Nano-attapulgite Functionalization by Silane Modification for Preparation of Covalently-integrated Epoxy/TMPTMA Nanocomposites

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Nano-attapulgite (nano-AT) particles organically-modified with the silane-containing epoxide groups were incorporated into a mixture of trimethylol-1,1,1-propane trimethacrylate, a tri-functional acrylate (TMPTMA) and methyl-hexahydrophthalic anhydride (MeHHPA)-cured CER was prepared for nanocomposites. The surface modification with silane of nano-AT was characterized by means of Fourier transform infrared spectroscopy (FTIR), and the results showed that the characteristic peaks of silane, such as 2966, 2886, 1010, 804 and 750 cm⁻¹ were observed in the FTIR spectra of nano-AT modified by silane, which indicated that silane coupling agent had already been grafted successfully on the surface of AT nanoparticles. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to investigate the microscopic structures of nanocomposites. The microscopy results displayed that a uniform dispersion of organically-modified nano-AT by silane in the polymeric matrix was obtained, which led to the improvement of the macroscopic properties of nanocomposites. The macroscopic properties of nanocomposites, such as impact strength, storage modulus, tan δ, thermal stability and the dielectric properties were measured. It is found that within the range of 10 to 20 pbw the higher the nano-AT modified by silane concentrations the greater is impact strength of nanocomposites where at 30 pbw it reaches 11.2 kJ/m² in contrast with 5.9 kJ/m² of the CER/TMPTMA system. Dynamic mechanical analysis (DMA) results showed that a glass transition temperature (T_g) found in nanocomposites was assigned to the epoxy phase modified by TMPTMA. With increase in nano-AT modified by silane concentration there were gradual higher values in both T_g and the storage modulus of nanocomposites. Additionally, the results of thermogravimetric analysis (TGA) revealed that thermal stability of nanocomposites was apparently improved in comparison with the CER/TMPTMA system. Dielectric measurements showed that the resulting nanocomposites also displayed quite different dielectric behaviours compared with the CER/TMPTMA system.

INTRODUCTION

Thermosetting resins are widely applied in adhesives, moulding compounds, coating and composites, owing to their attractive combination of stiffness, strength, high heat distortion temperature, thermal and environment stability, creep resistance and excellent processability. Unfortunately, the high density of cross-linking for cured systems could cause high brittleness and poor crack resistance at room temperature, which is practically one of the main
limitations on their wider and more effective applications. Therefore, many researchers up to this day have paid great attentions to the subject of toughening of thermosetting resins [1-4].

The bulk content of epoxy resins, when used, is usually modified by different approaches. There are many approaches used for toughening high performance epoxy resins [2,5,6], and one of the most important methods is to incorporate the inorganic fillers into the pure epoxy, e.g. glass beads [6], layered silicates [7-12] and carbon nanotubes (CNTs) [13], and so on. The epoxies filled with rigid particles would lead to significant increases in strength and stiffness of the materials.

In order to toughen epoxy resins, two approaches and techniques were adopted in this study: (i) epoxy resin as the matrix of the polymer has been modified by a tri-functional monomer, such as trimethylol-1,1,1-propane trimethacrylate (TMPTMA), and they can form a sequential polymer interpenetration networks as previously achieved by our group [14-16]; (ii) a kind of natural nanofibrillar silicate clay (attapulgite, AT) functionalized by silane coupling agent has been employed to toughen and strengthen the modified epoxy. Attapulgite is a type of natural fibrillar silicate clay mineral. In comparison with other fibrous or rod-like nanofillers, attapulgite with fibrous morphology in nanometer scale has the immense reserve in the world, and its processing is neither difficult nor expensive, which is useful to apply in industry. Then, this fibrous clay can be used as an attractive candidate instead of the expensive carbon nanotubes and carbon nanofibrillar as fillers in nanocomposites [17-19]. Bradley [20] first proposed the structure of attapulgite with a theoretical half unit cell formula of Si₈O₂₀Mg(Al)(OH)₂(H₂O)₄·4H₂O. The smallest structure unit of attapulgite is a fibrillar single crystal with high aspect ratio. The interactions between attapulgite single crystal, mainly van der Waals forces and hydrogen bonds, are extremely small, facilitating the separation of attapulgite microagglomerates into single crystals upon large shear or chemical modification [21]. In addition, attapulgite has a large surface area and good mechanical strength. These properties make attapulgite an ideal material for reinforcement [22-24].

Another objective of this article is to explore the influence of nano-AT concentration on dielectric properties of the nanocomposites. To our knowledge, there are few published reports investigating both the effects of nano-AT particles on the dielectric properties of nanocomposites and the epoxy/TMPTMA IPNs incorporated by OAT prepared by solution compounding method. It should be noted that the development and application of thermoplastic and thermosetting nanocomposites filled with organically-modified nanoscale materials have been the hot topics in recent years [25,26].

Because of the agglomeration of clay particles in nanometer range, the pretreatment of nano-AT is an important solution to improve the dispersion of the clay in polymer. In this study, the nano-AT particles have been modified by silane coupling agent. There are abundant -OH groups on the surface of attapulgite single crystals, which are favourable to form stable chemical bonding with the silane coupling agent. At the other chain ends of silane coupling agent, the epoxy groups interact with the epoxy resins to form a cross-linked network structure, thus it is possible to predict that this method would modify the macroscopic properties of nanocomposites.

In this paper, a novel sequential interpenetrating polymer network has been synthesized from 3,4-epoxycyclohexylmethyl-3’-4’-epoxycyclohexane carboxylate (CER) and trimethylol-1,1,1-propane trimethacrylate, a tri-functional acrylate (TMPTMA). It may be the first time in employing a kind of special silane containing the same epoxide groups as the matrix resin to modify the nano-OAT particles. The CER/TMPTMA/OAT nanocomposites have been prepared by physical blending and they are characterized by FTIR spectroscopy. The relationships between the microstructures of nanocomposites and their macroscopic properties have been explored in detail by means of SEM, TEM, DMA, TGA and dielectric measures. The results show that the macroscopic properties of the nanocomposites strongly depend on their microstructure.

**EXPERIMENTAL**

**Materials**

The commercially available grade of epoxy resin,
used in the current study, was 3,4-epoxycyclohexyl-
methyl-3’-4’-epoxycyclohexane carboxylate (marketed under the trade designation ‘UVR6105’), purchased from Dow Chemical Company, USA. The curing agent used was methyl-hexahydrophthalic anhydride (MeHHPA, marketed under the trade designation ‘LHY-807’), purchased from Shanghai Li Yi Science & Technology Development Co., China. The latent accelerator used was Neodymium(III) acetylacetonate hydrate (Nd(III)AcAc, marketed under the trade designation ‘FLQ-1’), purchased from Qinyang Tianyi Chemical Co., China. The modifier agent was trimethylol-1,1,1-propane trimethacrylate, a trifunctional acrylate (marketed under the trade designation ‘TMPTMA’) obtained from Jinshi Tech-development Co., China. Initiator, dicumyl peroxide (DCP) was purchased from Aldrich, (USA). [2-(3,4-Epoxycyclohexyl)ethyl]trimethoxy-silane (marketed under the trade designation ‘KBM-303’) was acquired from Shin-Etsu Silicone International Trading (Shanghai) Co. Attapulgite (AT, specific surface area: 300-400 m²/g) was purchased from Anhui Mingmer Mineral Co., China.

The structures of the raw materials are given in Scheme I.

Characterizations and Measurements

Fourier Transform Infrared Spectroscopy (FTIR)
The study by FTIR was applied in order to characterize the changes between the AT particle modified and unmodified by KBM-303. The blends of nano-AT particles and KBr powders were pressed into pellets by a hydraulic pressure machine. The pellets were measured with a Paragon 1000 (Perkin Elmer, USA) with the resolution of 4 cm⁻¹, and the spectra were recorded in 500-4000 cm⁻¹ region.

Scanning Electron Microscopy (SEM)
For visualization and analysis of the treatment effects of nano-AT particles modified by KBM-303, a Vega 5135 scanning electron microscope (SEM) by Tescan (Japan) was used. The samples of the nano-AT unmodified and modified by KBM-303 were prepared by suspending the solid powder in ethanol under ultrasonic vibration for 20 min before the SEM examination. One drop of the prepared suspension was applied onto copper platforms. Ethanol volatilized completely, and the copper platforms were sputter-coated with a thin layer of gold palladium alloy prior to SEM observation. In order to observe the dispersion of OAT particles in polymeric matrix, the facture surfaces of the impact testing samples were coated with thin gold layers of about 100 Å. The facture surfaces were examined at the activation voltage of 5.0 kV. Observation was carried out in secondary electrons (SE) or back-scattered electrons (BSE).

Transmission Electron Microscopy (TEM)
The dispersion morphology of the fibrous clays in the CER/TMPTMA system nanocomposites was investigated on a Jeol-100CX transmission electron microscope (TEM, Japan) using an acceleration voltage of 120 kV. All samples were microtomed by a
diamond knife into 50-80 nm thick slices.

Dynamic Mechanical Analysis (DMA)

The tangent delta and the storage modulus of the cured samples were measured with TA 2980 dynamic mechanical analyzer (USA) at single cantilever mode. The geometry of specimens was 25 mm × 5.0 mm × 1.3 mm (length × width × thickness). Scans were conducted in a temperature range of 50 to 250°C at a heating rate of 3°C/min and frequency of 1 Hz.

Thermogravimetric Analysis (TGA)

In order to investigate the thermal stability of the hybrid composites, TGA was performed using a Cahn TG systems 41 thermogravimetric analyzer (USA). The samples were heated up to 800°C from the ambient temperature at the heating rate of 5°C/min under air atmosphere.

Dielectric Measurements

The dielectric breakdown tests of the cured samples were performed at room temperature using 50 Hz, 100 kV high voltage transformer (Shanghai Lanpo High Voltage Technology & Equipment Co., China). The cured samples were inserted between two spherical electrodes with the radii of 10 mm, and then the measuring electrode system containing the measuring specimen was immersed in a tank filled with silicon oil so as to prohibit the flashover along the surface of the specimen. During testing, the applied voltage was raised step by step (the voltage ratio between adjacent steps was 2 [27]), and the voltage at each step was kept for 1 min. The initial test voltage was 20 kV and the rate-of-rise of the test voltage was 2 kV/min. All tests were carried out on at least two samples pre-treated in similar conditions like the dielectric breakdown tests.

Dielectric responses were measured using a CONCEPT 40 brand frequency impedance analyzer (Novocontrol, Germany) within a comparatively wide frequency range of 1 kHz to 10 MHz and at room temperature.

Impact Properties Measurement

Charpy impact tests were carried out using a RAY-RAN universal pendulum impact system (UK) at an ambient temperature. Specimens for impact tests were obtained according to ASTM D-256. At least eight samples were repeatedly tested for identification of the bend and impact properties of each kind of nanocomposites.

Hybrid Nanocomposites Preparation

Preparation of the Modified Nano-AT Particles

The nano-AT particles were dried in a vacuum oven at 120°C for 24 h and an appropriate amount of the silane (0.5-1% (by weight) based on the weight of AT particle) was added into a 500 mL three-necked flask, equipped with a mechanical stirrer and a reflux condenser, and mixed in high purity acetone (about 5% (by weight) based on the weight of silane) by stirring at 110-120°C for at least 8 h. After filtration, the silanized powders were dried in a vacuum oven at 120°C for 2 h to remove the solvent and the silane molecules that were not well bonded and thus would not significantly contribute to the joint strength. The probable schematic reaction between nano-AT particles and silane coupling agent is presented in Scheme II. The mechanism could be simply described as follows: in the first step, -Si-OCH₃ groups in the silane were hydrolyzed by water into -Si-OH groups. In second step, the condensing reaction between the -Si-OH groups of silane and -OH groups on the surface of AT occurred, which led to the grafting of silane into the surface of AT.

Preparation of the Hybrid Composites

The hybrid composite specimens were fabricated by a recommended solvent method which is used in many other studies [28] involving the use of a solvent. In this process, the UVR6105, latent catalyst, and/or modified nano-AT particles were weighed according to the formulation in Table 1 and dissolved in high dimethyl benzene and mixed thoroughly by stirring for at least 10 min at an ambient temperature and then sonicated for 10 min. Finally, the uniform mixture was obtained. The mixture was subjected to de-gassing at 100°C for 30 min to remove the solvent. Subsequently, a stoichiometric amount of MeHHPA was added to the mixture and stirred for 5 min at 100°C until it was completely dissolved in the mixture. The resulting mixtures were cured in the open stainless steel moulds for 4 h at 135°C and then...
post-cured at 165°C for 14 h. Table 1 shows the components and their weight contents used in the present study.

### RESULTS AND DISCUSSION

#### Modification of Nano-AT Particle

It is well known that the investigation of polymer nanocomposites is faced with considerable challenges owing to the nanoscale of the nanometer materials and concentration [29]. The main problems are to create full dispersion in the polymer matrix and a good interface between nanoparticles and the polymer matrix to achieve the necessary load transfer for enhanced mechanical response in high performance polymers. Maintaining a strong nanometer material/polymer interface and good dispersion are always crucial for good mechanical properties. However, a strong mismatch of the surface energy between AT nanoparticles and thermosetting resin causes the interface incompatibility and the poor dispersion, thus resulting in poor adhesion between them. These problems can be resolved through selectively organo-functionalizing AT nanoparticles, and subsequently binding them chemically to thermosetting resin. The application of various silane surface-treatment agents (also serving as silane coupling agents [30]) has been found to be effective for improving dispersion and adhesion between AT nanoparticles and polymeric matrix, which also enhances the mechanical properties of the nanocomposites. There have been many reports that focus on the effects of coupling agents on the mechanical properties of epoxy composites [31,32].

In this study, to enhance the dispersion and interface adhesion between AT nanoparticles and epoxy matrix, a silane monomer, [2-(3,4-epoxycyclohexyl)ethyl]trimethoxysilane has been chosen as coupling agent to functionalize AT nanoparticles. This selected silane has two different functional groups, one which is reactive with the epoxy resin and the other reacts with the surface of AT nanoparticles. Coupling agent can hydrolyze in aqueous solution (e.g., the acetone which is used in the present study contains a small amount of water) and its methoxy...
groups will transform into hydroxyl groups. After the reactions of hydroxyl groups with those on the surface of AT nanoparticles, an active coating of nano-AT particles is obtained. The epoxide groups at the other ends of silane can react with the epoxy during the curing process. The dispersion of AT nanoparticles is thus enhanced by silane coating. Thus, the interacting force between the AT nanoparticles and epoxy matrix is improved because of the enhanced chemical bonding between the AT nanofillers and the epoxy matrix. Figure 1 gives the FTIR spectra of the raw and modified nano-AT powders.

As shown in Figure 1, the spectra of silane-modified AT nanoparticles are very similar to those of raw AT nanoparticles, but some differences can still be detected. Compared with the spectrum of pure AT, the new absorption peaks at 2966 and 2886 cm\(^{-1}\) are observed in the spectrum of organo-AT samples, which are due to the oscillation of C-H bond [33]. Meanwhile, the new absorption band at 1447 cm\(^{-1}\) due to -CH\(_2\)- scissoring and -CH\(_3\)- asymmetric bending deformation, and the bands at 804 and 750 cm\(^{-1}\) should be ascribed to epoxide groups, which confirm the organification of AT nanoparticles. The strong absorption band near 1010 cm\(^{-1}\) corresponds to the stretching vibration of Si-O-AT bond [34]. In addition, the absorption band at 3720 cm\(^{-1}\) is due to the surface hydroxyl groups of the AT, the absorption bands at 3547 cm\(^{-1}\) and 1649 cm\(^{-1}\) are ascribed to the stretching vibration and deformation vibration of the

![Figure 1. FTIR Spectra of raw AT and AT modified by silane (KBM-303).](image)

interfibrillar water [35] which can be apparently found to decrease. These changes of characteristic peaks indicate that silane coupling agent has already been grafted successfully on the surface of AT nanoparticles.

The morphology of attapulgite before and after organic modification can be observed directly by means of SEM as shown in Figure 2. It is found that AT is a kind of clay with fibrous morphology, and the diameter of particles is about 50 nm and the length is near to several thousands of nanometer. This high length-diameter ratio of AT is favourable to enhance the mechanical strength of polymer materials. Just as shown in Figure 2a, because of van der Waals force between fibrous clay in AT, the pure AT would agglomerate or bundle together in large scale and it is difficult to find a single fibrous clay. As shown in Figure 2b, however, numerous single fibrous clays can be observed clearly. This indicates that the inter-
action between the AT single clay is weakened after organic modification and thus the large AT agglomerates could be broken down to primary particles.

Morphology of the Hybrid Composites
The overall properties of a composite material are determined not only by the parent components, but also by the phase morphology and interfacial properties of the composite. In order to analyze the relationship between the properties of hybrid composites with both structures and morphology, SEM and TEM measurements are employed in this study. It is greatly regarded that roughness of the fracture sample provides a wealth of information on the extent of plastic deformation and can be adopted to correlate with the bulk mechanical performance. Therefore, it is of great significance to observe the detail of fracture surface. The morphology of the surfaces of the fractured impact specimens is investigated by SEM as shown in Figure 3.

As shown in Figure 3, the fracture surface of OAT0 is fine, rather smooth and monotonous except for some markings of river line near the crack initiation sites (Figure 3a), which resembles a typical mechanism of brittle fracture, revealing that the resistance to crack propagation is very low. Also, rougher fracture surfaces and a greater number of dispersed phases are visible in the samples of OAT-filled nanocomposites with concentration of OAT increasing (Figures 3b, 3c and 3d). Therefore, some conclusions can be easily predicted from these SEM images: (i) the modification with silane coupling agent can contribute to the distribution of attapulgite in the polymeric matrix; (ii) the addition of attapulgite nanoparticles modified by silane coupling agent into the CER/TMPTMA systems could lead to

![Figure 3. SEM mapping micrographs of the impact fracture surfaces of the different composites: OAT0 (a), OAT10 (b), OAT20 (c) and OAT30 (d) (mag.: ×3k).](image-url)
toughness enhancement of the systems; (iii) the excessive loadings of attapulgite nanoparticles modified by silane coupling agent may result in larger aggregates of fillers, which lead to poorer toughness in the nanocomposites.

One of the most important questions in the nano-filled composites is the dispersion of fillers because nanoparticles dispersion in polymers can affect the final nanocomposites properties. Thus, to optimize OAT nanoparticles dispersion in the CER/TMPTMA systems, it is necessary to investigate and quantify the dispersion, which can be done by visualizing the nano-OAT themselves, the interface and the effects of OAT on the surrounding matrix by means of TEM. Figure 4 displays TEM micrographs of different nanocomposites.

As can be seen from Figure 4a, the diameter and length of a single crystal is about 50 nm and several thousands of nanometer, respectively. Just as shown in Figures 4b and 4c, OAT nanoparticles are fully located in polymeric matrix, which reveals that the OAT nanoparticles modified by silane have excellent compatibility and good dispersibility in the matrix. As the concentrations of OAT nanoparticles increase the

![Figure 4. TEM Micrographs of the raw AT (a), and the hybrid nanocomposites: OAT10 (b), OAT30 (c), and the magnified micrograph of OAT30 (d).](image)
dispersibility becomes constantly better, especially, when the concentration of OAT nanoparticles is 30 pbw, OAT nanoparticles display partial aggregation (Figure 4c). It can be seen from Figure 4d that there is a good interfacial adhesion between OAT nanoparticles and polymer phase. Because silane containing epoxide groups have been grafted onto the surfaces of OAT nanoparticles, there exist partial covalent bondings of nanoparticles inside polymeric network, which lead to the excellent compatibility between OAT nanoparticles and polymeric matrix.

**Mechanical Properties of the Hybrid Composites**

Strength is a key property that basically decides the suitability of a material for usage in structural application. Figure 5 displays the impact fracture strengths of the unmodified and the hybrid composites. It should be noted from Figure 5 that the impact strength values of nanocomposites are higher than those of CER/TMPTMA systems, which can be explained that the epoxide groups on the surface of OAT particles take part in curing reactions of matrix, leading to the incorporation of -Si-O- segments on the surface of OAT particles inside the networks of the matrix. Additionally, just as shown in Figure 7 it is also found that within the range of 10 to 20 pbw the higher the OAT concentrations, the greater would be the impact strength. The impact strength of nanocomposite with 30 pbw is up to 11.2 kJ/m² in contrast with 5.9 kJ/m² of the CER/TMPTMA system. However, it is apparent that at concentration of OAT below 30 pbw, the impact strength of nanocomposite displays a slight increasing tendency. A possible factor may contribute to the dispersion states of the inorganic filler in the polymer matrix. One well-known explanation is that either the partial aggregates of OAT particles restrain the crack deflection and/or plastic deformation zone size or fracture failure occurs in the filler/matrix interfacial zone, and thus fracture failure takes place where the crack can propagate in OAT particles. From SEM images in Figure 3 and TEM images in Figure 4, the micro-aggregates of OAT particles grow more and more with the increase of OAT concentrations. A relatively smaller toughening effect may occur owing to the existence of the segregated domains [36,37]. It is clearly found that OAT particles display the distinct agglomeration behaviour when its content is at 30 pbw, which can serve as the stress concentrators leading to premature and brittle failure. This has already been testified by the impact fracture in SEM images (Figure 3).

The dynamic mechanical responses, e.g., the storage modulus, $E^*$, and $\tan \delta$ versus temperature diagram for the different composites are displayed in Figure 6. As shown in Figure 6a, it is clear that the storage modulus at 50°C of the nanocomposite is higher than that of the CER/TMPTMA systems, and with increases in OAT concentration in CER/TMPTMA systems, the storage modulus in both glass and rubbery states of nanocomposites apparently improves. The increase of modulus as a function of OAT loading means that OAT particles can serve as effective fillers to strengthen CER/TMPTMA systems, an indication that the incorporation of OAT has improved the stiffness of the nanocomposites. Those phenomena can be explained by the fact that the OAT particles modified by silane create an obstacle to the molecular mobility of polymeric matrix. The storage modulus graphs show a sharp decrease in the temperature range of 170-220°C, which correlates with the glass transition temperature ($T_g$).

The damping property ($\tan \delta$) as the ratio of the dynamic loss modulus to the dynamic storage modulus is related to the molecular motions and phase transitions. Two important conclusions can be drawn

![Figure 5. Impact strength of nanocomposites based on IPNs/OAT.](image)
from the relaxation peak shown in Figure 6b [38]: (i) it reflects the overall rigidity of the material. As shown in Figure 6b, the value of \( \tan \delta \) of the nanocomposites decreases with OAT concentration, revealing the increasing trend of rigidity of the nanocomposites and (ii) the damping measurements also give practical information on the glass transition temperature. As can be seen in Figure 6b, the glass transition temperature (\( T_g \)) value of the CER/TMPTMA systems is 210°C, which is lower than that of nanocomposite, revealing that the addition of OAT particles into the CER/TMPTMA systems creates an obstacle in molecular mobility of polymeric matrix because of the existence of chemical bonds between the surface of OAT particles and epoxy molecules. Finally, it can be observed that the damping peak becomes broader with the OAT content increasing. Such a phenomenon has been also reported in an earlier publication [38]. It is admitted that there exists a non-linear relationship between the relaxation peak height and the concentration of OAT particles. It is assumed that the presence of fillers has increased the damping caused probably by either particle-particle friction where particles hold one another as in weak agglomerates or particle-polymer friction where there is no adhesion at the interface [39]. This result is in good agreement with Figures 3 and 4.

**Thermal Properties of the Hybrid Composites**

It is well known that the thermal stability of the resulting nanocomposites is strongly associated with their network structures and the distribution of the fillers in those matrices [14]. In order to understand the influence of the nanofillers on thermal stability and thermal degradation behaviour of the nanocomposites, thermogravimetric analysis (TGA) measurement is carried out in air atmosphere. TGA and DTG results of the pristine CER/TMPTMA systems and CER/TMPTMA/OAT nanocomposites with different concentrations of OAT are depicted in Figures 7 and 8, respectively. The TGA data are summarized in Table 2.

Just as shown in Figure 7, it is found that the initial degradation temperature of the CER/TMPTMA...
system begins at about 320°C. However, the onset temperature of decomposition tends to slight increase in most samples having different weight fractions of OAT nanofillers, and the initial degradation temperature of nanocomposites with different concentrations of OAT is almost similar. It is worth noting that the maximum weight loss rates of nanocomposites are distinctly increased as compared with the CER/TMPTMA system, revealing that the addition of OAT into the CER/TMPTMA system leads to an increase in temperature of the maximum rate of weight loss. Of interest is that there exists the second thermal decomposition reaction between 450°C and 600°C, which could be assigned to the decomposition reaction of the TMPTMA component, while the first thermal decomposition reaction may be attributed to the decomposition reaction of the CER-anhydride component. This can be also used to prove the existence of IPNs in the cured CER/TMPTMA systems and in good accordance with the results from our previous work [14].

From Figure 8, it is also found that CER/TMPTMA system exhibits a two-stage decomposition process and the first-stage decomposition occurs at a relatively lower temperature (at about 346.7°C) and the second-stage weight loss at about 410°C (marked I in Figure 8). However, in the case of nano-OAT addition into CER/TMPTMA systems, a weight loss process is observed at about 580°C (marked II in Figure 8), which may be attributed to decomposition of OAT.

It can be clearly seen from Table 2 that the addition of OAT into CER/TMPTMA systems leads to the improvement of temperature stability, since temperatures corresponding to all the listed characteristic weight losses are higher than those of CER/TMPTMA systems, and the residual weights at the listed characteristic temperature improve gradually with increase in OAT content.

It can be deduced from the above experimental results that the CER/TMPTMA system loaded by OAT nanofillers has increased the thermal stability, which may be explained by the fact that the thermal insulation effect of OAT particles will preferably lead to heat absorption, resulting in the onset of polymeric chains to degrade at higher temperature [40-43]. Another reason may derive from the barrier effect caused by diffusion of both the volatile thermo-oxidation products into the gas and oxygen from the gas phase into the polymer in the presence of the clay [44]. It is found that the thermal degradation temperatures of the composites have been improved gradually with increased content of OAT nanoparticles. It can be explained that the active silane grafted on OAT particles improves the interacting forces between the OAT nanoparticles and polymer molecules. Particularly, the epoxide groups of silane have taken part in the curing reaction of epoxy. The chemical bonds are formed between OAT nanoparticles and epoxy molecules, which create

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<th>Sample</th>
<th>$T_{0.5}$ (°C)</th>
<th>$PDT_{(max)}$ (°C)</th>
<th>Char yield (%) up to 500°C</th>
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<td>346.7</td>
<td>2.011</td>
</tr>
<tr>
<td>OAT10</td>
<td>367.9</td>
<td>354.8</td>
<td>4.848</td>
</tr>
<tr>
<td>OAT20</td>
<td>369.4</td>
<td>359.7</td>
<td>6.666</td>
</tr>
<tr>
<td>OAT30</td>
<td>370.9</td>
<td>358.8</td>
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Figure 8. The experimental DTG curves of nanocomposites based on IPNs/OAT.
obstacles to both the molecular mobility of matrix and the diffusion and penetration of low-weight molecules produced during the thermal degradation. These lead to improvement of the thermal stability of the nanocomposites. Additionally, due to hydrolysis reaction of the active silane grafted on OAT particles with water to form silanols and the reaction condensation of silanols to form Si-O-Si bond in composites, the incorporation of -Si-O-Si- segments in the networks of matrix plays important roles in improving the thermal stability.

**Dielectric Measurements of the Hybrid Composites**

As it is well known, the dielectric properties of nanocomposites are obviously dependent on their microstructures. From the above experimental results, it can be predicted that nanocomposites studied here should own unique dielectric properties. Some insights into the way that concentration of OAT affects the dielectric properties of nanocomposites may be obtained by examining the variation of ac breakdown voltage, loss tangent (\(\tan \delta\)), permittivity (\(\varepsilon\)) and impedance. Therefore, these dielectric properties of nanocomposites have been evaluated as described in the next paragraph.

Dielectric breakdown tests of polymers usually involve multiple samples due to statistical variation in recorded values of breakdown strength. Even though the samples are identical, the extent of breakdown strength of the specimens may be large. The dielectric breakdown data are known to be in good agreement with the Weibull distribution, which can be expressed by eqn (1) [45].

\[
F(Et) = 1 - \exp \left[ - \left( \frac{Et}{Et_s} \right)^\beta \right] 
\]

(1)

where \(Et_s\) is the scale parameter or the characteristic parameter, \(Et\) is the random variable (the measuring values of the cumulative breakdown strength), \(F(Et)\) indicates the cumulative failure probability for the Weibull distribution. The scale parameter, \(Et_s\), represents the cumulative dielectric breakdown strength required for 63.2% of tested specimens to fail. The shape parameter, \(\beta\), a dimensionless number is a measure of scattered values of the cumulative breakdown strength for \(Et = Et_s\) and determines the shape of the probability density function.

To compare experimental results with maximum likelihood regressions, the experimental cumulative probabilities of failure [46] can be estimated by:

\[
F(i, N) = \frac{i - 0.3}{N + 0.4}
\]

(2)

where \(i\) is the ith data, the data being ranked from the lowest to the highest values, and \(N\) is the sample size.

Figures 9 and 10 give the Weibull statistical characteristics of the cumulative breakdown strength of the cured CER/TMPTMA specimens with different weight fractions of OAT and the dependence of the cumulative breakdown strength on the OAT concentration, respectively. It can be seen clearly that the cumulative breakdown strength apparently tends to increase with the OAT concentration increasing up to 20 pbw and it hardly increases beyond 30 pbw, which shows that there is an optimum weight fraction of the OAT (about 20 pbw to 30 pbw). This makes it possible for the introduction of OAT to play the positive role in improving the dielectric breakdown characteristics of the cured CER/TMPTMA system. The apparent increase of the characteristic dielectric breakdown strength (called the scale parameter of the Weibull distribution) with the OAT concentration increasing in the range of 0 pbw to 30 pbw may be
probably attributed to the increase in the compactness of the CER/TMPTMA systems due to rod-like OAT nanofillers. Moreover, owing to the chemical surface modification, there are some epoxide groups on the surface of OAT. These groups can take part in the curing reactions between the anhydrides and epoxy resin, which lead to bond formation between the epoxy resins and OAT particles. These bondings of epoxy to OAT can give a layer of "immobilized" polymer, which forces the resin chains to become immobile [47]. The decrease in the segmental mobility influences the background resins’ cumulative electrical strengths.

The slope in the Weibull statistical plot (namely, the shape parameter, $\beta$, for the Weibull statistical distribution) of the CER/TMPTMA systems with different OAT concentrations is shown in Figure 11. It is found that the shape parameter, $\beta$, for the considered materials is increased with the increase of OAT concentration, implying lower scattered experimental data. It is well known that if any two insulating materials or structures have nearly the same value of Weibull shape parameter, their breakdown mechanisms can be considered similar to each other [48]. Then, the above experimental results suggest that the overall homogeneity of the nanocomposites is enhanced by the dispersion of rod-like OAT nanofillers.

The frequency dependency of the dielectric loss tangent ($\tan \delta$) and permittivity ($\varepsilon$) for different nanocomposites with a variety of OAT concentrations in the comparatively wide frequency range of $10^{-2}$ to $10^6$ Hz were tested and are shown in Figures 12 and 13, respectively.

It can be seen in Figure 12 that the significant $\tan \delta$ behaviours of the nanocomposites with different concentrations of OAT are observed in extra-low frequency range below 0.1 Hz, where the $\tan \delta$ values of the CER/TMPTMA IPNs with and without OAT tend to decrease sharply with increase in frequency. It should be noted that the $\tan \delta$ value in the extra-low frequency range is found to be much higher in nanocomposites than in cured CER/TMPTMA specimens, and the $\tan \delta$ values of the nano-
composites improve gradually with increases in OAT concentrations. The theory of the dielectric [49] can be employed to well interpret the tan $\delta$ behaviours of these cured thermosetting systems in the extra-low frequency range: the dielectric loss caused by ac electric field can be attributed both to the conduction loss due to motions of free ions and to the relaxational loss due to the motion of electric dipoles, as shown in eqn (3):

$$\tan \delta = \frac{\gamma + \varepsilon_0 (\varepsilon_s - \varepsilon_{\infty})}{\omega^2 \tau} \frac{\tau^2}{1 + \omega^2 \tau^2}$$

(3)

where $\varepsilon_0$ is the dielectric constant (8.85×10$^{-12}$ F/m), $\varepsilon_{\infty}$ and $\varepsilon_s$ are the dielectric permittivities when the frequencies of the applied electric field are infinitely large and nearly the same as zero, respectively, $\gamma$ is the ionic conductivity, $\omega$ is the angular frequency of the applied voltage and $\tau$ is the relaxation time of the dipole polarization.

When a dielectric is placed in ac electric field with the frequency below 0.1 Hz, the frequency is so low (nearly the same as dc electric field) that dipoles inside the dielectric move quite slowly and can be extremely thought to be "frozen" in the state of orientation towards the applied electric field, leading to the conclusion that the dipole relaxed polarization can be nearly neglected as it hardly contributed to the dielectric loss in the extra-low frequency range. Moreover, it is well known that the lower the frequency of the applied electric field, the larger the ionic current would flow through a dielectric. Because the angular frequency, $\omega$, is nearly equal to zero in the extra-low frequency range, eqn (2) can be rewritten as:

$$\tan \delta \approx \frac{\gamma}{\omega \varepsilon_0 \varepsilon_{\infty}}$$

(4)

It is obvious from eqn (4) that the lower the frequency and the higher the ionic conductivity, the larger would be the dielectric loss tangent.

For most commercial applications utilizing epoxy resins, it is necessary to add a kind of accelerator usually in the form of a base, acid, or organometallic compound into the formulation to speed up the rate of curing at elevated temperatures, which results in the existence of a large amount of ionic substances in the epoxy system. In the current study, the addition of natural fibrillar silicate attapulgite modified by silane coupling agent having a constantly high level of ionic content improves the ionic content of epoxides.

Figure 13 demonstrates the frequency dependency of permittivities of nanocomposites at different OAT concentrations. It can be seen from Figure 15 that in the frequency range, the dielectric permittivities of the resulting nanocomposites tend to increase with OAT concentration. Such dielectric behaviours may be mainly attributed to the addition of OAT into CER/TMPTMA systems, which results in increasing number of the electrically charged impurities [50]. It is worth noting that when the concentration of OAT is relatively low, for example, below 20 pbw, the dielectric permittivity of nano-composite is slightly higher than that of the CER/TMPTMA system, but when the concentration of OAT is beyond 30 pbw, the dielectric permittivity of nanocomposite is apparently higher than that of the CER/TMPTMA system, which may be attributed to the dispersion of nano-OAT in the resulting nano-composites. Just as it is observed in the above morphological characterizations, the higher the concentration of OAT nanofillers in the hybrid system there would be poorer dispersion of nanocomposites. The poor dispersion of nanofillers results in some defects in
the hybrid system. Additionally, the agglomerated nanofillers should act as the electrically charged impurities, which lead to higher permittivity in nanocomposites.

Impedance methods are widely used to characterize ferroelectric materials as the electrical properties of such materials which largely depend on fillers, fillers boundary and/or interface/polarization contributions. Figure 14 displays the variation of real part of impedance of different nanocomposites with frequency at room temperature. It is observed that the magnitude of $Z'$ of pure polymer decreases with increase in frequency, and that of nanocomposites displays a relaxation process at lower frequency (about $10^{-1}$ Hz), which may be due to the release of space charges. The curves also indicate an increase in ac conductivity with frequency. It can reliably say that these results may be related to the dispersion states and concentrations of fillers in polymer matrix.

**CONCLUSION**

In this study, the CER/TMPTMA systems containing organophilically modified OAT nanofillers have been synthesized to combine different properties of individual components, so that the relationships between properties and structures of the hybrid nanocomposites are found in detail. The distribution of nanofillers and the structural evolutions for the host matrix have been observed by means of SEM and TEM. According to the morphological observation and the characteristic analysis, it has been found that the organophilic treatment of attapulgite contributes to uniform distribution of nanofillers in the polymeric matrix. According to DMA measurements, with increases in OAT nanoparticles concentration, the glass transition temperature ($T_g$) values of the nanocomposites gradually increase, and the storage modulus of the hybrid nanocomposites displays an increasing trend at room temperature. Mechanical measurements have shown that the addition of nano-OAT particles into the CER/TMPTMA systems could lead to improvement of the impacting strength, and that when the concentrations of nano-OAT particles are 30 pbw, the impact strength of nanocomposite is twice higher than that of the CER/TMPTMA system. The thermal stability properties of the hybrid nanocomposites are significantly improved in comparison with the CER/TMPTMA systems. The dielectric measurement results have shown that the addition of AT modified by the silane coupling agent into the CER/TMPTMA system lead to significant differences in electrical properties from the CER/TMPTMA system. The macroscopic properties of the hybrid nanocomposites are determined by their components, concentration, dispersion and the morphological structure.

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