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Viscoelastic and thermal properties of full and partially cured DGEBA epoxy resin composites modified with montmorillonite nanoclay exposed to UV radiation

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ABSTRACT

Effects of UV radiation and associated elevated temperature on properties of polymeric composites have been well documented, limiting the scope of their usage in outdoor applications. In order to improve on this limitation, current study focused on incorporating nanoparticles into epoxy polymer composites and delay onset of deleterious effects of UV radiation by partially curing these samples. Samples were fabricated and cured to 80% conversion (partially cured) based on isothermal cure kinetic studies. Influence of 1, 2 and 3 wt. % loading of montmorillonite nanoclay on the cure behavior and development of physical properties of these composites were evaluated. Results of the study revealed that for optimization of modified epoxy composite properties a different curing cycle was necessary due to interaction of different amounts of nanoclay and epoxy molecules. Fabricated samples infused with 1, 2 and 3 wt. % montmorillonite nanoclay were exposed to 2500 h of continuous UV radiation, where effects of UV radiation on viscoelastic and thermal properties were evaluated and compared with identical set of fabricated samples using manufacturers' recommended cycle (fully cured). Addition of nanoclay increased the viscoelastic properties, and at the end of the study, storage modulus and activation energy of decomposition of partially cured samples evolved over exposure time, while fully cured samples degraded over the same period. Samples cured to 80% showed delayed UV radiation degradation effects.

1. Introduction

Wide use of polymers as matrix for fiber reinforced polymer composites used as replacements of structural parts in civil infrastructure, aerospace, automobile and marine applications subjects them to variety of environmental attacks [1–4]. As a result they are exposed to extensive amount of UV radiation and other environmental attacks over the course of their service life, affecting their thermal and viscoelastic properties. These attacks ultimately diminish their attractiveness and viability as competitive replacements to metals and other engineering materials. Several research attempts have been made to circumvent this issue using several fillers with different polymer systems each with diverse results including blended polymers as reported in literature [5–10]. Montmorillonite nanoclay (MMT) has been used as one of many types of nanofiller in modifying polymer systems to overcome some of the drawbacks associated with UV radiation exposure and elevated temperatures. MMT as nanofiller offer several benefits, such as improved thermal, viscoelastic [3,11,12] and mechanical properties [11,13]. Furthermore, MMT has shown to have the ability to influence degradation mechanisms often caused by prolonged exposure to UV radiation and elevated temperatures [8–10]. Presence of MMT in polymers has also shown the ability to minimize moisture absorption and enhance fire retardancy properties in MMT infused polymeric composites [2–4,14,15]. These abilities have been attributed to inherent morphology of MMT which prevent the escape of volatiles during decomposition and moisture ingress during exposure. As these nanoclays are infused into polymers, their structure influences chemistry of the mixture, affecting rheological and viscoelastic properties, and cure behavior leading to different cure cycles based on the type and amount of nanoclay modifier in the final composite [16,17].

Pandey et al. [9], Woo et al. [10], Singh et al. [18] and Kumar et al.[19] independently investigated the influence of UV radiation exposure on properties of polymeric composites infused with MMT nanoclays. Role of MMT on photo-oxidation and photo-thermal activities in polymers exposed to UV radiation has widely differed based on several reports [20–22]. Transition elements in MMT

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invariably affect the rate of photo-initialized chemical reactions leading to different outcomes of different MMT systems. The same was observed in a recent study [23] where SC-15 was modified with different MMT nanoclays and characterized. Surface of each of these nanoclays has been modified with different organic modifiers and results of the study showed that not only does surface modification affect mechanical and thermal properties; it also influenced interactions between UV rays and epoxy molecules.

In many instances when polymeric composites are exposed to UV radiation, most of their properties are enhanced during the initial stages due to residual crosslinking prior to the onset of damaging effects of UV radiation [24,25]. Other studies have also harnessed the energy of UV radiation to cure epoxy thermosets to form composites [25–27]. Energy of UV rays at 340 nm reaching the surface of earth is high enough to dissociate most bonds present in polymers resulting in material brittleness and loss of strength and other properties as reported by Guillet [28] and several others [8–10,19]. In some of the reports [23,29–32] presence of MMT in polymers led to increased photo-oxidation activities resulting in decreased thermal diffusivity and viscoelastic properties, while others have reported enhanced thermal stability [12,18,21]. Material brittleness and development of microcracks have been the most common outcomes of extensive exposure of polymer composites to UV radiation, leading to loss of mechanical properties. In order to minimize UV radiation effects on polymer composites, attempts were made to utilize the energy of UV radiation to allow partially cured epoxy composites to undergo post curing while delaying onset of deleterious effects of UV radiation. It is therefore speculated that having montmorillonite nanoclays in partially cured epoxy composite could help alleviated longevity related issues caused by UV exposure of polymeric composite materials and extend their service life.

In the current study different amounts of montmorillonite nanoclay – Nanomer® I.28E was used as nanofiller in modifying SC-15 epoxy resin to fabricate full and partially cured (80% without post curing) epoxy nanocomposites and exposed to 2500 h of UV radiation. Influence of different amounts of MMT on thermal and viscoelastic properties of SC-15 composites were characterized every 500 h of UV conditioning.

2. Experimentation

2.1. Materials

Two part diglycidyl ether of bisphenol A (DGEBA) based epoxy resin system, SC-15 was modified with 1–3 wt. % montmorillonite nanoclay – Nanomer® I.28E (MMT) used in fabricating samples for this study. SC-15 was acquired from Applied Poleramic Inc. with typical chemical structure shown in Fig. 1. Nanomer® I.28E is 2:1 phyllosilicate smectite clay acquired from Sigma Aldrich with typical chemical structures in Fig. 2. Surface of the clay has been modified with 25–30 wt. % of quaternary trimethyl stearyl ammonium with coefficient of cation exchange capacity (CEC) of 93.7 meq/100 g. Surface of most nanoclays has been modified with organic modifiers to enhance miscibility and reduce tendency of agglomeration [33,34].

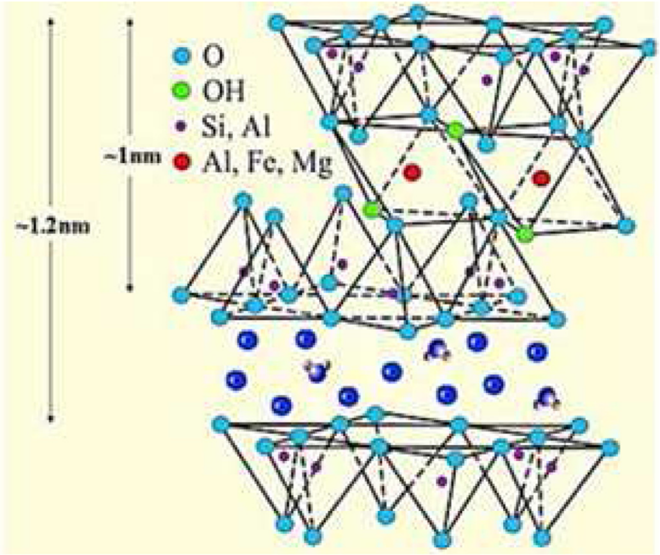


Fig. 2. Typical chemical structure of montmorillonite nanoclay [2].

2.2. Sample preparation

Samples for the study were fabricated using SC-15 epoxy resin system (neat) and SC-15 modified with 1–3 wt. % MMT. MMT was first dried in conventional oven, allowed to cool and dispersed into measured SC-15 epoxy resin part A using magnetic stirring technique. SC-15 part A mixed with MMT was stirred for 24 h to ensure uniform distribution of nanoclay. Part B of SC-15 epoxy system was then added in a mass mixing ratio of 100 part A to 30 part B. The mixture was mechanically stirred, desiccated and small amounts of each composition were characterized to study influence of MMT on cure behavior of SC-15.

2.3. Fabrication of partial and fully cured neat and nanocomposites

In order to fabricate partially cured epoxy composites for the study, influence of each MMT loading on cure behavior of SC-15 was first studied using differential scanning calorimetry (DSC) Q1000 from TA Instruments operating in isothermal mode. The instrument was purged with dry nitrogen flowing at a rate of 50 ml/min. Small amounts (8–10 mg) of desiccated neat and modified SC-15 epoxy solution were placed into aluminum hermetic pans and scanned at isothermal temperatures of 60, 70, 80 and 90° C while data were being recorded by the system. Obtained data were analyzed using TA Instruments' Specialty Library, where conversion versus time curves was generated for each system. Samples for the study were subsequently fabricated using conversion time versus temperature curves obtained from DSC results to cure each sample to required degree of conversion without post curing.

Fabrication of fully cured samples was done according to manufacturers' recommended cycle. Desiccated mixture of SC-15 part A and B was poured into molds and allowed to cure in ambient temperature for 24 h followed by 4 h of post-curing and properties

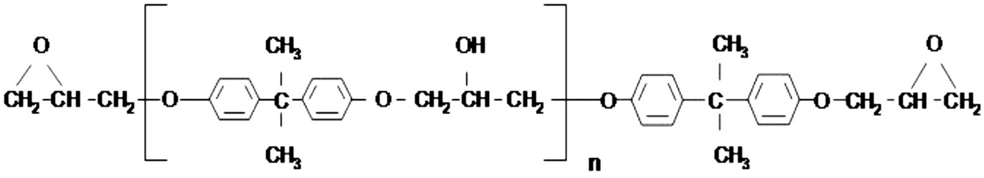


Fig. 1. Typical chemical structure of DGEBA.

characterized. Nanocomposite samples used in the study were fabricated using the same parameters above without taking into account the effects of MMT on rheological properties such as viscosity, gelation and cure behavior of MMT infused SC-15 epoxy systems.

2.4. *Sample conditioning*

Fabricated partial and fully cured neat and nano-infused epoxy composite samples were subjected to continuous UV radiation over a period of 2500 h using accelerated weathering chamber QUV/SE (Q-Lab, Ohio). The QUV/SE mimics real world environmental conditions similar to those under which these composites operate during service life, where meaningful data can be acquired at relatively short time. QUV/SE was equipped with 340 nm fluorescent lamps and set to a temperature of 60 °C and irradiance of 0.90 W/m^2. Thermal and viscoelastic properties of exposed samples were characterized every 500 h of UV exposure and data compared to that of unexposed.

2.5. *Thermal characterization*

Viscoelastic behavior of partial and fully cured neat and nanocomposites exposed to variable amounts of UV radiation was studied using Dynamic Mechanical Analyses (DMA) equipment Q800 from TA Instruments Inc. Q800 was operated in dual cantilever mode at a frequency of 1 Hz and an amplitude of 15 μm. Samples were machined and tested according to ASTM D4065-03 [35]. Influence of different amounts of MMT on thermal stability of SC-15 composite samples as they were exposed to UV radiation and persistent elevated temperatures was also studied using thermogravimetric analyses (TGA). TA Instruments' Q500 was used where the equipment was purged with dry nitrogen flowing at 60 mL/min and sample weights maintained between 13 and 15 mg. Three samples were scanned at 10 °C/min during TGA studies. Data from the test were analyzed to determine onset and decomposition temperatures as function of degree of cure as samples were exposed to different amounts of UV radiation.

3. Results and discussion

3.1. *Cure kinetics*

Properties of most epoxy polymer composites generally depend on processing parameters including constitute materials, viscosity, curing temperature and time. Epoxy cure reactions with amine hardener involve reaction between epoxide group and primary amine, followed by reaction between excess epoxide group and secondary amine from the hydroxyl groups which increases reaction rate at the onset and subsequent slow down due to onset of gelation [17]. Presence of MMT during curing typically affects rheological properties influencing gelation and development of viscoelastic leading to formation of ultimate properties of the final composites [36].

Cure reactions in epoxy systems have been studied extensively [37–41] using different techniques and data analyzed using several models. However, in almost all the techniques heat released during curing can be related to the degree of cure in epoxy and other kinetic parameters related to the process. In the current study, isothermal DSC scans were used in studying behavior of neat and compared with that of nanoclay infused epoxy systems to determine time and temperature required to cure each composition to desirable conversion. During curing the relationship between cure rate ($d\alpha/dt$) and degree of cure α, can be expressed as follows:

$$\frac{d\alpha}{dt} = k\alpha^m(1-\alpha)^n \tag{1}$$

where m and n are the reaction orders, k the reaction rate constant, which can be determined based on the initial rate $\alpha = 0$. k is assumed to have an Arrhenius relationship, i.e.

$$k = A\exp(-E_a/RT) \tag{2}$$

Fig. 3(a and b) shows experimental thermograms obtained from isothermal DSC scans for all samples cured at 70 and 80 °C, where different rates of cure of each system were observed. Maximum rate of chemical conversion occurred at different times for each system based on the composition. It also revealed the dependency of cure temperature on rate of chemical conversion based on composition as reported in literature [37,39]. Analyzing the obtained data using TA Instruments' Specialty Library, conversion time versus temperatures curves were generated for each composition, from which time required to cure each sample for the study was determined at specific temperature as shown in Fig. 4. Results of the study showed that time to cure each sample considered under the study to 80%

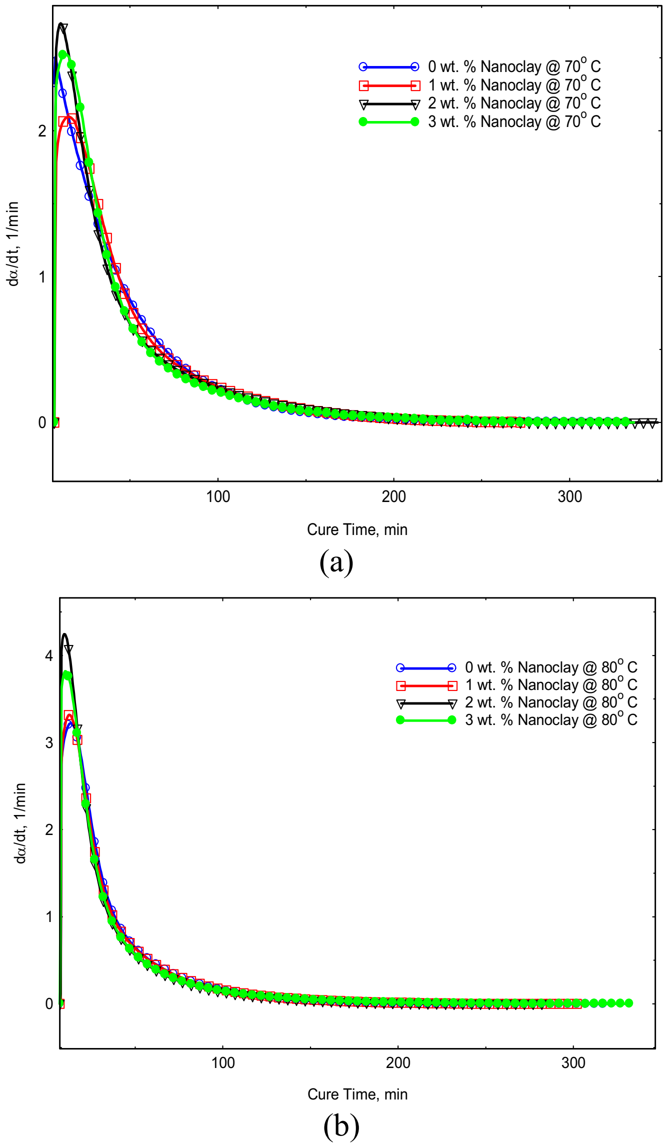


Fig. 3. Rate of conversion versus cure time for all samples at (a) 70 and (b) 80 °C.

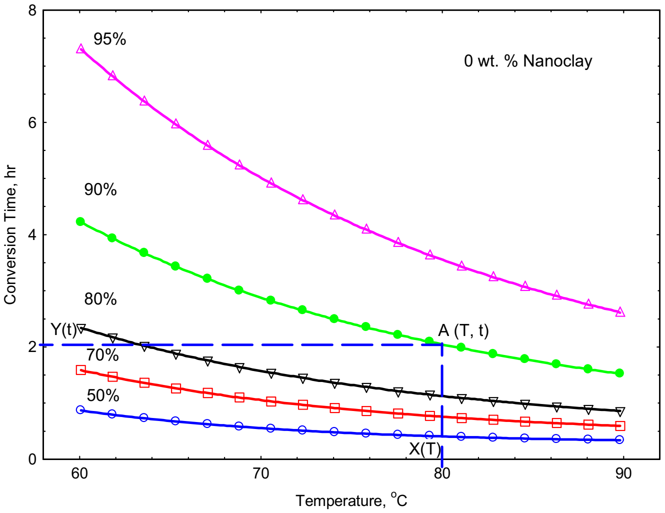


Fig. 4. Determination of cure times and temperatures for desirable conversion.

conversion using isothermal curing temperature of 80 °C was approximately 68, 54, 77 and 65 min for neat, 1, 2 and 3 wt. % MMT, respectively.

Further analysis of DSC data also indicated that activation energies of reaction were different for each system as expected, with 1 wt. % samples showing the least value of about 29 kJ/mol, while neat, 2 and 3 wt. % showed 35, 32 and 33 kJ/mol, respectively. These activation energies reflect the influence of different amounts of MMT contents on cure kinetics of SC-15, such as cure time, viscosity, conditions of gelation and vitrification, and finally ring opening of epoxide groups during curing. In a separate study, viscosity increased with increasing clay content, while gel time decreased with increasing clay content. Increasing gel time requires more energy to bring the reaction species together to cause gelation and vitrification leading to increased cure time. These factors tend to influence not only cure kinetics, but also development of viscoelastic and mechanical properties of the final composites based on the amount of nanoclay used. From the results it can be seen that activation energy of reaction was a function of MMT content and points to the catalytic behavior of MMT during SC-15 curing in the form of lower activation energy. Also time to cure 1 wt. % MMT infused samples to 80% conversion was lower compared to unmodified SC-15 sample and other nanocomposites. Overall, samples with 1 wt. % MMT manifested most catalytic behavior compared to other SC-15 nanocomposites in the form of lower cure time and lower activation energy, thus catalytic effect decreased with increasing clay content as also been reported in literature [42,43].

3.2. UV radiation 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 these samples were conditioned to 500 h of UV radiation visual changes began to occur in each exposed surface. Surfaces of post-conditioned samples showed yellowish discoloration due to interaction between epoxy molecules on the exposed surface and photons from UV radiation [19, 28]. These interactions in the presence of oxygen lead to photo-oxidation degradation in polymers producing ketones, peroxides and chromophoric species responsible for the discoloration and microstructural changes [10,44]. These ketones and other hydrocarbons react with oxygen giving rise to formation of alkoxy and hydroxyl radicals which initiates secondary reaction of hydrogen abstraction to form hydroperoxides increasing the degradation kinetic of different materials during thermal degradation [44]. Also these interactions and subsequent rates of chemical degradation have been shown to be sensitive to the frequency of UV light as well as time and frequency of exposure [45].

As samples went through 1000–1500 h of exposure yellowish discoloration on each exposed surface became intense. Beyond 1500 h of exposure, surface discoloration intensified particularly among MMT infused samples and became indistinguishable. This explains unique interaction between the epoxy molecules and UV rays caused by the presence of organic modifiers in MMT [20,23,29]. Role of different organo-modified nanoclays in epoxies during photo-oxidation degradation in polymers has been widely studied and shown to influence the degradation mechanism based on the type and quantity of clay loadings and polymer system being used. Hence different thermal stabilities outcomes are reported in literature [29–33].

3.3. Morphological characterization

Degree of nanoclay dispersion in various modified SC-15/nanoclay composites was studied using XRD technique, where diffraction patterns were obtained for Nanomer® I.28E clay powder and those from the various nanocomposites used in the study. Results of the study are shown in Fig. 5, with prominent diffraction peak obtained from Nanomer I.28E clay occurring at $2\theta = 3.60°$, corresponding to intergallery d-spacing of 7.91 Å. Due to highly organized silicate layers in nanoclays, the relative high intensity XRD peak observed around 2θ value of 3.60° of nanoclay powder was attributed to the morphology of silicate layers of MMT. Diffraction patterns obtained from fabricated epoxy/clay nanocomposites showed broader peaks at higher 2θ values, suggesting intercalation of epoxy molecules into the intergallery spacing. Intensities of these broad peaks, however, were lower compared to that of nanoclay powder, and among the nanocomposites intensity of the peaks increased with increasing MMT clay content in the nanocomposite. The broader peaks indicate a relative lack of orderliness of nanoclay platelets in each epoxy/clay composites, thus the system formed may be a combination of exfoliated platelets and intercalated or only the later. Furthermore,

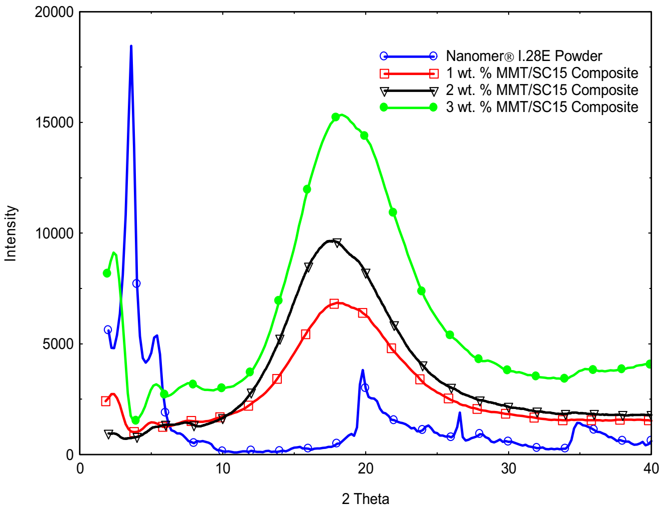


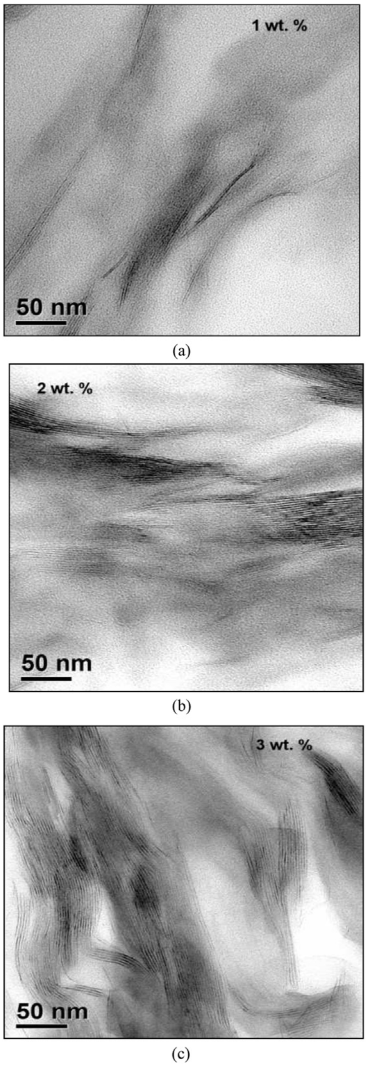
Fig. 5. X-ray diffraction patterns of Nanomer® I.28E and SC-15 with 1–3wt. % Nanomer® I.28E loadings.

intergallery *d*-spacing determined from the diffracted peaks was 21.03, 16.32 and 16.11 Å for 1, 2 and 3 wt. % nanocomposites, respectively. These values when compared to that obtained from nanoclay powder show significant intergallery opening of the nanoclay platelets in each nanocomposite, confirming the intercalation of epoxy molecules into the gallery of the clay platelets. However, TEM micrographs obtained from each nanocomposite at different locations to compliment XRD studies showed mainly intercalated morphologies of the various MMT loadings as shown in Fig. 6.

3.4. Thermal characterization

3.4.1. Influence of MMT on viscoelastic properties

Typical experimental thermograms obtained from DMA scans of unconditioned partial and fully cured samples are shown in Fig. 7. Storage modulus and damping effects (tan δ) of each sample are plotted as functions of temperature from 30 to 180 °C, where glass transition temperature was determined from the peak of tan δ curve. Addition of MMT to SC-15 resulted in increased storage modulus at 30 °C regardless of the degree of cure, albeit at different extent. Addition of 1, 2 and 3 wt. % MMT enhanced storage modulus at 30 °C by 12, 2 and 6% and by −5, 4 and 1% for full and partially cured samples, respectively.



(a)

(b)

(c)

Fig. 6. TEM micrographs of (a) 1, (b) 2 and (c) 3 wt. % MMT samples.

Tables 1 and 2 show average values of storage moduli and glass transition temperatures obtained from three samples of each set. At the onset of the study, addition of different amounts of MMT showed slight enhancements in storage modulus values with 1 wt. % showing the most. Glass transition temperature on the other hand showed lower values compared to neat samples. Worth noting that storage modulus for fully cured samples were relatively lower compared to those partially cured. However, fully cured samples showed broader elastic region, an indication of higher crosslinking resulting in tougher and better materials. This can be confirmed from glass transition temperature data obtained during DMA studies indicated in Table 2.

Fig. 8 shows average results from all samples considered under the study while undergoing several hours of UV radiation exposure. It can be seen from the data that as samples went through conditioning storage moduli increased slightly for fully cured samples. Enhancements in viscoelastic properties of fully cured MMT samples peaked at different exposure times prior to onset of damaging effects of UV radiation on material property. For example, maximum storage modulus for fully cured samples was observed at 500, 1000 and 1500 h of exposure for 1, 2 and 3 wt. % respectively. Peak values of storage modulus constituted approximately 13, 25 and 19% for 1, 2 and 3 wt. %, respectively, compared to unexposed neat sample. Glass transition temperatures on the other hand showed a different trend, with modest increase with the addition of MMT at room temperature or at onset of the study. As samples were exposed to UV radiation, glass transition temperature for neat SC-15 gradually increased from 110 °C and peaked at 118 °C after 1000 h before decreasing till the end of the study. On the other hand, glass transition temperatures of all MMT infused samples peaked at 500 h of exposure and went through several changes till the end of the study as can be seen in Fig. 8c.

For obvious reasons, glass transition temperatures of partially cured samples were lower compared to their fully cured counterparts. Glass transition temperature for unconditioned partially cured samples decreased with increasing clay content. This trend however changed after the first 500 h, where glass transition of MMT infused samples became higher than neat, with samples infused with 1 wt. % MMT showing the highest values (Fig. 8d). The observed higher values of Tg in 1 wt. % samples were attributed to higher degree of dispersion and restrictive movement of epoxy molecules trapped between the clay platelets [45]. Other studies [16,46] conducted using epoxy-clay systems reported increased glass transition temperatures while an opposite effect has been reported by Garea et al. [47]. Storage modulus on the other hand decreased immediately after 500 h of exposure. The decrease, however, constituted an enhancement when compared with control samples (fully cured) at every stage of the study as can be seen in Fig. 8b.

At the end of the study fully cured samples showed relatively higher values of storage moduli when compared to their unexposed counterpart. The increase in storage modulus was approximately 6, 20 and 11% for neat, 2 and 3 wt. % respectively, while 1 wt. % showed a decrease of about 5% from their respective unexposed counterpart. UV radiation exposure may have created a condition for much needed post-curing or residual crosslinking of the polymer chain molecules leading to increased crosslinking density and formation of stronger bonds. Based on assumption of highly exfoliated morphology and display of high catalytic behavior of 1 wt. % cured under the same processing parameters, we speculate that samples infused with 1 wt. % MMT were overly cured. And as a result exposure to UV radiation during the study led to material brittleness with little room for residual crosslinking. Conversely,

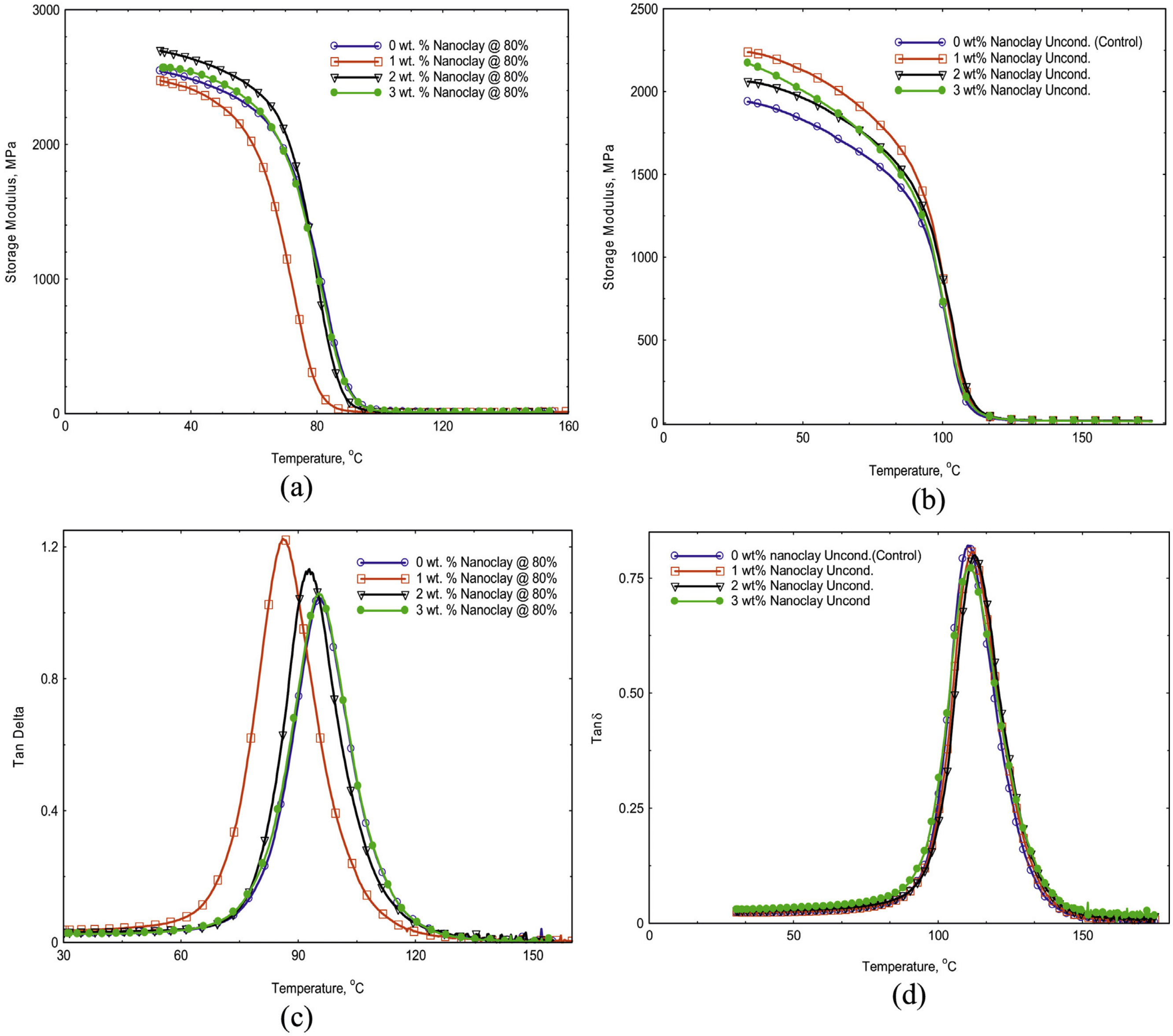


Fig. 7. Experimental plots of storage modulus for (a, b) and tan δ curves (c, d) for full and partially cured unconditioned samples as functions of temperatures, respectively.

samples with 2 and 3 wt. % MMT underwent several enhancements in the course of exposure, affirming the above statement. The findings reinforce the assertion made earlier that addition of nanofiller to polymers may require different processing parameters to achieve optimum properties. On the other hand, degradation in storage modulus for 3 wt. % samples at the end of the study was attributed to increased activities between UV radiation and presence of higher volume of MMT.

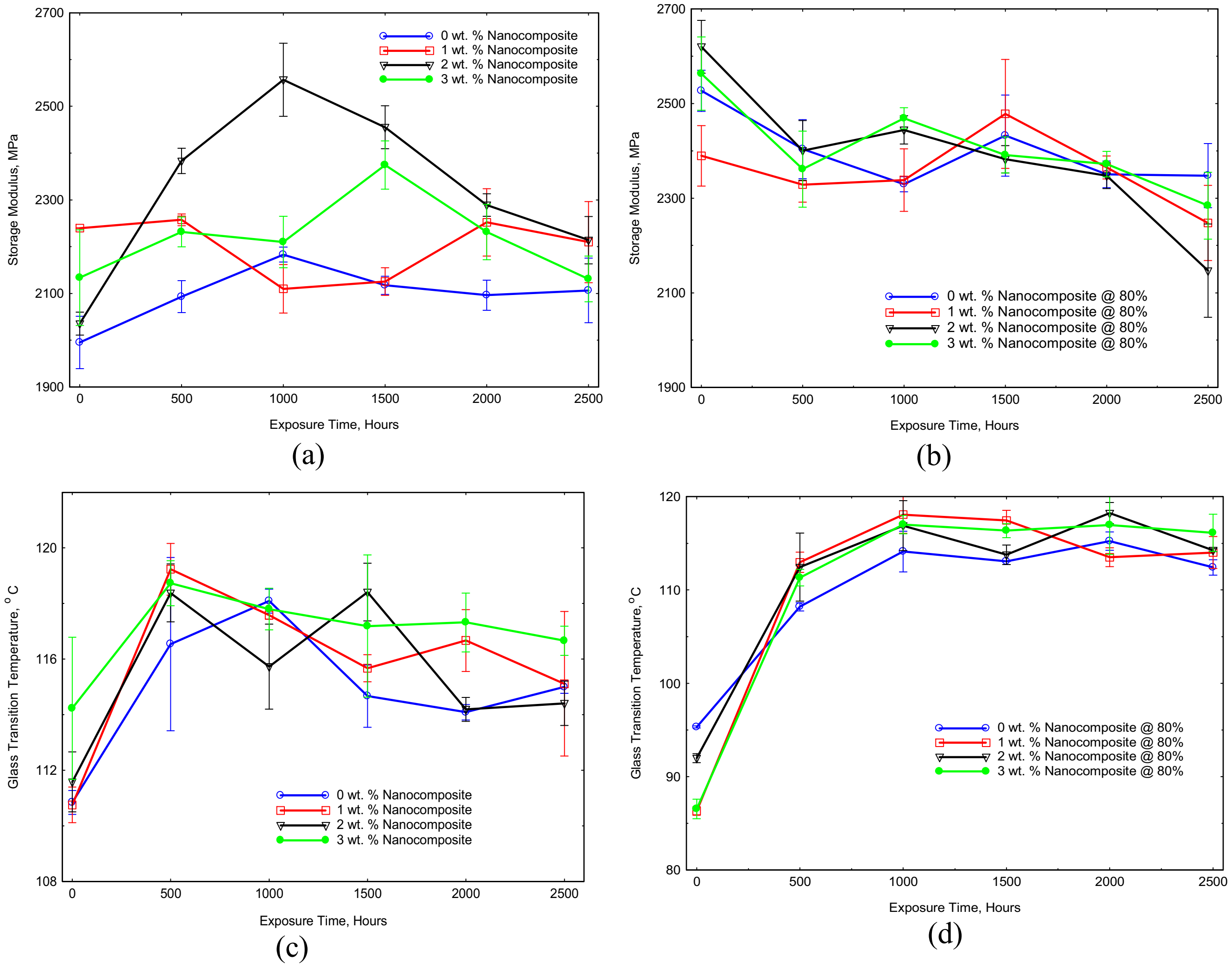
Partially cured samples at the end of the study showed a decrease in storage moduli compared to their respective unexposed samples by 7, 6, 18 and 11% for 0, 1, 2 and 3 wt. % samples respectively. The decrease, however, constitutes an increase when compared to that of fully cured samples with the exception of 2 wt. % samples as shown in Table 3. Samples with 2 wt. % showed worse retention of storage modulus when partially cured, while showing the most retention in the case of fully cured samples. Although storage moduli values were higher in partially cured samples it revealed a more damaging effect of UV radiation on these samples compared to fully cure and to their respective unconditioned counterpart. One explanation could be that chemical bonds in partially cured samples were relatively weaker and therefore required less energy from the UV rays to devour them, hence less

Table 1
Summary of storage modulus at onset of the study.

Samples	Partially cured	% Change	Fully cured	% Change
0 wt. % Nanoclay	2337.67 ± 175.31	–	1995.00 ± 56.00	–
1 wt. % Nanoclay	2542.67 ± 4.11	8.77	2239.50 ± 0.50	12.26
2 wt. % Nanoclay	2665.67 ± 296.24	14.03	2035.50 ± 24.50	2.03
3 wt. % Nanoclay	2494.33 ± 36.30	6.70	2133.67 ± 102.16	6.95

Table 2
Summary of glass transition at onset of the study.

Samples	Partially cured	% Change	Fully cured	% Change
0 wt. % Nanoclay	95.32 ± 0.11	–	110.84 ± 0.43	–
1 wt. % Nanoclay	86.32 ± 0.47	−9.44	110.75 ± 0.64	−0.08
2 wt. % Nanoclay	91.98 ± 0.47	−3.50	111.58 ± 1.08	0.67
3 wt. % Nanoclay	86.54 ± 1.05	−9.21	114.23 ± 2.56	3.06



(a) (b)

(c) (d)

Fig. 8. Average viscoelastic properties: storage moduli of (a) fully and (b) partially, and glass transition temperatures of (c) fully and (d) partially cured samples.

effective in withstanding UV radiation. Also, with higher cross-linking density effect of nanoclay on storage modulus was more pronounced, where higher loading of nanoclay led to better viscoelastic property retention after UV radiation exposure. It can also be argued that there was competing effects of UV radiation on material property thus between enhancing and degrading the properties.

Table 4 shows comparison of average glass transition temperatures for partial and fully cured samples at the end of the study. Unlike storage modulus, glass transition temperature of 2 wt. % partially cured samples improved over the course of the exposure time compared to the rest of the MMT samples which decreased. However, 2 wt. % fully cured samples showed a decrease in glass transition temperature compared to neat and other MMT infused samples. Fig. 9 shows a comparison of storage moduli of unconditioned and UV conditioned partially and fully cured samples, depicting the change that occurred between the samples at the end of the study. Worth noting that although storage moduli decreased across the board with exposure time, elastic region for partially cured samples improved till the end of the study as shown in Fig. 9b. Furthermore, changes in storage moduli and glass transition temperatures for each samples over the entire study were compared and presented in Fig. 10. It was observed that the difference between glass transition temperatures of partially and fully cured samples narrowed or became close to each other at different times. For example, in neat samples this occurred between 1500 and 2000 h, whiles samples with 1, 2 wt. % occurred at 1000 h and 3 wt. % occurred almost at the end of the study. On the other hand, a wide variation in storage moduli was observed as each sample went through conditioning, with 2 wt. % samples showing an

Table 3
Comparison of average storage moduli after 2500 h of UV radiation.

Samples	Partially cured	% Change	Fully cured	% Change
0 wt. % Nanoclay	2347.67	–	2106.33	–
1 wt. % Nanoclay	2247.67	−4.26	2209.67	4.91
2 wt. % Nanoclay	2146.67	−8.56	2214.01	5.11
3 wt. % Nanoclay	2284.02	−2.71	2131.11	1.18

Table 4
Comparison of glass transition temperatures after 2500 h of UV radiation.

Samples	Partially cured	% Change	Fully cured	% Change
0 wt. % Nanoclay	115.56	–	115.00	–
1 wt. % Nanoclay	113.88	−1.45	115.11	0.10
2 wt. % Nanoclay	116.43	0.75	114.41	−0.51
3 wt. % Nanoclay	113.11	−2.12	116.66	1.44

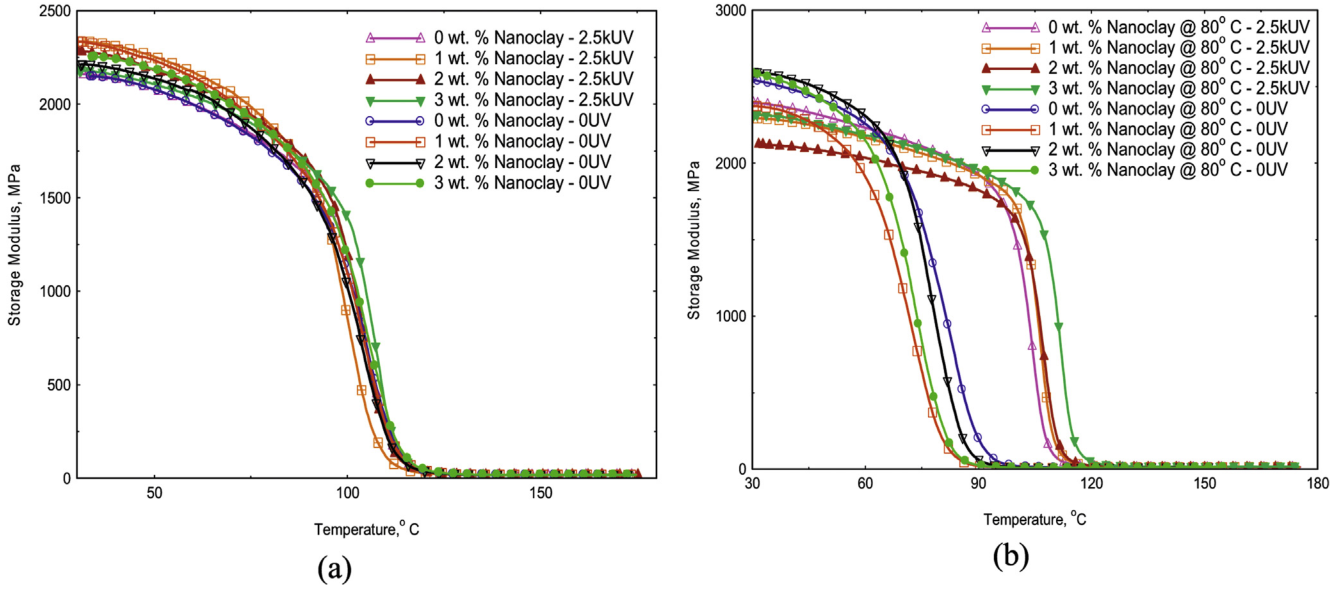


Fig. 9. Comparison of storage moduli of all samples between unexposed and exposed to 2500 h (a) fully and (b) partially cured.

interesting trend. It showed the least variation between partial and fully cured samples after first 500 h till the end of the study, and the only partially cured sample that showed lower storage modulus compared to its fully cured counterpart.

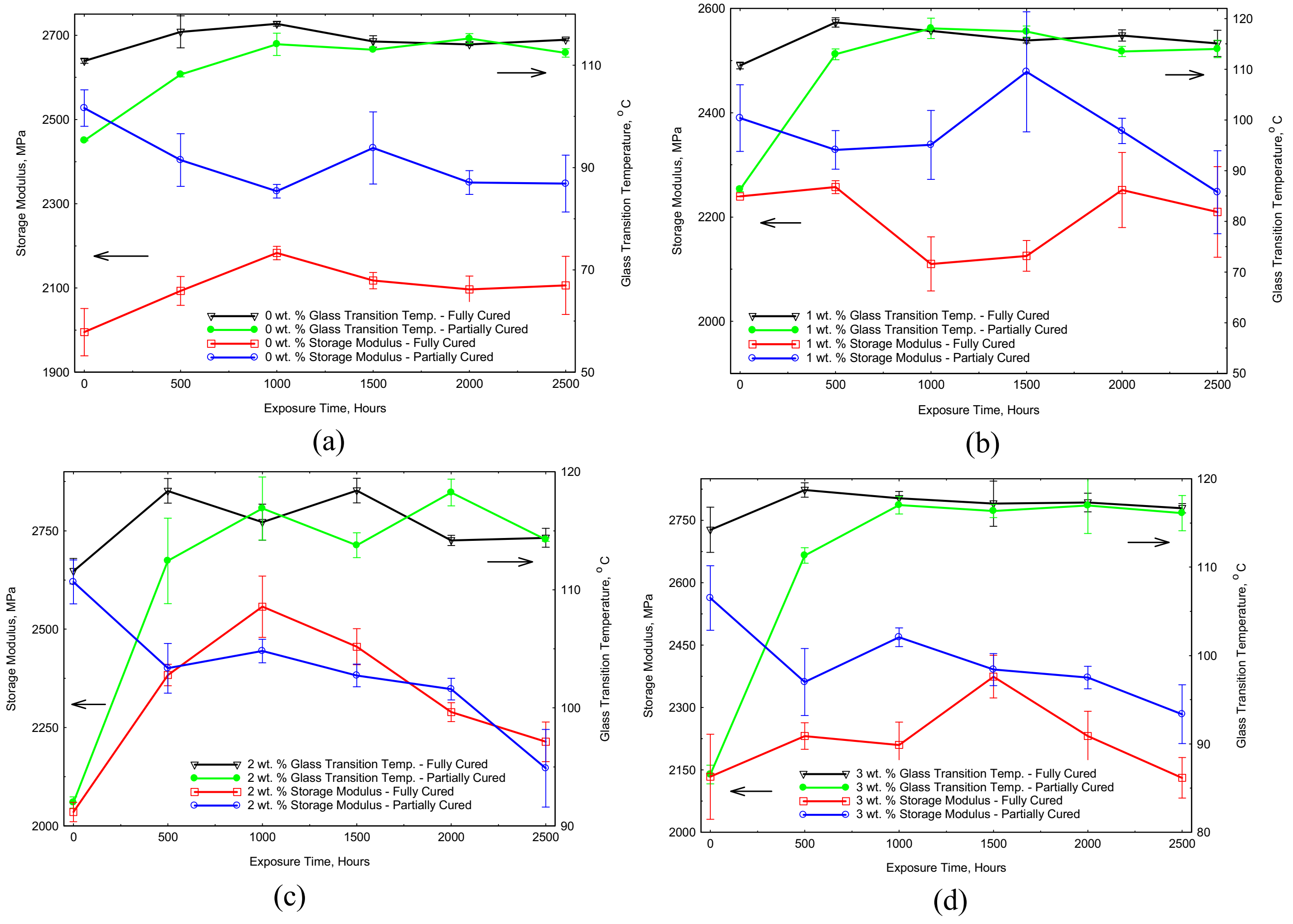
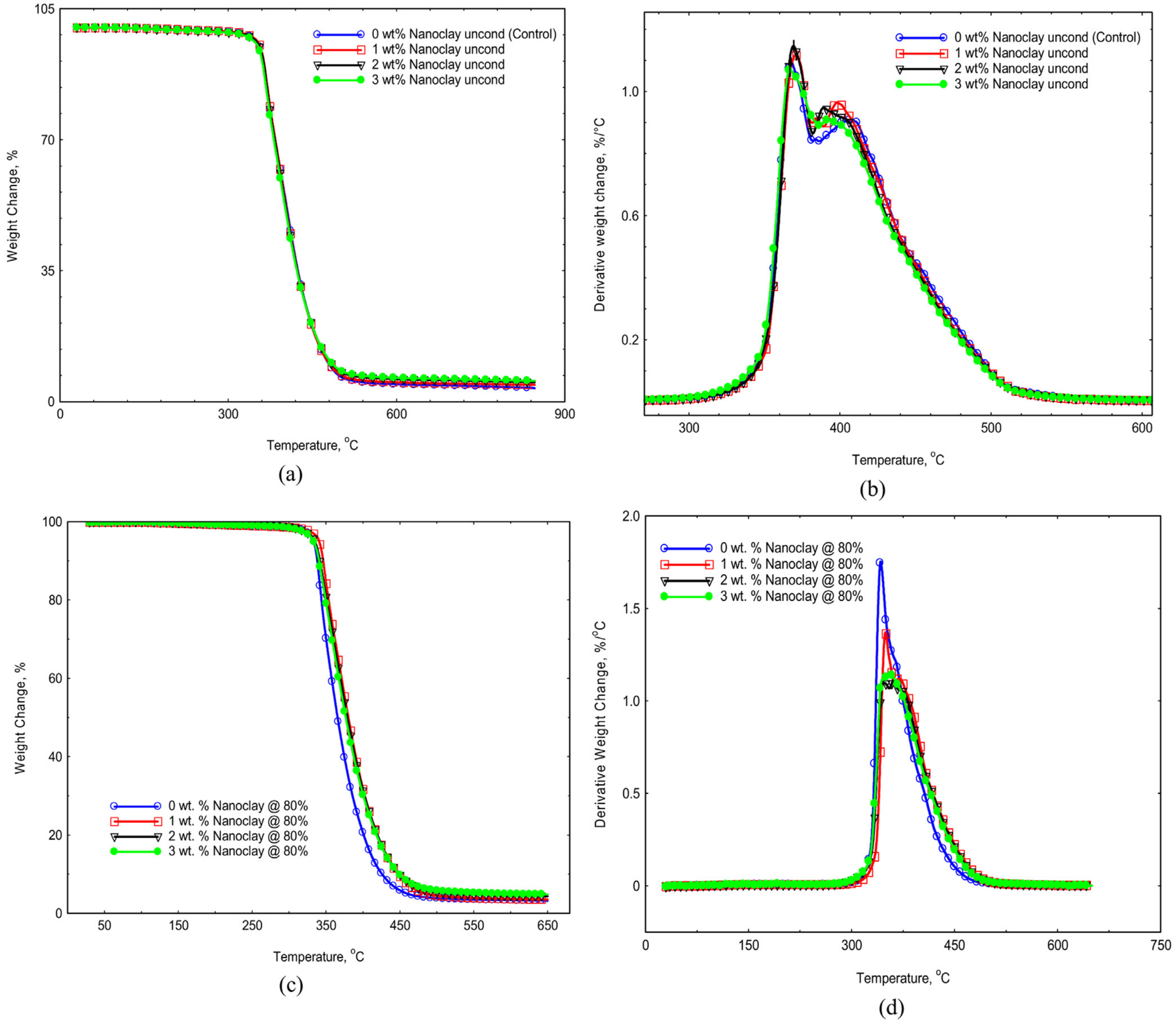


Fig. 10. Comparison behavior of glass transition temperature of each sample as function of exposure time.

3.4.2. *Thermal stability characterization*

Thermal stability enhancements in most MMT infused polymers samples have been ascribed to inherent structure of MMT, which prevents the escape of volatiles during decomposition. Degradation of epoxy composites in part depends on formation and retention of hydroxyl group during curing which retard the rate of decomposition when released during degradation. Influence of MMT on thermal stability of SC-15 epoxy composites under the study was done using conventional TGA experiments, where three samples from each set were scanned at 10 °C/min from 30 to 650 °C. Thermograms obtained for unconditioned partial and fully cured samples are shown in Fig. 11(a and b) and corresponding derivative curves in Fig. 11(c and d). Degradation parameters such as onset of degradation, temperature at which 5% of the original mass is lost (T_5), and decomposition temperature (T_p) determined from the peak of derivative weight lost curve obtained from each sample sets. Fig. 12(a–d) shows comparative behavior of onset of decomposition and decomposition temperatures of partial and fully cured samples as they were conditioned over the duration of the study.

During thermal decomposition of polymeric materials due to several degradation mechanisms acting independently or simultaneously on the material, degradation mechanism may take different forms, hence there is no particular mechanism associated to any system [48]. These mechanisms may consist of side-group elimination, random chain scission and depolymerization resulting in the formation of free radicals which further degrades the polymer over time. Many of these mechanisms depend on the constituent components, type and strength of the bonds present. At the onset of the study, it was observed that addition of MMT insignificantly influenced onset and decomposition temperatures regardless of degree of cure, with residue increasing with clay content. However, during UV radiation conditioning onset of decomposition temperatures decreased with increasing aging regardless of the composition particularly among MMT infused samples. This behavior showed among MMT samples validates the assertion that presence of MMT in polymers exposed to UV radiation can be more detrimental [20,29,31]. Interaction of UV rays and polymer molecules with MMT particles has shown to produce more free radicals which intend sever the bonds in epoxy composites resulting in loss of material properties. Although decomposition temperatures were observed to follow identical trend particularly among nanoclay samples (Fig. 12(c and d)), there were slight



(a) (b) (c) (d)

Fig. 11. Typical TGA thermogram of sample cured according to (a, b) manufacturers' cycle and (c, d) to 80% conversion.

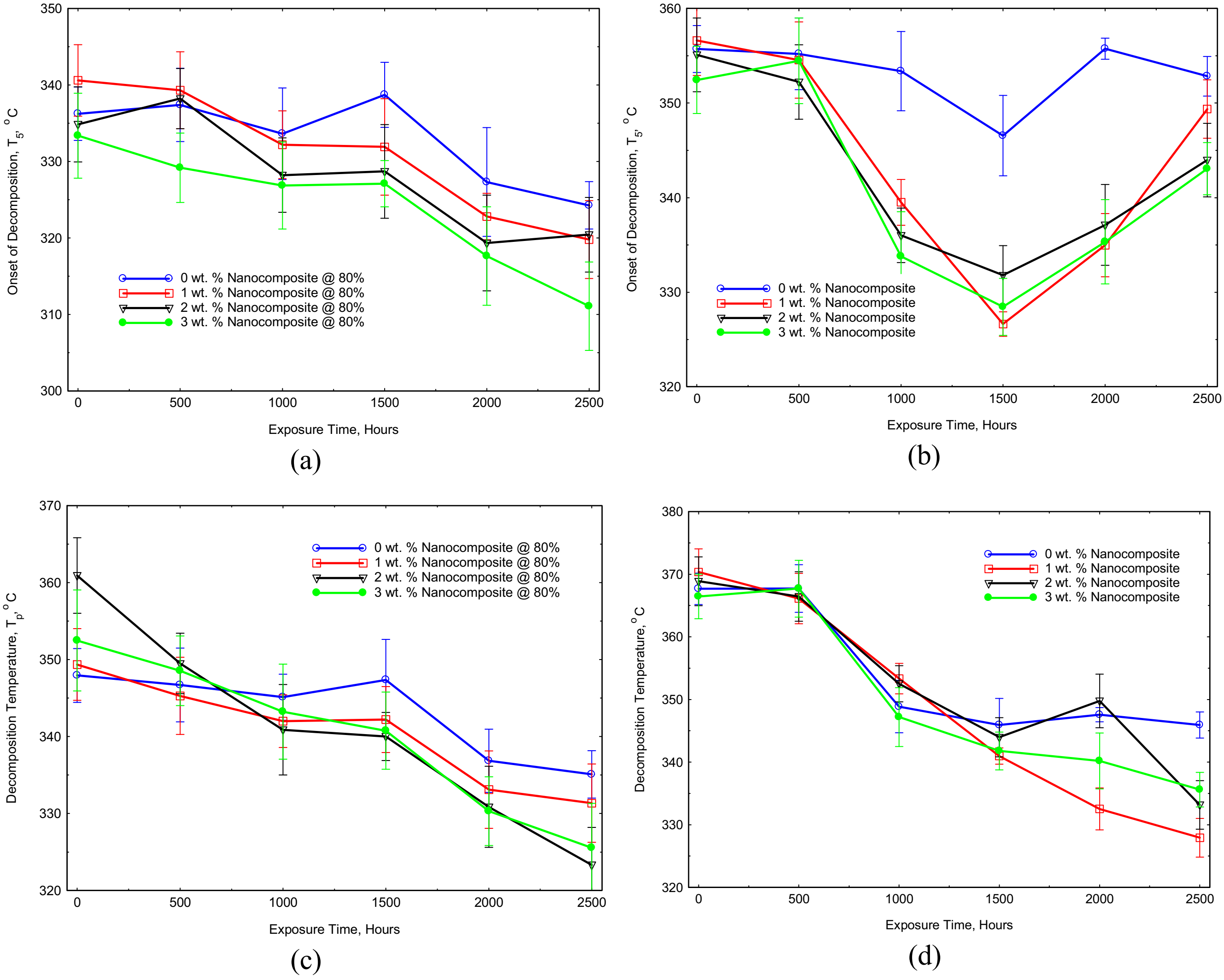


Fig. 12. Comparison of (a, b) onset of decomposition and (c, d) decomposition temperatures of partial and fully cured samples as function of exposure time.

variation due to different amounts in each sample. The results showed that presence of MMT in the epoxy composite used for this study exacerbated the effects of UV radiation when compared to neat samples cured to the same degree.

4. Conclusion

Results from the study showed that different amounts of montmorillonite nanoclay can have different effects on the cure behavior of DGEBA leading to different property enhancements. Addition of 1 wt. % showed higher catalytic effect possibly due to better dispersion. Viscoelastic properties of partially cured SC-15/MMT composites showed higher values prior to and during UV radiation degradation, although there was immediate degradation which stabilized after 500 h of exposure. It also showed that degree of degradation varied based on the MMT loading and degree of cure. For partially cured systems, rate of thermal stability degradation was lower compared to fully cured systems modified with MMT regardless of the percent weight loading of MMT. Activation energy of decomposition showed higher values in partially cured systems during UV radiation exposure.

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