MECHANICAL AND THERMAL PROPERTIES OF CARBON/EPOXY NANOCLAY COMPOSITES EXPOSED TO SYNERGISTIC EFFECT OF UV RADIATION AND CONDENSATION

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Abstract

The objective of this work was to investigate the mitigating effects of montmorillonite nanoclay (MMT) if any, on the properties of carbon fiber reinforced composites (CFRC) infused with different weight percentages of MMT and exposed to UV radiation and condensation. Composites used in this study were control and with 1- 3 wt. % of nanoclay. Samples were exposed to 15 days of continuous UV radiation and condensation using QUV/SE accelerated weathering system. Mechanical and thermal properties were characterized by compression tests, thermo-gravimetric analysis (TGA) and dynamic mechanical analyses (DMA) according to ASTM standards. Surface morphology of exposed samples was characterized through Scanning electron microscopy (SEM). These properties were characterized every 120 hours of exposure. Samples exposed to condensation did not follow any specific pattern, although there was a decrease in mechanical properties in all samples.

1. Introduction

Response of polymeric materials to harsh environmental conditions has been one of the major concerns during their usage in engineering applications, due to the viscoelastic nature of polymers. Polymeric composites once exposed to UV radiation absorbs the UV rays which in turn initiates photo-oxidation reaction in the matrix leading to formation of radical chemical groups and subsequent chain reaction [1-2]. This is also known as thermo-oxidation degradation of polymers. Thermo-oxidation degradation involves changes in both physical and chemical structures of the epoxy composites, which includes oxidation, chain scission and or cross-linking and subsequent weight loss result of which reduces the viability of material usage in structural application. Degradation mechanisms in polymers have shown to consist of thermal and thermo-chemical degradation. Thermal and photo-oxidation are due to the energy of the UV photons incident on the surface of the matrix, which interacts with the polymer molecules changing the thermodynamic equilibrium of the system. When UV photons are active, energy level is high enough to dissociate chemical bonds in the polymer chains [3] leading to the formation of microcracks on the surfaces and eventual matrix erosion. Also UV radiation inadvertently affects the viscoelastic properties in the form of elevated temperature, lowering the storage modulus and glass transition temperature. Polymer composites materials become susceptible to impact damage due to their relative brittleness. Subsequent exposure of these materials to moistures poses less challenge to moisture absorption or seeping through the cracks and weakening of the fiber-matrix interfacial bonds [2]. Absorption of moisture into the epoxy leads to hydrolysis and plasticization. Hydrolysis is reversible short term moisture absorption and desorption phenomenon with minimum damage to the polymer. Prolonged moisture absorption leads to permanent damage which results in thermo-physical, mechanical changes and also changes in the chemical structure and ultimate deterioration of material properties especially due to hydrothermal aging raising durability issues [4].

Moisture absorption by epoxies and fiber reinforced polymer composite materials depends on a variety of factors such as temperature, filler type, strength of the interfacial bonds between the fibers and the matrix, flaws such as voids and fiber orientation during processing [5]. Exposure of polymeric composites to sequential UV radiation and moisture

conditioning could accelerate the aging process than exposure to either one of the environmental factors or conditioning.

This study seeks to investigate effects of MMT loading on the thermal and mechanical properties of samples exposed to both UV radiation and condensation in comparison to neat samples with no MMT.

2 Materials and Conditioning

2.1 Materials and sample preparation

Materials used for the study were commercially available SC 15 epoxy, a bisphenol A based epoxy which comes in two parts, A and B from Applied Poleramics Inc, montmorillonite nanoclay I.28E (MMT) from Nanocor® used as a filler, and satin weave carbon fiber used as a reinforcement to fabricate both neat and nanocomposite samples. Surface of the MMT clay has been modified by the supplier, enhancing the chemical bonding between the epoxy molecules and the nanoclay, and ultimately increasing the cross-linking density. Dispersion of MMT into the epoxy system was done using magnetic stirring for about 5-6 hours and subsequent infusion into the pre-arranged fiber cloth using VARTM technique. Fiber cloths alignment is critical, since any fiber misalignment promotes moisture absorption [4] and ultimately affects the mechanical properties of the final laminate. Laminates fabricated for this study were neat composites with no nanoclay and those with 1-3 wt. % loading of MMT. Laminates were allowed to cure over a 24 hour period in ambient temperature followed by post curing in an oven at a temperature of 100^{o} C for 2 hours, according to manufacturer's recommendation. The post cured laminates were machined for sample preparation for variety of tests and conditioning.

2.2 Conditioning

Samples were subjected to cyclic UV radiation and condensation in accordance with ASTM G-154 using 4 hours of UV radiation at 60° C alternating with 4 hours of condensation at 50° C over a period of 360 hours. QUV/SE (Q-Lab, Ohio) accelerated weathering chamber equipped with 340nm fluorescent lamps generating irradiance of 0.68W/m^2. Weight change of samples was monitored every 24 hours while mechanical and thermal properties were characterized every 120 hours.

2.3 Testing

2.3.1 Compression Tests

Quasi static compression test was performed using a 10 KN Instron Servo-hydraulic materials testing system (MTS-890) to investigate the rate-dependent behavior of the woven carbon fiber reinforced composites during quasi-static loading using ASTM D695-02. A set of five samples were tested from each laminate with dimensions of 12.75 x 12.75 x 5.0 mm. Samples from each type were tested under displacement mode with a constant cross head speed of 1.27 mm/min at room temperature translating into a strain rate of 1.63E-3 s^{-1}. Dynamic compression tests on the other hand were performed using Split Hopkinson Pressure Bar (SHPB) with three different pressures yielding strain rates of 421, 505 and 605s^{-1} respectively. During testing, the specimen was sandwiched between two identical steel bars known as incident and transmission bars. A striker bar of the same material as the incident bar impacted the incident bar which generated a longitudinal compressive incident stress pulse that traveled down the incident bar and was recorded by a strain gauge mounted on the incident bar. Part of the pulse reaching the incident bar and sample interface got reflected back into the incident bar in the form of a tensile pulse while the remaining traveled through the specimen into the transmission bar. Record of reflected pulse and transmitted pulse gave the strain rate and stress as functions of time respectively. Strain induced in the specimen was obtained by integrating the strain rate versus time plot. Strain rate ($\dot{\varepsilon}$), strain (ε), and stress (σ) of the specimen were determined by equations 1-3 [6] from reflected and transmitted pulses,

$$\dot{\varepsilon}(t) = -\frac{2C_0}{L_s}\varepsilon_R(t) \qquad (1)$$

$$\varepsilon(t) = -\frac{2C_0}{L_s}\int_0^t \varepsilon_R(t)dt \qquad (2)$$

$$\sigma(t) = \frac{\mathrm{E}_b\mathrm{A}_b}{\mathrm{A}_s}\varepsilon_T(t) \qquad (3)$$

Where, E_b, A_b and ρ_b; and E_s, A_s and ρ_s are the modulus, cross-sectional area and density of the bar

and specimen respectively, and $C_0 = \sqrt{E_b / \rho_b}$ is the longitudinal wave velocity in the incident bar, L_s is the specimen length and $\varepsilon_R(t)$ and $\varepsilon_T(t)$ are the time-dependent reflected and transmitted strains respectively.

2.4 Thermal Characterization

2.4.1 Thermogravimetric Analysis (TGA)

Effects of MMT on the thermal properties of both conditioned and unconditioned samples were studied using thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA) According to ASTM standards. Dynamic or non-isothermal TGA were performed according ASTM D3850-02using TA instruments Q500. The experiments were performed over a temperature range of 30° C to 850° C. at a heating rate of 10° C/min. Three samples were tested from each sample type with their weight in the range of 10-15mg. Samples were taken from both conditioned and unconditioned laminates and tested for comparison.

2.4.2 Dynamic Mechanical Analysis

Dynamic mechanical measurements were carried in three point bending mode in accordance to ASTM 4065-06 using TA instruments setup DMA Q800. Three rectangular samples with dimensions 60 x 13 x 3.5 mm^3 (length x width x thickness) were machined from each laminates, both conditioned and unconditioned for testing. The tests were performed at a frequency of 1 Hz and a heating rate of 5° C/min from 30° C to 180° C under nitrogen environment. The glass transition temperature (T_g) was determined using the maximum peak of the loss factor (tanδ) curve.

3 Results and Discussion

3.1 Surface Characterization

After conditioning, surface of all samples showed whitish discoloration due to chemical changes caused by the synergistic effects of UV and condensation. Physical changes such as presence of matrix cracking and surface roughness were observed throughout the samples. Morphological studies were conducted on the surfaces using scanning electron microscope (SEM) – JEOL JSM 5800. Distinguishable microcracks were observed on all the samples regardless of the percent weight loadings of MMT as indicated in figure 1.

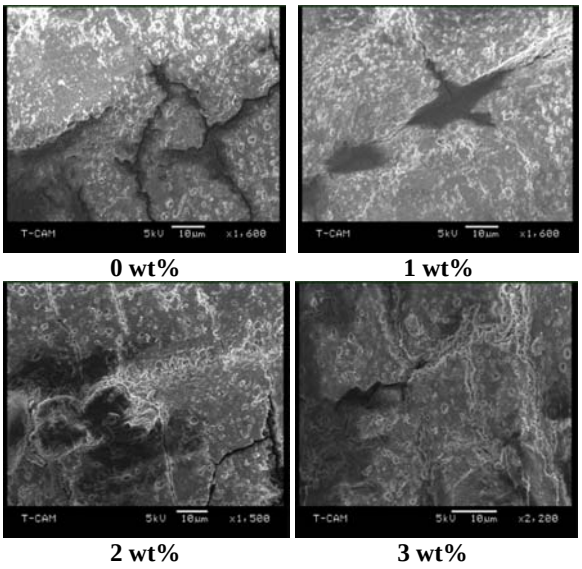

Figure 1. SEM of conditioned sample surfaces

During conditioning, moisture absorption was observed not to be obeying Fickian second law of diffusion, either due to limited exposure time or absorption characteristic of polymeric composites samples were non Fickian. Sample weighing was done right after the condensation cycle, where samples were removed from the chamber, wiped with clean tissue and weighed. At the end of the study, it was observed that the overall weight gained due to absorption of moisture by 2 and 3 wt% samples were approximately 0.10 and 0.11% respectively. Whiles, neat and 1 wt% was recorded as 0.20 and 0.16% weight gained. This could be attributed to the barrier property effect exhibited by the nanoclay which impedes moisture uptake.

3.2 Mechanical Tests

Quasi-static compression loading tests of unconditioned and conditioned samples showed enhancements in both strength and modulus with increasing content of nanoclay and the results are shown in tables 1 and 2 for baseline samples and those tested after 15 days. 3 wt% samples gave the best properties in terms of materials strength and

modulus with an increase of approximately 14% compared to the neat system at room temperature. A similar trend was observed with these material properties during the first 10 days of conditioning, with the strength increasing with increasing weight percent loadings of MMT. However, at the end of the study, 2 wt% samples showed better strength (33.30%) than 3 wt%, although 3 wt% showed the best modulus of 13.08 GPa constituting approximately 10% of enhancement when compared to the neat system at the end of the study. The enhancements can be attributed to the barrier property of the nanoclay preventing the absorption of moisture that leads to the deterioration in material strength when exposed to both UV and moisture at elevated temperature of 50° C. Modes of failure in all samples were mainly delamination and kink band formation. Typical stress-strain curves obtained from samples tested before and after conditioning are shown in figures 2 and 3.

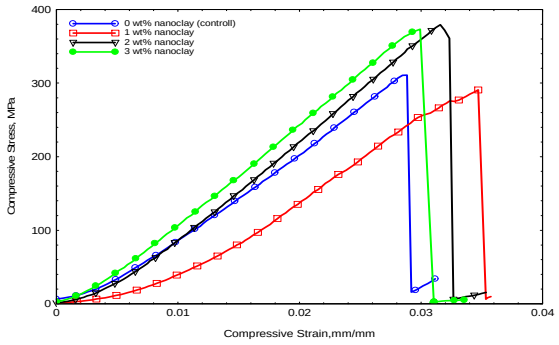

Figure 2. Compressive stress-strain curve of samples before conditioning

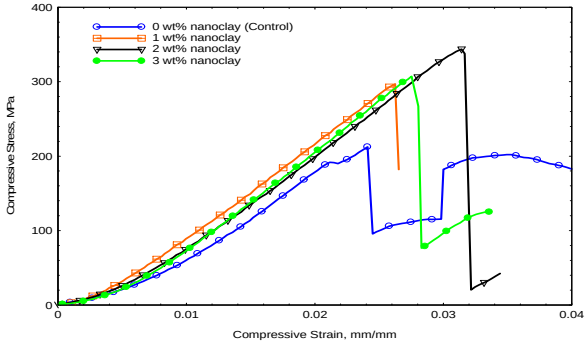

Figure 3. Compressive stress-strain curve of samples after conditioning

Table 1. Compressive strength of quasi-static tests

Strength, MPa	Room Temperature	% Change	UV-Conden.	% Change
0 wt%	265.82	-	245.56	-
1 wt%	275.07	3.48	324.29	32.06
2 wt%	304.95	10.29	327.34	33.30
3 wt%	326.27	22.17	302.17	23.05

Table2. Compressive modulus of quasi-static test

Modulus, GPa	Room Temperature	% Change	UV-Conden.	% Change
0 wt%	11.20	0.00	11.88	
1 wt%	11.34	1.25	12.46	4.88
2 wt%	12.20	8.93	12.88	8.42
3 wt%	13.20	17.86	13.08	10.10

At the end of the study period, it was observed that the modulus of all samples increased while the strength decreased when compared to their respective unconditioned samples at room temperature obtained prior to conditioning. It was observed that as the exposure time increases, the average compressive strength decreased for the neat system. For the samples with nanoclay strength decreased initially up to ten days before increasing for both 1 and 2 wt. % samples. However, the trend observed in 3 wt. % samples was inconsistent with the rest of the nanoclay infused samples, and a similar behavior was observed in modulus curves.

Typical dynamic stress-strain curves of conditioned and unconditioned samples at strain rate of $640s^{-1}$ are shown in figures 4 and 5. Examination of the stress-strain curves showed that all the samples including the neat exhibited linear elastic behavior up to a point before undergoing plastic deformation resulting in the complete failure of the samples at higher strain rates. Mode of failure in all samples varied from lower to higher strain rates. At lower strain rates, the failure mode in unconditioned samples was kinking, whiles delamination was observed in conditioned samples. However at higher strain rates, modes of failure in both conditioned and unconditioned samples were interlayer delamination,

fiber breakage, fiber pulled-out and buckling.

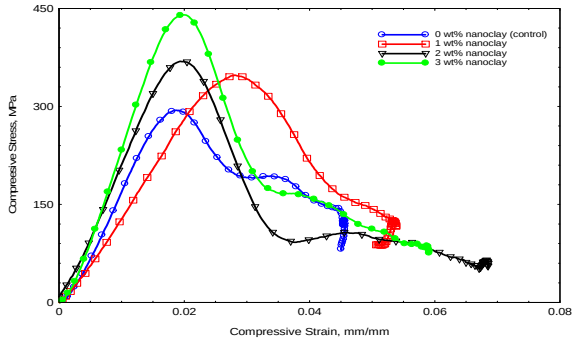

Figure 4. Compressive stress-strain curves of unconditioned samples at 640s^{-1}

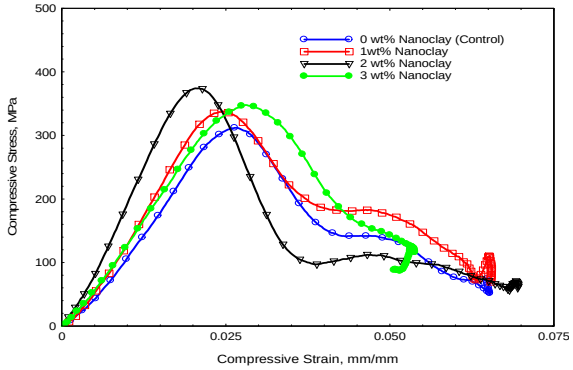

Figure 5. Compressive stress-strain curves of conditioned samples at 640s^{-1}

A strong rate dependency was observed in the modulus and peak stress obtained, and also on the ductility of the testing samples.

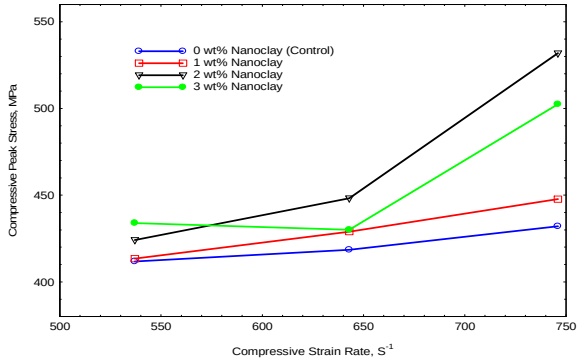

Figure 6. Compressive peak stress versus strain rate obtained from unconditioned samples

Generally, modulus and maximum strengths of these material increases as the strain rate increases while ductility decreases. This was observed in data obtained for the modulus of unconditioned samples tested as indicated in figure 6. A different trend was observed after conditioning as shown in figure 7. Similarly, test data obtained for compressive peak stresses from unconditioned and conditioned are shown graphically in figures 8 and 9, where no particular trend was observed. All the samples showed lower modulus and peak stress values after conditioning.

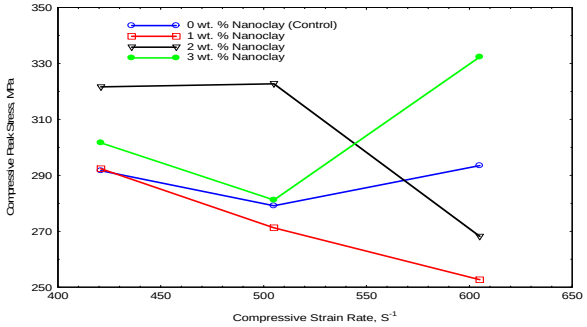

Figure 7. Compressive peak stress versus strain rate obtained from conditioned samples

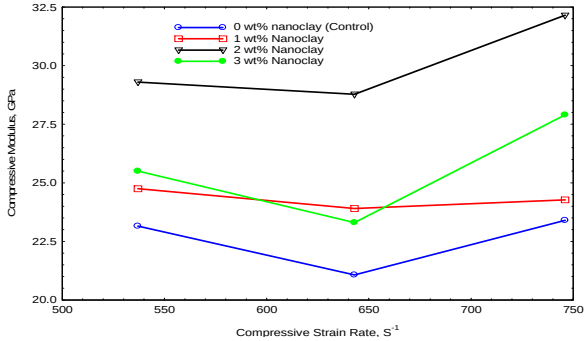

Figure 8. Compressive modulus versus strain rate obtained from unconditioned samples

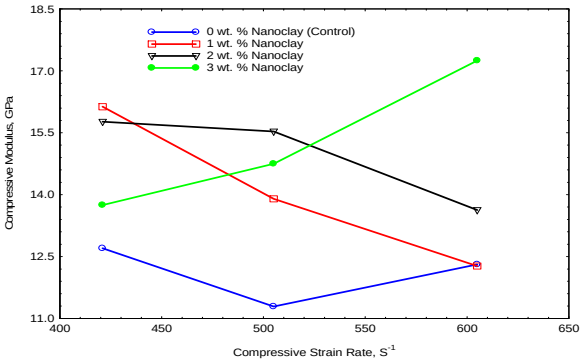

Figure 9. Compressive modulus versus strain rate obtained from conditioned samples

3.3 Thermal Analysis

Thermogravimetric curves obtained for unconditioned samples at room temperature showed the decomposition temperature for neat to be about 332° C and 336° C for nanophased samples. At the end of the study, a similar trend was observed with decomposition temperatures of all conditioned samples between 331° C and 335° C. These results show that the effect of montmorillonite had little to no effect on the decomposition temperature of the samples used for this study. Results of post conditioned samples showing decomposition temperature is shown in fig. 10.

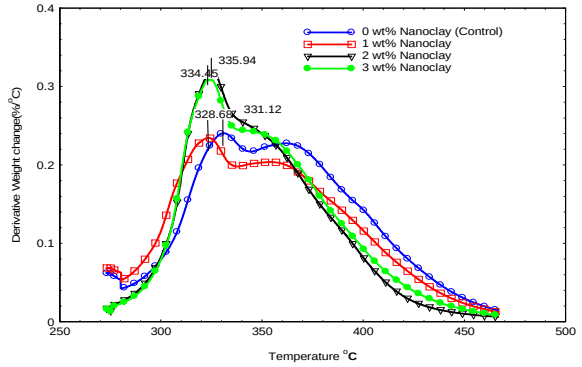

Figure 10. Decomposition temperatures of conditioned samples

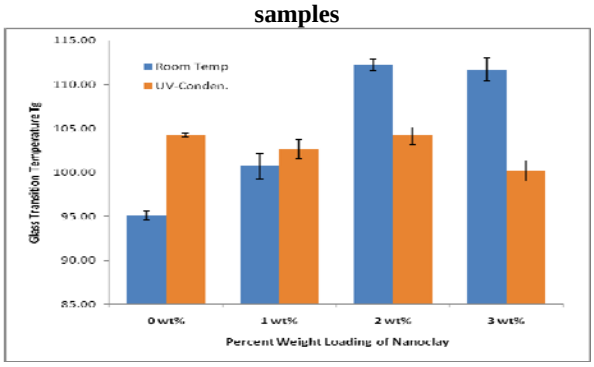

Figure 11. Effect conditioning on Glass Transition temperature

Effects of MMT on the viscoelastic properties were studied through dynamic mechanical analysis on samples before and after conditioning. Results of which are summarized in figures 11 and 12. The glass transition temperature for unconditioned samples showed improvements as the content of MMT increases, up to 2 wt% and a slight decrease in 3 wt% samples. However, samples tested after conditioning showed a decrease in glass transition temperature. 2 wt% and 3 wt% samples showed the most deterioration in glass transition temperature, while there were actually an increase in that of the neat system and 1 wt% samples. This could be due to the relaxation and segmental motion of the clay infused molecules as a result moisture absorption and desorption. There was no particular trend on the storage modulus. More investigations on this trend are underway.

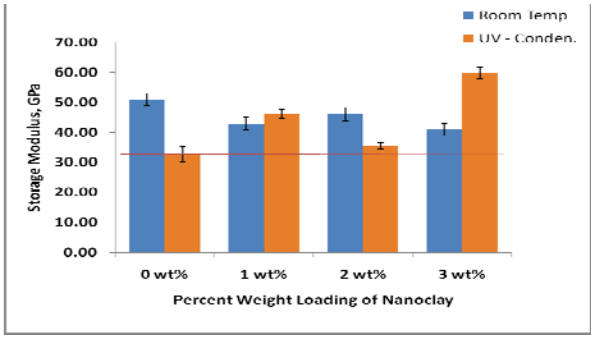

Figure 12. Storage modulus for unconditioned and conditioned samples

3.2 Summary

From the study, it was observed that the synergistic effect of UV and condensation can be detrimental to polymer composite, and the addition of nanoclay can mitigate the effects. There were degradation in all the measured properties; however, the residual strength and modulus were both higher in nanophased samples compared to neat samples. The addition of nanoclay enhanced the glass transition of the unconditioned samples at room temperature, however, the glass transition temperature decreased after conditioning.

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