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Biodegradable glycerol-derived alkyd resins were synthesized from glycerol and maleic anhydride by polycondensation reactions. One set of glycerol-derived alkyd resin/clay nanocomposites was successfully prepared by melt blending maleic anhydride-glycerol precursors with organoclays. These clays had been pretreated with methyl tallow bis-2-hydroxylethyl ammonium chloride salt (yielding a nanocomposite designated clay30B), and some samples of the clay30B were further treated with the diglycidyl ether of bisphenol A (DGEBA) (clay30BT). Resin/mica and resin/talc nanocomposites were also prepared, in the same way, to yield materials for purposes of comparison. The morphologies, thermostabilities, and mechanical properties of the resulting nanocomposites were investigated in detail. X-ray scattering results and transmission electron microscopy (TEM) images clearly indicated that 30BT was further delaminated by the DGEBA, and that the clay30B and clay30BT were mostly exfoliated and finely distributed in the alkyd resin matrix. These layered silicate fillers gave remarkable improvements in thermostability and mechanical properties even at very low loadings. Minimizing aggregation was more of a problem in the case of the mica and the talc, at least in this matrix.

Keywords: clay; glycerol-derived alkyd resin; mechanical properties; mica; talc

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INTRODUCTION

There is currently considerable interest in biodegradable polymers that can be used as alternatives to petroleum-based plastics to reduce environmental problems [1,2]. For example, such polymers can be derived from (a) sources such as poly(butylene succinate), poly(ε-caprolactone), poly(vinyl alcohol), aliphatic polyester and aliphatic-aromatic copolyesters, or (b) from renewable resources such as polyglycolide, polylactides, chitosan derivitives, or (c) from biosources such as corn, wood cellulose etc, or (d) from small molecules like butyric acid or valeric acid that give polyhydroxybutyrate and polyhydroxyvalerate and their copolymers (including Procter & Gamble's Nodax^{TM} resins) by bacterial reactions [3–6]. Obviously, biodegradable polymers made from renewable resources or natural sources are attracting much more attention because of the eco-friendliness resulting from their origins, in contrast to the fully petroleum-based biodegradable polymers, mainly because they have environmental and economic advantages [7,8].

Glycerol-derived alkyd resins are also a kind of biodegradable polymer, and are products of polycondensation reactions between a polybasic acid and polyhydric alcohol modified with fatty acid or drying oil [9,10]. In recent years, the increasing low-cost supply of glycerol from the production of biofuels has led to increasing interest in glycerol-based alkyd resins, particularly since they might be a useful type of biodegradable polymer. Traditionally, alkyd resins, as oil-modified polyesters, are among the most widely used resins in exterior solvent-based inexpensive coatings applications because of their high gloss and durability [11–13]. Alkyd resins possess flexibility to certain extents because of the long-chain fatty acid of the oil used in the modification procedures. The availability of better performing acrylic resins forced alkyd resins to become relatively minor in importance. However, it is estimated that alkyd resins still constitute 70% of the conventional binders used in surface coatings today [8]. Such thermoset resins could be very important in a wide range of applications, not only because of their excellent high gloss and durability, but also because of their being made from natural materials. Thus, alkyd resins are currently considered to be among the most promising biodegradable plastics because of their low production costs and easy processibility in large-scale production. However, some of the properties such as brittleness, low heat distortion temperature, high gas permeability, and low melt viscosity for further processing, etc. restrict their applications. Therefore, modification of the biodegradable alkyd resins through innovative technologies such as nanoreinforcement is an increasingly important challenge.

The introduction of layered silicates into polymeric materials has been a research focus for a number of years, since results from the Toyota Company showed that the introduction of only 2 vol% of exfoliated clay into Nylon-6 leads to an 87°C increase in glass transition temperature and doublings in Young's modulus and tensile strength [14–18]. The introduction of natural layered silicates such as clay, mica and talc into a biodegradable alkyd resin would mean that the resulting polymeric nanocomposites would be entirely made of non-petroleum dependable sources [19–21].

The present review gives a brief report on the preparations and morphologies of glycerol-based alkyd resin/layered silicates nanocomposites, as well as their thermal stabilities and mechanical properties.

Experimental

Materials

The glycerol-derived alkyd resin polymer, a kind of thermoset precursor material, was kindly provided by the Procter & Gamble Company. The precursor was maleic anhydride-glycerol oligomer (Fig. 1). It is a sticky solid, and becomes sufficiently liquid to pour if heated to 100°C. Southern Clay Products Inc. (Gonzales, Texas) provided a commercially available clay, Cloisite® 30B, which was a natural montmorillonite modified with methyl tallow bis-2-hydroxyethyl quaternary ammonium chloride (Fig. 2) (concentration of 90 mg/100 g clay). The average (001) d-spacing of this silicate layer was about 18.5 Å. The diglycidyl ether of bisphenol A (DGEBA) was kindly provided by the Dow Chemical Company (Midland, MI). Mica ($H_4Al_6K_2O_{24}Si_6$, 325 mesh, water ground) and talc ($3MgO \cdot 4SiO_2 \cdot H_2O$) O) were the products of Spectrum Quality Products Inc. Garden, CA and the Aldrich Chemical Company Inc., respectively. All organic solvents were high-performance liquid chromatography grades and were purchased from the Aldrich Company.

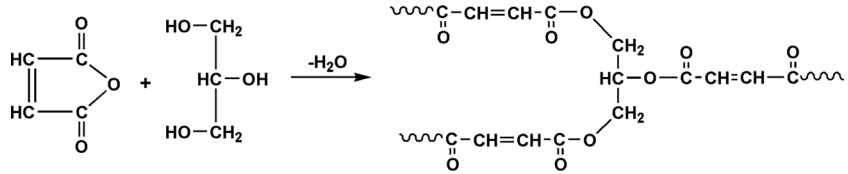


FIGURE 1 Schematic for the preparation of a glycerol-derived alkyd resin made from maleic anhydride and glycerol.

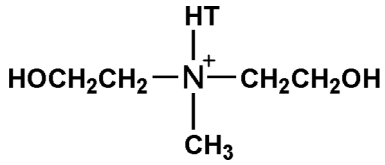


FIGURE 2 Quaternary ammonium salt used to treat the clay. Here T is tallow (~65% C18, ~30% C16, ~5% C14), and the anion is chloride.

Treatment of the Clay

To further enhance the polar interactions between the fillers and the alkyd resin matrix, the organoclay surfaces were additionally treated with a diepoxide, a diglycidyl ether of bisphenol A (DGEBA) with epoxy molar mass of 184 to 190 g/mol. The epoxy monomer was diluted with acetone in a volume ratio of 1 : 10. The organo-clay was first suspended in water, and then the desired amount of epoxy-acetone solution was poured into the mixture, which was then mechanically stirred at 50°C for 2 h. The mixture was completely dried in an oven, evaporating both the water and solvent. The weight ratio of DGEBA to alkyd resin in the finished composite was calculated from the molecular weight of epoxy and carboxyl contents of the resin.

Preparation of the Alkyd/Clay, Alkyd/Mica, and Alkyd/Talc Nanocomposites

Several concentrations of the clay30B, clay30BT, mica, and talc in the alkyd resins were investigated, specifically 2.5, 5.0, 7.5, and 10 wt% (relative to the total weight of the glycerol-derived alkyd resin). Briefly, the desired amount of one of these layered silicates was added to the glycerol-derived alkyd resin and mechanically stirred for 20 min in a flask at 80–90°C. The mica and talc had been strongly milled to a fine state of homogenous powders before mixing. The samples were then placed into Teflon™ molds and degassed under vacuum at 100°C for about 60 min, and then held at 100 °C overnight. In many cases, undesirable bubbles formed, but this was generally avoidable by better degassing at a temperature that gave a viscosity at which any bubbles easily escaped before the matrix solidified.

Characterization

XRD. X-ray diffraction (XRD) measurements of neat alkyd resin, the layered silicates, and the corresponding composites films were carried out at room temperature using an X-ray generator (a Siemens D500 diffractometer) (CuKα radiation, with 30 mA, 40 kV, $\lambda = 1.5406$ Å).

The 2θ scan range was 2 to 10°, with a step size of 0.05°, and a time per step of 1 sec.

TEM. Transmission electron microscopy (TEM) images were obtained using a JEM 1230 EX-II instrument (JEOL, Tokyo, Japan) operated at an acceleration voltage of 80 kV. All of the ultrathin sections (less than 200 nm) were obtained by microtoming, using a Super NOVA 655001 instrument (Leica, Swiss) with a glass knife. They were subjected to TEM observation without staining.

Thermogravimetric analysis (TGA). Thermogravimetric analysis of the alkyd thermoset and corresponding nanocomposites were carried out on a TA Instruments TGA 2050 Thermogravimetric Analyzer with nitrogen as purging gas. Tests were conducted from 40 to 600°C at a heating rate of 20°C/min.

Differential scanning calorimetry. The thermal behavior of the same materials was characterized using DSC measurements on a TA Instruments DSC 2010 at 130 ml/min nitrogen flow at a thermal rate of 10°C/min from −150 to 100°C.

Mechanical property measurements. The values of the moduli and tensile strengths of samples having dimensions of $30 \times 5 \times 1\,mm^3$ were measured at room temperature using a fully computerized Instron mechanical tester (Model 1122). The initial gauge length was 30 mm and the cross-head speed was 5 mm/min. The tensile properties of greatest interest were the Young's moduli and tensile strengths, and values were obtained as an average of at least five measurements.

RESULTS AND DISCUSSION

Morphology (XRD and TEM/ESEM)

Figure 3 shows the XRD patterns in the range of $2\theta = 2$–40° for the alkyd resin, clay30B, clay30BT, mica, and talc, and their corresponding composites containing various concentrations of the layered silicates.

The pattern of the neat alkyd resin is displayed as a baseline to compare the existence of diffraction peaks coming from the layered silicate dispersed in the matrix. The peak at $2\theta = 14$–30° of the neat glycerol-derived alkyd resin corresponds to the amorphous state of the matrix. There is no peak in the range of $2\theta = 2$–15°, which is an important range with regard to analysis of peak changes upon the introduction of the layered silicates.

Clay30B was the clay modified with methyl tallow bis-2-hydroxyethyl quaternary ammonium chloride with one alkyl tail,

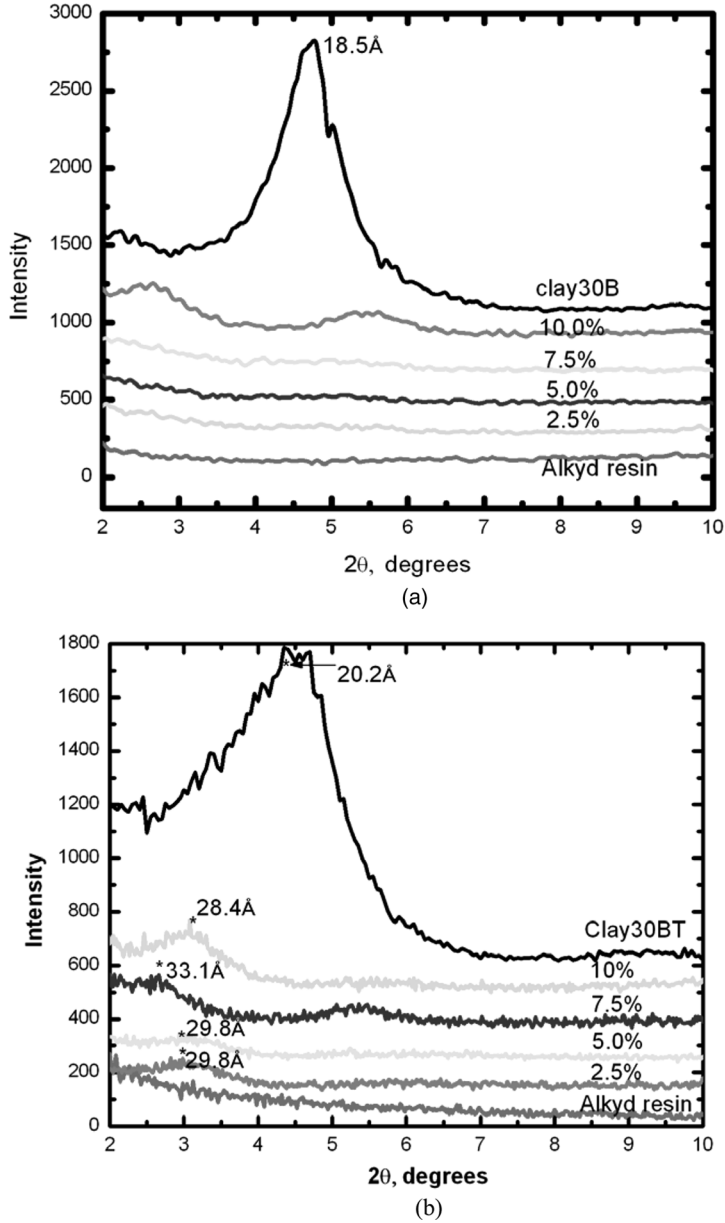
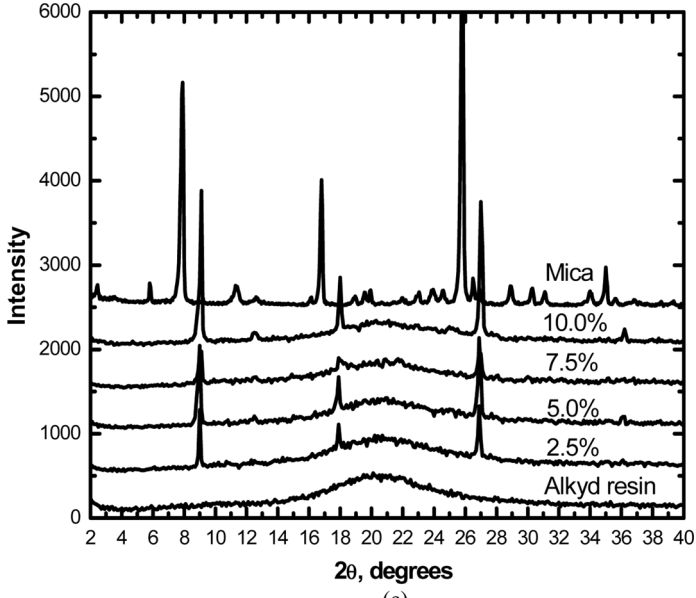
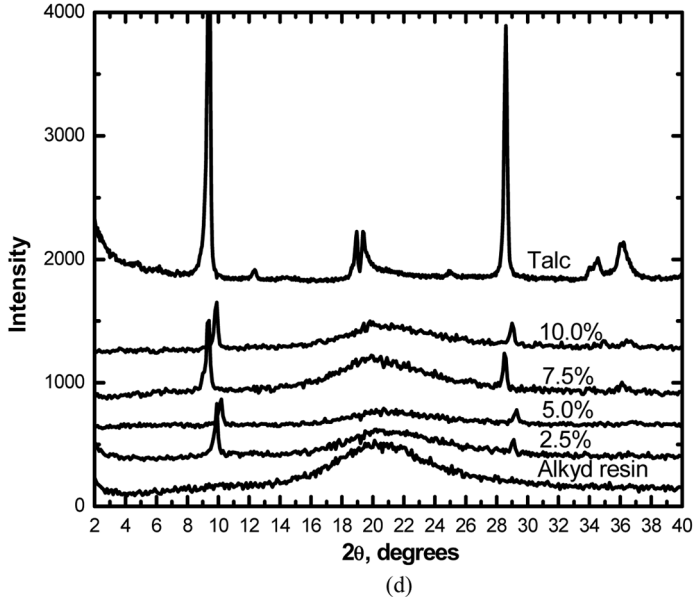


FIGURE 3 XRD results for alkyd resins reinforced with layered silicates. (a) Clay30B and its alkyd resin composites; (b) Clay30BT and its alkyd resin composites; (c) mica and its alkyd resin composites; (d) talc and its alkyd resin composites.



(c)



(d)

FIGURE 3 Continued.

which increased the space between two layers. Specifically, the d001 distance increased from 11.7 Å in Cloisite® Na^+ to 18.7 Å in clay30B.

There was no peak in the range $2\theta = 2$–15° in the alkyd resin/clay30B composites in which the content of layered silicate was less than 7.5%. This result indicates that the d-spacings between layers are so large that the fillers formed exfoliated structures. This exfoliation may have been brought about by the side chains of the matrix dispersing into the spaces among layers to exfoliate the layers, which facilitated by the reaction between the tallow modifiers chains of clay30B and the alkyd resin matrix. The reaction between the maleic-anhydride and the hydroxyl groups in the methyl tallow 2-hydroxyethyl quaternary ammonium on the surface of clay30B is proposed in the schematic in Figure 4. The characteristic peak of the neat clay30B was still evident in the composites when the content of clay30B was over 5.0% but much lower than that of 30B, which demonstrated that the clay30B was not well exfoliated in the matrix when its concentration was relatively high and thus formed only intercalated structures.

It is clearly indicated in Figure 3b that clay30BT was further delaminated by the reaction with DGEBA, from 18.5 Å to 20.2 Å, compared

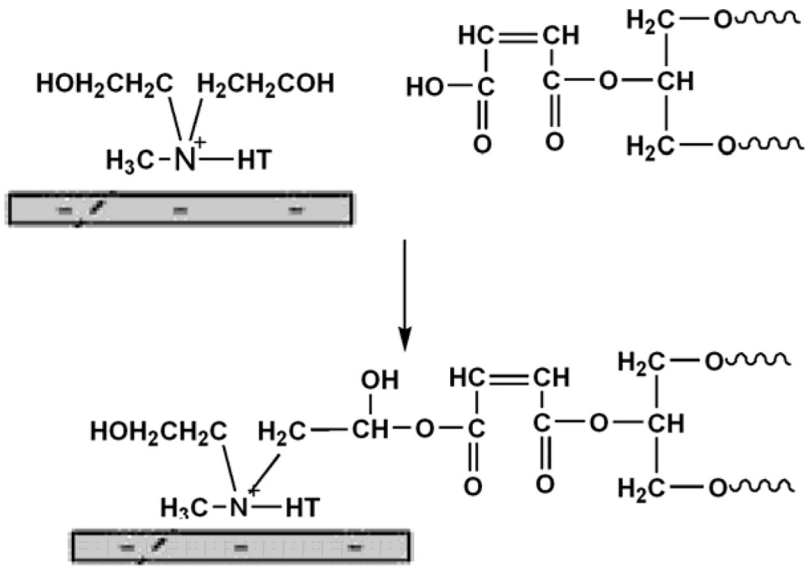


FIGURE 4 Schematic of the reaction of alkyd resin precursor with the 30B clay.

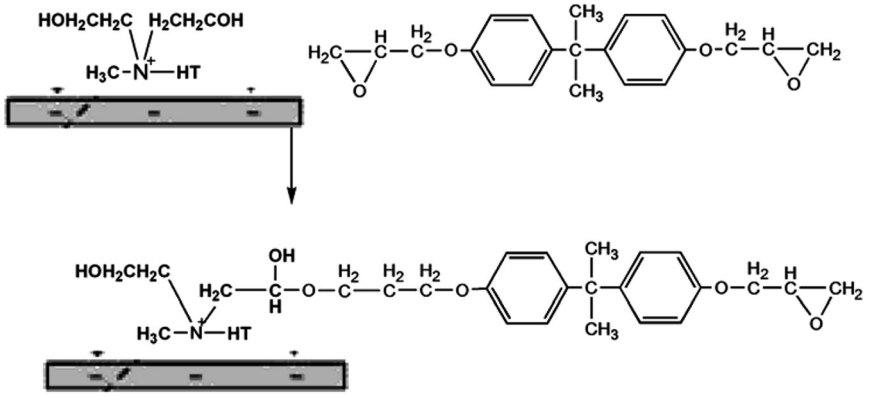


FIGURE 5 Schematic of the reaction of DGBEA with the clay30B.

with clay30B. The proposed reaction mechanism could be explained by the sketch in Figure 5, in which the hydroxyl groups on the surface of clay30B may react with the epoxy of DGEBA. The introduction of DGEBA did indeed expand the d-spaces among the layers.

A similar phenomenon occurred in the clay30BT composites. There was no discernible peak from the clay30BT in the composites over the range 2–10° when the content of the clay30BT was less than 7.5%, which means that the clay30BT was almost completely exfoliated. The characteristic peak for the clay30BT became weaker when the clay content was over 7.5%. The plain peak of the resin/30BT composite compared to that of the neat clay30BT indicates an increase in d-spacing and more intercalated structures in the polymer matrix. The figure also clearly shows that there were weak peaks in the XRD result for resin/clay30BT nanocomposites, even in the resin/clay30BT composite with 10.0% of clay30BT, which indicated that the clay30BT was almost fully exfoliated in the alkyd resin matrix, since the cross linking between maleic-anhydride and DGEBA could also have taken place during curing.

The XRD pattern for the alkyd resin/mica composites (Fig. 3c) showed that the characteristic peak of mica was still present in the composites. The same results were obtained in the alkyd resin/talc composites (Fig. 3d). The results showed that the mica and talc could not be intercalated applying the usual melt blending methods. The results were somewhat different from the results reported in the Nodax™/mica and Nodax™/talc composites, in which mica and talc were intercalated or even exfoliated and well dispersed during ultrasonic treatment at low concentrations [4].

In order to check the internal nanometer-scale morphologies of the nanocomposites, XRD was supplemented by TEM, which provides direct visualization of the morphology, atomic arrangement, spatial phase distribution, and structural features of a selected sample area. Figure 6 shows the TEM images of the naocomposites: (a) glycerol-derived alkyd resin/clay30B −5.0%; (b) glycerol-derived alkyd resin/clay30BT −5.0%; (c) glycerol-derived alkyd resin/mica −5.0% and (d) glycerol-derived alkyd resin/talc −5.0%, where the dark entities are intercalated silicate layers. From the TEM results in Figure 6a and b, it is clear that the stacks of clay30B and clay30BT forming the clay crystallites were now well dispersed in the polymer matrix. TEM results in Figure 6c and d also demonstrate that mica and talc could be dispersed into small agglomerates by the milling and shear during melt blending.

Thermal Stability

The thermal stabilities of the alkyd resin/layered silicate composites series were determined from the thermogravimetric results. Figure 7 shows an example of a TGA trace obtained for the neat alkyd resin thermoset system. The onset and the end set temperature were determined from the intersection of the two tangents, and the peak degradation temperatures were determined from the inflection points on the curves.

Table 1 presents values for the (i) onset temperature, (ii) the end set temperature, (iii) the temperature interval ΔTemp between these two temperatures, (iv) the degradation peak temperature, and (v) the total weight loss at 500°C. These results showed that the onset temperature was increased to ca. 345°C for the alkyd resin/clay30BT nanocomposite, to 330°C for the alkyd resin/mica composites, and to 342°C for the alkyd resin/talc composites, compared with the onset temperature 321.2°C for the neat alkyd resin thermoset. Similarly, the end temperature was increased to ca. 436°C for the alkyd resin/clay30BT nanocomposite, to 426°C for the alkyd resin/mica composites, and to 425°C for the alkyd resin/talc composites, compared with the onset temperature 344.7°C for the neat alkyd resin thermoset. The improvement of thermostability obviously results from the introduction of layered silicates, such as clay30BT, mica and talc. Specially, the larger improvement in the alkyd resin/clay thermosets relative to the other two series is obviously from the exfoliated structure in alky resin/clay30BT as opposed to the less-effective intercalation in the alkyd/resin/mica or alkyd resin/talc composites. The interval temperature between degradation onset and end set remained nearly constant

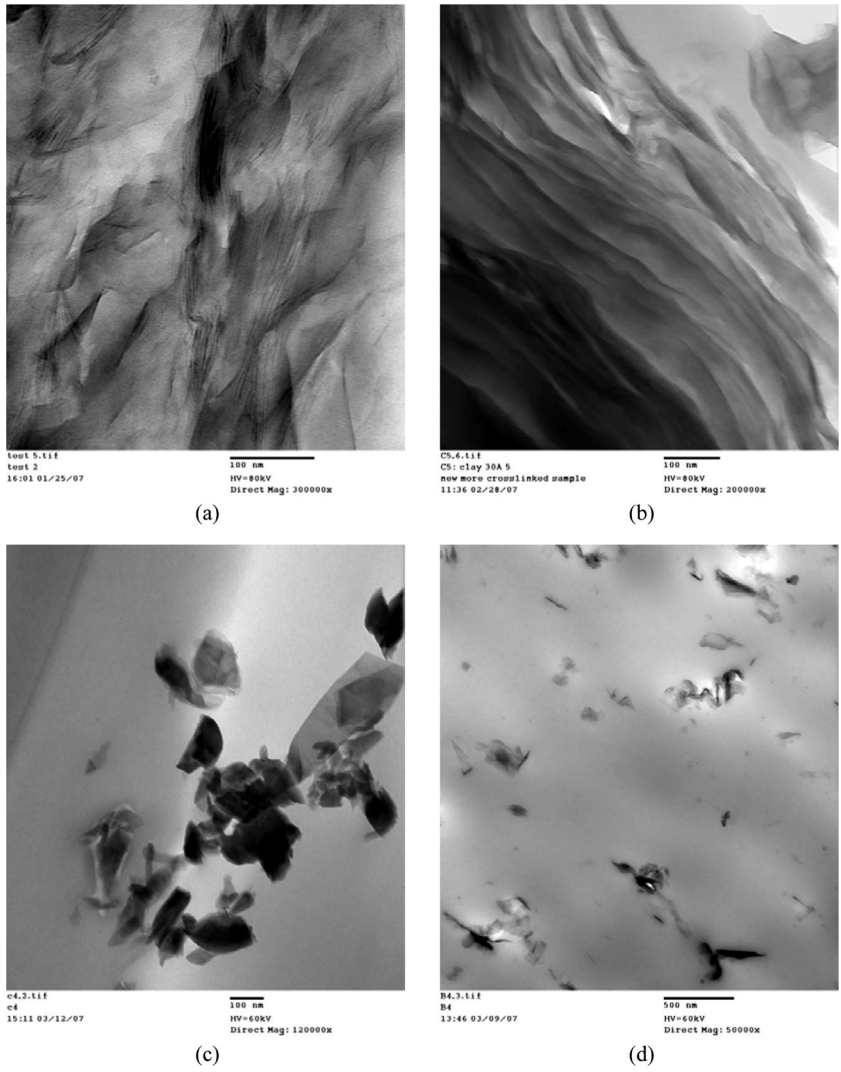


FIGURE 6 TEM results showing the dispersion of clay30B and clay30BT in the alkyd resin. (a) Alkyd resin/clay30B 5.0%; (b) Alkyd resin/clay30BT 5.0%; (c) Alkyd resin/mica 5.0%; (d) Alkyd resin/talc 5.0%.

around 90°C for the alkyd resin/clay30BT thermosets and alkyd resin/mica thermosets, and ca. 80°C for the alkyd resin/talc thermosets. However, the interval temperatures were increased by about 65°C compared with that for the neat alkyd resin thermoset.

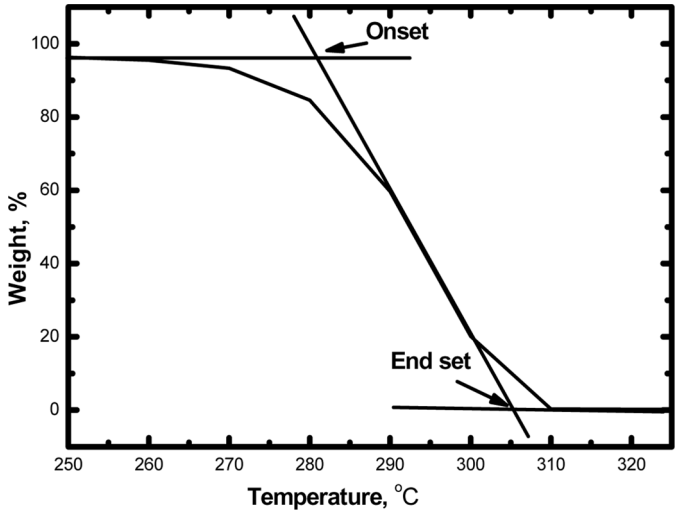


FIGURE 7 Determination of onset and end set temperature from the thermogravimetric results on an alkyd resin thermoset.

The total weight losses of the composites at 500°C were not generally in direct proportion to the amount of layered silicates incorporated. Reductions of weight loss with increases in layered silicates concentration were of course observed, as expected.

TABLE 1 Thermal Stability Parameters of Various Alkyd Resin/Layered Silicate Systems as Determined from TGA

Filler	Filler loading	Onset temp (°C)	End set temp (°C)	ΔTemp (°C)	Degradation peak (°C)	Total wt. loss @500°C (%)
None	0	321.2	344.7	23.5	344.7	100.0
Clay30BT	2.5	349.2	437.1	87.9	403.0	79.6
	5.0	345.8	437.8	92.0	407.2	78.1
	7.5	346.5	437.1	90.6	408.0	76.5
	10.0	345.0	436.2	91.3	408.0	75.6
Mica	2.5	335.9	432.1	96.2	393.1	78.1
	5.0	336.7	427.1	90.3	395.6	76.6
	7.5	336.6	426.3	89.8	394.1	76.4
	10.0	328.4	426.3	97.9	394.5	74.1
Talc	2.5	342.8	431.9	89.1	402.8	79.8
	5.0	344.3	425.6	81.4	398.1	75.9
	7.5	344.3	425.6	81.4	399.7	74.4
	10.0	344.3	425.0	80.7	400.4	72.2

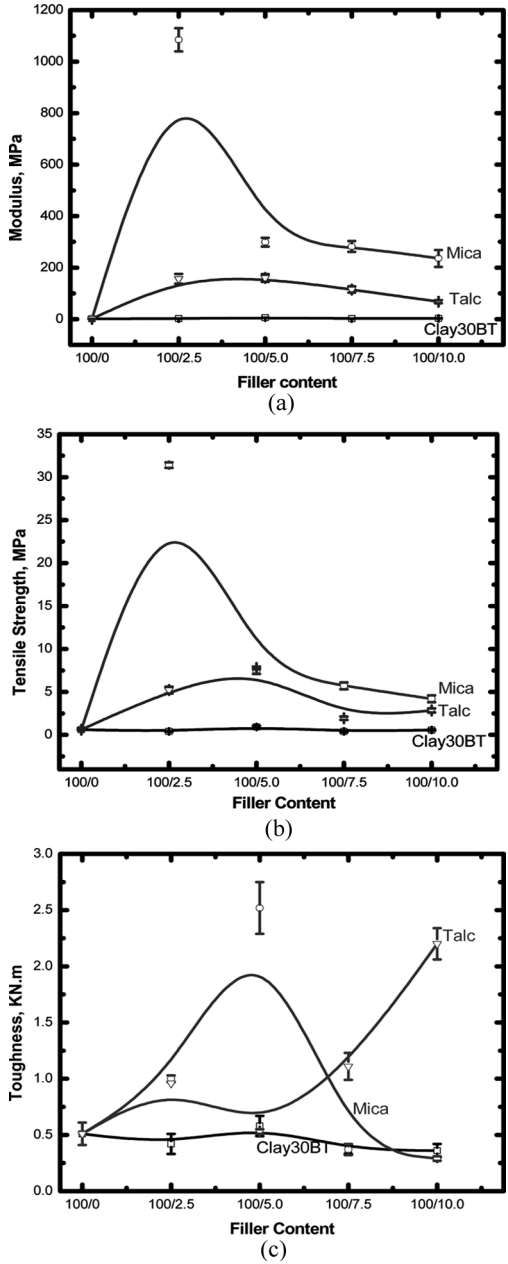


FIGURE 8 Mechanical properties of glycerol-derived alkyd resin/layered silicates (clay30BT, mica, talc) nanocomposites: (a) Young's modulus, (b) tensile strength, (c) toughness.

Mechanical Properties

Figure 8 shows the tensile properties obtained at 25°C for the neat alkyd resin and the alkyd resin/layered silicate composites. The properties include (i) Young's modulus, (ii) tensile strength (defined as the stress at break) and (iii) toughness. As shown in Figure 8, there was almost no increase in the mechanical properties including Young's modulus, tensile strength and toughness of alkyd resin/clay30BT composites compared those of pure alkyd resin thermoset. This is due to the fact that the fine dispersion and exfoliated layered clays in the alkyd resin may also act to decrease the gas permeability of the matrix, which would prevent the low molecular weight molecules such as water from permeating through the matrix during cross linking, especially when the matrix had a high viscosity [22]. However, as shown in Figure 8, both the Young's modulus and tensile strength of the composites were greatly improved in alkyd resin/mica and alkyd/talc composites compared to those of the pure alkyd resin thermoset. Of particular interest is that even very small amounts of the mica or talc gave significant reinforcement of the alkyd resin thermoset. Large amounts of mica or talc ($>5.0\%$) did not improve the Young's modulus and tensile strength as much. Similar results were obtained for the toughness of the alkyd resin/mica thermosets. However, the toughness of the alkyd resin/talc did increase with increasing amounts of talc.

CONCLUSIONS

Alkyd resin/clay nanocomposites were successfully prepared by melt blending maleic anhydride-glycerol precursors with organo-clays that had been pretreated with methyl tallow bis-2-hydroxylethyl ammonium chloride salt (clay30B) and the clay further treated with DGEBA (clay30BT). XRD and morphology results clearly indicated that 30BT was further delaminated by the DGEBA, and that the organoclays were mostly exfoliated and well dispersed in both series of alkyd resin nanocomposites, and this led to considerable improvements in thermostabilities. The mechanical properties including Young's modulus, tensile modulus, and toughness, remained comparable to those of the corresponding neat alkyd resin thermoset. Although the mechanical properties of these glycerol-anhydrid alkyd resins were found to be greatly improved, there are still problems such as further minimizing the formation of aggregates in the case of mica or talc in the polymer matrix.

Additional research also should be carried out to establish the morphologies, mechanical properties, and biodegradabilities of these

interesting clay-based materials. It would also be important to investigate the modification by introducing in-situ silica by the sol-gel method [23,24], and other layered inorganic fillers such as expanded graphite [25,26]. Microcellular foams would also be of interest, particularly in the case of the graphite, since the percolation threshold concentration for electrical conductivity should be extremely low for such an anisometric filler.

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