DYNAMIC MECHANICAL ANALYSIS OF GRAPHITE PLATELET AND NANOCLAY REINFORCED VINYL ESTER, AND MWCNT REINFORCED NYLON 6,6 NANOCOMPOSITES

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ABSTRACT

This paper describes investigations on dynamic mechanical analysis (DMA) of nylon 6,6 thermoplastic reinforced with 1.25 and 2.5 wt. percent multi-wall carbon nano tubes (MWCNT), and Derakane 411-350 vinyl ester thermoset reinforced with 1.25 and 2.5 wt. percent Cloisite 30B nanoclay and exfoliated graphite nanoplatelets (xGnP). Visco-elastic materials exhibit the characteristics of both elastic solid and viscous liquid. This dual behavior which is both time and temperature dependent has been characterized by dynamic oscillation and creep experiments performed at various isothermal temperatures. Viscoelastic properties such as storage modulus (E'), loss modulus (E"), damping, glass transition temperature (T_g) and creep behavior were compared for the different nanocomposites. Short range creep tests were performed at isothermal conditions and the time-temperature superposition principle was utilized to generate creep-strain master curves at a reference temperature.

An increase in storage modulus was observed with increasing reinforcements in all the cases. Glass transition temperature and loss factor also showed an increase for vinyl ester with nano clay and graphite platelets. For MWCNT /nylon 6,6 nanocomposites, a marginal decrease in loss factor was observed with increasing reinforcement of MWCNT while glass transition temperature remained almost the same. The effect of reinforcement greatly improved the creep-resistance of both nylon 6,6 and vinyl ester, with 2.5 wt. percent nano clay /vinyl ester exhibiting the maximum creep-resistance. The extent of creep-strain increased with increasing temperature, with 2.5 wt. percent graphite /vinyl ester exhibiting the maximum relative creep at its glass transition temperature.

KEY WORDS: Viscoelasticity, Creep Behavior, Nanotechnology

1. INTRODUCTION

Composite materials with polymer matrices exhibit viscoelastic behavior which is directly related to molecular structure and formulation differences [1]. The behavior of composites is dominated by the fiber properties if the composites are loaded along the fiber direction. However, in practical applications, a composite structure could experience various loading conditions [2]. Even in a simple loading case, the stress state in nano-composites could be multi-axial and non uniform due to the complex interaction between the nanoparticles and matrix. Nano reinforcement of engineering materials can impart remarkable structural (e.g., stiffness) and physical (e.g., low CTE) property advantages to the matrix [3]. For example, nanolayered reinforcement can impart greater thermal stability [4], making the polymer less flammable [5].

The unparalleled characteristic of nano clay layers to boost mechanical properties of an engineering polymer (nylon-6) was first demonstrated by Toyota [6]. With only 4.2 wt. % nano clay, the modulus doubled and heat distortion temperature increased by $80^{o}C$ compared to the pristine polymer.

These tremendous improvements in properties directed many works to model and characterize the mechanical behavior of nanocomposite materials. Several studies have attempted to model the mechanical behavior of single-wall carbon nano tube, applying molecular mechanics. The dynamic modulus, damping, low-velocity impact response and acoustic absorption coefficients of nanoparticle enhanced composites have been characterized by the authors. Molecular Dynamic (MD) simulations were used for obtaining the elastic constants for different matrices reinforced with single and multi-wall carbon nanotubes [7]. The flexural dynamic modulus and damping of nylon 6,6 reinforced with different wt. percents of multi-wall carbon nano tubes (MWCNT) were determined experimentally using the impulse-frequency response vibration technique [8].

The interlaminar shear strengths of glass fabric /vinyl ester composites treated with various single wall carbon nanotubes were significantly improved with respect to that of the composite control samples. The equivalent or improved in-plane properties like flexural strength and other Z-axis mechanical properties of composite laminates could also be obtained. Potential for single wall-carbon nanotubes to enhance the interface properties of laminates through a toughening effect, fiber-bridging mechanism and direct reinforcement of the matrix was demonstrated [9].

An accurate knowledge of time-temperature dependent behavior and proper constitutive modeling are prerequisites for predicting the overall stress-strain response of nano-reinforced composites. The principle of time-temperature superposition is usually applied because it extends the range of frequencies or time of viscoelastic properties beyond that measurable. This concept comes from observations that the time scales of motions of constituent molecules of polymers are affected by temperature [10].

An attempt is made in this paper to characterize the viscoelastic behavior of nylon 6,6 reinforced with different wt. percent multi-wall carbon nano tubes, and vinyl ester thermoset reinforced with nano clay /graphite platelets. Dynamic oscillation and creep tests were performed with a DMA and the principle of time-temperature superposition was applied to characterize the viscoelastic behavior of these nanocomposites.

2. EXPERIMENTAL

2.1 Experimental Setup DMA tests were performed in accordance with ASTM D4065-01: "Standard Practice for Plastics: Dynamic Mechanical Properties: Determination and Report Procedures" [11] using a Q800 DMA (TA Instruments, USA) and recommendations of the machine manufacturer [12-13]. Schematic of Q800 DMA is shown in Figure 1.

Q800 DMA is a controlled stress with combined motor and transducer (CMT) machine in which motor applies force and displacement sensor measures strain. Force and amplitude are the raw

signals recorded by the machine. Stiffness is then calculated directly from force and amplitude and modulus is calculated by multiplying the stiffness by the appropriate geometry factor. Geometry factor for single cantilever clamp [12] is calculated by:

$$GF = \frac{1}{F}\left[\frac{L^3}{12I} + 2S(1+\upsilon)\frac{L}{A}\right] \quad (1)$$

where: L = *span length of the specimen.*
A = *sample cross sectional area* (mm^2)
I = *geometric moment* (mm^4) = ($bh^3/12$)
h = *sample thickness (mm)*
b = *sample width (mm)*
F = *clamping factor (nominally 0.9)*
S = *shearing factor (nominally 1.5)*
υ = *Poisson's ratio (nominally 0.44)*

As can be seen from the formula, the geometry factor is an exponential function of length and thickness. Hence, it is important that due care is taken in measurement of the sample dimensions. A digital vernier caliper with a least count of 0.005 mm was used in these tests and the average of length, width and thickness at 5 different locations was recorded. A variation of less than 0.03 mm was observed in the dimensions of each individual sample.

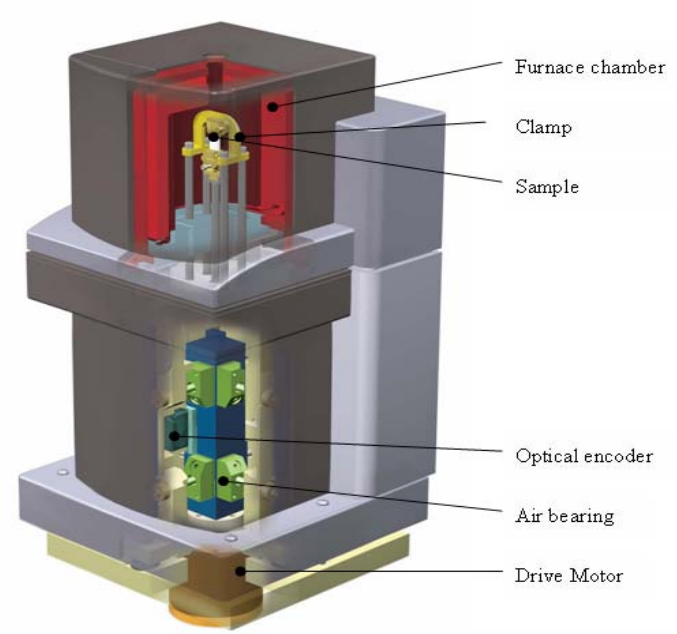

Figure 1. Schematic of TA instruments model Q800 DMA [14]

Several trial runs were performed for finalizing the sample boundary conditions. Three-point bend clamp was used for oscillatory testing of MWCNT /nylon 6,6 nanocomposites and single-cantilever clamp was used for nano-clay and graphite platelet reinforced vinyl ester nanocomposites. Three-point bend clamp used had a span of 50 mm with friction free rollers to nullify the clamping effect due to variation of shape as shown in Figure 2(a). Single-cantilever

clamp used had a span of 17.5 mm as shown in Figure 2(b). All creep tests were performed using single-cantilever clamp. A torque of 1.13 N.m (10 lb-in) was used for clamping the sample in single-cantilever clamp.

(a) 3- Point Bending (b) Single- Cantilever

Figure 2**.** DMA clamps used for testing

2.2 Sample Preparation Prismatic samples with nominal dimension of 58 x 9.9 x 3 mm (2.3" x 0.39" x 0.12") were milled from the manufacturer supplied plates for oscillatory tests using three-point bending clamp. Samples with dimension of 18.5 x 10.0 x 1.6 mm (0.73" x 0.39" x 0.06") were milled for creep tests using the single-cantilever clamp.

2.3 Experimental Procedure

2.3.1 Oscillatory tests MWCNT reinforced nylon 6,6 nanocomposites were tested using three-point bend clamp with a span of 50 mm at a frequency of 1 Hz and a displacement amplitude of 25 μm. Testing was done over a temperature range of -50°C to 150°C with a temperature ramp of 3°C per minute. A pre-load of 1 N and a force track of 125% were used. Three samples were tested from each configuration.

Vinyl ester nanocomposites were tested using single-cantilever clamp with 17.5 mm span, at a frequency of 1 Hz and displacement amplitude of 25 μm with a temperature ramp rate of 3°C per minute from -50°C to 150°C. Two samples were tested from each configuration in this case.

2.3.2 Creep tests Creep measures the flow properties of a material when subjected to a constant load. Nylon 6,6, vinyl ester and their nanocomposites were tested using single-cantilever clamp with a span of 17.5 mm and a pre-load stress of 3 MPa. Specimen dimensions were $18.5 \times 10 \times 1.6$ mm and two samples were tested from each configuration.

Short-term creep tests were carried out with Q800 DMA analyzer by subjecting the samples to a constant load over 30 minutes duration at isothermal temperatures. The room temperature (RT) fluctuated between 28-30°C. Data from short creep tests performed at various isothermal temperatures could be superposed (shifted) to a reference temperature to create the long-term

creep behavior. A temperature range of 28°C through 100°C was chosen, as this covered the glass transition temperature for all the nanocomposites investigated in this research.

The sample was initially equilibrated at 28°C for about 4 minutes to make sure that the sample temperature settles down. After equilibrium, the sample was subjected to a fixed stress of 3 MPa for about 30 minutes. The temperature was then incremented by 4°C and the above procedure executed all over again. This procedure was repeated till the final temperature of 100°C. The raw data signals at various temperatures were exported into rheology data analysis software as TTS signals, and the shifting mechanism is adopted at a prescribed reference temperature for creep-strain data.

All calibrations viz. position, electronics, force, dynamic and clamp calibrations were done and thermocouples were aligned properly before performing a test as prescribed by manufacturer.

3. RESULTS AND DISCUSSION

3.1 Oscillatory Test Results Figures 3 and 4 show typical outputs of MWCNT /nylon 6,6 reinforced nanocomposites for storage modulus, loss modulus and loss factor as a function of temperature. Glass transition temperature reported here is from the peak of loss modulus, as per ASTM D4065-01 [11], and loss factor (damping) from peak of tan δ curve.

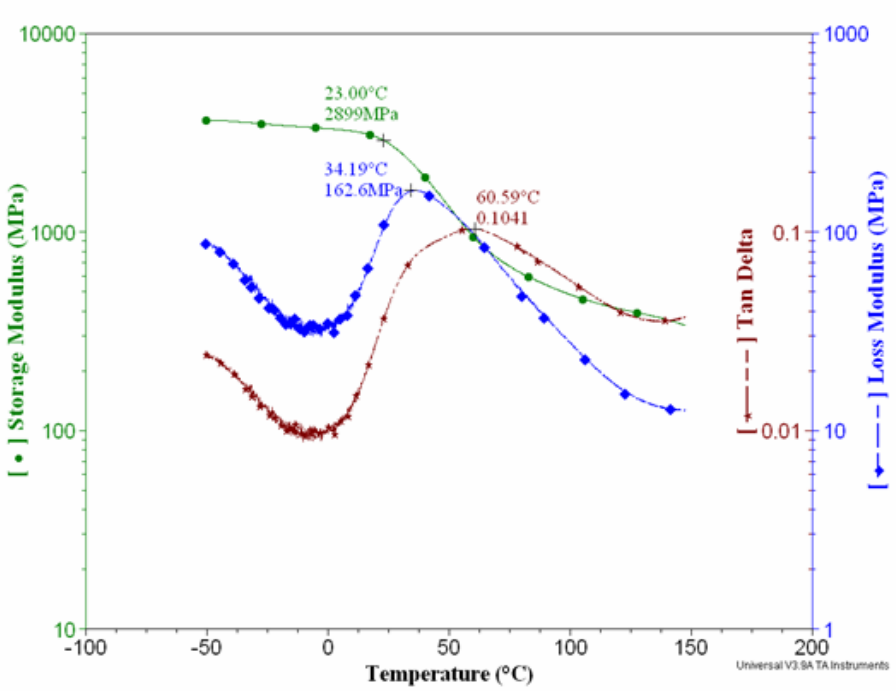

Figure 3. Dynamic modulus and damping for pure nylon 6,6

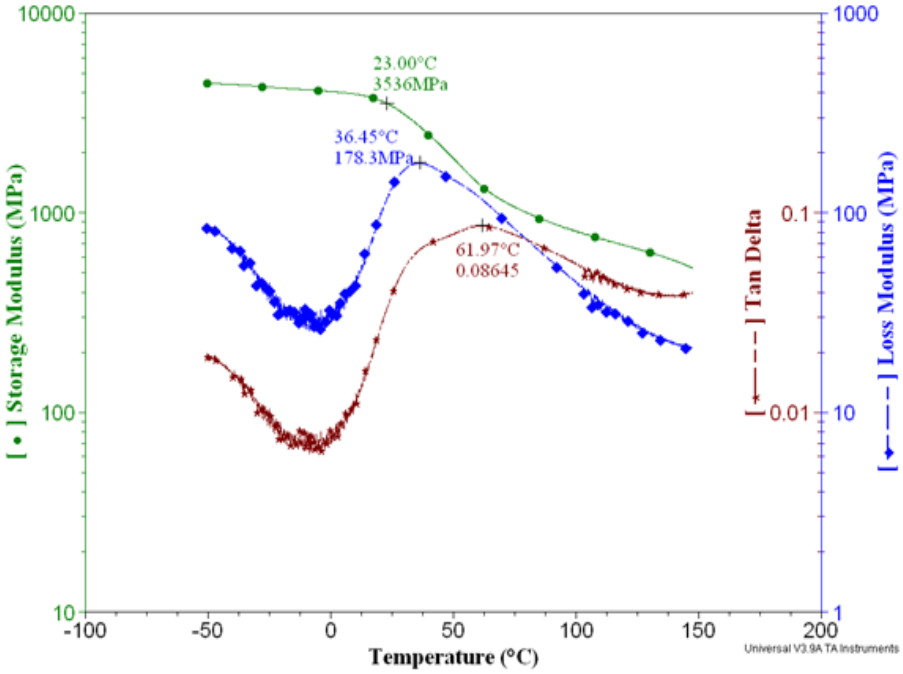

Figure 4. Dynamic modulus and damping of nylon 6,6 with 2.5 wt. percent MWCNT

Figures 5 to 7 show the comparison of storage modulus, glass transition temperature and loss factor (3-point bend) with respect to temperature and MWCNT reinforcement for the nylon 6,6 nanocomposites. Storage modulus increased with increasing MWCNT reinforcement in all the cases for nylon 6,6 nanocomposites. A marginal decrease in loss factor was observed with increasing reinforcement of MWCNT while glass transition temperature remained almost the same.

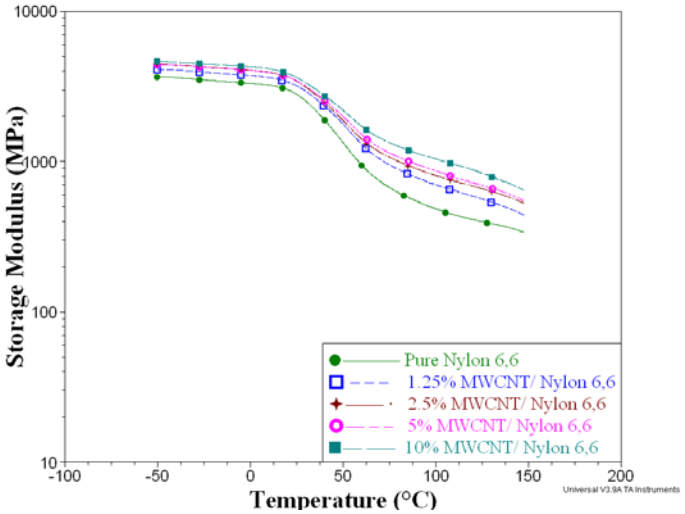

Figure 5a. Storage modulus of MWCNT/ nylon 6,6 nanocomposites vs. temperature

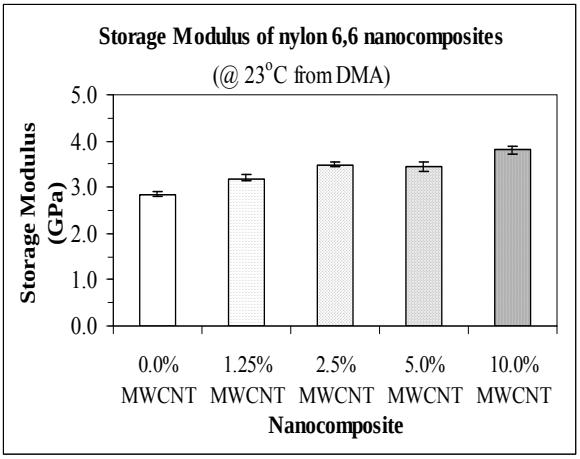

Figure 5b. Storage modulus of MWCNT/ nylon 6,6 nanocomposites at 23 °C from DMA

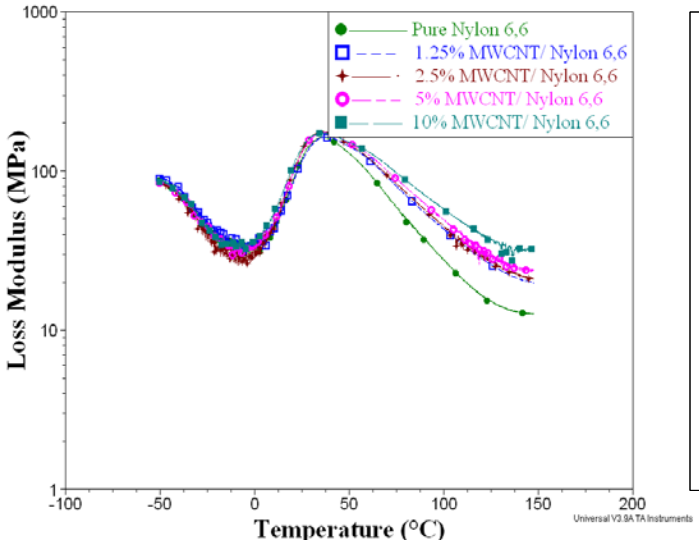

Figure 6a. Loss modulus of MWCNT/ nylon 6,6 nanocomposites vs. temperature from DMA

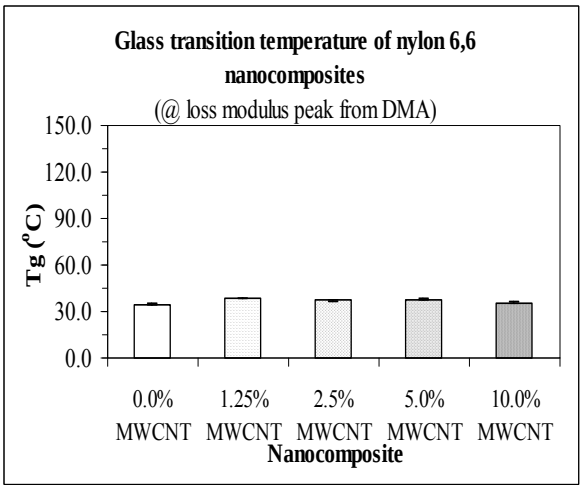

Figure 6b. Glass transition temperature of MWCNT /nylon 6,6 nanocomposites at peak of loss modulus from DMA

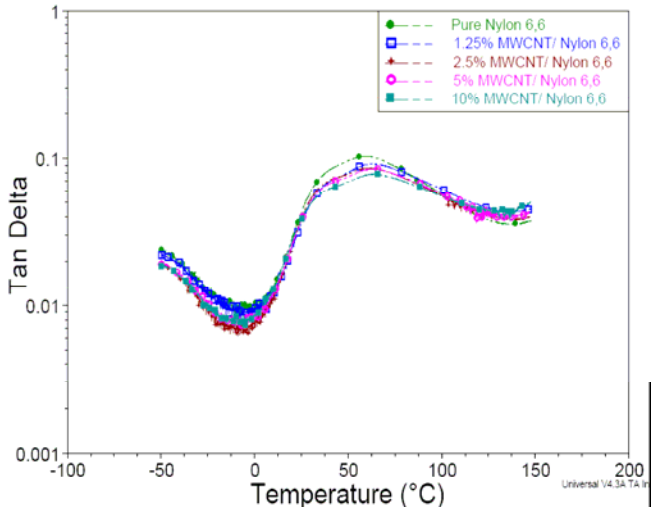

Figure 7a. Tan delta of MWCNT/ nylon 6,6 nanocomposites vs. temperature

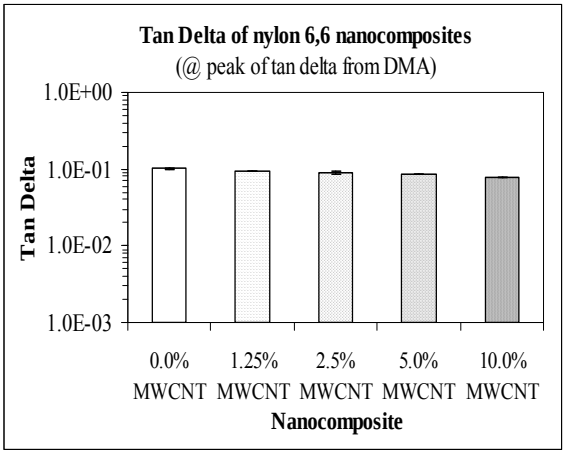

Figure 7b. Loss factor of MWCNT/ nylon 6,6 nanocomposites at peak of tan δ from

Figures 8 and 9 show typical outputs of storage modulus, loss modulus and loss factor for pure vinyl ester and reinforced with graphite platelets. Note that the figures show the output of one sample tested with single cantilever clamp and the highest tan δ peak value is considered to be α.

It is also to be noted that only one distinct α peak was observed in case of the 2.5 wt. percent graphite platelet reinforced vinyl ester.

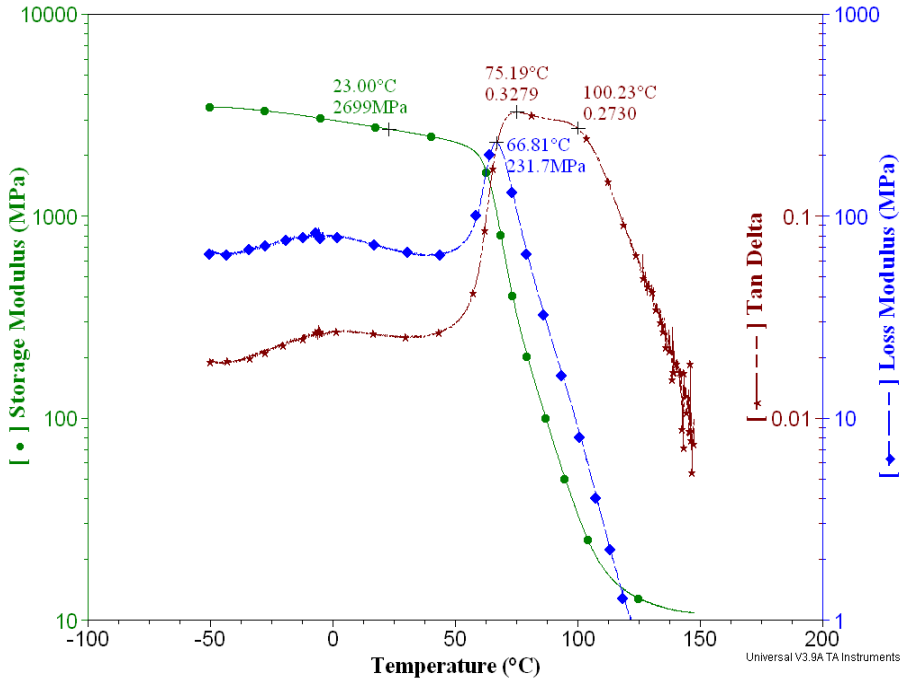

Figure 8. Dynamic modulus and damping for pure vinyl ester

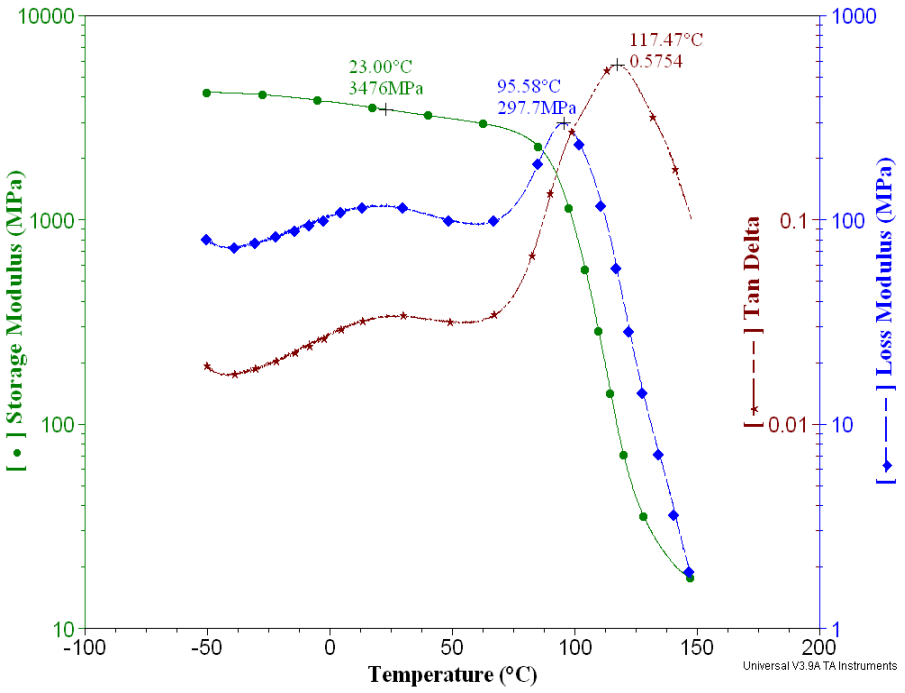

Figure 9. Dynamic modulus and damping for vinyl ester with 2.5 wt. percent graphite platelets

Figures 10 to 12 show the comparison of storage modulus, glass transition temperature and loss factor with respect to temperature for vinyl ester and effects of nano clay and graphite platelet reinforcement on the above properties with single-cantilever clamp. Storage modulus, glass transition temperature and loss factor showed an increase with greater reinforcement of nano clay and graphite platelets.

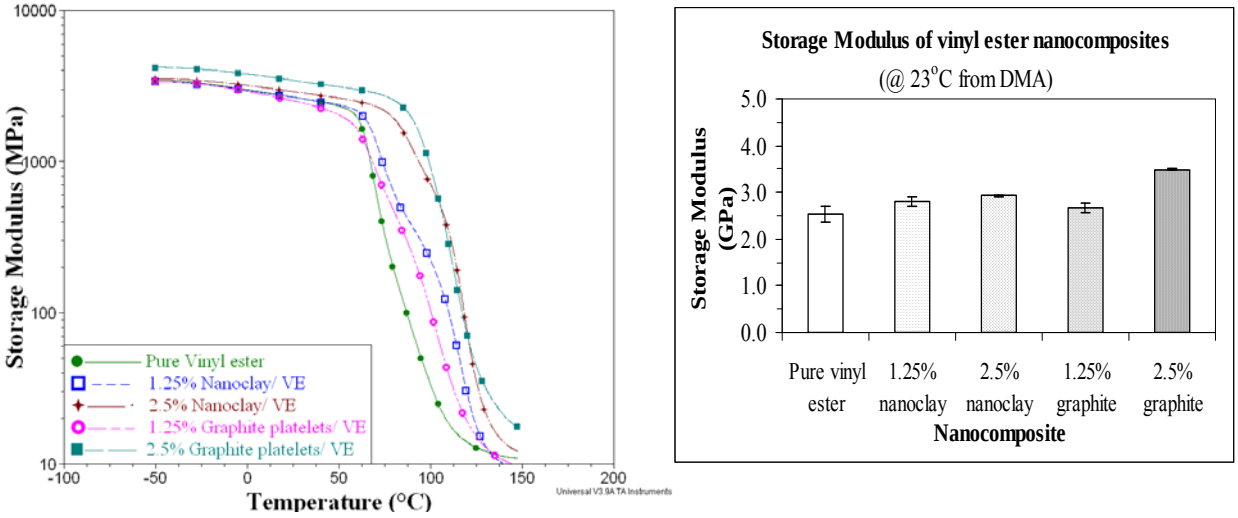

Figure 10. Storage modulus of vinyl ester nanocomposites versus temperature and nano-reinforcement at 23 °C from DMA

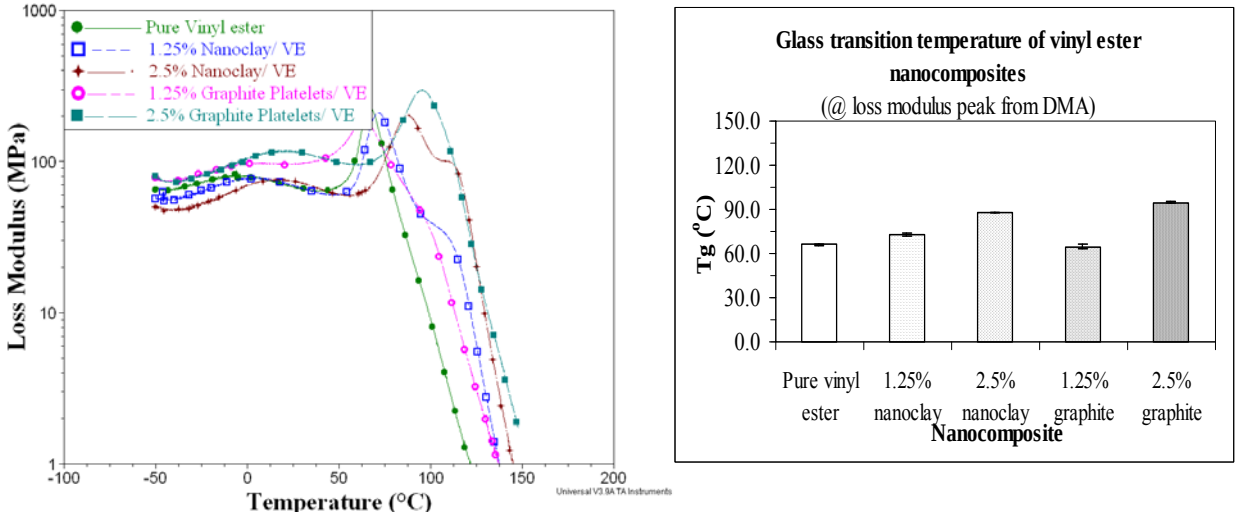

Figure 11. Glass transition temperature of vinyl ester nanocomposites at loss modulus peak from DMA

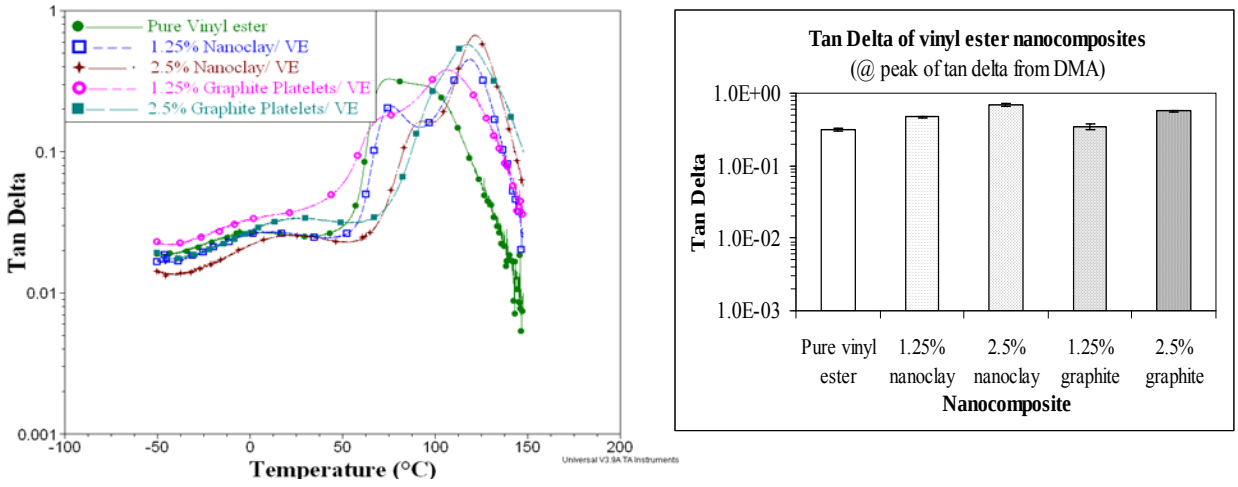

Figure 12. Loss factor of vinyl ester nanocomposites at peak of tan δ from DMA

Figures 13 to 15 show a comparison of the storage modulus, glass transition temperature and loss factor of nylon 6,6, vinyl ester and their nanocomposites. Storage modulus of MWCNT/ nylon 6,6 nanocomposites is greater than that of vinyl ester nanocomposites, where as glass transition temperature and loss factor are higher for nano-clay and graphite platelet vinyl ester nanocomposites compared to MWCNT /nylon 6,6.

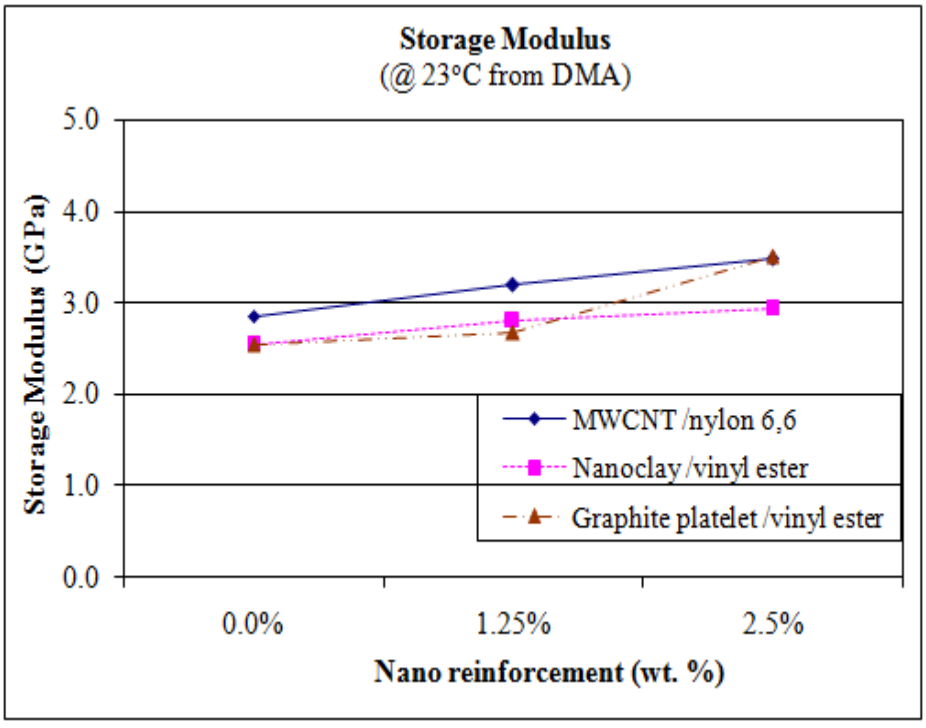

Figure 13. Storage modulus of nylon 6,6 and vinyl ester nanocomposites

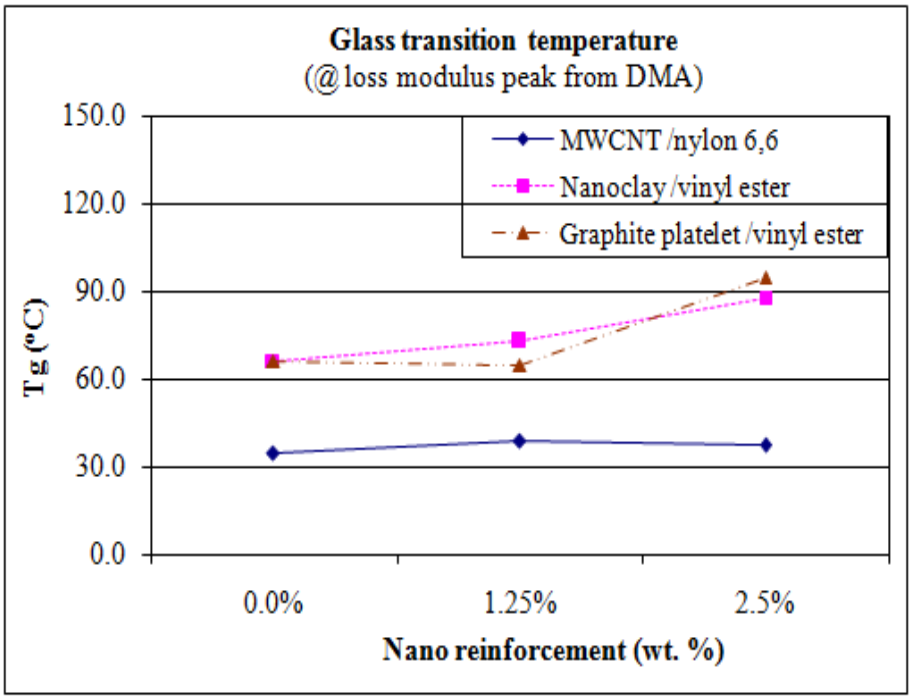

Figure 14. Glass transition temperature of nylon 6,6 and vinyl ester nano composites

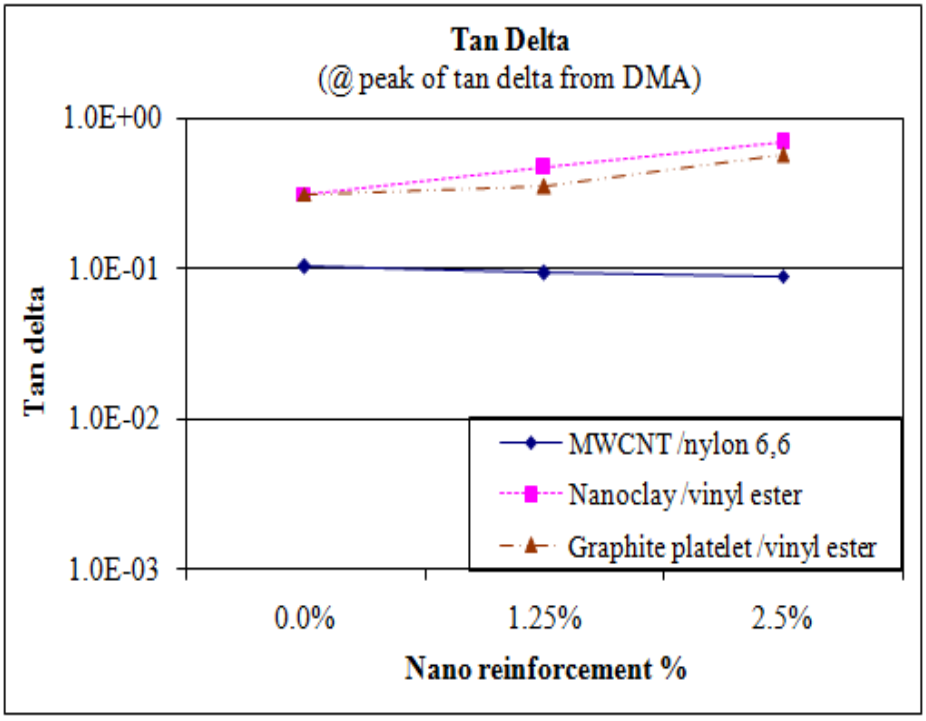

Figure 15. Loss factor of nylon 6,6 and vinyl ester nanocomposites

3.2 Creep Results To investigate the time dependent effects of reinforcing nylon 6,6 with multi-wall carbon nanotubes and vinyl ester with graphite platelet and nano clay, creep tests were performed on both pure, 1.25 and 2.5 wt. percent reinforced nanocomposites. To establish the linear viscoelastic range for both pure nylon 6,6 and vinyl ester, creep data were plotted as compliance (1/MPa) versus applied stress. The compliance curves should overlap in the linear viscoelastic range. The effect of applied stress from 2 to 4 MPa on creep compliance for both nylon 6,6 and vinyl ester was found to be less than 5 % (as shown in Figures 16 and 17) and therefore the creep behavior can be considered to be linear in this range. As such, a 3 MPa creep stress was applied for all tests to better evaluate the relationship between molecular structure and viscoelastic behavior in the linear range [15].

Creep-strain data over 30 minutes test duration were gathered for the MWCNT /nylon 6,6 nanocomposites at various temperatures as typical plots from DMA (Figures 18 and 19). Results are plotted (Figures 20-22) in terms of relative creep (defined as a percentage of instantaneous or initial strain) vs. nano reinforcements [16]. No clear relationship could be observed regarding the effect of temperature on the relative creep over 30 min test duration for a given MWCNT /nylon nanocomposite. However, the highest creep occurred near the glass transition temperature ($39^{\circ}C$) for 1.25 wt. percent MWCNT /nylon 6,6. Unlike the case for MWCNT /nylon 6,6 nanocomposites, the effect of temperature on creep response is more pronounced for nano-clay and graphite vinyl ester nanocomposites. For example, the creep responses for 2.5 wt. percent nano-clay and graphite platelet vinyl ester nanocomposites increased by 134% and 360% respectively, at their respective glass transition temperatures of $\sim 88^{\circ}C$ and $\sim 95^{\circ}C$.

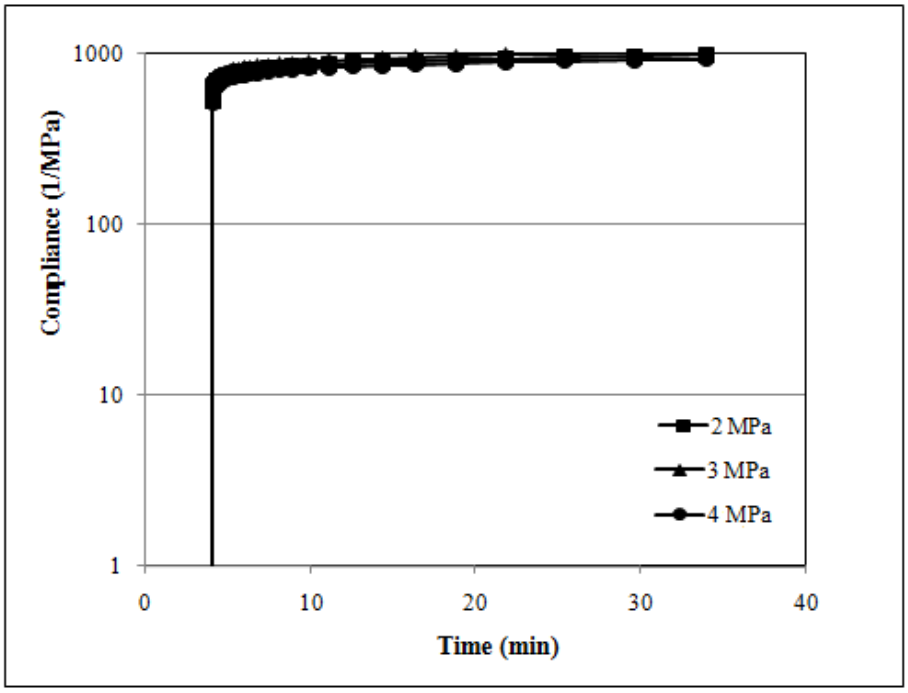

Figure 16. Creep compliance for pure nylon under different (2-4 MPa) preloads

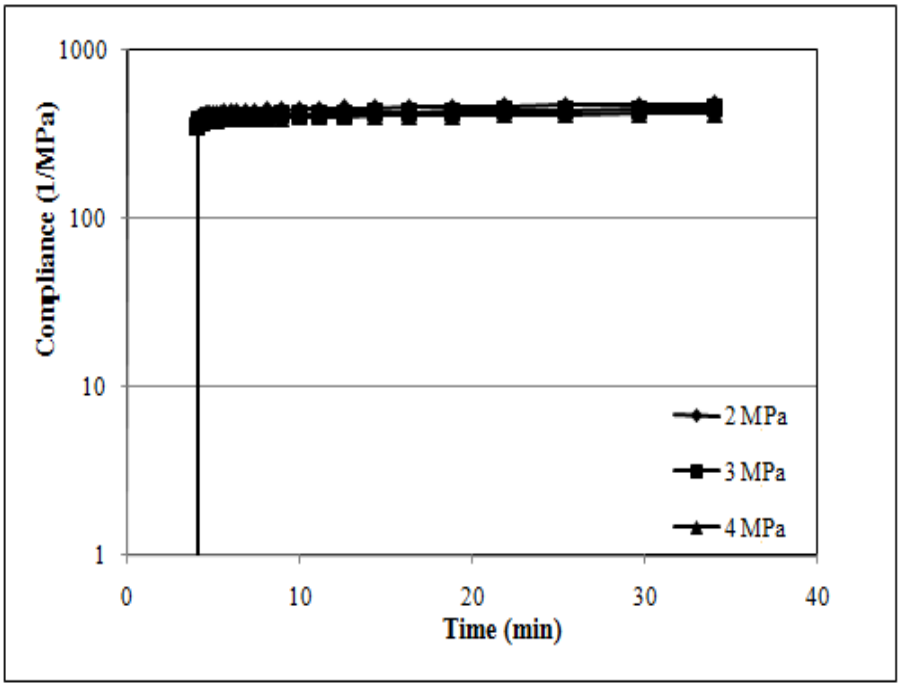

Figure 17. Creep compliance for vinyl ester under different (2-4 MPa) preloads

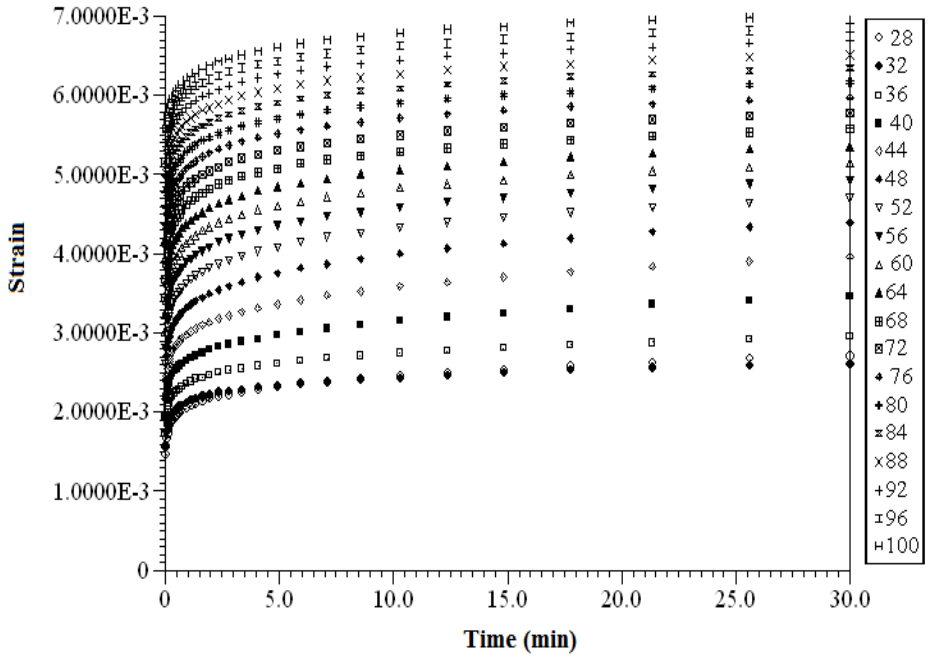

Figure 18. Typical DMA plot of creep-strain for pure nylon 6,6 over 30 min at various temperatures (^{o}C)

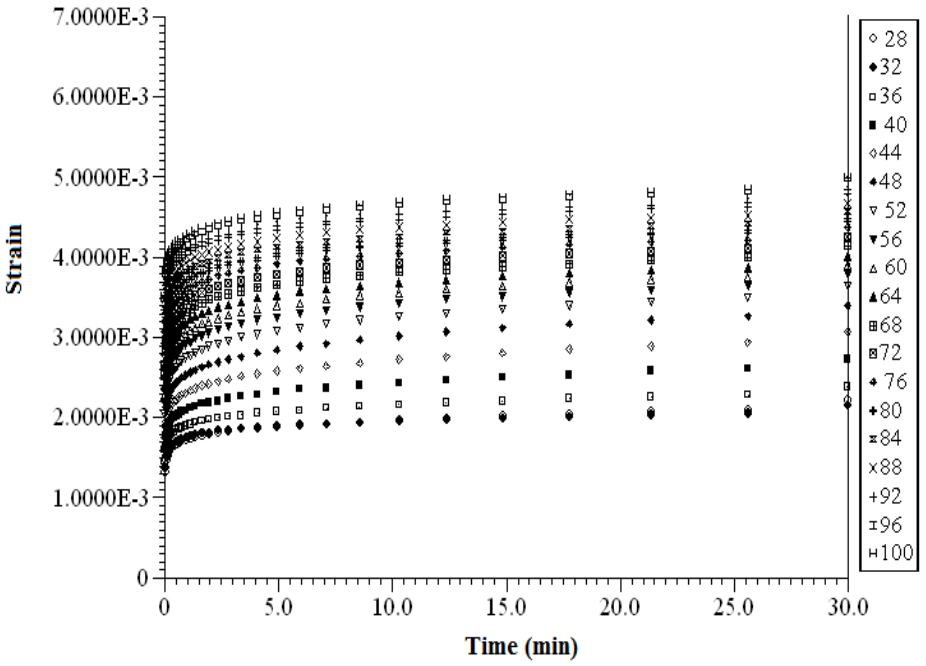

Figure 19. Typical DMA plot of creep-strain for 2.5 wt. percent MWCNT /nylon 6,6 over 30 min at various temperatures (^{o}C)

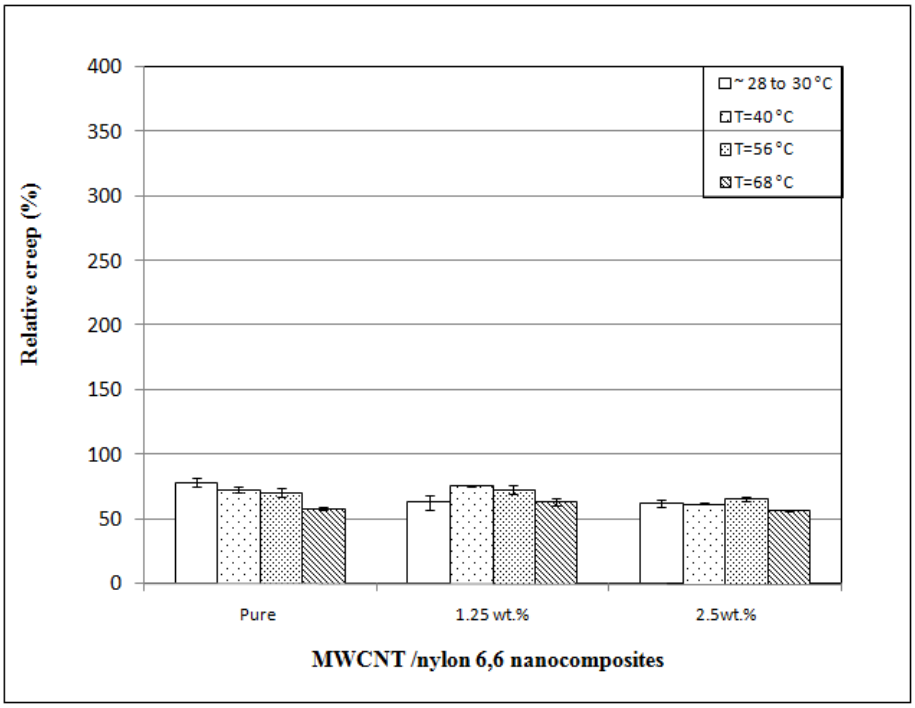

Figure 20. Relative creep for MWCNT /nylon 6,6 nanocomposites at various temperatures

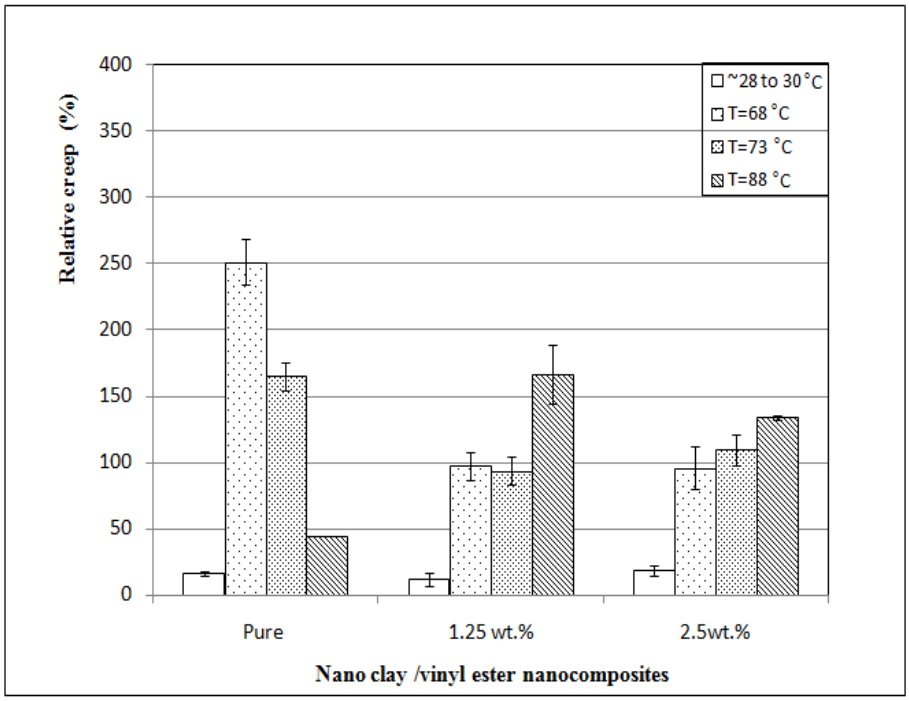

Figure 21. Relative creep for nano clay /vinyl ester nanocomposites at various temperatures

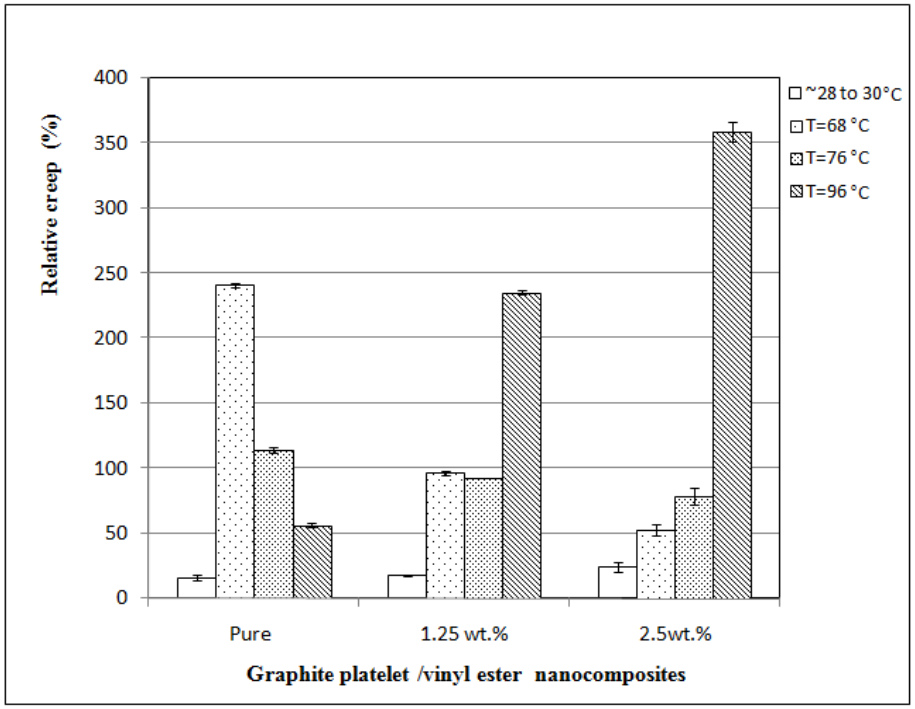

Figure 22. Relative creep for graphite platelet /vinyl ester nanocomposites at various temperatures

Master curves of creep were generated by post processing (shifting) of creep data at different temperatures to a reference room temperature (RT) for all the nanocomposites. Master curve of creep-strain for MWCNT /nylon 6,6 nanocomposites is seen in Figure 23. Creep initially started at a very high rate and subsequently decreased until it saturated at around11 years. The 1.25 wt. percent reinforced nylon 6,6 had lower creep compliance than pure nylon and the 2.5 wt. percent reinforced nylon 6,6 had the lowest. Nylon loaded with 1.25 and 2.5 wt percent had respectively 95% and 89% relative creep after 400 minutes, while the pure sample showed 116% relative creep as shown in Figure 24. This means that nylon 6,6 with 2.5 wt. percent MWCNT offers greater resistance to creep over a period of time.

Figure 25 summarizes the effect of nano clay and graphite platelets on relative creep of vinyl ester generated from shifting at various temperatures. The 2.5 wt. percent nano-clay vinyl ester was observed to exhibit the minimum relative creep of all the nanocomposites including graphite reinforced vinyl ester. For example, 1.25 and 2.5 wt. percent reinforced vinyl ester with nano clay composites had 228% and 182% relative creep respectively, compared to 528% for pure vinyl ester after 11 years duration. Moreover, vinyl ester with 1.25 wt. percent graphite has comparable relative creep characteristics with that of 2.5 wt. percent nano clay reinforced vinyl ester.

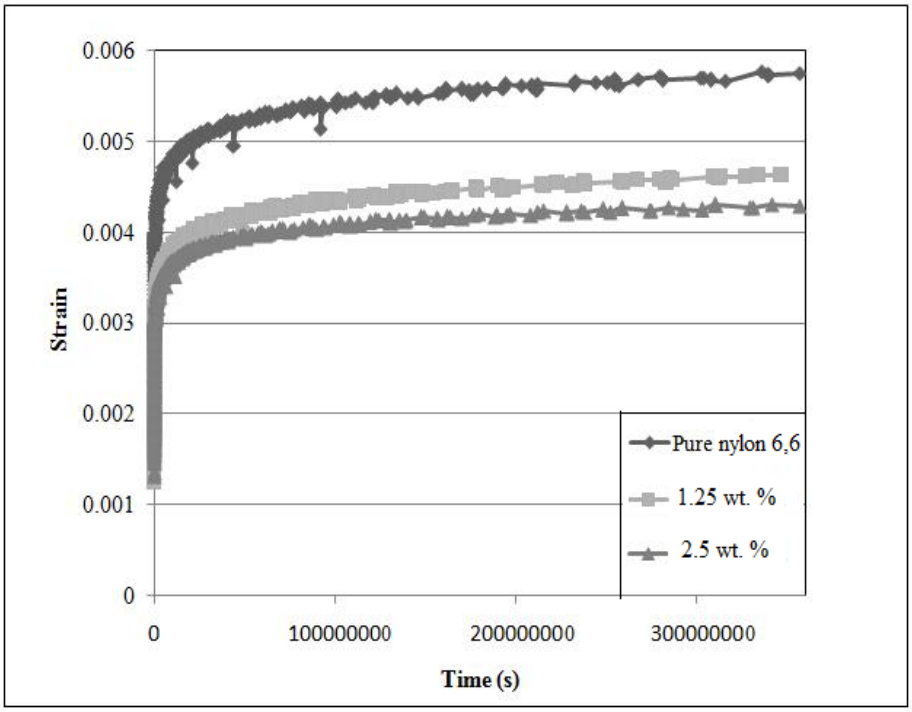

Figure 23. Master curve of creep-strain generated by shifting of creep data at different temperatures to reference temperature (~ 28 to 30 °C) for MWCNT /nylon 6,6 nanocomposites

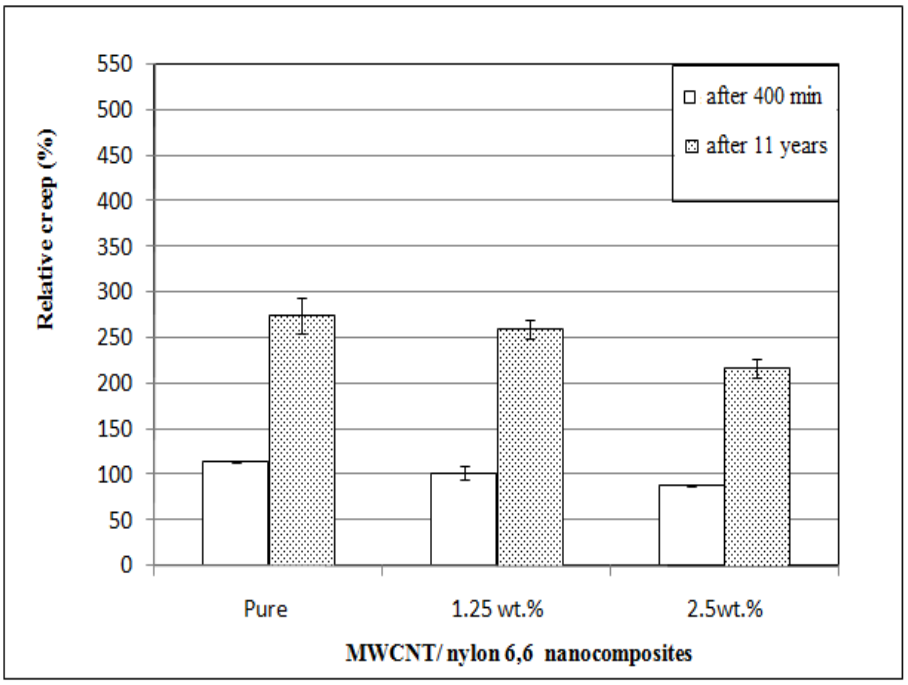

Figure 24. Relative creep for MWCNT /nylon6,6 nanocomposites generated from shifting of creep data at different temperatures to reference temperature (~ 28 to 30 °C)

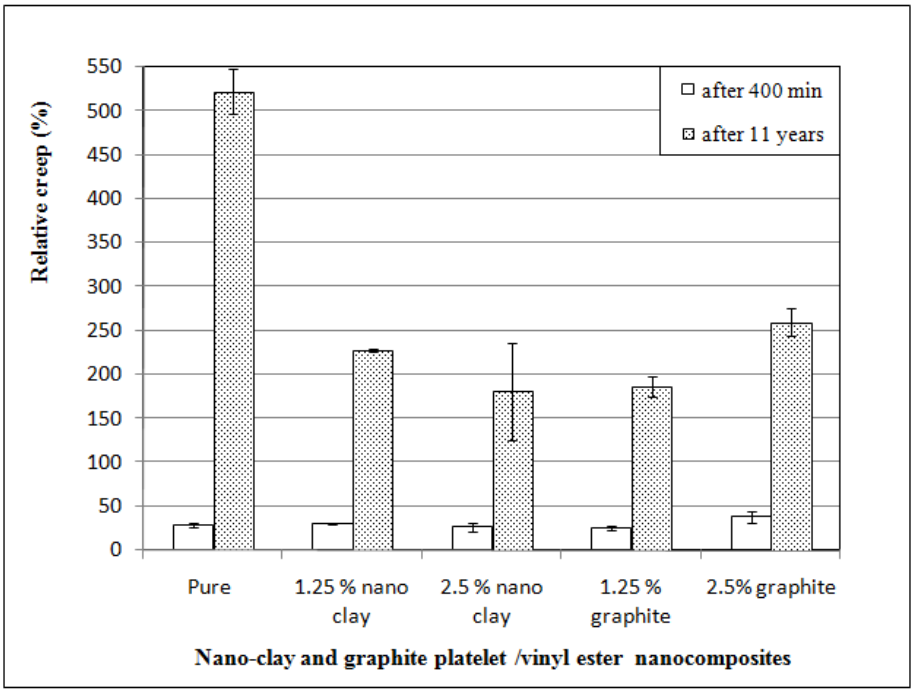

Figure 25. Relative creep for vinyl ester nano clay and graphite nanocomposites generated from shifting of creep data at different temperatures to reference temperature (~ 28 to 30 °C)

4. CONCLUSIONS

From DMA testing, it was observed that storage modulus of pure nylon 6,6 is greater than that of pure vinyl ester, where as glass transition temperature and loss factor are higher for pure vinyl ester compared to pure nylon 6,6. Storage modulus increased with increasing reinforcement in all the cases. It was also observed that storage modulus and glass transition temperature of 2.5 wt. percent graphite platelet reinforced vinyl ester is more than that of nanoclay reinforced vinyl ester, while loss factor is higher in case of 2.5 wt. percent nanoclay reinforced vinyl ester.

The effect of both temperature and time on creep response of nylon 6,6 reinforced with MWCNT and vinyl ester reinforced with nano clay and graphite platelets has been characterized using time-temperature superposition. The 2.5 wt. percent nano clay /vinyl ester had the lowest creep compliance (greatest creep-resistance) over time periods of 400 min and 11 years, when the creep data at different temperatures was shifted to a reference room temperature (RT). Relative creep at the glass transition temperatures was less for MWCNT /nylon 6,6 nanocomposites, however, than that for vinyl ester reinforced nanocomposites. The 2.5 wt. percent graphite platelet reinforced vinyl ester had 360% relative creep, whereas the 2.5 wt. percent MWCNT /nylon 6,6 had only 63% relative creep at their respective glass transition temperatures.

5. ACKNOWLEDGMENT

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