THERMAL AND VISCOELASTIC PROPERTIES OF SC-15 EPOXY RESIN COMPOSITES MODIFIED WITH MONTMORILLONITE NANOCLAY EXPOSED TO UV RADIATION

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1 Introduction

Wide use of polymers as matrix for fiber reinforced polymer composites used as replacements of parts in aerospace, automobile and marine applications exposes them to a variety of environmental attacks, where their thermal and viscoelastic behavior are often affected. Several research attempts have been made to resolve some of these drawbacks, where different fillers have been explored with different polymer systems with reported variations in desirable properties [1-4]. Montmorillonite nanoclay (MMT) used as nanofiller has several benefits, such as improved thermal and mechanical properties, and has shown the prospect of impeding degradation mechanisms often caused by prolonged exposure to UV radiation and elevated temperatures [5]. Microstructural changes in polymers due to nanoclay addition leading to polymer property enhancements are controlled by numerous processing factors [6, 7], including interfacial chemistry and molecular mobility during curing, reaction time, enthalpy, vitrification, activation energy of reaction and viscoelastic properties [8-10].

There are contravening reports about increased photo-oxidation activities in polymers exposed to UV radiation due to the presence and interaction of transition elements used during surface modifications of MMT to ensure compatibility with host polymers [11]. These transition elements in MMT invariably affect the rate of photo-initialized chemical reactions leading to different outcomes of different MMT systems. In a recent study MMT nanoclays with different surface modifications were used in modifying DGEBA epoxy and exposed to UV radiation [12]. Result of the study showed that not only does surface modification affect mechanical and thermal properties; it also influences interactions between UV rays and epoxy molecules.

Studies have also shown that in many instances where polymeric composites are exposed to UV radiation, most of their properties are enhanced during the initial stages prior to the onset of damaging effects of UV radiation [13, 14]. Energy of UV rays at 340nm is high enough to dissociate most bonds present in polymers resulting in material brittleness and loss of strength and other properties [14, 15]. Therefore bonds formed between nanoclay and epoxy molecules may be strong enough to retard this process leading to extended service life and overcome longevity related issues caused by UV exposure in polymeric composite materials.

In the current studies, different amounts of montmorillonite nanoclay Nanocor® I.28E was used as nanofiller to modify SC-15 epoxy resin commonly used as matrix for FRP. Influence of different amounts of MMT on thermal and viscoelastic properties of SC-15 composites were characterized after 2500 hours of UV conditioning.

2 Materials and Conditioning

2.1 Materials

Commercially available two part diglycidyl ether of bisphenol A (DGEBA) based SC-15 epoxy resin system from Applied Poleramic Inc., with typical chemical structure shown in Fig. 1. Montmorillonite nanoclay - Nanomer® I.28E (MMT) used as nanofiller from Nanocor® was obtained from Sigma Aldrich with typical chemical structure shown in figure 2.

![Fig. 1. Typical chemical structure of DGEBA](image-url)
2.2 Sample Preparation and Fabrication

Samples for the study were fabricated using unmodified SC-15 epoxy resin system modified with 1-3 wt. % MMT. MMT was first dried in conventional oven prior to dispersing into SC-15 epoxy resin part A using magnetic stirring technique. SC-15 containing MMT was stirred for 24 hours to ensure uniform distribution of nanoclay. Part B of SC-15 epoxy system was subsequently added in a mass ratio of 100 part A to 30 part B. The mixture was then stirred mechanically followed by desiccation and finally poured into molds and cured to fabricate samples according to manufacturers’ recommended cycle. Thus, samples in the molds were cured in ambient temperature for 24 hours followed by 4 hours of post curing and properties characterized.

2.3 Nanocomposites

Most properties of epoxy polymer composites generally depend on the processing parameters including viscosity and curing temperature. Epoxy cure reactions with amine hardener involve epoxide group reacting either with primary or secondary amine from the hydroxyl groups increasing the rate of reaction at the onset and subsequent slow down due to onset of gelation [7]. Presence of MMT during curing typically affects rheological properties influencing gelation and development of viscoelastic and ultimate properties of the final composites. Hence, reported enhancements in material property associated with nanocomposites.

2.4 Conditioning

Behavior of SC-15 epoxy composites infused with nanoclay in outdoor settings where UV radiation and other environmental attacks are imminent was studied using an accelerated weathering chamber QUV/SE (Q-Lab, Ohio). The QUV/SE equipped with 340nm fluorescent lamps and operated at a temperature of 60°C and irradiance of 0.90W/m² simulates real-life environmental conditions. In this work, samples were exposed to up to 2500 hours of conditioning. With these parameters, every 500 hours of UV exposure generated in the chamber of the equipment mimics conditions of yearly UV radiation dosage in Montgomery, Alabama.

2.5 Characterization

Characterization of material properties throughout the study was done on each epoxy composite prior to and post UV radiation conditioned for comparison.

2.5.1 Dynamic Mechanical Analysis

Influence of different amounts of Nanomer® I.28E on viscoelastic properties of various SC-15 epoxy composites were studied prior to and after conditioning using dynamic mechanical analyses (DMA). TA Instruments’ Q-800, operating in dual cantilever mode at an oscillation frequency of 1Hz and amplitude of 15μm was used in this study. Samples were machined and tested according to ASTM D4065-03. DMA scans were performed at 5°C/min from 30 to 180°C, where glass transition temperature was determined from the peak of Tan delta curve.

2.5.2 Thermogravimetric Analysis

Thermal stability of SC-15 composite samples modified with various amounts of MMT was studied using thermogravimetric analysis (TGA) using TA Instruments’ Q-500. The Q-500 equipment was purged with dry nitrogen flowing at 60 mL/min with each sample weighing between 13–15mg. Furthermore, samples were scanned at three other
scanning rates (5, 20 and 30°C/min) to determine activation energy of decomposition along with 60-minute half-life. Data from the test were analyzed to determine how different amounts of MMT influences decomposition kinetic parameters of SC-15 prior and post UV exposure.

3.0 Results

High-resolution TEM micrographs were obtained throughout the samples to establish nanoclay dispersion for various MMT compositions under the study. Properties enhancements with the incorporation of nanoclay have been well established to have dependency on the degree of dispersion, and interaction with the host polymer molecules to form strong interfacial bonding [11]. TEM gives a qualitative analysis of nanoclay dispersion in the epoxy composites. Given the same manufacturing technique, we assume a complete dispersion of MMT within 1 wt. % clay loading.

Therefore, TEM studies were performed on 2 and 3 wt. % samples and are shown in figure 3 (a, b). The micrographs obtained represent typical exfoliated structure and loose intercalated tactoids in ordered stacked.

3.2 Conditioning

During sample conditioning in QUV/SE chamber only one surface of each sample was exposed to UV radiation. At the onset of the studies, there was slight distinction in color between the different SC-15/MMT compositions and neat samples. As samples were conditioned to 500 hours of exposure, there were visual changes in exposed surfaces. Exposed surfaces of post conditioned samples showed yellowish discoloration due to interaction between epoxy molecules on the exposed surface and photons from UV radiation. Yellowish discoloration began and progressed up to 1000 hours of exposure. After 1500 hours of exposure, surface discoloration intensified and the intensity of discoloration increased with increasing clay content, particularly among MMT infused samples. This indicates peculiar interaction between the epoxy molecules and UV rays caused by the presence of MMT. The metals (Fe²⁺) used in clay modification may have been responsible for the discoloration as studies have indicated [17-19].

After 1500 hours, there was no visual distinction between all samples as discoloration intensified. The interaction led to formation of microcracks, which over time act as micro channels for moisture and other environmental attacks. SEM micrographs obtained from the surface of each sample after 1500 hours of exposure are presented in figure 4, showing multiple cracks with different sizes throughout the samples. Micro crack formation increased after 1500 hours and crack sizes increased with increasing clay content. SEM studies indicated the growth of grooves between the cracks especially for neat and 1 wt. % samples, while 2 wt. % and 3 wt. % samples showed much less. Presence of the cracks also act as stress concentration sites, reducing load bearing capacity and thermal diffusivity of these types of materials. At the end of the study, SEM micrographs showed indistinguishable microcracks throughout the samples.

Fig. 3. TEM micrographs for 2 and 3 wt. % MMT loading respectively.
3.4 Viscoelastic Property

Addition of MMT showed a slight increase in viscoelastic properties at the onset of the study with 1 wt. % showing the most enhancement of about 12 %, possibly due higher degree of exfoliation. On the other hand glass transition temperature remained unchanged for 1 and 2 wt. % samples and a mere 3 % improvement for samples with 3 wt. % loading of MMT with typical thermograms shown in figure 4 and average values in figure 5. Influence of nanoclay reinforcements on cure behavior of thermosets has also been widely reported in literature [7-10]. However, in the current studies, all samples were fabricated using the same processing parameters with no consideration for the influence of MMT on cure behavior leading to reported results.

Fig. 4. SEM micrographs of exposed (a) neat, (b-d) 1 – 3 wt. % sample surfaces exposed to 1500 hours UV.

Fig. 5. Typical DMA thermogram of sample cured according to manufacturers’ cycle.
As samples went through conditioning, there were slight improvements in the storage modulus of all samples during the initial stages, perhaps due to residual crosslinking. This was particularly much needed energy to complete the crosslinking process in MMT samples, based on the previous assumption and studies reported in literature. Viscoelastic properties of each MMT loadings peaked at different times prior to the onset of material property degradation. For example, maximum storage modulus was observed for 1, 2 and 3 wt. % after 500, 1000 and 1500 hours of exposure respectively. However, glass transition temperatures peaked after 500 hours of exposure for all nanoclay infused samples, while that of neat was observed after 1000 hours.

Peak values of storage modulus constituted approximately 13, 25 and 19 % for 1, 2 and 3 wt. % respectively compared to unexposed neat samples.

Glass transition temperatures on the other hand were observed to be 8, 7, and 7 % for 1, 2 and 3 wt. % MMT respectively.

At the end of the study, although storage modulus decreased after peaking, it actually constituted 6 and 9% improvements for neat and 2 wt. % respectively and remained unchanged for 1 and 3 wt. % samples.

### 3.5. Thermo-Mechanical Properties

Dimensional changes during thermo-mechanical analysis (TMA) depend on the strength of the bonds within the network chains and mobility of the chain segments during glass transition. Segmental mobility of polymer chains within a network leads to creation...
of free volume, which reduces thermal diffusivity, mechanical and viscoelastic properties, and makes such materials susceptible to solvent penetration [20]. Generally, thermal expansion is a reversible phenomenon with less impact on the overall strength of bonds; however, significant occurrences can influence the life expectancy of polymers. Therefore, coefficient of thermal expansion values can be used as a measure to compare strength and durability of different polymer compositions. Behaviors of SC-15 composites under the study were different as expected with typical thermographs graphically represented in figure 7, and summary of the results in Table 1. The results showed that addition of nanoclay increased the coefficient of thermal expansion (CTE) before and after transition. The observed increase in CTE can be attributed to an increased intermolecular bond length due to nanoclay addition, and subsequently decreasing the intermolecular force of attraction leading to ease of molecular movement.

Samples with 2 wt. % showed maximum pre transition CTE value, approximately 38% higher than that of neat, while the difference between pre and post transition CTE values showed minimum value. This may be due to formation of stronger chain networks between epoxy molecules and MMT nanoclay particles preventing segmental mobility of the molecules during glass transition hence lower values.

Additionally, lower values in CTE differences meant there was less free volume created by the movement during transition, and therefore, further heating beyond the transition point may lead to degradation. Worth noting that during thermal cycles at high temperatures, plastics not only soften, but can also undergo thermal degradation leading to questions about their durability.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Coefficient of Thermal Expansion CTE, µm/(m·° C)</th>
<th>CTE difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 wt. %</td>
<td>75.50±2.45</td>
<td>106.30</td>
</tr>
<tr>
<td>1 wt. %</td>
<td>81.09±2.57</td>
<td>97.11</td>
</tr>
<tr>
<td>2 wt. %</td>
<td>104.30±1.24</td>
<td>76.57</td>
</tr>
<tr>
<td>3 wt. %</td>
<td>80.30±6.23</td>
<td>94.73</td>
</tr>
</tbody>
</table>

Fig. 9. TMA thermograms of post cured SC-15/nanoclay samples exposed to 2500 hours UV.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Coefficient of Thermal Expansion CTE, µm/(m·° C)</th>
<th>CTE difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 wt. %</td>
<td>79.93±3.56</td>
<td>101.74</td>
</tr>
<tr>
<td>1 wt. %</td>
<td>76.34±5.43</td>
<td>115.82</td>
</tr>
<tr>
<td>2 wt. %</td>
<td>76.31±7.67</td>
<td>107.76</td>
</tr>
<tr>
<td>3 wt. %</td>
<td>81.64±4.42</td>
<td>103.39</td>
</tr>
</tbody>
</table>

Table 1. CTE of unconditioned neat and nanophased SC-15 composite samples

Table 2. CTE of unconditioned neat and nanophased SC-15 composite samples

Fig. 8. TMA thermograms of unconditioned neat and nanophased SC-15 composite samples.
Typical thermograms at the end of the study shown in figure 9 showed more settled behavior during glass transition compared to unconditioned where material behavior varied widely. Summary of CTE at the end of the study is presented in table 2.

3.2 Thermogravimetric Analysis (TGA)

Inherent structure of MMT has been shown to trap volatiles during decomposition leading to enhanced thermal properties [21] and also has the tendency to prevent moisture absorption in the event of moisture exposure. Influence of different amounts of MMT on thermal stability of SC-15 was studied under conventional TGA experiments, where three samples from each set were scanned at 10°C/min from 30 to 850°C. Typical thermograms are shown in figure 10(a) and corresponding derivative curves in Fig. 10(b). Onset of degradation was determined as the temperature at which noticeable weight change and was considered mass loss at 5% of the original mass, while decomposition temperature was determined from the peak of the derivative weight loss curve. Onset and temperatures at which 50% of the original material is lost are reported as T_s, T_50 respectively and presented in table 3. Results from TGA on unconditioned samples showed insignificant onset and decomposition temperatures along T_50 values. Thermal decomposition of polymeric materials can be complex in nature involving several mechanisms acting individually or simultaneously, and therefore difficult to define degradation mechanism for any particular system [22]. Degradation may take different forms based on the type and strength of the bonds present, such forms as side-group elimination, random scission and depolymerization [22] resulting in the formation of free radicals which further degrades the polymer over time.

Thermal stability and degradation of cured epoxy resin thermosets typically depends on the hydroxyl group formation and structure of amine curing agent used during curing [23]. During UV radiation conditioning, kinetic parameters remained unchanged for the first 500 hours, after which there was gradual decrease till the end of the study. However between samples exposed to the same amount of UV radiation, kinetic parameters remained identical such as observed in unconditioned samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T_s, °C</th>
<th>T_50, °C</th>
<th>T_decomp, °C</th>
<th>Residue, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 wt. %</td>
<td>355.72</td>
<td>406.50</td>
<td>367.67</td>
<td>3.37</td>
</tr>
<tr>
<td>1 wt. %</td>
<td>356.62</td>
<td>405.20</td>
<td>370.34</td>
<td>4.53</td>
</tr>
<tr>
<td>2 wt. %</td>
<td>355.10</td>
<td>404.41</td>
<td>368.87</td>
<td>5.19</td>
</tr>
<tr>
<td>3 wt. %</td>
<td>352.45</td>
<td>403.27</td>
<td>366.45</td>
<td>5.54</td>
</tr>
</tbody>
</table>

To further determine the influence of different amount of MMT on thermal stability, activation energy of decomposition was determined for each
sample, based on data obtained from the thermal parameters at the maximum rate of decomposition from each heating rates, using Flynn – Wall – Ozawa method. Activation energy of decomposition measures thermal stability between different polymer composite systems, and was observed to increase gradually during the initial exposure. As samples go through several hours of UV exposure, activation energy of decomposition evolved possibly due to residual crosslinking in all samples except samples with 2 wt. % MMT which slightly decreased. After 1000 hours of UV radiation, most of the decomposition parameters decreased till the end of the study and summary of the result shown in table 4. Activation energy of decomposition on the other hand increased gradually with exposure time and reached maximum values for all samples after 2000 hours. Worth noting that activation energy of decomposition of nanophased samples was higher than the neat system in all cases as can be seen in table 5.

Values of activation energy of decomposition as expected were different and varied based on the composition of the system. The decomposition behavior observed with all samples in nitrogen was a single step; however, the derivatives of the weight loss curves showed a second peak relatively close to the main decomposition peak (Fig. 10b). At higher heating rates, intensity of the main decomposition peak diminishes while the secondary peak gained prominence in all nanophased samples, emphasizing the dependency of mechanism of decomposition on the composition of the material.

Table 4. Decomposition parameters of Neat and nanophased SC-15 composites exposed to 2500 hours of UV radiation

<table>
<thead>
<tr>
<th>Sample</th>
<th>T5, °C</th>
<th>T50, °C</th>
<th>Tdecomp, °C</th>
<th>Residue, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 wt. %</td>
<td>334.21</td>
<td>374.34</td>
<td>360.18</td>
<td>1.66</td>
</tr>
<tr>
<td>1 wt. %</td>
<td>336.60</td>
<td>378.63</td>
<td>359.88</td>
<td>2.17</td>
</tr>
<tr>
<td>2 wt. %</td>
<td>331.32</td>
<td>380.32</td>
<td>350.38</td>
<td>3.21</td>
</tr>
<tr>
<td>3 wt. %</td>
<td>333.54</td>
<td>381.08</td>
<td>345.42</td>
<td>3.80</td>
</tr>
</tbody>
</table>

Table 5. Activation energy of decomposition of neat and nanophased SC-15 conditioned samples

<table>
<thead>
<tr>
<th>Sample/Exposure Time, hr</th>
<th>Activation Energy of Decomposition, KJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 wt. %</td>
</tr>
<tr>
<td>0</td>
<td>112.20</td>
</tr>
<tr>
<td>500</td>
<td>109.18</td>
</tr>
<tr>
<td>1000</td>
<td>141.29</td>
</tr>
<tr>
<td>1500</td>
<td>167.92</td>
</tr>
<tr>
<td>2000</td>
<td>216.73</td>
</tr>
<tr>
<td>2500</td>
<td>121.18</td>
</tr>
</tbody>
</table>

Summary

From the results, it can be seen that thermal and viscoelastic properties degradation due to UV radiation exposure did not follow any particular trend. Different amounts of MMT influenced these properties differently. Although addition of MMT to SC-15 epoxy resin had insignificant influence over onset and decomposition temperatures, there was significant influence on the activation energy of decomposition.

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References

The text seems to be a citation list, likely from a scientific journal, containing information on various studies, articles, and research works. It includes a mix of references to different fields within polymer science and technology, suggesting an extensive review of literature. Here is a structured representation of the text: