SELECTIVE CLAY PLACEMENT WITHIN A SILICATE-CLAY EPOXY BLEND NANOCOMPOSITE

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ABSTRACT

A clay-epoxy nanocomposite may be prepared by dispersing a layered clay in an alkoxy epoxy, such as a polypropylene oxide based epoxide before combining the mixture with an aromatic epoxy to improve the nanocomposite’s thermal and mechanical properties.

11 Claims, 7 Drawing Sheets
Dispersing a clay material in an alkoxy epoxy to form a dispersed clay

Add dispersed clay to aromatic epoxy

Stir mixture

Cool mixture

Add curing agent

Degass

Cure

Figure 1
Figure 2
Figure 4
Figure 6 (a)

Figure 6 (b)
SELECTIVE CLAY PLACEMENT WITHIN A SILICATE-CLAY EPOXY BLEND NANOComposite

ORIGIN OF THE INVENTION

The invention described herein was made by an employee of the United States Government and may be manufactured and used only by or for the Government for Government purposes without the payment of any royalties thereon or therefore.

BACKGROUND

Many epoxy based composites used for structural applications in the aerospace industry are composed of toughened epoxy resins. Epoxy monomers containing aromatic moieties tend to have a greater melt viscosity than the alkoxyl based monomers. In addition, epoxy resins composed of solely aromatic epoxy tend to be glassy whereas the flexible alkoxyl based epoxy resins tend to be rubbery. Such resins typically exhibit sub-optimal mechanical properties relative to the glassy resins, for example, lower yield stress.

Dispersing an organically modified layered silicate clay in a polymeric matrix to form a nanocomposite may improve the resulting material’s mechanical properties including increasing yield stress. However, when such a clay is added to a polymeric matrix, the resulting material may lose properties in other areas such as a decrease in glass transition temperature $T_g$ and reduced ductility and toughness.

BRIEF SUMMARY

Epoxy blended nanocomposites containing both rigid aromatic and flexible alkoxyl components were prepared with clay added as a strengthener. The clay was initially dispersed in the polypropylene oxide based epoxy and then combined with an aromatic epoxy to form the blended epoxy resin. The aromatic component of the blend contributes rigidity and higher temperature capability to the material whereas the alkoxyl component is the more flexible, mechanically weaker, component of the blend. When a clay is dispersed in the blend of aromatic and alkoxyl, the clay tends to reside close to the aromatic components, due to electronic interactions between the aromatic ring and the clay sheet. Addition of clay to the alkoxyl based epoxy first, physically places the clay in the toughening, more flexible component of the material, the mobility of the clay is optimized and the mechanically weaker phase is reinforced, thus improving the mechanical properties of the material. Blending epoxies produced both glassy and rubbery nanocomposites at room temperature, depending on the aromatic to alkoxyl ratio.

The accompanying drawings, which are incorporated in and constitute a part of the specification, illustrate various example systems, methods, and so on that illustrate various example embodiments of aspects of the invention. It will be appreciated that the illustrated element boundaries (e.g., boxes, groups of boxes, or other shapes) in the figures represent one example of the boundaries. One of ordinary skill in the art will appreciate that one element may be designed as multiple elements or that multiple elements may be designed as one element. An element shown as an internal component of another element may be implemented as an external component and vice versa. Furthermore, elements may not be drawn to scale.

DESCRIPTION OF DRAWINGS

FIG. 1 is a flowchart showing a procedure for making a nanocomposite.
psi under nitrogen and the temperature was ramped from -50 °C to 250 °C at a rate of 10 °C/min. Disappearance of the (001) peak suggested an exfoliated morphology.

Transmission electron microscopy (TEM) specimens were obtained by microtoming nanocomposite samples, 20 to 70 nm thick, and floating the sections onto Cu grids. 

The XRD pattern of the pre-dispersed clay, FIG. 4, shows two diffraction peaks, 410 and 420. The peak at 2θ=4.8°, d_{001}=1.7 nm, 430, corresponded to the as-received Cloisite 30B. Following intercalation of the alkoxy component of the blend, the peak intensity decreased by approximately 50%, 410, and a second diffraction peak, 420, appeared at 2θ=2.4°, d_{001}=3.4 nm, corresponding to clay layers intercalated with the alkoxy component.

In FIG. 5(a), a TEM image is shown of a nanocomposite with an epoxy ratio of 70 aromatic to 30 alkoxy with clay concentration of 5 wt %. In FIG. 5(b) a TEM image is shown of a nanocomposite with an epoxy ratio of 70 aromatic to 30 alkoxy with clay concentration of 5 wt %. In FIG. 5(c), a TEM image illustrates dispersion of 2 wt % Cloisite 30B in a nanocomposite with an epoxy ratio of 90 aromatic to 10 alkoxy. These figures show the level of dispersion and the areas where the clay is more separate than others.

A Perkin Elmer High Pressure Differential Scanning calorimeter (HP-DSC) was used to determine T_g of the epoxy samples. The resin (8-12 mg) was weighed and placed into a sealed aluminum DSC pan. The tests were performed at 200 psi under nitrogen and the temperature was ramped from -50° C to 250° C at a rate of 10° C/min.
In general, resin modulus increased with either increased aromatic content or increased clay content. For example, the highly aromatic 90:10 nanocomposite has a much higher modulus, 3.1 x 10^4 ± 4 x 10^4 GPa, as compared to 6 x 10^4 ± 7 x 10^4 GPa for the lower aromatic 50:50 nanocomposite. However, up to 67% increase in modulus was also observed in the 50:50 blend when comparing the base resin blend to the resin blend with 5 wt% pre-dispersed Cloisite 30B. The difference in modulus between the samples containing 2 wt% clay, straight addition as compared to the samples with pre-dispersed clay was an increase of 1.3 x 10^4 GPa and an increase of 1.7 x 10^4 GPa for 5 wt% clay addition. In the 70:30 nanocomposite, placing the clay in the alkoxy component resulted in an 60% increase in modulus for the nanocomposite with 2 wt% pre-dispersed clay as compared to the base resin blend, without a corresponding decrease in toughness.

The yield stress also increased with increased aromatic or clay content, again with greater values of strength attained by pre-dispersion. Selectively placing the clay in the alkoxy component was also a significant benefit to the yield stress of most 70:30 nanocomposites made. Addition of 2 wt% pre-dispersed clay increased σ_y by 40% without a corresponding decrease in toughness, relative to the base resin. Addition of 5 wt% pre-dispersed clay increased σ_y by 63%, also without a significant change in the material toughness. The least dramatic influence was observed with the 90:10 resins. In this case, pre-dispersion of the clay had no effect on the overall properties. This may be attributed to the already low concentration of flexible component present in the system. Therefore, the σ_y values of the nanocomposites in the 90:10 series are reduced relative to the base resin because these nanocomposites fail earlier than the base resin. It should be noted that the 50:50 resins also did not yield, therefore the yield stress represented the stress at failure.

In regards to toughness, the nanocomposites in the 50:50 series were rubbery at room temperature and only showed improved toughness when the clay was pre-dispersed in the alkoxy epoxy component. The nanocomposite toughness increased despite the increase of strength and modulus, as evidenced by an increase of 30 MPa for the 2 wt% pre-dispersed nanocomposite and 25 MPa for the 5 wt% pre-dispersed nanocomposite, which is more than a 100% overall increase in calculated toughness resulting in a stronger/stiffer composite.

In general, the mechanically weaker, rubbery regions improved with clay addition to a greater extent than the more rigid, glassy, materials, in terms of strength, modulus, and toughness. Therefore, pre-dispersing offered the greatest benefit in mechanical properties to systems which were initially rubbery, or mechanically weaker than a similar glassy system. The materials with higher T_g values have stronger chemical bonds and while these materials still showed improved properties with clay additions, the enhancements were not as significant as seen in the rubbery materials with the lower T_g.

The blend compositions with greater aromatic content generally resulted in a higher T_g. It was observed that the T_g generally dropped following simple mixing of Cloisite 30B into the epoxy blends. For example, the day offered little or no enhancement of T_g for 90:10 or the 50:50 series of resins. Both, an increase in plasticization and a reduction in the crosslink density typically cause a decrease in T_g. Each of these are plausible contributors to the observed drop in T_g.

The effect of pre-dispersing the clay in the alkoxy component was to recover the initial T_g drop. Pre-dispersion forced the clay into the more mobile component, thus reinforcing the nanocomposite with the pre-dispersion step to the nanocomposite. Selectively placing the clay in the alkoxy component had no effect on the yield stress of most 70:30 nanocomposites made. Addition of 2 wt% pre-dispersed clay increased σ_y over 40% without a corresponding decrease in toughness, relative to the base resin. Addition of 5 wt% pre-dispersed clay increased σ_y by 63%, also without a significant change in the material toughness. The least dramatic influence was observed with the 90:10 resins. In this case, pre-dispersion of the clay had no effect on the overall properties. This may be attributed to the already low concentration of flexible component present in the system. Therefore, the σ_y values of the nanocomposites in the 90:10 series are reduced relative to the base resin because these nanocomposites fail earlier than the base resin. It should be noted that the 50:50 resins also did not yield, therefore the yield stress represented the stress at failure.

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### Table 2

<table>
<thead>
<tr>
<th>Clay Content</th>
<th>T_g (°C)</th>
<th>T_g (°C)</th>
<th>T_g (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% clay</td>
<td>63 +/- 2</td>
<td>32 +/- 2</td>
<td>0 +/- 1</td>
</tr>
<tr>
<td>2% 30B</td>
<td>62 +/- 2</td>
<td>29 +/- 1</td>
<td>-1 +/- 2</td>
</tr>
<tr>
<td>(pre-dispersed)</td>
<td>67*</td>
<td>41*</td>
<td>0*</td>
</tr>
<tr>
<td>5% 30B</td>
<td>66 +/- 1</td>
<td>30 +/- 8</td>
<td>-2 +/- 2</td>
</tr>
<tr>
<td>5% 30B</td>
<td>65*</td>
<td>45*</td>
<td>0 +/- 3</td>
</tr>
</tbody>
</table>

*Data from one sample.

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The single $T_g$ reported within each system indicated a miscible system. Correspondingly, macrophase separation within these blends was not observed by SEM. However, the results collected did suggest a level of phase separation, which allowed for manipulation of the material properties. For example, the 70:30 blend contained 2.3 times, by weight, the amount of aromatic component over alkoxy; (2x by volume). While the flexible (alkoxy) component was likely well integrated into the blend, there would remain large regions composed solely of the aromatic component. As such, an affinity between the silicate clay and the aromatic segment which pulled the clay into these regions would render the flexible component deficient in clay content. The SEM images in FIGS. 7(a) and 7(b) show distinct regions of the 70:30 blend containing significant quantities of clay, 710, while adjacent regions of the blend are essentially absent of clay, 720.

The 50:50 series contained nearly equal quantities of both aromatic and alkoxy components. In this case, SEM images in FIG. 8(a) and 8(b), show much greater homogeneity in the dispersion of the silicate clay, relative to the 70:30 blend of FIG. 7. The disparity in silicate distribution within the 70:30 system had significant influence in the nanocomposite properties, and allowed manipulation of those properties by selectively placing the clay in the alkoxy region.

Significant benefit from pre-dispersion was observed within the mechanical property data. In this case, positioning the silicate reinforcement within the flexible component allowed improved mobility of the clay, translating into improved composite strength and modulus.

Evidently the clay did reside in a specific region of the blend as provided by SEM images. Furthermore, the increase in $T_g$ on pre-dispersing the clay suggested that the clay restricted epoxy chain motion within the mobile component of the blend. Tensile test data from the epoxy blends revealed that the mobility of the silicate layers within the matrix offered improved resin toughness. This was seen by the improved toughness and significant enhancement in strength within the pre-dispersed 50:50 resins, relative to other resins in the series which are glassy at room temperature.

While the systems, methods, and so on have been illustrated by describing examples, and while the examples have been described in considerable detail, it is not the intention of the applicants to restrict or in any way limit the scope of the appended claims to such detail. It is, of course, not possible to describe every conceivable combination of components or methodologies for purposes of describing the systems, methods, and so on provided herein. And while several examples have been provided at different epoxy ratios (70:30 vs 50:50), it should be evident to one skilled in the art that Applicant is also claiming mixtures comprising an equivalent ratio between 70:30 and 50:50 of aromatic epoxy to alkoxy epoxy or aliphatic epoxy, respectively. Additional advantages and modifications will readily appear to those skilled in the art. Therefore, the invention, in its broader aspects, is not limited to the specific details, the representative apparatus, and illustrative examples shown and described. Accordingly, departures may be made from such details without departing from the spirit or scope of the applicants' general inventive concept. Thus, this application is intended to embrace alterations, modifications, and variations that fall within the scope of the appended claims. Furthermore, the preceding description is not meant to limit the scope of the invention. Rather, the scope of the invention is to be determined by the appended claims and their equivalents.
10. The method as set forth in claim 9, where the first temperature is at least 40° C.

11. A method of preparing a toughened clay-epoxy nanocomposite comprising: preparing a curable composition according to the method as set forth in claim 9; and curing the curable composition according to a curing protocol to form a toughened clay-epoxy nanocomposite, where the curing protocol includes heating at a second temperature for a period of time and heating at a third temperature greater than the second temperature for a period of time.