Biobased nanocomposites from clay modified blend of epoxidized soybean oil and cyanate ester resin

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A B S T R A C T

Novel bio-based nanocomposites were prepared by blending surface modified natural clay with epoxidized soybean oil (ESO) and cyanate ester resin (CE). A convenient method was employed to modify the attapulgite (ATT) clay by adsorbing the poly(ethylene glycol) diglycidyl ether (PEGDE) onto the clay surface, which was confirmed by the appearance of a new peak of infrared spectroscopy due to hydrogen bonding and chelation. Thermogravimetric analysis (TGA) showed that the amount of PEGDE adsorbed on ATT was influenced by PEGDE concentration in acetone solution. Scanning electron microscope (SEM) and transmission electron microscope (TEM) results showed that nanoscaled ATT dispersed well in the blend of epoxidized soybean oil (ESO) before and after curing. The thermal-physical and mechanical properties were evaluated by dynamic mechanical analysis (DMA), TGA and tensile mechanical test. The nanocomposites showed higher glass transition temperature and modulus, and the tensile strength of the nanocomposites was reinforced as compared to that of ESO/CE blends.

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1. Introduction

Vegetable oil, as the cheapest and most abundant biological feedstock, has been studied extensively in recent years for composites and coating materials because of its advantages such as low toxicity and inherent biodegradability [1–4]. With systematic study, for example, Mohanty et al. [5–7] investigated the epoxidized linseed oil based epoxy materials; Adekunle et al. [8] and Mustata et al. [9] tested the performance of soybean oil composites, it is found that these renewable polymers could serve as an alternative to the traditional petroleum-based polymers through innovative design, because these novel bio-based polymers could be more cost-effective and eco-friendly than the existing petroleum-based polymers.

When bio-based polymers are used to replace part of the highly crosslinked thermosetting resins, the toughness of modified blend is usually increased. However, the modulus, tensile strength and thermal stability are decreased at the same time [10], which limited the application of these polymers in composites and coatings.

To solve this problem, one of the convenient ways without sacrificing eco-friendliness is organic–inorganic nanocompositing technique. Previously, many inorganic nanoparticles have been applied to modify polymer systems [11–14], such as layered silicates [15], TiO2 [16], ZnO [17] and rod-like silicates [18], which increased the mechanical properties of the composites due to their intrinsic properties.

However, the large specific surface of nanoparticles always results in aggregation, and their polar surface leads to poor compatibility with polymer matrices [19]. As a result, it’s difficult to prepare nanocomposites with well dispersed nanoparticles via simple mixing. Therefore, nanoparticles are surface modified to improve their dispersibility. For example, Chen et al. [20] studied the organically modified oxidized multi-walled carbon nanotubes, and found that they can be well dispersed in epoxy matrix and improved thermo-mechanical performance of the material; Wang et al. [21] found that the surface modified TiO2 had a finer dispersion and better compatibility than bare TiO2; Fu et al. [22] investigated the organically modified clay with polyhedral oligomeric silsesquioxane (POSS).

The natural clay attapulgite (ATT) belongs to a family of hydrated magnesium silicates with a fibrous structure of approximately 20 nm in diameter and several micrometers in length scale, which gives ATT larger surface area and stronger absorptive capacity than those of any other natural minerals [23]. These properties, as well as good mechanical strength and thermal stability, make ATT an ideal candidate to reinforce polymeric materials. However, ATT has not received much attention in the application of thermostets even though Nuit et al. [24] found that ATT could improve the mechanical properties and dimensional stability of epoxy resins significantly. Although some procedures have been developed to modify the ATT [24–26], it is still necessary to explore some methods more convenient and practical for the actual application.
Recently, poly(ethylene oxide) (PEO) has been applied as a modifier for layered nanoparticles due to its interactions with metal ions, e.g. Tunney et al. [27] obtained high performance aluminosilicate nanocomposites with PEO surface-modified kaolinite. This arouses our interest in the modification of ATT by PEO for the preparation of new bio-based materials.

In our previous works, cyanate ester resin, a widely applied coating and structural material in microelectronic industry, was modified by epoxidized soybean oil (ESO), which improved the toughness of cyanate significantly and lowered down the water sorption at the same time, while this modification further made the material more cost-effective and environment friendly [28]. The blend was then reinforced by in situ generated nano-silica [29] to compensate the drop in thermal and modulus due to the introduction of ESO, however, this in situ generation method was tedious and required well controlled hydrolysis process.

As a result, in this study, a convenient PEO surface modification method was applied for ATT to improve its compatibility with the bio-based cyanate materials; while the PEO was further functionalized with epoxy group (PEGDE) to improve its interaction with resin matrix. The effect of PEGDE concentration and ATT contents on the thermal and mechanical properties of composites was investigated in this article.

2. Experimental

2.1. Materials and sample preparation

The cyanate ester resin (CE), 1,1’-bis(4-cyanatophenyl) ethane, with a cyanate equivalent of 132 g/eq was obtained from Shanghai Huifeng Technical & Business Co. (Shanghai, China). Epoxidized soybean oil (ESO) (oxirane content as 6.8%) was obtained from Shanghai Tongxin Chemical Auxiliary Plant (Shanghai, China). Poly(ethylene glycol) diglycidyl ether (PEGDE) as an oligomer of 10 units and $M_n \approx 526$ was received from Aldrich Co. The chemical structures of PEGDE, ESO and CE resin are shown in Fig. 1. Attapulgite (ATT) nano-rods (Attagel 50) were provided by Engelhard Co., United States. Copper (II) acetylacetonate and nonylphenol were provided by Sigma–Aldrich.

Attapulgite was baked in muffle furnace at 500 °C for 6 h before modification. For surface modification, ATT was first dispersed in acetone with 1 wt%, and then different amounts of PEGDE were added, the suspensions were stirred vigorously for 6 h and sonicated for 2 h at room temperature. The suspensions were filtered and washed with acetone for three times, and then the obtained white powders were dried in vacuum at 60 °C for 24 h.

The blend of CE and ESO in a weight ratio of 80:20 was selected due to its best performance as compared with other ones in both toughness and water sorption [28] and prepared by the procedure we have reported previously. The modified ATT was dispersed into the blend with vigorous stirring and ultrasonication for 1 h. Then the modified blends were cured with copper (II) acetylacetonate as a catalyst and nonylphenol as a co-catalyst at 177 °C for 2 h, and postcured at 210 °C for 2 h. The weight ratio of the CE-ESO/catalyst/co-catalyst was 100:0.05:2. The samples were designated as Table 1, where CES means CE-ESO blend.

2.2. Measurement

Fourier transform infrared spectroscopy (FTIR) was performed at ambient temperature with a Thermo Nicolet Nexus 440 Spectrometer, 4 cm⁻¹ resolution and 32 scans were used.

Thermal gravimetric analysis were performed with a Pyris 1 TGA equipment (Perkin Elmer Inc, USA) under air flow of 40 ml/min. The heating rate is 10 °C/min and the temperature range was from 50 °C to 800 °C.

The curing conversions and reaction rates were determined by Perkin-Elmer differential scanning calorimeter (DSC, Pyris 1). The samples were isothermally cured at 177 °C under a nitrogen flow of 20 ml/min. The calorimeter was calibrated using an indium standard (heat flow calibration) and an indium–lead–zinc standard (temperature calibration). The samples weighed approximately 5–10 mg.

The melt viscosity variations of the composites during curing reaction were recorded with an ARES-4A rheometer (TA Instrument, USA). The samples were tested under a parallel plate mode and a controlled strain of 1% to ensure that the measurements were performed under linear viscoelastic conditions.

The morphologies of the fully cured samples were observed by scanning electron microscope (SEM, Tescan TSM163MM). The samples were fractured in liquid nitrogen and coated with a fine gold layer before observation.

The dynamic mechanical properties were performed with a Netzsch dynamic mechanical analysis (DMA 242) operating in the single cantilever mode at an oscillation frequency of 1.0 Hz. The
Recently, Fig. 3.1. the peak collected hydrogen at 1040-79. The tensile mechanical properties of cured samples were performed at room temperature with an Instron-5565 universal tester at a tensile speed of 20 mm/min. The samples were prepared into dumbbell shape specimens according to China State Standard GB 1040-79. For each sample, ten replicates were tested to give an average value.

3. Results and discussion

3.1. Surface modification of ATT

The adsorption of polymers on clay is important in many applications such as drilling fluids, ceramics, paints, sludge dewatering, desliming, soil science and organoclay. Adsorption behaviors of poly(ethylene oxide) (PEO), which has the same backbone structure as PEGDE, on several metal oxides in aqueous systems have been reported [27,30–33]. The hydrogen bonding between the surface silanol (SiOH) groups and the ether oxygen in the PEO was proposed to be the mechanism for the adsorption of PEO on silica. Recently, Deng [34] and Shen et al. [35] have reported the adsorption of PEO on smectite, where the layer charge may be the reason of adsorption.

For the natural clay modified systems in our study, as there are lots of silanol groups and cations such as magnesium and aluminum on the ATT surface, one would expect that the adsorption of PEGDE on the ATT surface could be enhanced by the cooperation effect of hydrogen bonding and the layer charge. To verify this point, FT-IR spectra of PEGDE, ATT, and ATT-PEGDE which was prepared by dispersing ATT into 10 ppm PEGDE acetone solution are shown in Fig. 2. Compared with the FT-IR spectra of PEGDE and ATT, a new peak appeared at 3615 cm⁻¹ in the FT-IR spectra of modified ATT, which corresponds to the formation of hydrogen bonding between silanol group and PEGDE according to the report of Alabugin and coworkers [36]; while the new peak appeared at 989 cm⁻¹ may correspond to the chelation between oxygen atom and cations on ATT surface. The adsorption mechanism of PEGDE on ATT is proposed as shown in Scheme 1.

In another aspect, the PEGDE could also self-aggregate mutually because of Van der Waals force between molecules. To study the effect of PEGDE/ATT ratio on the surface adsorption behavior, different concentrations of PEGDE in acetone solution were studied. The amount of PEGDE adsorbed on ATT surface is measured by thermogravimetric analysis (TGA), which was performed as a function of temperature at a heating rate of 10 °C/min under air atmosphere. TG curve of the ATT clay (Fig. 3) shows ca. 8.5% weight loss with an increase in temperature, including a small weight loss by the increase of temperature ranging from 400 to 600 °C and a larger one from 400 to 600 °C due to the occurrence of weight loss of water. In contrast, the ca. 97% weight loss of PEG occurs near 400 °C, resulting from thermal decomposition of the sample.

The amount of PEGDE adsorbed on ATT surface is about 1.6 wt% (shown in Table 2 as calculated from Fig. 3) when the PEGDE concentration is very low in acetone solution (1 ppm). However, the amount of PEGDE chelated with ATT surface increases to 8 wt% when the PEGDE concentration in acetone solution is enhanced to 1%. That could be the result of PEGDE self-aggregation.

3.2. Curing behavior of resin and nanocomposites

The isothermal curing processes of the nano-clay modified bio-based composites have been studied by DSC. Fig. 4 shows the isothermal curing conversions of CES and its nanocomposites with various conditions cured at 177 °C isothermally. The incorporation of nano-clay and its subsequent surface treating with PEGDE show clear effect on the curing behaviors. From Fig. 4a, it can be observed that the isothermal curing conversions of nanocomposites are lower than that of CES-blend. Composites containing ATT without surface treating shows the lowest curing rate, while systems with surface treated ATT show higher curing rate even though they are still lower than that of CES-blend. By comparing the blend with and without PEGDE (0.5 wt%), one can find that the incorporation of PEGDE essentially shows limited effect on the curing behavior even though it decreases curing rate and enlarges final curing conversion slightly.

The effect of fillers (or nano-particles) on the curing rate of thermosetting polymers has been studied by numerous researchers [37–40]. Depending on the surface properties, nano-particles may either increase or retard the curing process from catalyzing or adsorption of polar monomers due to high surface energy [39,41,42]. In this study, the surface untreated ATT may adsorb the catalyst or part of cyanate ester monomer and thus decrease

<table>
<thead>
<tr>
<th>Composites</th>
<th>ATT-1 ppm</th>
<th>ATT-10 ppm</th>
<th>ATT-100 ppm</th>
<th>ATT-1%</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEGDE(wt%)</td>
<td>1.6</td>
<td>6.5</td>
<td>6.8</td>
<td>8.0</td>
</tr>
</tbody>
</table>

* 1 wt% ATT dispersed in acetone solution with different concentration of PEGDE.
the curing rate. After chelated with PEGDE, this kind of surface adsorption is diminished. Therefore, surface treated ATT show little influence in regarding the curing behaviors of CES-blend system even though the PEGDE concentration changes. Only at the later stage of curing process, the addition of nano-clay slows down curing as the nanoparticles decrease the mobility of reacting species. The rheological behaviors are closely related to the isothermal curing process. The evolution of intrinsic viscosity at the early stage of curing process of the composites cured at 177 °C isothermally is shown in Fig. 4b. The addition of ATT and the content increase of PEGDE enlarge the initial viscosity of uncured composites (as shown in Table 3), while the increase of intrinsic viscosity of CES-blend is quicker than that of the nanocomposites, which also confirms that the incorporation of ATT retards the curing reaction.

3.3. Morphology of cured resin and nanocomposites

The morphologies and dispersion of ATT nano-rods in blends are shown in Fig. 5. The unmodified ATT nano-rods have been dispersed in the composite but in form of self-aggregation (Fig. 5a), which is confirmed by TEM microscopy of the cured sample, as shown in Fig. 5b. While for ATT modified with PEGDE in acetone solution, the resulting composites show well-dispersed clay particles in the matrix (Fig. 5c–f).

However, an interesting phenomenon is observed if one compares the nanocomposites with CES-blend. The dispersed phases in CES-blend (Fig. 6a) have disappeared with the addition of ATT particles (Fig. 5). In other word, the addition of ATT changes the phase separation and fracture behavior of CES materials greatly, which have been reported before and the reason may be that the nanoparticles form growing center for the dispersed phase during phase separation [29,43,44].

To verify this point, the fracture surface of CES-10-ppm-2 is etched in chloroform to eliminate the effect of crack on surface structure. As shown in Fig. 6b, except a few large phases, the dimension of dispersed phase drops significantly. The addition of PEGDE into CES-blend can also decrease the dispersed phase size (Fig. 6c), but the phase size is still much larger than that of ATT modified nanocomposites. From Fig. 6d, it can be found that the surface modified ATT are well dispersed within the composites. In other words, the well-dispersed nanoparticles provide growing centers for the epoxidized soybean oil phase, and consequently the dimension of these phases drops remarkably due to the wrapping of dispersed phase onto the nano-clay surface.

3.4. Thermal and mechanical properties of cured resin and nanocomposites

The thermal and mechanical properties of the composites are influenced by the introducing of ATT and the morphologies of nanocomposites. The temperature dependence of storage modulus ($G'$) and tan $\delta$ of nanocomposites are collected by dynamic mechanical analysis (DMA) (as shown in Fig. 7). In our previous work, it has been found that the storage modulus of ESO/CE blend decreases dramatically with the addition of ESO. In this study, the storage modulus of CES-10 ppm-2 and CES-100 ppm-2 are much higher than that of ESO/CE blends, and the storage modulus of the CES-1 ppm-2 is higher than that of ESO/CE blend at the temperature above 80 °C (As shown in Fig. 7a). However, the storage modulus of

![Scheme 1. Schematic representation of the hydrogen bonding and chelation of PEGDE and ATT.](image-url)
Fig. 5. Morphologies of CES composites cured isothermally at 177 °C for 2 h and postcured at 210 °C for 2 h. (a) CES-none-2, (b) TEM microscopy of CES-none-2, (c) CES-1 ppm-2, (d) CES-10 ppm-2, (e) CES-100 ppm-2, (f) CES-1%-2.
Table 3
The initial viscosity before curing (at 177 °C) and tensile mechanical properties of cured ESO/CE/ATT composites and ESO/CE blend.

<table>
<thead>
<tr>
<th>Composites</th>
<th>CES Blends</th>
<th>CES-none-2</th>
<th>CES-1 ppm-2</th>
<th>CES-10 ppm-2</th>
<th>CES-100 ppm-2</th>
<th>CES-1%-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial viscosity (Pa.s)</td>
<td>1.97 ± 0.25</td>
<td>3.55 ± 0.37</td>
<td>3.90 ± 0.46</td>
<td>5.06 ± 0.58</td>
<td>7.59 ± 0.66</td>
<td>9.43 ± 0.78</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>59 ± 2.6</td>
<td>40 ± 1.9</td>
<td>55 ± 2.1</td>
<td>64 ± 2.3</td>
<td>61 ± 2.4</td>
<td>38 ± 1.8</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>8.3 ± 0.5</td>
<td>5.0 ± 0.4</td>
<td>6.3 ± 0.5</td>
<td>8.8 ± 0.6</td>
<td>7.6 ± 0.5</td>
<td>6.4 ± 0.4</td>
</tr>
</tbody>
</table>

CES-None-2 is lower than that of ESO/CE blend, which could result from the poor surface conditions of ATT. The self-aggregated ATT in the blend has disrupted the highly crosslinked polymer network and the storage modulus decreases as a result of lower crosslinking density [45] and additional free volume due to the nanoparticle interface.

CES-1 ppm-2 has the highest Tg and CES-none-2 has the second highest due to the interaction of nanoparticles with CES matrix. The surface modification of ATT, as in the case of CES-1 ppm-2, increases the Tg of the nanocomposites; however, further increasing of the PEGDE concentration for ATT surface modification decreases the Tg of composites, due to the plastification effect of PEGDE adsorbed on ATT surface. As a result, CES-1%-2 shows the lowest Tg, which is even lower than CES-blend without ATT particles.

This could be further confirmed by Fig. 8, which shows the influence of modified ATT content on the storage modulus and tan δ.

Fig. 6. Comparison of morphologies of samples at different conditions. (a) SEM of CES-blend; (b) CES-10 ppm-2 sample etched in Chloroform; (c) CES-blend with 1 wt% of PEGDE; (d) TEM of CES-10 ppm-2.
Fig. 7. DMA characterization of ESO/CE/ATT composites of different PEGDE content. (a) Storage modulus with temperature; (b) tan δ with temperature.

CES-100 ppm-2 shows the highest storage modulus at low temperature. The Tg of nanocomposites decreases with the increase of ATT content. Considering the mentioned plastification effect, one would expect that, as the content of surface treated ATT increases, the Tg of nanocomposites would become lower, due to stronger plastification effect.

The thermal stability of the bio-based cyanate ester nanocomposites with various ATT concentrations and surface treating conditions have also been investigated by thermogravimetric analysis (TGA) under air atmosphere (as shown in Fig. 9). The addition of ATT improves the thermal stability of bio-based cyanate ester nanocomposites as in the case of CES-none-2, since nano-particles hinder the mobility of polymer chains at lower temperature. However, the increasing of PEGDE concentration and surface treated ATT content decrease the initial degradation temperature of nanocomposites due to the plastification effect of PEGDE, which corresponds well with what is observed in the DMA test results.

The tensile mechanical properties of ESO/CE/ATT composites and ESO/CE blend are shown in Table 3. The tensile strengths of CES-1 ppm-2, CES-10 ppm-2 and CES-100 ppm-2 are much higher than that of CES-None-2. However, the strength of CES-1%-2 is close to that of CES-None-2, which could be due to aggregation of ATT nano-rods. In addition, the elongations at break of CES-1 ppm-2, CES-10 ppm-2, CES-100 ppm-2 and CES-1%-2 are higher than that of CES-None-2. Obviously, the modification of ATT nano-rods with PEGDE in acetone solution at lower concentration (1 ppm, 10 ppm and 100 ppm) could improve the tensile mechanical properties of

Fig. 8. DMA characterization of ESO/CE/ATT composites of different ATT content. (a) Storage modulus with temperature; (b) tan δ with temperature.

Fig. 9. TGA curves of the CES-blend and its nanocomposites with different PEGDE content (a) and different ATT content (b) after cured at 177 °C for 2 h and postcured at 210 °C for 2 h.
composites. Moreover, the tensile strength of CES-10 ppm and CES-100 ppm–2 have been enhanced compared to that of ESO/CE blend and their elongation at break has little fluctuation with the addition of ATT nano-rods.

4. Conclusions

The nano-clay could be surface treated by PEGDE due to the chelation of PEG backbone with metal ions, which has been confirmed by the weight loss variations in TGA, and the new adsorption peaks corresponding to the hydrogen bond between the chelation shown in FT-IR spectroscopy. The modified ATT nano-rods could be well dispersed in the ESO/CE blend in order to prepare bio-based nanocomposites with improved mechanical properties. The storage modulus of nanocomposites containing ATT of moderate surface treatment are much higher than that of ESO/CE blend, but non-treated ATT or surface treated ATT with high concentration PEGDE would deteriorate the performance of materials. In addition, the SEM and TEM results of the samples have shown that nano-particles could serve as the nuclear centers for dispersed phase and thus facilitate the formation of a much finer phase structure.

Acknowledgements

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