epoxy resins modified with rigid silica particles (Fig. 7b–f) are quite different from that of the pure epoxy resin (Fig. 7a). The fracture surface of the pure epoxy resin is very smooth with uniform crack direction, which reveals the characteristic of brittle fracture. As for the epoxy/silica hybrid materials, the fracture surface appears rough and irregular appearance. And the fracture strips divert to different directions, which disperse stress and resistance to crack propagation because of the energy-absorbing mechanism introduced by the rigid silica particles, which indicates the characteristic of toughening fracture. This well agrees with the impact resistance property of the cured epoxy resins modified by the rigid silica particles.

4. Conclusions

A new hybrid material incorporating epoxy/silica has been successfully prepared via Sol-gel by mixing the nanoparticles with epoxy resin in the hybrid system. The $-Si(OEt)_3$ group has been introduced to the epoxy chain end by founctionalizing partially epoxy group with APTES. In the hybrid, covalent bond between the polymer chain and the inorganic network was formed. These hybrid materials are found to be of good optical transparency and improved properties over pure epoxy resin.

The increase of the total silica content results in hybrid materials properties such as impact strength, tensile strength, glass transition temperature (T_g) and thermogravimetric temperature enhanced. This indicates that epoxy/silica posses better roughness than that of the pure epoxy resin.

Acknowledgements

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References

1. D. MAXWELL, A. J. KINLOCK and R. J. YONG, *J. Mater Sci.* **3** (1984) 9.
2. A. F. YEE and R. A. PEARSON, *J. Mater Sci.* **21** (1986) 2462.

3. T. IIJIMA, TOCHIMOTO and M. TOMOI, *J. Appl. Polym. Sci.* **43** (1991)1685.
4. B. Z. JANG, J. Y. LIAN, L. R. HWANG and W. K. SHIH, *J. Reinf. Plast.* **8** (1989) 312.
5. C. CARFAGNA and L. NICOLAIS, *J. Appl. Polym. Sci.* **44** (1992) 1465.
6. C. SANCHEZ and B. LEBEAU, *MRS Bull.* **26** (2001) 377.
7. T. OGOSHI, H. ITOH, K. M. KIM and CHUJO Y, *Macromolecules*. **35** (2002) 334.
8. W. STOBER, A. FINK and BOHN E, *J. Colloid Interf. Sci.* **26** (1968) 62.
9. C. J. BRINKER and G. W. SCHERER, "*Sol-Gel Science:* the Physics and Chemistry of Sol-Gel Processing" (A Cademic Press London, 1990).
10. E. F. VANSANT, P. VAN DER VOORT and K. C. VRANCHEN, "Characterization and Chemical Modification of Silica Surface" Elsevier Amsterdam, (1995).
11. J. C. RO and I. J. CHUNG, *J. Non-Cryst. Solids*. **18** (1991) 130.
12. R. JOSEPH, S ZHANG and W. FORD *Macromolecules*. **29** (1996) 103.
13. A. R. SIEBERT, *Acs. Adv. Chem. Ser.* **208** (1984) 179.
14. MAĚJKA LIBOR, DUŠEK KAREL, PLEŠTIL JOSEF and LEDNICKÝ FRANTIŠEK, *Polymer.* **40** (1998) 171.
15. WETZEL BERND, HAUPERT FRANK and ZHANG MING QIU, *Comp. Sci. Techn.* **63** (2003) 2055.
16. Z. H. HJUANG, K. Y. QIU, Y. WEI and J. POLYM, *Sci. A Polym. Chem.* **35** (1995) 2403 .
17. Z. AHMAD, M. I. SARWAR and J. E. MARK, *J. Appl. Polym. Sci.* **63** (1997) 1345.

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