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Synthesis of novel epoxy-group modified phosphazene-containing nanotube and its reinforcing effect in epoxy resin

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ABSTRACT

In this work, novel epoxy-group modified phosphazene-containing nanotubes (EPPZTs) were successfully synthesized through the reaction between epichlorohydrin and phosphazene-containing nanotubes with active hydroxyl groups. The structure was characterized by Fourier transform infrared spectroscopy (FTIR) and the morphology was investigated by scanning electron microscopy (SEM). EPPZTs/epoxy resin composites were prepared by introducing EPPZTs into epoxy resin matrix (EP618). Impact strength and tensile strength of the composites with different content of EPPZTs were tested and SEM was used to study the dispersion of EPPZTs in polymer matrix. The best effect in reinforcing the matrix was observed when the content of EPPZTs was 0.1%. The thermal stability of the composites was studied by thermo gravimetric analysis (TGA) and it was found that the addition of EPPZTs effectively increased the residue and decreased the weight loss rate.

1. Introduction

Epoxy resins have many advantages such as low manufacturing cost, low shrinkage, great chemical resistance and good mechanical properties. They are widely used in coatings, adhesives, electronic devices, automobiles and space vehicles [1–4]. However, its brittle nature and fire risk restrict its application in some advanced fields. To further improve the physical and mechanical performance of the epoxy resins, researchers have developed a lot of additives and modifiers such as calcium carbonate, pearl shell powders, silica, titania, alumina, montmorillonite and carbon nanotubes (CNTs) [5–11]. Among all the approaches, the addition of carbon nanotubes is seen as the most promising one because researchers want to transfer CNTs' excellent mechanical, thermal and electrical properties to the polymer matrices [12]. Researchers have developed many methods to modify CNTs to make them disperse in the polymer matrices more easily [13]. The complex modification process always destroys the complicated structure of the CNTs which results in the loss of mechanical or electric properties of the CNTs [14]. Developing a new kind of nanotubes at low cost which has a homogeneous dispersion in the polymer matrices without complex modification will be of great significance in this field.

Phosphazenes is a new kind of hybrid organic–inorganic materials with alternating nitrogen and phosphorus atoms in the main chains. Phosphazene-containing materials have been used as flame retardant materials, optical materials, biomaterials, electrode materials, membrane materials, etc. [15–19]. In our previous study, the world's first phosphazene-containing nanotube (PZT) was synthesized through one-pot reaction with controllable morphology, simple process, high yield and low cost [20]. The synthesized PZTs show great heat resistance, radiation resistance and fire retardancy. It is easier for PZTs to disperse in the

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polymer matrices attribute to the hybrid organic–inorganic structure. By changing the molar ratio of the monomer, PZTs with active hydroxyl groups were synthesized by our team [21]. This information is encouraging because the hydroxyl groups can be functionalized with many other active molecules or molecular chains. This made the modification of the PZTs much more convenient and it may help expand the methods for introducing PZTs into polymer matrices. For example, the PZTs can be introduced to epoxy resin to reinforce the resin matrix as they are expected to have a homogeneous dispersion in the matrix to create a CNT-like effect. Meanwhile the great flame retardancy of PZTs can be transferred to the epoxy resin matrix. Up to now, there has not been any literature reporting the PZTs' addition in the epoxy resin, so this work is the first to report the preparation of PZTs/epoxy resin composites and its comprehensive properties.

In this work, PZTs with active hydroxyl groups were synthesized and modified with epoxy groups in mild conditions to yield epoxy-group modified phosphazene-containing nanotubes (EPPZTs). The structure was characterized by Fourier transform infrared spectroscopy (FTIR) and the morphology was detected by scanning electron microscopy (SEM). The dispersibility of the nano-particles in the epoxy resin (EP618) matrix was studied by scanning the surface under SEM. The curing temperature was investigated by differential scanning calorimeter (DSC) when 4,4′-diaminodiphenylmethane (DDM) was used as curing agent. The impact strength and tensile strength of the EPPZTs/epoxy resin composites with different proportion of EPPZTs were tested. The thermal stability of the cured composites was tested by thermo gravimetric analysis (TGA).

2. Experimental

2.1. Materials

Hexachlorocyclotriphosphazene (HCCP) was purchased from Aldrich and purified through sublimation before use. Tetrahydrofuran (THF) was obtained from Shanghai Chemical Reagents Corp. (Shanghai, China) and dried before use. 4,4′-Diaminodiphenylmethane(DDM), epichlorohydrin, 4,4′-sulfonyldiphenol (BPS), ethanol, acetone and triethylamine (TEA) were purchased from Shanghai Chemical Reagents Corp. (Shanghai, China) and used without further purification. Epoxy resin 618 (EP618) was purchased from Shanghai Haiqu Chemical Industrial Corp. The structure of EP618 is shown in Fig. 1 and its average epoxy value is 0.51 (the term "epoxy value" represents the fractional number of epoxy groups contained in 100 g of resin).

2.2. Fourier transform infrared spectroscopy (FTIR)

The characterization of FTIR was conducted on a Perkin–Elmer Paragon 1000 Fourier transform spectrometer at room temperature. The synthesized nano-particles were mixed with KBr powder at the proportion of 1:100 and then the mixture was made a disk under high pressure. The disk was scanned by the spectrometer for four times.

2.3. Scanning electron microscopy (SEM)

SEM was performed on a JEOL JSM-7401F SEM at an accelerating voltage of 5 kV and an S-2150 (Hitachi Ltd., Japan) SEM at an accelerating voltage of 15 kV. The samples were pasted on a copper platform by conductive tapes.

2.4. Thermo gravimetric analysis (TGA)

The thermal stability was tested on a Perkin–Elmer thermal gravimetric analyzer. The samples (about 10 mg each) were heated from 20 °C to 800 °C at a heating rate of 20 °C min^{-1} at the N_2 atmosphere.

2.5. Differential scanning calorimeter (DSC)

The curing temperature was determined on a Perkin–Elmer Pyris 1 DSC instrument at a heating rate of 10 °C min^{-1} from 0 °C to 300 °C at a N_2 atmosphere. On the same instrument, glass transition temperatures of the cured composites were tested at the heat rate of 10 °C min^{-1} from 20 °C to 300 °C at a N_2 atmosphere.

2.6. Mechanical performances

Impact strength was tested on RAY-RAN Universal Pendulum Impact System Testing Equipment in IZOD (unnotched) mode. The sample size was 80 mm × 10 mm × 4 mm. Tensile strength was tested on the INSTRON 4465 Universal Testing System. The sample size was 80 mm × 10 mm × 4 mm.

2.7. Synthesis of the epoxy-group modified phosphazene-containing nanotubes

2.7.1. Step 1: synthesis of the phosphazene-containing nanotubes with active hydroxyl groups (PZTs)

The ratio of HCCP and BPS described in the literature [21] was changed to yield PZTs containing active hydroxyl groups (shown in Fig. 2): 0.87 g of triethylamine (8.64 mmol) was added to a solution of HCCP (0.50 g,

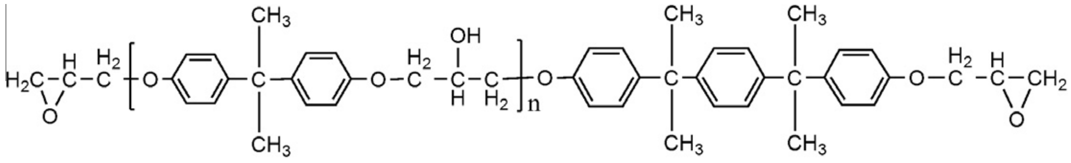

Fig. 1. Structure of EP618.

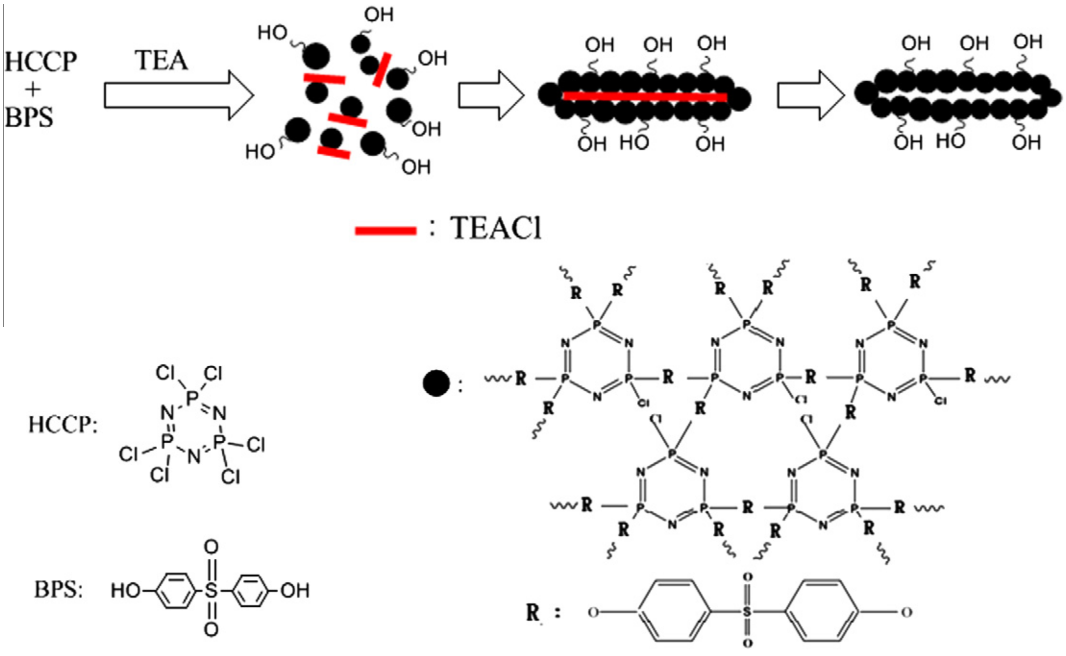

Fig. 2. Schematic synthesis procedure of PZTs.

1.44 mmol) and BPS (1.44 g, 5.76 mmol) in THF (100 mL). The reaction mixtures were kept in an ultrasonic bath (100 W, 80 kHz) at room temperature for 3 h. The product was filtrated and then washed three times with THF and deionized water.

The filtered solid was dried in vacuum oven and the PZTs were obtained as white powder (yields: 82%).

2.7.2. Step 2: synthesis of epoxy-group modified phosphazene-containing nanotubes (EPPZTs)

The synthesis procedure of EPPZTs is shown in Fig. 3. 0.3 g of the PZT powder was added to 50 mL THF in a 100 mL flask. The mixture was kept in the ultrasonic bath (240 W, 80 kHz) for 10 min. Then 9 g of epichlorohydrin was added to the flask and the water bath was heated to 60 °C. Four milliliters of 3% NaOH solution was added to the flask dropwise. The reaction was maintained for 5 h. The solid product was washed with acetone, deionized water and ethanol.

The solid obtained was dried in vacuum oven to yield epoxy-group modified phosphazene-containing nanotubes (EPPZTs).

2.8. Preparation of the EPPZTs/epoxy resin composites

The epoxy resin(EP618) was mixed with acetone in a flask in the ultrasonic bath (240 W, 80 kHz). EPPZTs were added to the mixture and the ultrasonic bath lasted for 30 min. The mixture was kept in the vacuum oven until the solvent was removed. Then the melted curing agent DDM was added to the mixture of EPPZTs/epoxy resin. They were stirred quickly to get a homogeneous dispersion before they were poured into the mold. The curing process was at 100 °C for 2 h, 150 °C for 3 h and 250 °C for 3 h.

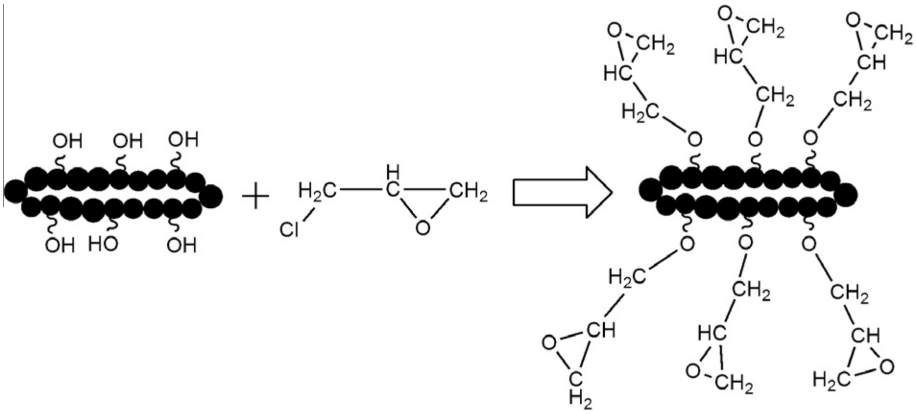

Fig. 3. Schematic synthesis procedure of EPPZTs.

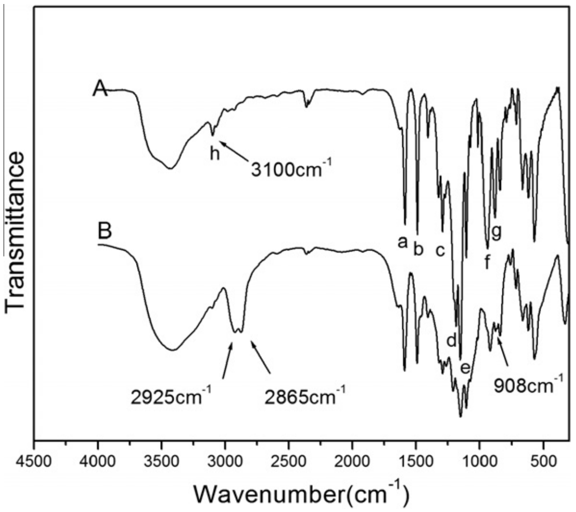

Fig. 4. FTIR spectra of (A) PZTs and (B) EPPZTs.

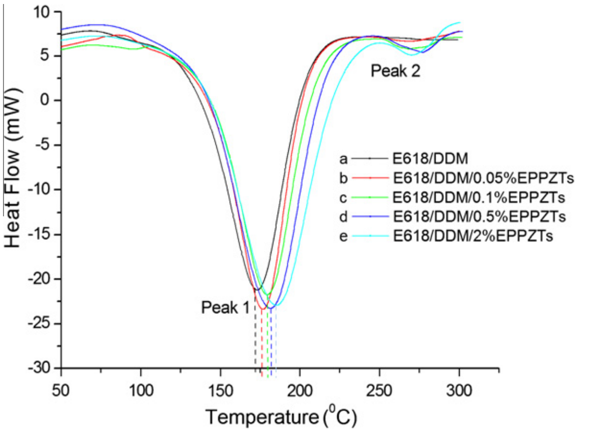

Fig. 6. DSC thermo grams of the curing reactions of composites.

3. Results and discussion

3.1. Characterization of PZTs and EPPZTs

The reaction which generated PZTs occurred in a solution of tetrahydrofuran (THF) with triethylamine (TEA) as an acid acceptor. HCCP and BPS dissolved in THF and the reaction between them generated hydrogen chloride (HCl). The triethylamine absorbed the HCl to form TEACl, which accelerated the polymerization. During the polymerization, TEACl was precipitated out and the nanometer-sized rodlike crystals were formed. The polymerization reaction between HCCP and BPS occurred on the surface of the rodlike crystals. As the polymerization proceeded, crosslinked polymers were produced. The use of ultrasound was very important because this made the polymers exist in the form of nano-particles. The high surface energy of nano-particles made it easy for them to adhere onto the nanometer-sized TEACl crystals to grow to a core–shell structure. Then the core was removed and the nanotubes were formed.

The FTIR spectra of PZTs and EPPZTs are shown in Fig. 4. The absorption peak at 3100 cm^{-1} (h) indicates the presence of –OH. The peaks at 1590 cm^{-1} (a) and 1480 cm^{-1}

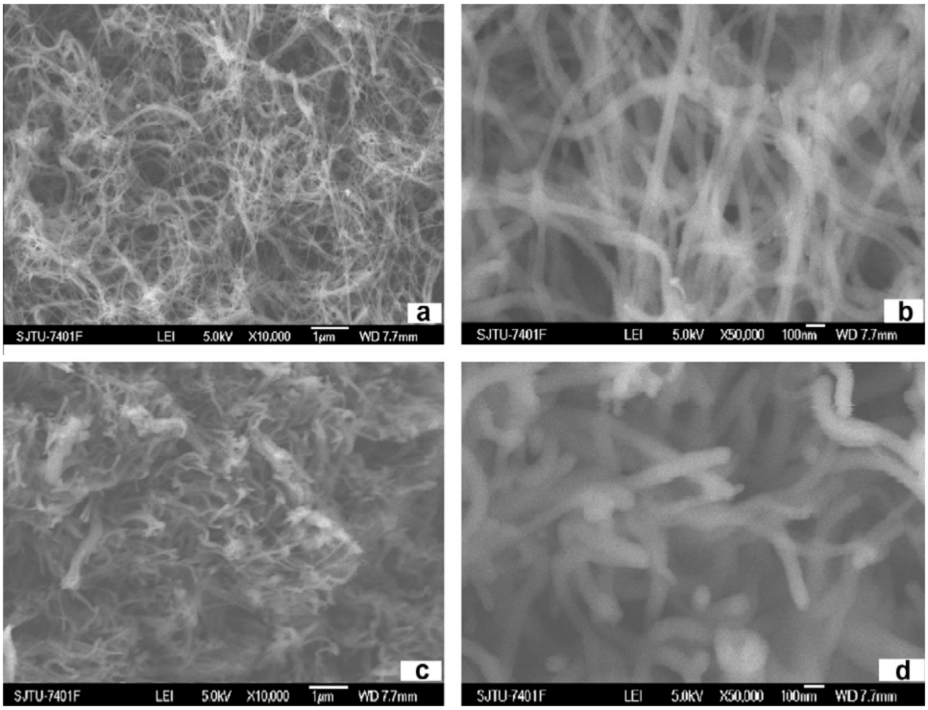

Fig. 5. SEM images of (a) PZTs × 10,000; (b) PZTs × 50,000 (c) EPPZTs × 10,000 and (d) EPPZTs × 50,000.

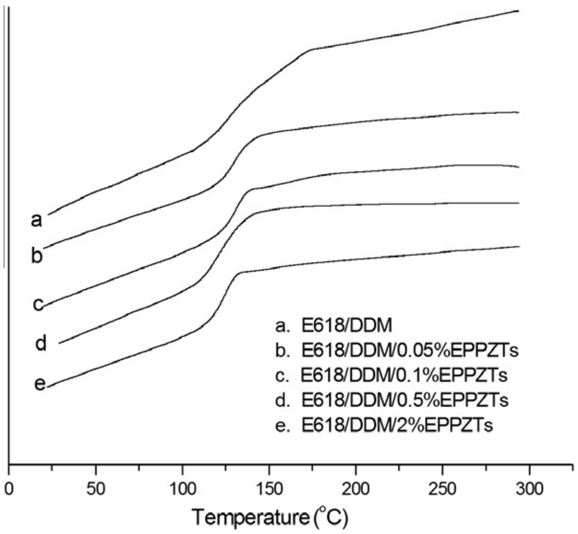

Fig. 7. Glass transition of EPPZTs/epoxy resin composites: (a) pure epoxy resin; (b) 0.05%EPPZTs; (c) 0.1% EPPZTs; (d) 0.5% EPPZTs and (e) 2% EPPZTs.

(b) correspond to benzene ring; the peaks at 1294 cm^{-1} (c) and 1150 cm^{-1} (e) correspond to O═S═O; the peak at 1187 cm^{-1} (d) corresponds to P═N; the peak at 940 cm^{-1} (f) corresponds to P–O–Ar; the peak at 875 cm^{-1} (g) corresponds to P–N. The difference between A and B is marked in the figure. After the modification of PZTs with epoxy groups, the peak at 3100 cm^{-1} corresponding to –OH becomes weak while the peak at 908 cm^{-1} corresponding to epoxy group and the peaks at 2925 cm^{-1} and 2865 cm^{-1} corresponding to $–CH_2$ appear. This indicates that the epichlorohydrin has reacted with the active –OH in PZTs and the EPPZTs have been successfully synthesized.

3.2. Morphology of PZTs and EPPZTs

The images of PZTs and EPPZTs from SEM are shown in Fig. 5. PZTs were noodle-like as image a and image b showed. They were several micrometers in length and their outer diameters were about 80–90 nm. When the PZTs were modified with epoxy groups, the outer diameters seemed not being changed a lot but the surface was obviously not as smooth as that of PZTs. This was mainly because the small molecules of epoxy groups did not coat the whole tube to form a new layer outside the PZTs but the groups interspersed on the PZTs through chemical bonds (C–O) to form EPPZTs (shown in c and d). When the EPPZTs were added to the resin matrix, the epoxy groups interspersing on the tube reacted with curing agent such as DDM which contains $–NH_2$ to make the tube firmly exist in the matrix to reinforce the material.

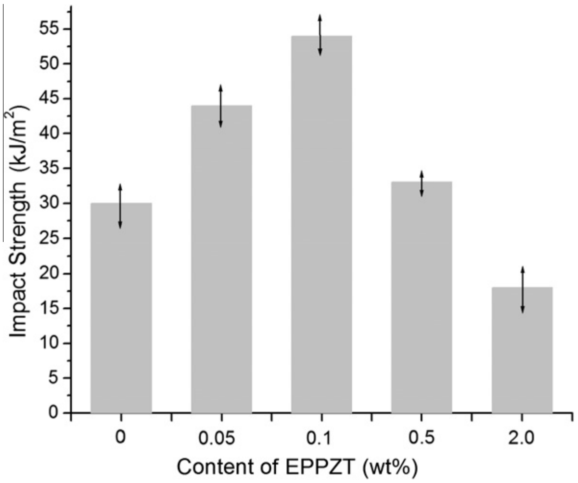

Fig. 8. Impact strength of EPPZTs/epoxy resin composites.

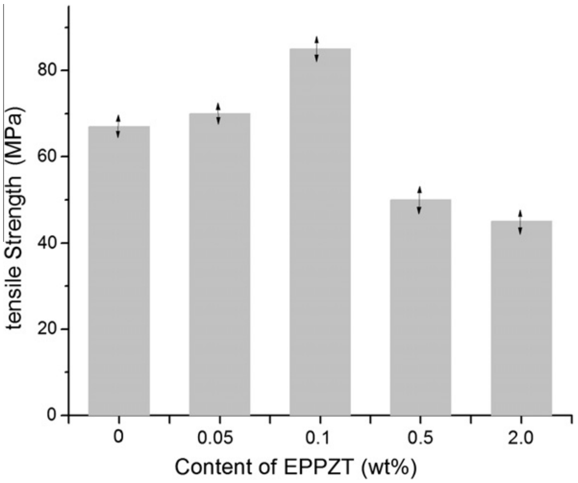

Fig. 9. Tensile strength of EPPZTs/epoxy resin composites.

3.3. Curing of the EPPZTs/epoxy resin composites

Determination of the curing temperature was important when preparing completely-cured EPPZTs/epoxy resin composites. DSC was used to study the curing process because the curing reaction was always accompanied by heat release [22]. In Fig. 6, curve a representing the reaction between curing agent DDM and EP618 showed the exothermic peak was at 170 °C. When EPPZTs were added to the mixture, as curve b–e showed, the peaks appeared at higher temperature. It was found that as the percentage of EPPZT increased, the curing peak temperature increased by 3–5 °C. The reason for the climbing of the curing temperature was supposed to be that the EPPZT particles hindered the movement of the EP618 chain segments to make the reaction a little more difficult. Literatures have mentioned that the brittleness of epoxy resins was mainly due to the rapid cross-linking reactions leading to high cross-link density [23]. In our work, EPPZTs played a role like tougheners lowering the rate of curing. In curve b–e, peaks at 270 °C can be observed. These peaks represented the reaction between EPPZTs and DDM at higher temperature. It was evidence that the epoxy groups in EPPZTs were active and they had chemical bonds linking with the epoxy resin matrix.

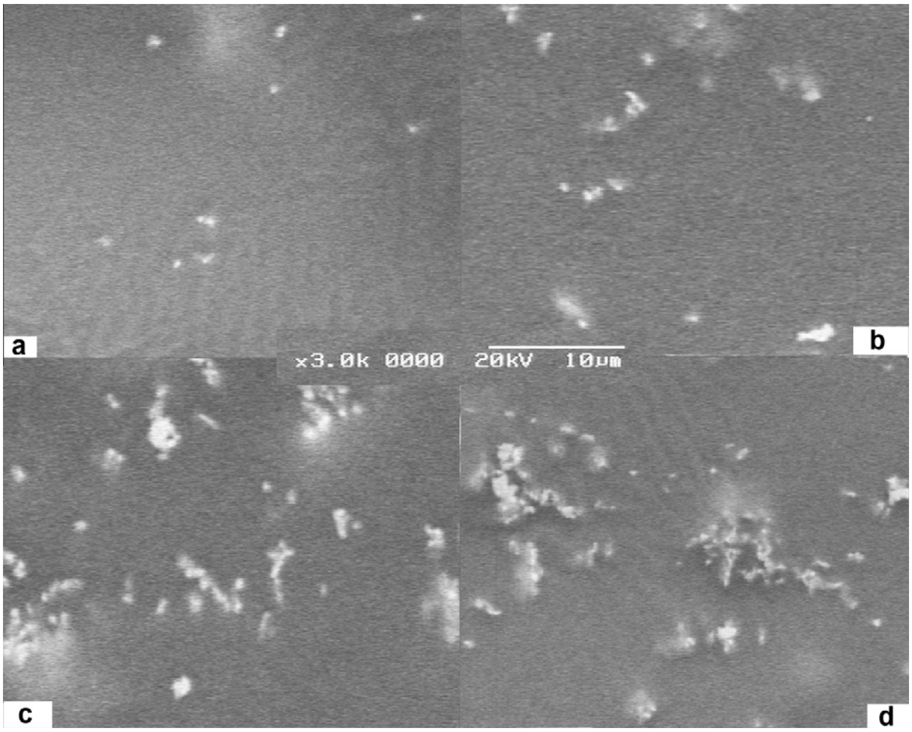

Fig. 10. Dispersion of EPPZTs in the composites: (a) 0.05%EPPZTs; (b) 0.1% EPPZTs (c) 0.5% EPPZTs and (d) 2% EPPZTs.

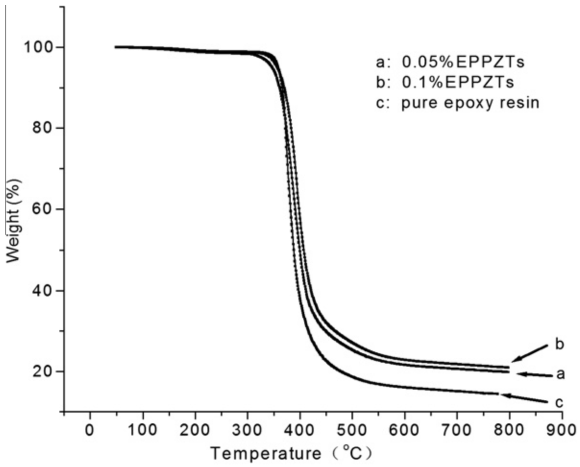

Fig. 11. TGA curves of EPPZTs/epoxy resin composites: (a) 0.05%EPPZTs; (b) 0.1% EPPZTs and (c) pure epoxy resin.

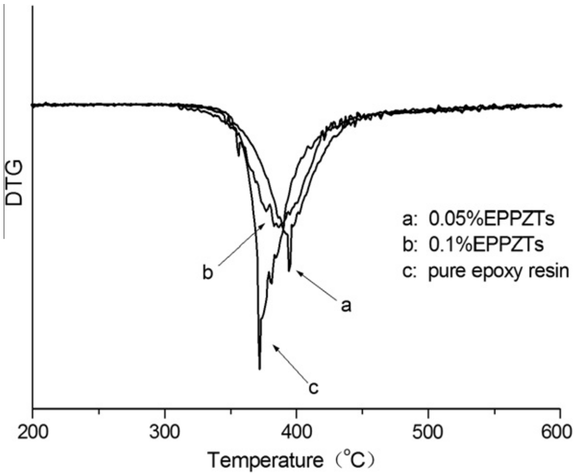

Fig. 12. DTG curves of EPPZTs/epoxy resin composites: (a) 0.05%EPPZTs; (b) 0.1% EPPZTs; (c) pure epoxy resin.

Glass transition of the composites was tested by DSC and the curves were shown in Fig. 7. The result agreed with the curing process studied in the section above, the addition of EPPZTs tended to reduce the glass transition temperature of the composites. As the percentage of EPPZTs increased, more agglomerates were generated and these particles, especially the inner part of the particles had little chance to meet the curing agent which made them not easy to cure in the cross-linking net. As the "not-easy-cure" part increased, the glass transition temperature decreased. However, there was just a slight drop measured from 135 °C to 125 °C even when the EPPZTs reached the percentage of 2%.

3.4. Mechanical performances

The cured EPPZTs/epoxy resin composites were investigated concerning their mechanical properties by impact test and tensile test. Fig. 8 showed the impact strength of the investigated samples and Fig. 9 showed their tensile strength. The impact strength increased at low contents of EPPZTs: at 0.05%, it rose up to 44 kJ/m^2 from 30 kJ/m^2; at 0.1%, it reached the highest point 53 kJ/m^2. This can be explained by the CNT-like effect, especially due to the strong interaction between amino-groups of DDM and epoxy groups in the EPPZTs. However, when the content of EPPZTs increased to 0.5% or even higher, the impact strength showed a decline: at 0.5%, it was 32 kJ/m^2 and at 2.0% it went down to 18 kJ/m^2. This can be explained by the increasing amount of agglomerates and these agglomerates sometimes act as imperfections in a composite.

The tensile properties were also studied and the resulting values were shown in Fig. 9. The tensile strength changed in the trend similar to the impact strength. The reference sample was 67 MPa and it had a slight increase by 2 MPa at the content of 0.05%. It climbed to 84 MPa as the highest point when the content increased to 0.1%. Then the tensile strength decreased as the content of EPPZT increased (at 0.5% it was 48 MPa and at 2.0% it was 45 MPa). This can also be explained by the inhomogeneous dispersion of EPPZTs in the epoxy resin matrix. Agglomerates in the matrix always showed negative effect.

The mechanical tests showed when the content of EPPZT was 0.1%, both the impact strength and the tensile strength of the composite reached the highest point. The mechanical properties had a close relationship with the dispersion of EPPZTs in the matrix. So the surfaces were studied by SEM to identify the influence of the EPPZTs on the matrix strength.

3.5. Morphology of the surfaces

EPPZTs were dispersed in the epoxy resin matrix in the ultrasonic bath. It was reported that CNTs may undergo rupture in such a situation [24]. But EPPZTs did not suffer from any rupture during the dispersion process due to the flexibility of the molecular skeleton of phosphazene. The composites with different weight percentage of EPPZTs were investigated by SEM and the dispersion of EPPZTs can be seen in Fig. 10. When the addition of EPPZTs was 0.05% (a) and 0.1% (b), they dispersed homogeneously in the matrix attribute to the hybrid organic–inorganic structure of phosphazene. When the percentage rose to 0.5% (c), the EPPZTs begun to agglomerate. As image c showed, particles of 4–5 μm were found though most of the EPPZTs dispersed in the matrix in a relatively homogeneous manner. The image of 2% EPPZTs (d) showed more micro-scale particles and the ability to form agglomerates lead to the poor performance in mechanical tests. The SEM images agreed with the results of mechanical tests and the dispersion of EPPZTs can well explain the negative effect in matrix strength when the percentage of EPPZT rose to 2%.

3.6. Thermal stability of EPPZTs/epoxy resin composites

Thermal stability is very important to polymeric material so the EPPZTs/epoxy resin composites were investigated by TGA as illustrated in Fig. 11. The pure sample (c) lost 10% of its weight at about 360 °C. The composites with 0.05% EPPZTs (a) and 0.1% EPPZTs (b) had little change in the initial decomposition process. But it was obvious that the two composites generated higher residue valued 21% and 22% compared to 14% of the pure sample. This may be explained by the existence of phosphorus content in EPPZTs and the higher residue may contribute to the flame retardant properties [25]. We can also get a conclusion that the EPPZTs/epoxy resin composites had a lower mass loss rate as the DTG curves showed in Fig. 12. The peak of the mass loss rate for pure sample (c) reached 39%/min, however, the addition of EPPZT made it decrease to 24%/min (a) and 27%/min (b).

4. Conclusion

Novel epoxy-group modified phosphazene-containing nanotubes (EPPZTs) were successfully obtained through two convenient steps and were used to reinforce the epoxy resin matrix. The EPPZT/epoxy resin composites were prepared successfully. The mechanical tests showed when the addition of EPPZTs was 0.1% (weight percentage), the impact strength was 53 kJ/m^2 and the tensile strength was 84 MPa, both reaching the highest point. The investigation of the surfaces showed the mechanical properties had a close relationship with the dispersion of EPPZTs in the matrix. The agglomerates may become the drawbacks of the composites. The thermal stability analysis showed the addition of EPPZTs effectively increased the residue and decreased the weight loss rate.

The conveniently-getting phosphazene-containing nanotubes showed good performance in improving epoxy resin matrix in our research. This was encouraging because PZTs may also be introduced to other polymer matrices to give a positive effect. What's more, PZTs had inherent active groups and they were easy to modify so it may provide many other possible ways to add PZTs to other polymer matrices.

Acknowledgments

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