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Effect of Surface Functional Modification of Nano-Alumina Particles on Thermal and Mechanical Properties of Epoxy Nanocomposites

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Abstract

Surface organic molecule modification of nanosized alumina particles is an effective way to improve its dispersion in polymer and to enhance the properties of polymer nanocomposites. In the present study, γ-aminopropyl triethoxysilane was used as a surface modification agent to react with the hydroxyl group on the surface of nanosized alumina. The properties of the modified alumina particles were characterized by FT-IR spectra, particle-size analyzer and transmission electron microscope (TEM). The nanocomposites of the epoxy resin filled with nano-sized alumina before and after surface modification were fabricated by physical blending. The mechanical behaviour and heat resistant properties of the composites were investigated. The results showed that the effective chemical bonds were formed between nano-alumina particles and γ-aminopropyl triethoxysilane after modification. Compared to the non-modified particles, the modified alumina nanoparticles exhibited a good dispersibility, and distributed uniformly in the epoxy matrix. The epoxy matrix filled with the modified nanoparticles showed a shorter gel time and a higher curing degree. The composites filled with modified nano-alumina revealed the optimum improvement of heat resistance. The composites with 3 wt% weight fraction modified particles had higher thermal decomposing temperature and glass transition temperature, and they were raised by 11 and 10°C relative to that of the neat resin, respectively. The modified alumina nanoparticles had better enhancement effect on epoxy matrix. The ultimate flexural strength and flexural modulus of the composites with 3 wt% modified particles increased by 55 and 77.1%, respectively; the impact strength of the composites containing 5 wt% modified particles increased by 24.7% relative to the neat resin, and the impact fracture surface presented ductile fracture features.

Keywords

Nanocomposites, surface modification, mechanical properties, heat resistance

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1. Introduction

The inclusion of inorganic fillers into polymers for engineering applications is primarily aimed at improvement in the mechanical properties. These fillers can be chosen as fibers (carbon, glass) or particles, such as ceramic powders. The inclusion of micrometer sized particulates into polymers can favourably stiffen the material and may also increase the strength under certain load conditions. But it has to be considered that they yield a detrimental effect on some important properties of the matrix polymers, such as processability and the material's resistance against impact [1, 2]. A large amount of research work has been done to overcome this basic problem. Among them, the introduction of nanoparticles instead of microparticles into the polymers is a very effective approach. It was verified experimentally by some researchers that nanoparticles of metallic or inorganic type effectively reinforce polymer matrices [3, 4].

Nanosized alumina, as particulate filler, has been widely used in the field of insulation materials as it can improve dielectric performance and thermal conduction of the organic polymers [5, 6]. But the nanoparticles are prone to cluster in the polymer matrix and cannot form stable nanocomposites due to high specific surface area and energy, and so the properties of the composites are far below the theoretical values. The stability of the hybrid nanocomposites requires that nano-sized filler can be easily dispersed in the polymer and form strong chemical bonds with the organic moieties. Thus, to yield a better compatibility between the filler and the host polymeric materials and even dispersion of the filler in polymer, the use of coupling agents is recommended [4, 7]. Siloxane of various kinds has been widely used as coupling agents between nanoparticles (e.g., nano-alumina) and polymeric resins [8]. The coupling process can be accomplished *via* the chemical reaction between the triethoxy groups of silane molecules and the hydroxyl groups on the surface of nanoparticles, whereas other functional groups of silane molecules, which are generally amine, epoxy, etc., can be retained. Dharmendra *et al.* [9] have reported the formation of Si–O–Al bonds between nano-thick alumina platelets and 3-glycidoxypropyl trimethoxysilane (GPS). The nano-thick alumina platelets functionalized with GPS distributed uniformly in the epoxy matrix, and the composites demonstrated higher tensile strength. You *et al.* [10] investigated the surface organic modification of nano-SiO_2 and its effect on the properties of epoxy nanocomposites. They have shown that Si–O–Si bonds were formed between nano-SiO_2 particles and GPS. The surface functional modification of nano-SiO_2 improved the dispersion of nano-SiO_2 particles in the epoxy matrix, and the nanocomposite filled with the silica treated by GPS showed better heat-resistance behaviour. John *et al.* [7] modified the surface of multi-walled carbon nanotubes with γ-aminopropyl triethoxysilane in order to improve their dispersion in epoxy and thus improve the mechanical properties of nanocomposites. Additionally the research that the silane coating improved the electrical and flexural properties of the nanocomposites of silver nanoparticles/epoxy has also been reported [4].

In the present study, γ-aminopropyl triethoxysilane was used as a surface modification agent to control the surface properties of nano-alumina particles. The surface properties of modified particles were analyzed. The microstructure, the mechanical properties and thermal properties of the modified nano-alumina/epoxy composite were also investigated.

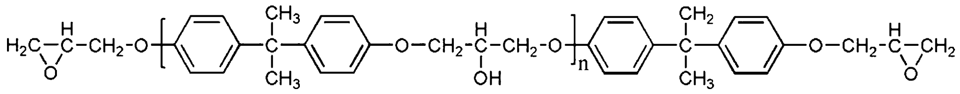
2. Experimental

2.1. Materials

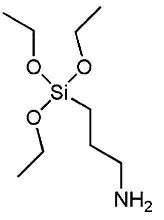
Nano-alumina, with an average diameter of 40 nm, was provided by the Jiangsu Hehai nanometer materials Co. Ltd., China; γ-aminopropyl triethoxysilane with purity of 99% supplied by Dow Corning Chemicals was used for silane functionalization of nanoparticles. The matrix was an epoxy polymer-based bisphenol A resin, diglycidyl ether of bisphenol A, with 178 g/epoxy equivalent, manufactured by Shanghai Organic-Resin Co. Ltd., China. An amine hardener, polyamidoamine (PAA), served as curing agent (Shanghai Organic-Resin Co. Ltd., China). Chemical structures of epoxy and silane coupling agent are shown in Fig. 1.

2.2. Surface Modification of Nano-Alumina Particles

The γ-aminopropyl triethoxysilane (5 g) was added in an aqueous ethanol solution prepared by the volume ratio of ethanol:water = 1:9 (250 ml). The solution was stirred for 5 min. Then the nano-alumina particles dried at 120°C for 6 h (50 g) were dispersed in the above solution with a mechanical stirrer in an atmosphere of nitrogen for 1–2 h, and ultrasonic action for 10 min. The temperature of nanoparticle modification was controlled at 40–50°C. After the reaction, the powders were separated by centrifuging and washed by acetone for some time and then dried in a vacuum oven at 80°C for 12 h.



Diglycidyl ether of bisphenol A



3-aminopropyltriethoxysilane

Figure 1. Chemical structures of diglycidyl ether of bisphenol A and 3-aminopropyl triethoxysilane.

2.3. Nanocomposite Processing

Epoxy matrix nanocomposites reinforced by the nano-alumina particles before and after the modification were fabricated by physical blending using a 'high shear' laboratory-mixing device. Prior to the blending, the nanoparticles were dried at 80°C for 4 h. The epoxy resin was preheated in the same way for a better wetting of the particles. After incorporating the particles into the resin, the mixture was stirred at 80°C. Then, it was subjected to high shear mixing at 140 rpm for 20 min at 80°C. Next, it was sonicated in a ultrasonic bath for 40 min at 80°C. After the ultrasonication, the nano-alumina/resin mixture was degassed at room temperature until most of entrapped bubbles were removed completely. Then, 2 phr (parts per hundred resins) of curing agent (PAA) were slowly mixed into the mixture. After stirring for 10 min at 130°C, the mixture was poured into a rubber mould with an aluminium film, and then the mixture was cured for 3–4 h at 150°C. The nano-alumina particles were added in different percentages of 1, 2, 3, 5 and 7 wt% with regard to epoxy monomer mass.

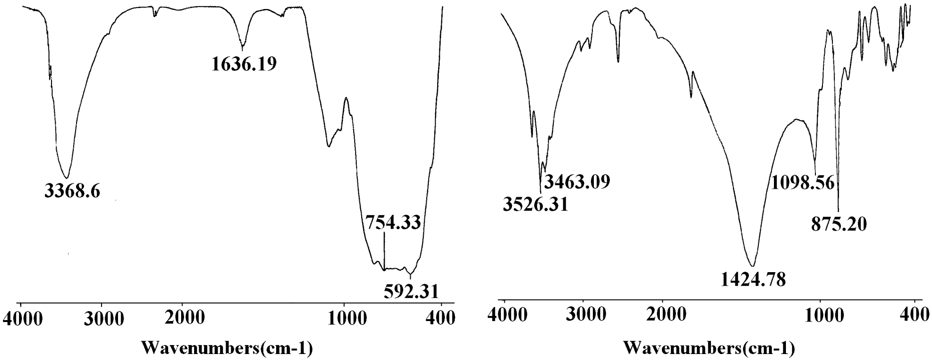
2.4. Characterization

Fourier transform infrared (FT-IR) measurements were performed on a Perkin Elmer FT-IR spectrometer (model: Paragon 1000) to identify surface functional groups of modified nano-alumina. The size distribution of the particles of nano-alumina was tested on N4Plus particle size analyzer, and the samples were dispersed in ethanol by ultrasound to get better dispersion. Transmission electron microscopy (TEM, Hitachi H-660) was used to examine the microstructure of composites. Flexural properties were determined by conducting a three-point bending test. The tests were performed on a CMT6104 electronic universal testing machine with a 1000 N load cell at a cross-head rate of 1.0 mm/min using $60 \times 25 \times 2.4$ mm^3 specimens, according to the ASTMD-790 standard test. Five specimens were tested for each composite. Thermo-gravimetric analyses (TGA) were carried out on a DTG-60H thermal analyzer made by Japan Shimadzu Corporation with a heating rate of 20°C/min from 0 to 600°C under nitrogen air. Differential scanning calorimetry (DSC) measurements were performed between 30 and 150°C at 10°C/min heating rate with TA Q100. Scanning electron microscopy (SEM) examinations on a Philips-XL30 were used to study the morphology of fracture surfaces from flexural testing. The fracture surfaces of the specimens were sputter-coated with gold prior to their observation.

3. Results and Discussion

3.1. Characterization of Surface-Modified Nano-Alumina

Figure 2 shows the FT-IR spectrum of non-modified and γ-aminopropyl triethoxysilane modified nano-alumina. From the spectra analysis, it is clear that there are significant differences between two patterns. As shown in Fig. 2(a), a broad peak



(a) (b)

Figure 2. FT-IR spectrum of nano-alumina, (a) non-modified nano-alumina, (b) γ-aminopropyl triethoxysilane modified nano-alumina.

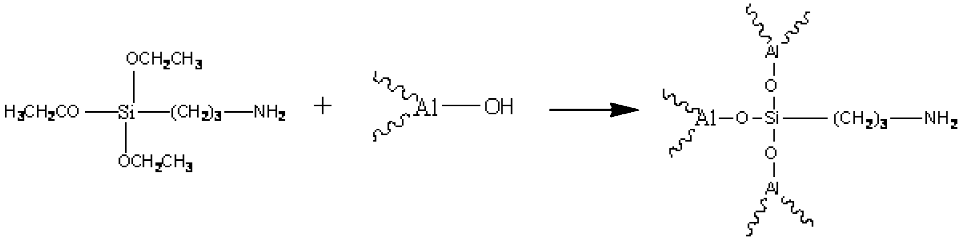
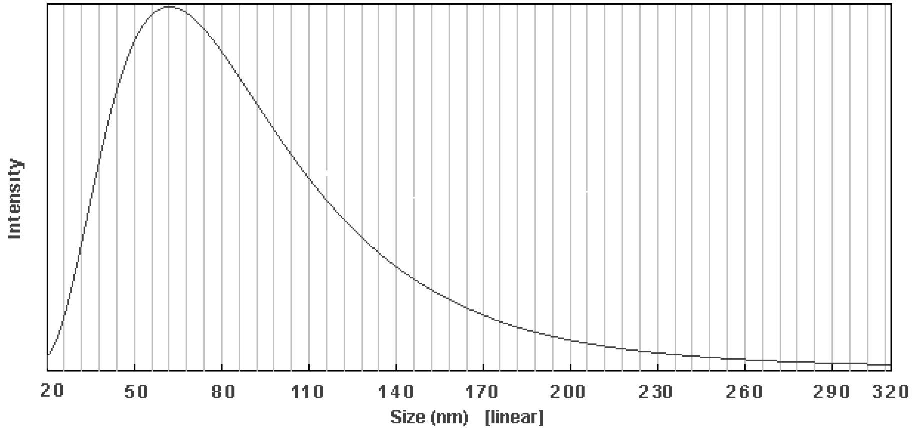


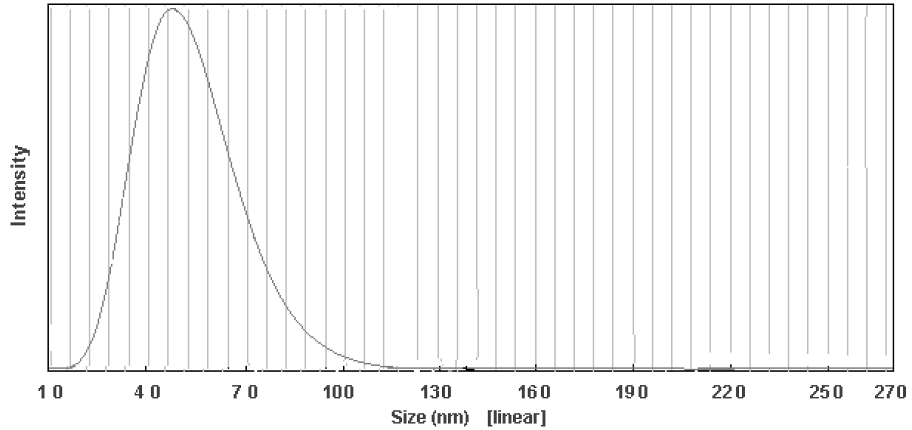
Figure 3. Schematic representation of reaction mechanism between the silanols groups and the hydroxyl groups.

is observed at around 754 cm^{-1}, which is a characteristic absorbance peak of alumina. The band at 3368.6 cm^{-1} is attributed to the presence of hydroxyl groups (–OH) on the surface of the alumina nanoparticles that are hydrogen bonded either to absorbed water molecules or to each other [11, 12]. In comparison, the above peaks disappear in the infrared spectrum of the modified alumina (see Fig. 2(b)), which means that the chemical bond structures of the surface of modified alumina nanoparticles are changed. Absence of the –OH peak indicates that the hydroxyl groups are consumed, which has decreased the concentration of hydroxyl on the surface of the alumina. It is suggested that the chemical reaction occurred between the γ-aminopropyl triethoxysilane and –OH groups on the surface of nano-alumina. The reaction mechanism includes the hydrolysis of γ-aminopropyl triethoxysilane forming reactive silanols (Si–OH) and then the condensation reaction of silanol groups (Si–OH) with –OH groups. The reaction mechanism can be illustrated as in Fig. 3. The peak at 1098.56 cm^{-1} which is not present in the FTIR spectrum of non-modified alumina is attributed to the Si–OH bond [13] that resulted from the hydrolysis of γ-aminopropyl triethoxysilane transforming most of the Si–O–C_2H_5 into Si–OH [9]. In addition, the new absorptions at 3526.31, 3463.09, 1424.78 and 875.20 cm^{-1} appear in the infrared spectrum of the modified alumina. The absorption peaks at 3526.31 and 3463.09 cm^{-1} are attributed to the stretching vibration of –NH_2 groups introduced by γ-aminopropyl triethoxysilane, and the 1424.78 cm^{-1} peak is believed to be a nonlinear Si–O bond formed by the reaction between alumina and silane [14]. The 875.20 cm^{-1} peak corresponds to the stretching vibration of the Si–O bond [13]. From the evidence mentioned above, it is further confirmed that the chemical bond was formed between γ-aminopropyl triethoxysilane and alumina.

The particle size distributions are shown in Fig. 4. Figure 4(a) and (b) show the particle size distribution curves of non-modified and γ-aminopropyl triethoxysilane modified nano-alumina, respectively. Comparison of Fig. 4(a) with (b) shows that the non-modified particles (Fig. 4(a)) present a comparatively wide size distribution. Their mean particle size was 62.2 nm. While the size distribution of modified



(a)



(b)

Figure 4. Particle size distribution curves of nano-alumina, (a) non-modified nano-alumina, (b) γ-aminopropyl triethoxysilane modified nano-alumina.

particles (Fig. 4(b)) is obviously narrow, and the particle size is also decreased, their mean particle size is 50.1 nm, which indicates that the dispersion of modified alumina particles is much better than that of the original. This results mainly from γ-aminopropyl triethoxysilane on the surface of modified particles preventing agglomeration between two adjacent particles. The test values of particle size of nano-alumina are higher than the actual values: the reason for this is that the particle size measured by the particle size analyzer is the hydrated particle size, and the hydration size of the particle is slightly bigger than the actual size due to the agglomeration of nanoparticles in the solution.

3.2. Dispersion of Nanoparticles in Resin Matrix

Good dispersion is critical for taking advantage of nanoscale particles and obtaining optimized properties. Figure 5 shows TEM micrographs of the dispersion of the alumina nanoparticles before and after the modification in epoxy matrix. A comparison of Fig. 5(a) with (b) shows that the non-modified particles mainly exist in the form of agglomerations in the resin matrix, while the agglomerate size of modified particles is reduced greatly: a significant improvement in the nanoparticle distribution can be observed, which is mainly attributed to the surface treatment of the alumina nanoparticles by γ-aminopropyl triethoxysilane. It can be believed that alumina nanoparticles are prone to agglomerate due to having higher specific surface area and surface energy, which makes it difficult to disperse them in organic resin. After the modification, the surfaces of modified alumina nanoparticles are covered by γ-aminopropyl triethoxysilane. The surface energy of the particles is decreased by γ-aminopropyl triethoxysilane through the reaction between Si–OH

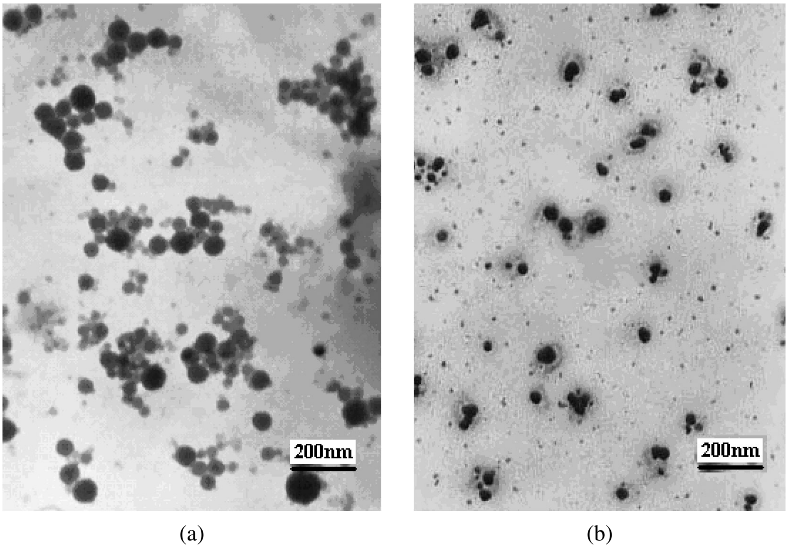


Figure 5. TEM micrographs of nanocomposites, (a) filled with unmodified alumina, (b) filled with modified.

groups and the hydroxyls on the surfaces of the alumina nanoparticles, which results in a decrease of clustering tendency of nanoparticles. Also, due to the surface groups, the structure of the modified particles is more compatible with the epoxy resin than that of the original particles, and the modified particles disperse more easily and are more stable in epoxy resin.

3.3. Curing of Nanocomposites

The curing degree of the resin-based composites is generally relative to the cross-linking degree of the reactive system. The higher is the degree of cross-linking, the higher is the curing degree and the shorter the curing time. Table 1 shows the gel times of the pure resin and the nanocomposites with 1, 2 and 3 wt% alumina particles at the temperatures of 25 and 80°C, respectively. As shown, compared to the pure resin, the gel times of non-modified nanocomposites are lengthened, while modified nanocomposites containing 2 and 3 wt% alumina particles are shortened, and the gel times of the system are decreased with the increase of alumina contents. The gel time of pure resin is increased due to the adding of the nanoparticles at lower weight fraction. It is seen that the gel time of pure resin is 37 min, while nanocomposite with 1 wt% nano-alumina is increased to 120 min (modified nano-alumina, 45 min) at 25°C. It can be believed that nanoparticles in the resin can act as obstacles in the diffusion and movement of the chain segments of resin macromolecules when the particle contents are lower, which makes cross-linking reactions of the macromolecules more difficult. So the cross-linking degree of the system is decreased and the gel time is increased. But the system viscosity is increased gradually and the reaction probability of functional groups between molecules is increased, and so the curing reaction is speeded up and the gel time is shortened with the increase of alumina nanoparticle contents. The gel times of nanocomposites with 3 wt% as-received and modified alumina nanoparticle con-

Table 1.
Gel time of pure resin and nanocomposites at the temperatures of 25 and 80°C (min)

Materials	Temperature	
	25°C	80°C
Resin	37	5.0
Nano-alumina/resin		
1.0 wt%	120	8.0
2.0 wt%	75	6.5
3.0 wt%	60	5.0
Modified-nano-alumina/resin		
1.0 wt%	45	6.5
2.0 wt%	30	4.5
3.0 wt%	25	3.5

tents are shortened to 60 and 25 min, and decreased by 60 and 20 min compared to nanocomposites with 1 wt% nanoparticle contents at 25°C, respectively.

It is very clear that the gel times of modified nanocomposites are shorter than that of non-modified nanocomposites, and it is significantly shortened under elevated temperatures. This is mainly attributed to higher cross-linking degree in modified nanocomposites than non-modified nanocomposites. In modified nanocomposites, amino groups are introduced on the surfaces of particles after surface modification of particles by γ-aminopropyl triethoxysilane. The cross-linking degree of the system is increased by the reaction between the amino groups and the epoxy, and the cross-linking reaction is speeded up with the increase of nanoparticle contents and the temperature, which makes the system cure more easily, thus shortening the gel times. As shown in Table 1, under the temperature of 25°C, the gel time of the modified nanocomposite containing 1 wt% nanoparticles is 45 min, whereas containing 2 and 3 wt% nanoparticles this is decreased to 30 and 25 min, respectively, and shortened by 75, 45 and 35 min compared to non-modified nanocomposites, respectively. Although the variational tendency of gel times at 80°C is the same as at 25°C, the curing reactions are speeded up, and thus the gel times of epoxy system are shorter at elevated temperature of 80°C. It can be seen that the gel times are shortened significantly by around 1/10 times whether it involves modified or unmodified nanocomposites at 80°C than at 25°C.

3.4. Thermal Properties

The effect of surface modification of the nano-alumina particles on the glass transition temperature (T_g) of the nano-alumina/epoxy nanocomposites was analyzed by DSC. T_g values were determined by the peak position of the curves, which are shown as a function of nanoparticle content in Fig. 6 and Table 2. It can be

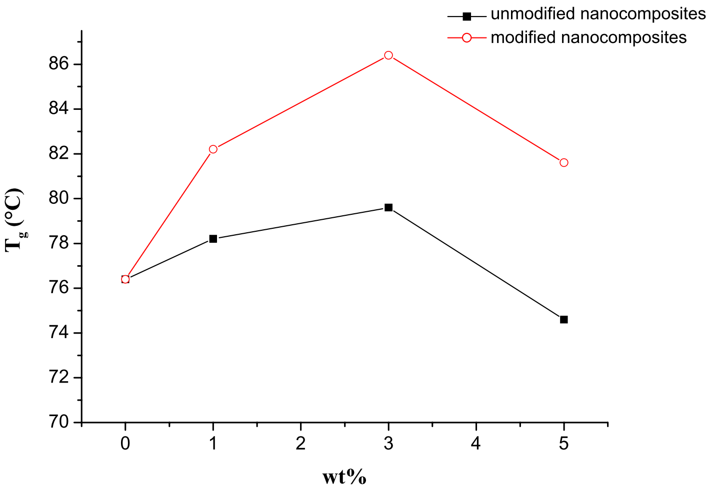


Figure 6. T_g *versus* particle contents curves of nanocomposites. This figure is published in color in the online version.

Table 2.
Glass transition temperature (T_g, °C) of neat resin and nanocomposites

	Glass transition temperature (T_g), °C			
	Neat epoxy	1.0 (wt%)	3.0 (wt%)	5.0 (wt%)
	76.4			
Unmodified alumina/resin	–	78.2	79.6	74.6
Modified alumina/resin	–	82.2	86.4	81.6

seen that only slight variations in T_g are observed for unmodified nanocomposites, while the values for modified nanocomposites are higher compared to the neat epoxy. As shown in Fig. 6, T_g increases with the increase of nanoparticle contents initially in two nanocomposites, in which the modified nanocomposites have faster increasing rate, with an increase of 10°C, whereas unmodified nanocomposite only increased by 3.2°C relative to the neat resin when the nanoparticle contents were 3.0 wt%. The difference in T_g can be attributed to the difference in the extent of cross-linking reactions of the epoxy system. As in the above analysis, the surface modification of nano-alumina particles by γ-aminopropyl triethoxysilane introduced a higher degree of cross-links in the modified nanocomposites than the unmodified nanocomposites and thus resulted in higher T_g. However, T_g decreases with the increase of particle contents when the contents exceed 3.0 wt%. This decrease in T_g may be caused by an increase in nanoparticle agglomeration when the content of nanoparticles is higher. The agglomerations of nanoparticles in resin matrix may function as defects, which make the macromolecules move easily, and T_g of the matrix is decreased [15]. T_g of unmodified nanocomposite with 5 wt% nanoparticles is lower than that for neat epoxy resin (decreased by 1.8°C). It is suggested that the dispersion of the nanoparticles in unmodified nanocomposite with 5 wt% nanoparticles will be even poorer.

Figure 7 depicts TGA curves of neat resin and the composites. Among them, Fig. 7(a), (b) and (c) show the nanocomposites with 1, 3 and 5 wt% addition of modified nanoparticles, respectively. Figure 7(d) is for composites containing 5 wt% as-received nano-alumina particles and Fig. 7(e) is the pure epoxy. Table 3 shows the onset decomposing temperature (T_d) of the materials and the weight loss of the composites by 50% temperature ($T_{50\%}$) data obtained from Fig. 7. From Fig. 7 and Table 3, it can be seen that the addition of nanoparticles, whether they are modified or unmodified particles, all have an influence on the heat resistance properties of the resin matrix. Introducing different content nanoparticles into epoxy resin can change the initial decomposing temperature of neat resin more or less. In comparison, 1 wt% addition of modified nanoparticles have only a slight influence on T_d of epoxy resin, whereas adding 3 wt% modified nanoparticles can significantly raise the thermal decomposition temperature by about 11°C. But the onset decomposing temperature of the composites is lower than that of neat resin when the particles

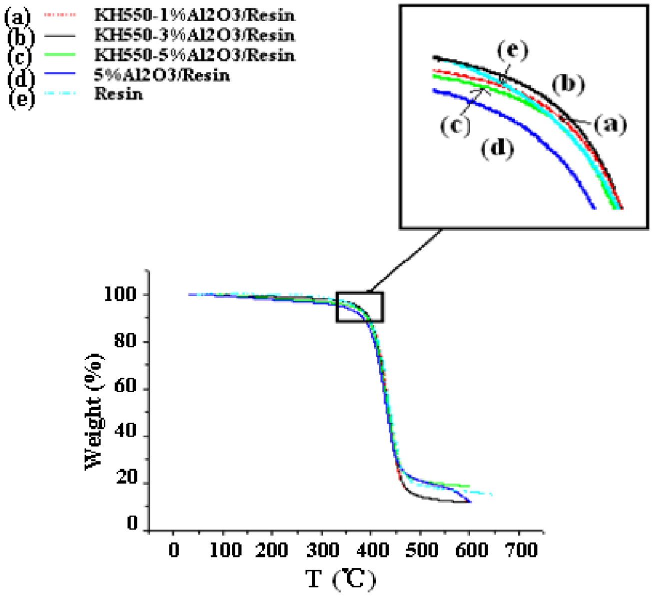


Figure 7. TGA curves of neat resin and nanocomposites. This figure is published in color in the online version.

Table 3.
Onset decomposing temperature (T_d) and weight loss by 50% temperature ($T_{50\%}$) data of neat resin and nanocomposites

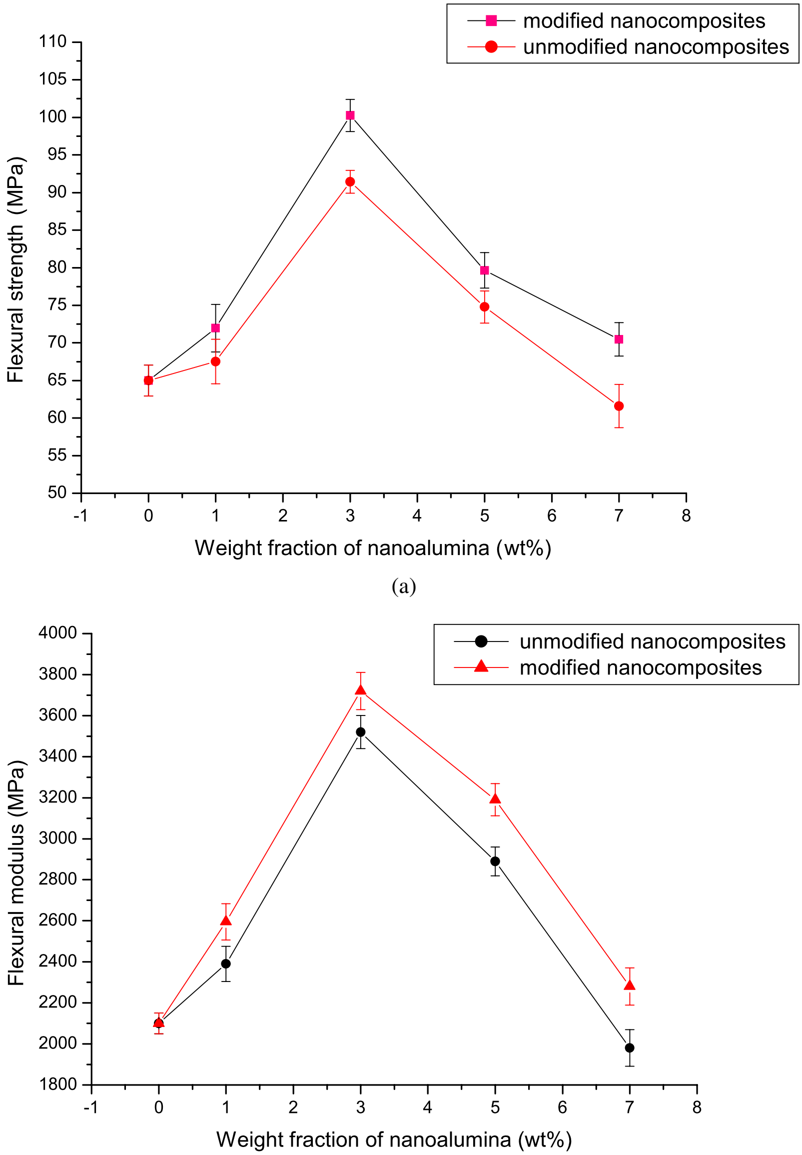
Materials	Temperature	
	T_d (°C)	$T_{50\%}$ (°C)
Resin	364.0	435.6
KH550-1 wt%Al_2O_3/resin	365.4	437.5
KH550-3 wt%Al_2O_3/resin	374.8	440.8
KH550-5 wt%Al_2O_3/resin	362.1	435.5
5 wt%Al_2O_3/resin	341.8	430.0

content is 5 wt%. T_d of the neat resin is 364.0°C, the nanocomposite with 5 wt% modified particles is 362.1°C, decreased by approximately 2°C, whereas T_d of the nanocomposite containing 5 wt% as-received alumina nanoparticles has a significant decrease of about 22°C.

As discussed above, addition of modified particles to epoxy increases the cross-linking density by the reaction of surface functional groups with the epoxy matrix during the curing process. The epoxy matrix with 3 wt% loading of modified nanoparticles has higher cross-linking degree compared to that of 1 wt% addition, and so it has higher thermal decomposing temperature. In comparison, for the composite with 5 wt% loading of modified nanoparticles, a decrease of the onset decomposing temperature was observed. It can be suggested that a significant increase in viscosity of the nanoparticle/epoxy mixture makes bubbles and agglomerates in the matrix when adding higher contents of nanoparticles (5 wt%). This relatively poor dispersion may result in some defects in the epoxy matrix, which can quicken the thermal decomposition rate of the matrix [15]. With regard to the epoxy with 5 wt% loading of as-received particles having a lower thermal decomposing temperature, it is also suggested that the dispersion of as-received particles in the matrix is poorer than that of modified particles. Also, from the data of $T_{50\%}$, it can be seen that the epoxy composites added by modified nanoparticles have better heat resistance compared to the epoxy with as-received nanoparticles.

3.5. Mechanical Properties

The bending tests were performed in order to evaluate the influence of surface functional modification of nanoparticles on the mechanical properties of epoxy resin composites. Figure 8 shows the flexural properties of epoxy nanocomposites based on unmodified and modified nanoparticles. As shown in Fig. 8, below 3 wt% particle contents, the flexural strength and flexural modulus are increased by the addition of nanoparticles, which play the role of reinforcement. The flexural strength and flexural modulus are decreased with increasing particle contents when the particle contents in composites are more than 3 wt%, which demonstrates that the role of reinforcement of nanoparticles is reduced. Comparison with as-received nanoparticles, nanoparticles modified by γ-aminopropyl triethoxysilane have better enhancement effect on the matrix, which indicates that the development of a strong interfacial bonding enables an effective stress transfer between the epoxy matrix and the modified particles. It is suggested that the use of modified nanoparticles in composites can improve efficiently the compatibility and dispersion of system, and particles can be integrated easily into the matrix structure by the chemical bonding formed between the surface functional groups of nanoparticles and the epoxy matrix. The new covalent bonds can provide strong interfacial shear stress and, therefore, crack propagation can be blunted by bringing up the crack faces of modified nanoparticles. As a result, more effective load transfer to the epoxy matrix can be obtained. In comparison, 3 wt% modified particles have the best enhancement effect on the epoxy resin. The flexural strength and flexural modulus of the composite with 3 wt% modified nanoparticles were increased by 55 and 77.1%, respectively, relative to the neat epoxy matrix, whereas the improvement was approximately 40 and 67.4%, respectively, in the case of unmodified-nanoparticles/epoxy nanocomposites. But the flexural strength and flexural modulus were decreased sharply when the particle contents exceeded 3 wt%. The decrease of flexural strength and flexural modulus for higher nanoparticle contents can be interpreted by an increasing susceptibility to agglomeration of nanoparticles. Because of their high surface energy and large aspect ratio and with increasing viscosity, it will be more difficult for the nanoparticles to disperse in the epoxy matrix when their contents are higher. This

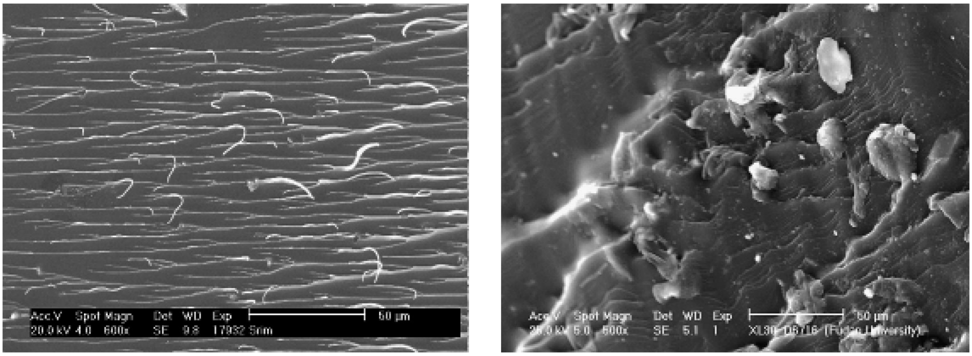


(a)

(b)

Figure 8. Flexural properties *versus* particle contents curves of nanocomposites. (a) Flexural strength, (b) flexural modulus. This figure is published in color in the online version.

will result in large size aggregates which deteriorate the mechanical properties of the composites. As in the above analysis, it might indicate the presence of an upper limit to the content of nanoparticles that can be added directly into epoxy resin for reinforcement action because of a significant increase in viscosity and probably also a saturation of nanoparticles addition which needs to be addressed.



(a) (b)

Figure 9. SEM images of impact fracture surface of nanocomposites, (a) filled with unmodified alumina, (b) filled with modified alumina.

The addition of nanoparticles into the epoxy resin has an effect on the toughness of the resin. The general tendency is that the ductility of the resin matrix is decreased by the addition of nanoparticles for higher nanoparticle contents. In order to further study the effect of surface modification of nanoparticle on the toughness of composites, the impact toughness of nanocomposites with the higher loading of 5 wt% was tested. The results show that the impact strength of the composites containing 5 wt% as-received nanoparticles is lower than that of the neat resin. The impact strength of neat resin is 8.33 kJ/m^2, while the composites with 5 wt% as-received nanoparticles is around 6.25 kJ/m^2, decreased by 33.2%, whereas for the modified nanocomposites, the impact strength of composites with 5 wt% modified nanoparticles is 10.39 kJ/m^2, increased by 24.7% relative to the neat resin. It is indicated that the surface modification of nanoparticles improves the ductility of epoxy resin matrix nanocomposites. In order to further verify this, the fracture surfaces of composites with as-received and modified nanoparticles after the impact test were observed with SEM.

Figure 9 shows the SEM images of the impact fracture surface of nanocomposites. In comparison, the fracture surface of the composites with 5 wt% as-received nanoparticles in Fig. 9(a) shows river lines which are the characteristics of brittle fracture behaviour. The fracture surface between the river lines is relatively smooth. The fracture surface of the composites filled with 5 wt% modified nanoparticles (Fig. 9(b)), however, shows substantial increase in the surface roughness and presents a large number of dimples, which is obvious toughness fracture.

4. Conclusions

Alumina nanoparticles were functionalized by silanization process using γ-aminopropyl triethoxysilane. The surface functional modification of the nanoparticles was confirmed by FT-IR and particle-size analysis. Epoxy nanocomposites with different as-received and modified alumina nanoparticle contents were prepared by physical blending. TEM observation demonstrates that the agglomeration of modified particles is much smaller, and the modified nanoparticles relatively evenly disperse in epoxy matrix compared to that of as-received particles. The system curing reaction is speeded up by addition of nanoparticles. In comparison, the modified nanocomposites have shorter gel time, especially under elevated temperature because of higher cross-linking density that resulted from the reaction between the modified particles and the matrix. The surface modification of nanoparticles has an effect on the Tg and onset decomposing temperature of the resulting composites. The composites with 3 wt% modified nanoparticles have better heat resistance. But the heat resistance properties of composites are decreased when the contents of nanoparticles are higher. This might result from poor dispersion of particles in the matrix. The alumina nanoparticles modified by γ-aminopropyl triethoxysilane have better enhancement effect on the epoxy matrix due to higher cross-linking degree and greater compatibility with the matrix. The composites with 3 wt% modified particles have a 55 and 77.1% improvement of flexural strength and flexural modulus, respectively, relative to the neat epoxy. However, the flexural strength and flexural modulus are decreased when the nanoparticle contents exceed 3 wt% due to the agglomeration of particles and the increased viscosity of the epoxy matrix at the higher particle contents. This indicates that there is an upper limit to the contents of nanoparticles that can be added directly into the epoxy matrix for reinforcement. The surface modification of particles improves the ductility of the epoxy resin matrix. The impact strength of composites with 5 wt% modified nanoparticles increased by 24.7% relative to the neat resin, and the impact fracture surfaces present the toughness fracture features.

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