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Preparation and characterization of epoxy nanocomposites by using PEO-grafted silica particles as modifier

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Abstract EP/SiO_2 nanocomposites, which contained PEO flexible chain, have been prepared via epoxy resin and PEO-grafted silica particles. The PEO-silica particles were obtained by endcapping PEO-1000 with toluene 2,4-diisocyanate (TDI), followed by a reaction with silica sols. The chemical structure of the products was confirmed by IR measurements, and the mechanical properties of composites such as impact strength, flexural strength, dynamic mechanical thermal properties were investigated. The results showed that the addition of the PEO-grafted silica particles to the epoxy/DDS curing system, the impact strength is 2 times higher than that of the neat epoxy. While the storage modulus and the glass transition temperature are a little changed. The morphological structure of impact fracture surface and the surface of the hybrid materials were observed by scanning electron microscope (SEM) and atomic force microscopy (AFM), respectively.

Introduction

Organic–inorganic nanocomposite materials have been regarded as new generation of high performance materials since they combine the advantages of the inorganic materials (rigidity, high stability) and the organic polymers (flexibility, ductility and processibility). Moreover, in comparison with macroscopic composites made of the same component phases they usually exhibit non-linear changes in optical, electrical, and thermal mechanical properties [1–4]. These hybrid materials are usually produced by sol–gel reaction, which consists of two steps: the first step is the hydrolysis of metal alkoxides, and the second step is the polycondensation of the resulting hydrolylsis product. There are many nanocomposite polymers, especially containing nano SiO_2 or nano TiO_2, which were prepared by the sol–gel approach and investigated with a focus on how the nanoparticles influence the mechanical, thermal, and optical properties and so on of the nanocomposite polymers and the relationship between structure and properties [5–8]. In these hybrid composites, epoxy resin (EP) has been widely applied as matrix polymers for the industrial and structural applications, including surface coatings, adhesives, painting materials, etc. However, the use of thermosetting materials is often limited by their toughness properties, which affect the durability of components and place strong constraints on design parameters. Impact resistance, fatigue behavior and damage tolerance are some of the properties influenced. For practical application, high strength and toughess are required. One approach is modification with soft particles such as rubber and thermoplastics, carboxyl-terminated acrilonitrile liquid butadiene-acrilonitrile liquid (CTBN) or amine-terminated butadiene-acrylonitrile rubber (ATBN) [9, 10]. However, these show the lower flexural strength and Young's modulus.

Recently, there has been a number of investigating mechanical properties of particulate reinforced epoxy composites. Incorporation of the rigid inorganic filler into various polymers or epoxy systems is a well-known technique to improve the physical, mechanical and thermal properties. Many researchers [11–15] have improved the

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toughness of epoxy resins by incorporating nano-particles, such as SiO_2, TiO_2, and Al_2O_3 particles etc. Kang et al. [16] studied the nano-SiO_2 particles prepared via sol–gel process. Then, the surfaces of the nano-SiO_2 particles were modified by substituting silanol groups into other functional groups through changing the degree of substitution. These surface-tailored nano-SiO_2 particles were filled into epoxy resin and the obtained EP/SiO_2 hybrid materials showed superior thermal property and a decrease in damping and high glass-transition temperature (*Tg*) with the filler contents.

In our previously work, we have described the preparation of EP/SiO_2–TiO_2 hybrid materials, which contained chain-extended urea—PEO and found that nano-particles could enhance tensile strength and impact strength of epoxy matrix [17]. In this project, the epoxy-based organic/inorganic hybrid materials were prepared using the bisphenol-A type epoxy resin and PEO-grafted silica particles as the organic and inorganic sources, respectively. The thermal, dynamic mechanical, and morphological properties of the epoxy/silica hybrids were examined and discussed in detail.

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% according to the supplier. PEO-1000 was of analytical grade and carefully got rid of water before use. Other reagents were purified by conventional methods. Tetraethoxysilane (TEOS)(chemical reagent grade) was ordered from XilongChemical Fractory, Guangdong, China. Toluene 2,4-diisocyanate (TDI)(80/20) was purified by distillation under vacuum.

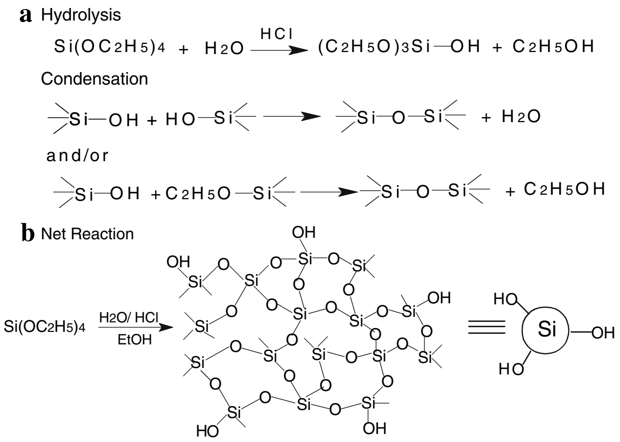
Fourier transformed infrared spectroscopy (FTIR) was recorded between 4000 and 400 cm^{-1} on a Perkin-Elmer 1710 spectrophotometer using KBr pellets at room temperature. The crystal behavior of the EP and EP/SiO_2 materials was analyzed by X-ray diffractometry (XRD: D/max-RB, Japan). The impact strength of the cured resins was determined by a charpy impact- testing machine (XJJ-50, Chende, PRC) according to China National Standard GB1043-79. The flexural strength and tensile strength were examined with a Shengzhen Reger RGT-5 universal testing system, at the flexural rate 2 mm/min. All the presented results are average of five specimens. Thermogravimetic analyses (TGA) was carried out using NETZSCH STA449 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 frequency of 1 Hz from –100 °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 $48 \times 5 \times 2.5$ mm^3. Atomic force microscopy (AFM) was carried out using AJ-IIIa analyzer (Shanghai AJ Nano-Science Development Co. Ltd) and the tapping mode was utilized. The scan size was about10 μm × 10 μm.

Preparation of silica sols

Tetraethoxysilane (TEOS) was hydrolyzed by mixing TEOS with ethanol and acidic water (PH = 5 with 1 M HCl) at molar ratio 1:8:4. The mixture was charged into a 250-ml round-bottom flask equipped with a reflux condenser, mechanical stirrer, and thermometer with a temperature controller, heated to (50 ± 1) °C for 3 h. Then the solution was condensed in vacuum at 60 °C for 2 h to obtain a sticky silica sols. The hydrolysis and condensation reactions involved in the process may be depicted in Scheme 1 [18].

Preparation of PEO-grafted silica particles

Into a three-necked round-bottomed flask, which was equipped with a stirrer, an N_2 inlet and a cooler. TDI (7.0 ml) dissolved in proper amount of acetone was added. Then an excessive amount of PEO-1000 (PEO-1000: TDI = 2:1) was dropped into the flask with 1 h. The solution was stirred for additional 17 h at 30 °C, and the yellow solution was obtained. Terminal of reaction was



Scheme 1

confirmed by determination of the isocyanate group content by means of titration. Then amount of silica sols and acetone mixture were dropped into above solution within 2 h, stirred at 30 °C for additional 2 day. The final precursor was obtained by getting rid of acetone under vacuum at 50 °C. The reaction should be depicted in Scheme 2.

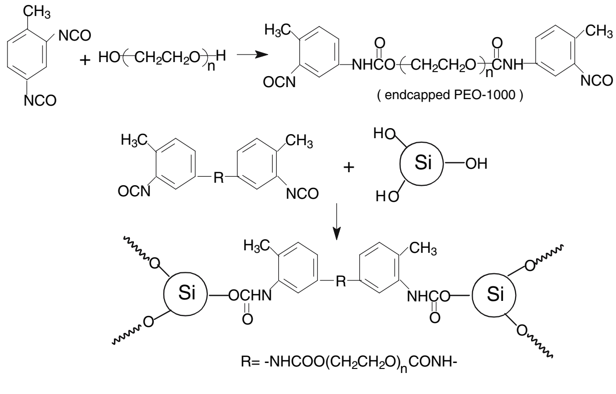
Curing procedure

A mixture of epoxy/silica-titatia hybrid precursor and a stoichiometric amount of DDS (30 g/100 g of epoxy resin) were degassed in vacuum at 130 °C for about 30 min. The resulting mixture was then cast into a preheat mold coated with silicone resin. All samples were cured at 130 °C for 2 h, 170 °for 2 h and 190 °C for 2 h. In the curing systems, some of the interfacial force between the PEO-grafted silica particles and epoxy resin had changed from the hydrogen bonding to Si–O–C covalent bond through the dehydration of the hydroxyl group in epoxy resin with the residual silanol group in the PEO-grafted silica particles at high temperature [19], interpenetrating epoxy/silica network was formed as the following scheme: silica network-epoxy-silica network.

Results and discussion

FT-IR spectra

Figure 1 illustrates the FT-IR spectra of (a) PEO-1000; (b) endcapped PEO-1000 with TDI; (c) PEO-grafted silica;(d) EP/SiO_2 nanocomposite. In (a), a distinct absorption peak at ~1100 cm^{-1} is in the region of C–O–C stretching for ether groups and the peak at 3507 cm^{-1} belongs to –OH group. In (b) the peak at~2275 cm^{-1} confirms the existence of –NCO groups. In (c) the peak at~2275 cm^{-1} disappeared and indicated that the –OH groups of silica sols reacted with the remaining –NCO groups of endcapped PEO-1000.The broad bands at the range of 1273–1037 cm^{-1} and 815–463 cm^{-1} caused by the presence of the Si–O–Si backbones bond [20]. Absorption bands at~1725 cm^{-1} in both (b) and (c) were mainly due to –C=O asymmetric stretching from urethane groups. In (d) the peak at 3442 cm^{-1} is characteristic of–OH stretching in a result of the Si–OH, which is an unreactive groups in inorganic networks, the peak at~1093, 815 cm^{-1} are the main absorption bands of Si–O–Si bond, is indicative of the network formation in the epoxy/silica hybrid materials [21].



Scheme 2

Size of PEO-grafted silica particles

PEO-grafted silica particles were obtained by a grafting process of PEO-1000 endcapped with TDI and silica sol, and the particles size were measured by a laser diffraction type particle size analyzer (NOVA 1200e, Quantachrome, USA). A particles size distribution is shown in Fig. 2. From this figure, the size of the majority of particles is about 5–40 nm. Consequently, the PEO-grafted silica particles are restrained at the molecular level, when it mixed with epoxy resin matrix, the mixing system was cured by molecular level in modified epoxy nanocomposites. The nanocomposites were transparent.

X-ray diffraction (XRD)

Figure 3 shows the XRD patterns of reagent grade silica (a) and pure epoxy resin (b) and epoxy resin/SiO_2 nanocomposite (c). Figure 3a shows that the peaks are very sharp, which belongs to crystallite structure. Figure 3b and c show a broaden peak, the contact angle (2θ) is ranging between 10°and 30°, and reveals the characteristic of amorphous peaks. But the nanocomposite exhibits a significant increase in intensity when silica nano-particles added to pure epoxy resin. This is attribute to the polymer chains in the nanocomposite are covalently bond (or crosslinked to) the inorganic networks.

Mechanical properties of epoxy/silica hybrid materials

Incorporation of micrometer inorganic particles into polymers often reduces strength properties of the composites except the stiffening effect. When the bonding between the filler particles and the matrix is poor, the flexural strength and tensile strength of micrometer particles filled composites is known to be reduced with rising filler content [22]. From Table 1, it may be seen that the above statements are inapplicable to the current epoxy/silica composites. Both tensile strength and bending strength increase with a rise in the silica concentration. That means the

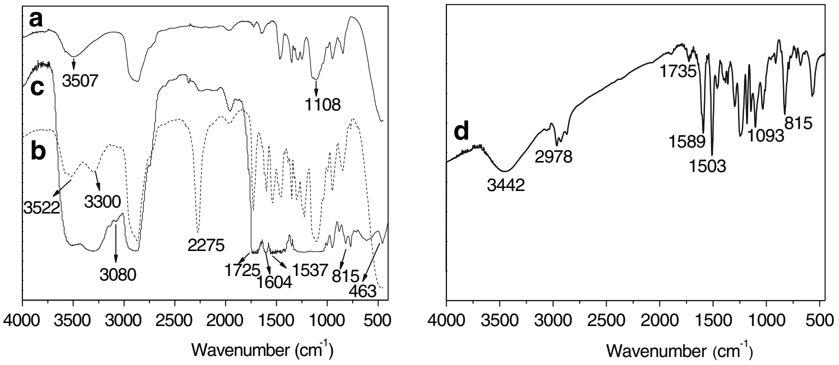


Fig. 1 FTIR spectra of EP/SiO$_2$ nanocomposite (**a**) PEO-1000; (**b**) endcapped PEO-1000 with TDI; (**c**) PEO-grafted silica; (**d**) EP/SiO$_2$

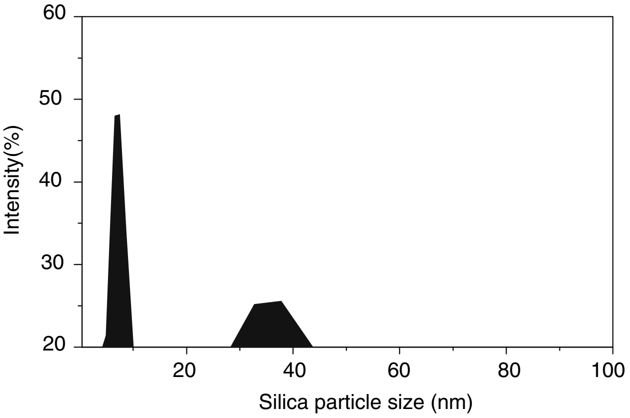


Fig. 2 Distribution of PEO-grafted silica particles

interfacial adhesion is so strong that the nano-particles are able to carry the applied load. As shown in Table 1, the impact toughness of the composites increases with silica content increasing. Since unnotched Charpy impact strength reflects the energy consumed before fracture, the results demonstrated that the nano-particles in the composites are able to induce plastic deformation of the surrounding matrix polymer to a certain extent under the conditions of high strain rate. The results of the Table 1 show the impact strength reaches the highest level when SiO$_2$ content is about 1.5 wt.%, the impact strength is almost two times as much as that of the pure epoxy resin. However, the declining trend of the mechanical properties of composites with increasing silica content, it probably due to the worse distribution of the nano-particles in the composites. This is understandable as the more nano-particles are added into epoxy resin, the more viscous the mixture and the more difficult the breaking-down of the agglomerated particles.

Thermal properties of epoxy/silica composites

The cured epoxy/silica composites samples were characterized with DSC and TGA to evaluate their thermal

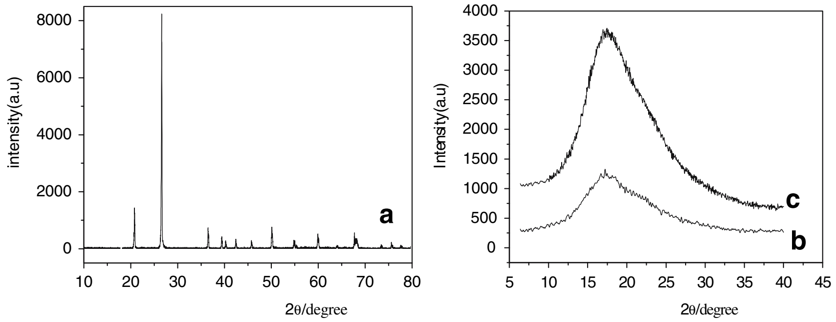


Fig. 3 X-ray spectra of (**a**) Reagent grade SiO$_2$; (**b**) pure EP; (**c**) EP/SiO$_2$ nanocomposite

Table 1 Mechanical properties of epoxy/silica composites

Silica content Wt.%)	Impact strength (kJ/m^2)	Tensile strength (MPa)	Tensile modulus (MPa)	Bending strength (MPa)
0	10.02	51.40	515.4	83.46
1.0	13.53	56.71	541.4	92.97
1.5	19.16	70.75	616.3	102.65
2.0	18.53	63.14	623.7	104.38
2.5	17.59	52.13	598.4	101.43

properties. The effect of silica nano-particles content on the glass transition temperature (*Tg*) was exhibited in Fig. 4. It can be seen that the addition of silica nano-particles by the PEO-grafted method has slightly enhanced the glass transition temperature (*Tg*). The increase in *Tg* is likely attributed to a loss in the mobility of chain segments of epoxy resin resulting from the silica nano-particles/matrix interactions. This observation is the same as for PA6/silica nanocomposites [23]. Some supporting data for this explanation are given in DMA.

Figure 5 shows the results of the thermal decomposition of the pure epoxy resin and the epoxy/silica composites. 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 334 °C while the epoxy resin/silica is 372 °C and 381 °C when silica content is 1.0 wt.% and 2.0 wt% at 10% weight loss, respectively. This is because the polymer chains in the composites are crosslinked to inorganic networks, a highly crosslinked density was obtained, and the thermal stability of the polymer components should be improved.

Dynamic mechanical thermal analysis

Typical dynamic mechanical spectra in the form of plots of storage dynamic modulus (E') and loss tangent($tan\delta$) as function of temperature are shown in Fig. 6. Figure 6a shows the storage modulus of the curing system modified by PEO-grafted silica particles, which containing PEO flexible chain. It may be seen that below 110 °C, the storage modulus of the modified curing system is approximate to that of the pure epoxy system. Generally, dynamic modulus would be decreased with the addition of the flexible chain spacer. However, PEO-grafted silica particles synthesized in this work consisted of flexible chain and silica rigid particles. The flexible chain is aimed to improve impact strength, and the rigid silica particles is intended to retain high dynamic modulus and thermal properties of the EP/SiO_2 hybrid materials. The rigid silica particles played a great role in enhancing the high dynamic modulus of epoxy resin modified by PEO-grafted silica particles.

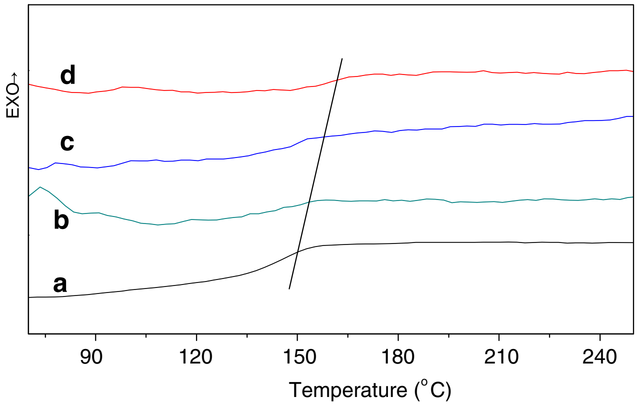


Fig. 4 Glass transition temperature of epoxy resin at different nano-SiO_2 contents (**a**) pure EP; (**b**) 1.0 wt.%EP/SiO2; (**c**) 1.5 wt.% EP/SiO2; (**d**) 2.0 wt.% EP/SiO2

Figure 6b shows the dynamic mechanical spectra for *tan* δ of the EP and EP/SiO_2 nanocomposites. Compared to the pure epoxy system, the peak glass transition temperature (*Tg*) of EP/SiO_2 nanocomposites slightly increased with rising silca contents. The increasing in *Tg* may be attributed to a loss in the mobility of chain segments of epoxy resin resulting from the silica particles/matrix interaction and impeded chain mobility. However, in the transiting region, on the other hand, the damping is high because of the initiation of the molecular chain segments and their stress relaxation.

Morphological structure of hybrids

The impact behavior of the modified system can be explained in term of morphology observed by SEM. Images shown in Fig. 7 are the microphotographs of the pure epoxy matrix and the composites. From the photograph (Fig. 7a), a smooth glassy fractured surface occurs, with cracks in different planes can be seen. This indicates brittle fracture of the pure epoxy resin, which accounts for its poor impact strength. As for the composites (Fig. 7b–d), the fracture surfaces show massive shear deformation, there are many indentations, deep cracks or pores on the fracture surfaces. This indicates that upon exposure of mechanical stress, the concentrating nano-particles appear to encourage shear yielding of the epoxy interlayers at the tip of the propagating crack, which continues throughout the entire volume. Energy is absorbed for such shear yielding leading to the increase in impact strength [24]. In addition to the above statement, the other possible reason for the rough fracture surface is attributed to the smaller phase separation and the special interaction between the nano-particles and

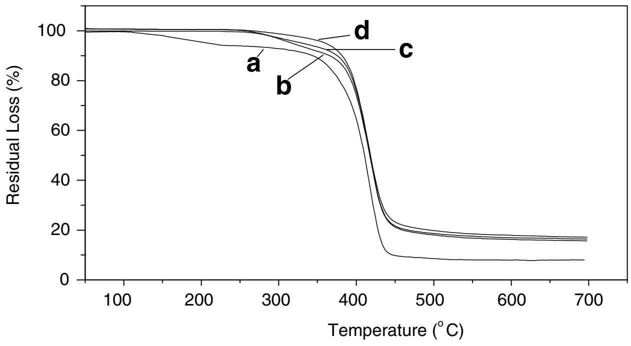


Fig. 5 TGA thermograms of (**a**) pure EP; (**b**) 0.5 wt.%EP/SiO_2; (**c**) 1.0 wt.% EP/SiO_2; (**d**) 2.0 wt.% EP/SiO_2

Fig. 6 DMTA curves of the neat epoxy and the EP/SiO$_2$ nanocomposites

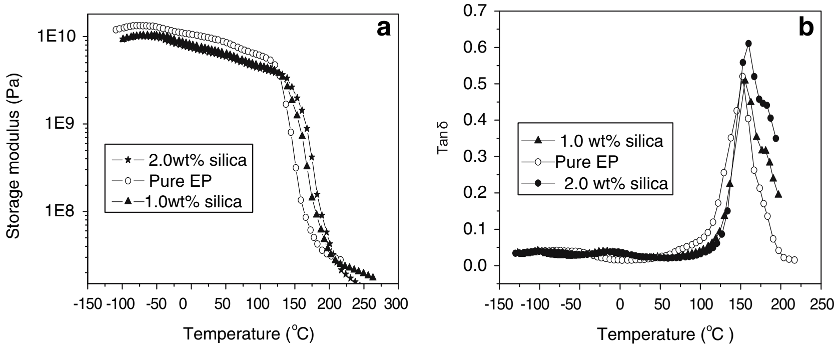
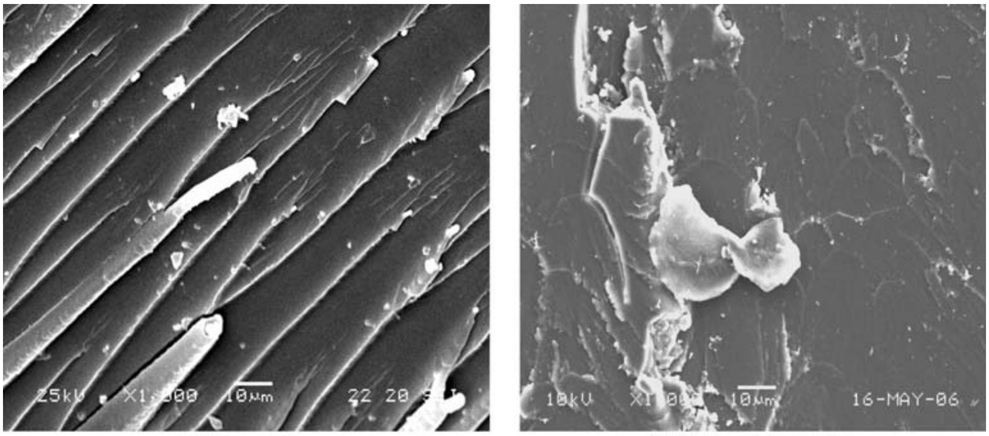
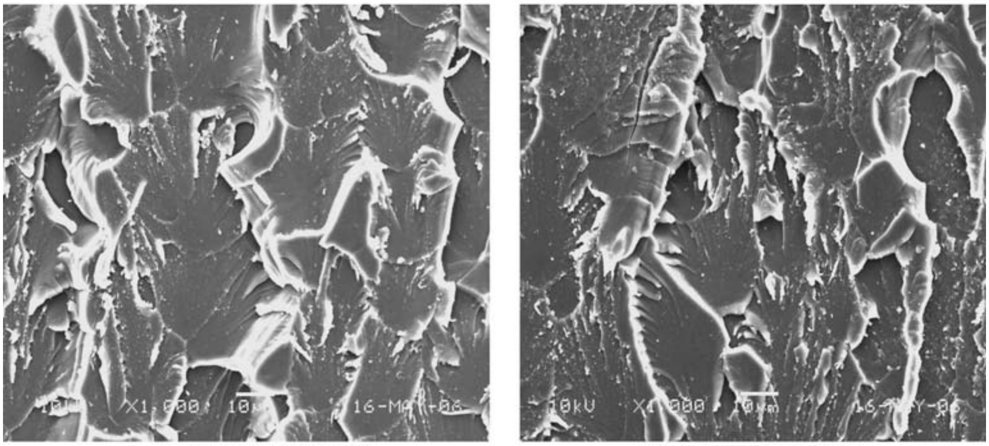


Fig. 7 SEM micrographs of the fracture surfaces for the pure epoxy resin and modified systems



(1) Pure EP (2) 0.5 wt % EP/SiO$_2$



(3) 1.0 wt % EP/SiO$_2$ (4) 2.0 wt % EP/SiO$_2$

the polymer that constrains the polymer chains' mobility and efficiency of the rearrangement.

Atomic force microscopy

The topographic morphology of epoxy/silica nanocomposites surfaces was scanned by AFM. Figure 8 reveals the representative pictures. The bright domains are attributed to the silica phase, while the dark domains are assigned to the epoxy network. These images show that the organic and inorganic phase are strictly interconnected with no major macroscopic phase separation that might have occurred during the curing process, the silica domains are embedded in the polymeric matrix with an average size around 10–20 nm. Compared with picture (**1**) and (**2**), there are a number of small bulges are observed on the interfaces, and

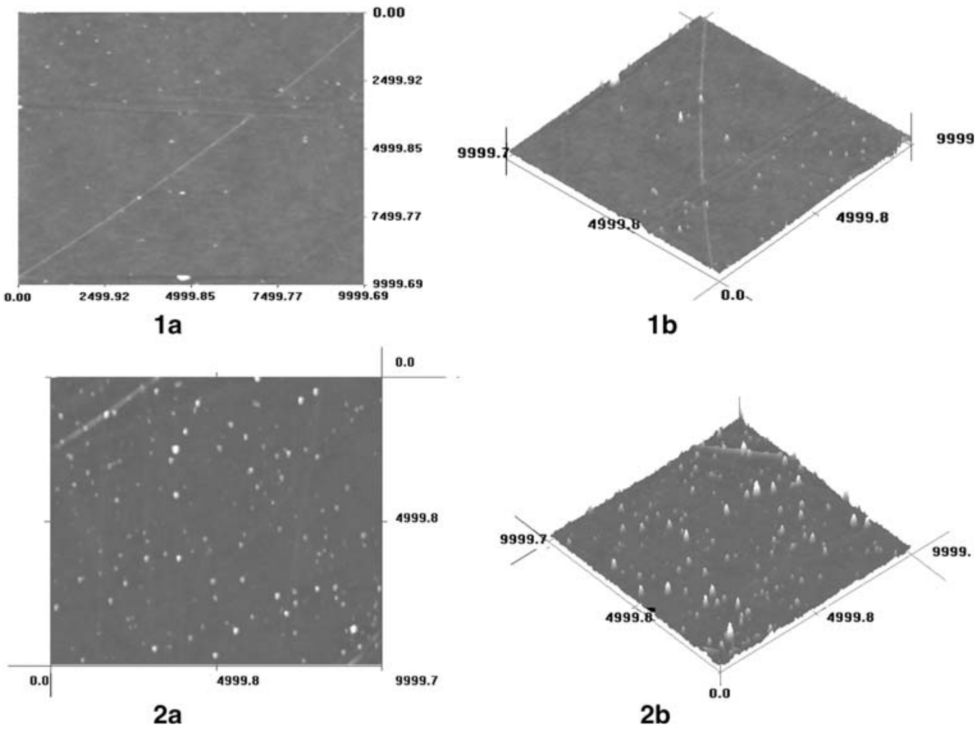


Fig. 8 AFM of (1**a**, 1**b**) 1.0 wt.% SiO_2; (2**a**, 2**b**) 2.5 wt.%SiO_2, where **a** and **b** indicate the two-and three-dimensional images, respectively

with increasing of the silica contents, the size of the bulges is also enhancing, indicating that some silica nano-particles exist at the interfaces. The 3D images show that the surface roughness (Rms) of the Fig. 8 (2b) is 0.696 nm, while Fig. 8 (1b) is 0.612 nm, then the Rms values of the composites have found to be increased with increasing contents of silica. These images may demonstrate that a strong bond has been formed between the PEO-grafted silica sols and the epoxy matrix in the composites.

Conclusion

EP/SiO_2 nanocomposites have been prepared successfully by epoxy resin and PEO-grafted silica particles using DDS as curing agent. The nanometer-scaled inorganic domains disperse homogeneously in epoxy matrix without macro-phase separation because there are interactions between the two phases and the aggregation behavior of SiO_2 was restricted by the introduction of endcapped PEO-1000 with TDI. It was found that the PEO-grafted silica particles containing PEO flexible chain could effective toughening modifier for the epoxy resin. The impact strength of the cured systems modified with PEO-grafted silica particles was two times higher than that of the pure epoxy. While the storage modulus and the glass transition temperature are a little changed, and the fracture surfaces of all modified systems display tough fracture feature.

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