

## **Effects of Bromination on the Viscoelastic Response of Vinyl ester Nanocomposites**

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Composite Structures and Nano-Engineering Research

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### **Abstract**

The viscoelastic properties, modulus (stiffness) and damping (energy dissipation) of 1.25 and 2.5 wt. percent nanoclay and graphite platelet reinforced Derakane 411-350 (non-brominated) and 510A-40 (brominated) vinyl ester have been studied over a range of temperature and frequency. Effects of frequency on the viscoelastic behavior were investigated using a Dynamic Mechanical Analyzer (DMA) by sweeping the frequency over three decades, from 0.01 to 10 Hz, and temperature range covering the glass transition regimes. Master curves were generated by time-temperature superpositioning of the experimental data at a reference temperature. The nano reinforced composites showed a drop in storage modulus with bromination. Nanocomposites with 1.25 and 2.5 wt. percent graphite had the highest storage modulus among brominated specimens. Bromination was also found to significantly increase the glass transition temperature ( $T_g$ ) and damping for all nanocomposites. Increase in,  $T_g$ , with bromination was probably due to the molecular weight effect. Among the brominated specimens, 1.25 wt. percent graphite platelet reinforced vinyl ester exhibited the best viscoelastic response with high damping and glass transition temperature, along with superior storage modulus over a longer time period.

**Keywords:** Nanocomposites, Viscoelastic properties, Bromination

## 1. Introduction

The DMA is a useful tool to study the effects of frequency and temperature on viscoelastic properties of composites. In dynamic mechanical analysis, the response of a material loaded in a sinusoidal excitation mode at either fixed or variable frequency is measured. The two main mechanical properties that are obtained from a DMA test are: storage modulus, which measures the maximum stored energy in the material per unit loading cycle, and loss modulus which is proportional to the energy dissipated by the material.

Most frequently, DMA measurements are carried out under constant displacement amplitude in a fixed-frequency deformation mode, in which the mechanical properties are function of temperature only. Other measurements that provide more information may include frequency sweep with temperature steps, to which time-temperature superposition (TTS) applied to predict the long-term time dependent properties of the material. The shifting model could follow either Williams-Landel-Ferry (WLF) model or the Arrhenius model [1], depending on the reference temperature at which the data are shifted. The WLF model is typically used to describe frequency/ temperature equivalency effects of polymers in the glass transition region [2].

The thermo-mechanical behavior of composites is quite complicated, and to address the dual behavior of a material which is time and temperature dependent, a costly and time-consuming experimental testing procedure would be required. The other approach is to take advantage of the time-temperature superposition principle which facilitates the construction of master curves. These master curves provide valuable information on the mechanical response of the material and enables the prediction of viscoelastic parameters beyond the accessible range.

Melo and Radford [3] developed a DMA-based approach to study the viscoelastic properties of fiber-reinforced (PEEK/IM7) composites. A mechanical model was developed, to describe the 3-D viscoelastic properties of a transversely isotropic material, based on five independent storage moduli and three values of damping (loss factor).

Magableh et al., [4] characterized the storage modulus ( $E'$ ), loss modulus ( $E''$ ), damping, glass transition temperature ( $T_g$ ) and creep behavior for nylon 6,6 thermoplastic reinforced with 1.25

and 2.5 wt. percent multi-wall carbon nano tubes (MWCNT), and Derakane 411-350 non-brominated vinyl ester thermoset reinforced with 1.25 and 2.5 wt. percent Cloisite 30B nanoclay and exfoliated graphite nanoplatelets (xGnP). Short range creep tests were performed at isothermal conditions, and the time-temperature superposition (TTS) principle was utilized to generate creep-strain master curves at a reference temperature.

Bakis and Temple-Boyer [5] studied the tensile creep response of coupon-type specimens made of epoxy reinforced with up to 3 wt % single-walled carbon nanotubes. Master creep compliance curves were constructed at 40 C reference temperature based on the time-temperature superposition principle and Findley- type creep law [6] for the creep-strain was fit to the master curves.

The deformation behavior of vinyl ester polymer under monotonic tensile loading and relaxation conditions was characterized and modeled by Plaseied and Fatemi [7]. The Standard Linear Solid model was used and modified to model the stress- strain behavior of this material over wide range of strain rate and temperatures.

Focus of our research is on developing stronger, safer and more cost-effective structures for the new generation naval ships; especially nanoparticle reinforced glass/carbon polymeric based composites and structural foams for blast/shock/impact mitigation. Fire, smoke and toxicity are of significant concern in ship structures. Bromination is a process at which the fire resistance performance of vinyl ester resin systems can be improved. The work reported here is an extension of previous work [4] on the viscoelastic behavior of non-brominated vinyl ester nanocomposites. An attempt has been made to experimentally characterize the dynamic storage modulus ( $E'$ ) and damping of brominated and non-brominated vinyl ester reinforced with 1.25 and 2.5 wt. percent nano-clay and graphite platelets as a function of temperature and frequencies. Dynamic mechanical testing has been used to perform multi-frequency (accelerated temperature measurements) and theoretical time-temperature superposition treatment of the data. Effects of bromination on the viscoelastic response of these vinyl ester nanocomposites are discussed.

## **2. Theory**

The time- temperature superposition principle is based on the fact that processes involved in molecular motion occur at larger rates at elevated temperatures. The change in property which

occurs relatively quickly at higher temperatures can be made to appear as if they occurred at longer times or lower frequencies simply by shifting the data with respect to time (1/frequency) [2]. By shifting the data with respect to frequency to a reference curve, a master curve is generated, which covers time (frequencies) outside the accessible range.

The relationship between the shifting factor,  $a_T$ , and temperature can be described through the Arrhenius model [2]. For this model, the degree of shifting was calculated in Equation (1).

$$\text{Log } a_T = \frac{E}{R(T - T_o)} \quad (1)$$

Where,  $E$ , is the activation energy associated with relaxation transition,  $R$ , is the gas constant (8.314 J/mole C) and  $T_o$  is the reference temperature.

### 3. DMA Experiments

#### 3.1. DMA setup

Dynamic measurements were carried out using the TA Instrument model Q800 DMA on prismatic specimens deformed in a single-cantilever clamping mode, with a span length of 17.5 mm.

Since a material's modulus is independent of geometry, equations relating the sample stiffness to the modulus depend on clamping conditions, sample shape and deformation mode. The calculation of stiffness for the single-cantilever clamp used in model Q800 DMA, along with appropriate correction factor is described in Ref [8]. Also included are stress and strain equations calculated from force and deformation amplitude, assuming linear viscoelastic behavior. The stiffness model, along with maximum stress and strain equations for a rectangular cross section sample tested with single-cantilever clamp [8] are given as:

$$E = \frac{K_s}{F_C} \frac{L^3}{12 I} \left[ 1 + \frac{12}{5} (1 + \nu) \left( \frac{t}{l} \right)^2 \right] \quad (2)$$

$$F_C = 0.7616 - 0.02713 \sqrt{\frac{L}{t}} + 0.1083 \ln\left(\frac{L}{t}\right) \quad (3)$$

$$\sigma_x = \frac{6 P L}{w t^2} \quad (4)$$

$$\varepsilon_x = \frac{3 \delta t F_c}{L^2 \left[ 1 + \frac{12}{5} (1 + \nu) \left( \frac{t}{l} \right)^2 \right]} \quad (5)$$

where:

$E$  = elastic modulus

$L$  = clamp span length

$K_s$  = measured stiffness

$t$  = sample thickness

$I$  = sample moment of inertia

$\nu$  = Poisson's ratio

$F_c$  = clamping correction factor

$\sigma_x$  = stress

$\varepsilon_x$  = strain

$P$  = applied force

$\delta$  = amplitude of deformation

### 3.2. Test description

The 1.25 and 2.5 wt. percent nanocaly and graphite platelet reinforced non-brominated and brominated vinyl ester nanocomposites were characterized by performing a multi-frequency isothermal mode, in which the sample is equilibrated at different temperatures and subjected to a series of frequencies. Specimens with dimensions of 35mm×10mm×1.6 mm were subjected to frequencies between 0.01 and 10 Hz with a temperature step rate of 4°C per minute starting from 30 C (RT) to 150 C. A very small displacement amplitude (25  $\mu m$ ) was applied since the analysis assumes linear viscoelastic characterization, and two specimens were tested from each configuration. The raw data was then fed to the Rheology data analysis software [8] to generate the master curves.

## 4. Results and discussion

### 4.1. Molecular weight

As shown in Figure 1, the densities of brominated vinyl ester nanocomposites are greater than that of the non-brominated samples. It should be noted that Bromine is a heavy atom and there are four Bromine atoms bonded in one molecule, which results in the molecular weight as well as the density being higher for brominated specimens. Specific gravity of 510A-40 brominated vinyl ester is about 1.23 while that of the non-brominated version 411-350 is 1.046.

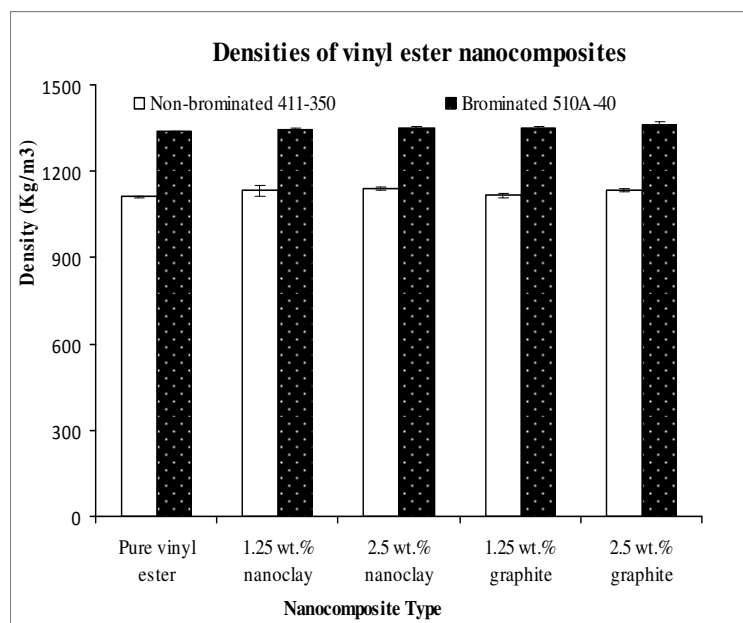


Figure 1. Densities of non-brominated (411-350) and brominated (510A-40) vinyl ester nanocomposites.

## 4.2. Storage modulus

The storage modulus versus temperature curve provides valuable information about the stiffness of a material as a function of temperature, and it is sensitive to structural changes such as molecular weight, fiber-matrix bonding and degree of crosslinking action [1].

Figures 2-4 show the storage modulus ( $E'$ ) for both brominated and non-brominated vinyl ester nanocomposites, as a function of temperature and frequency. The temperature range has been selected such that the tested samples pass through the thermo-mechanical transition region. The brominated nanocomposites showed an initial drop in storage modulus with nano-reinforcements (Figures 3 and 4). However, the 1.25 and 2.5 wt. percent graphite platelet reinforcements had the highest initial storage modulus (at 30 C) among the brominated specimens (Figure 5).

Higher initial storage modulus in fiber reinforced composite materials are in general attributed to good fiber/matrix bonding (cross linking), or higher initial molecular weight [1]. The loss in storage moduli for brominated nanoclay composites could be due to weak interfacial bonding between the nanoclay reinforcement and brominated resin (Figures 5). On the other hand, graphite platelets appear to be bonding better with the brominated resin resulting in higher storage modulus (Figure 5) compared to pure vinyl ester.

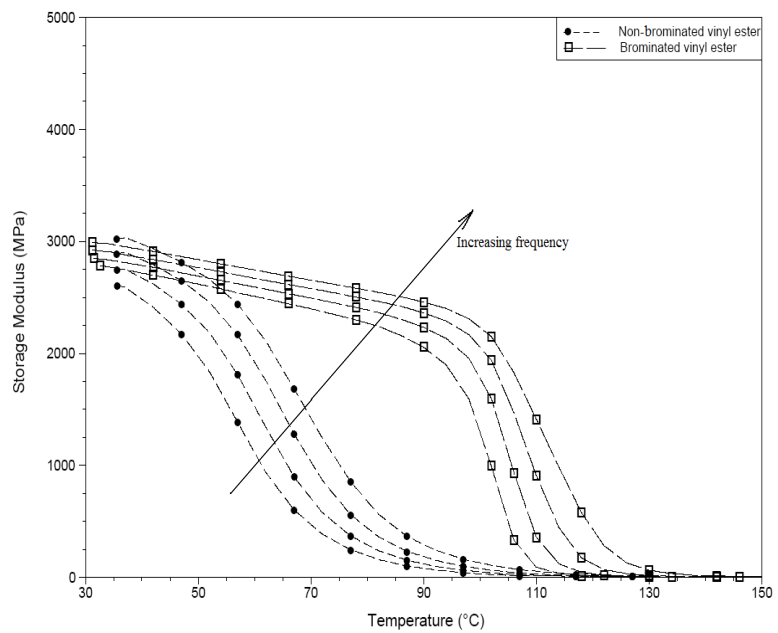


Figure 2. Storage modulus for pure vinyl ester with and without bromination.

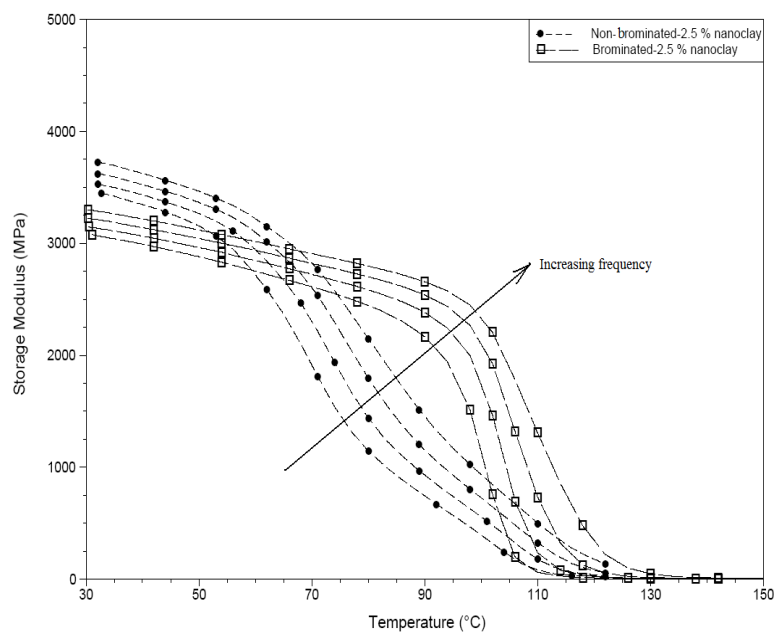


Figure 3. Storage modulus for 2.5 wt. percent nanoclay reinforced vinyl ester with and without bromination.

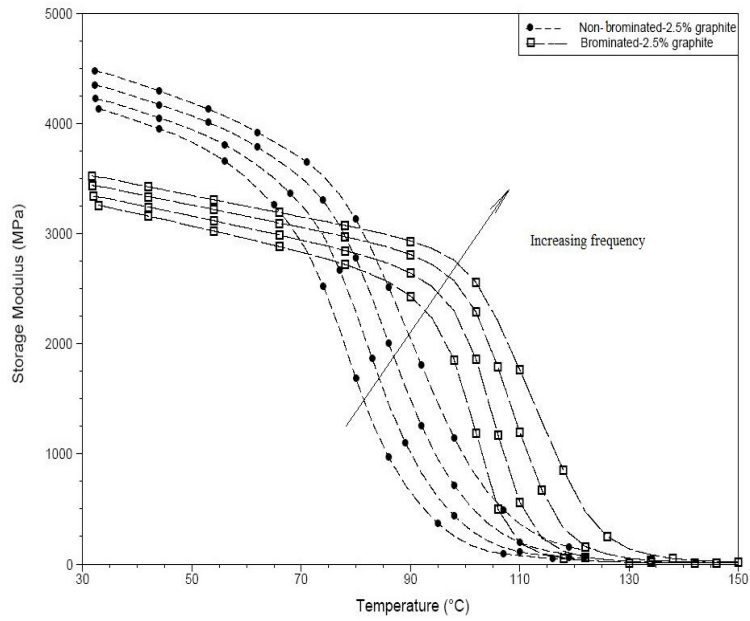


Figure 4. Storage modulus for 2.5 wt. percent graphite platelet reinforced vinyl ester with and without bromination.

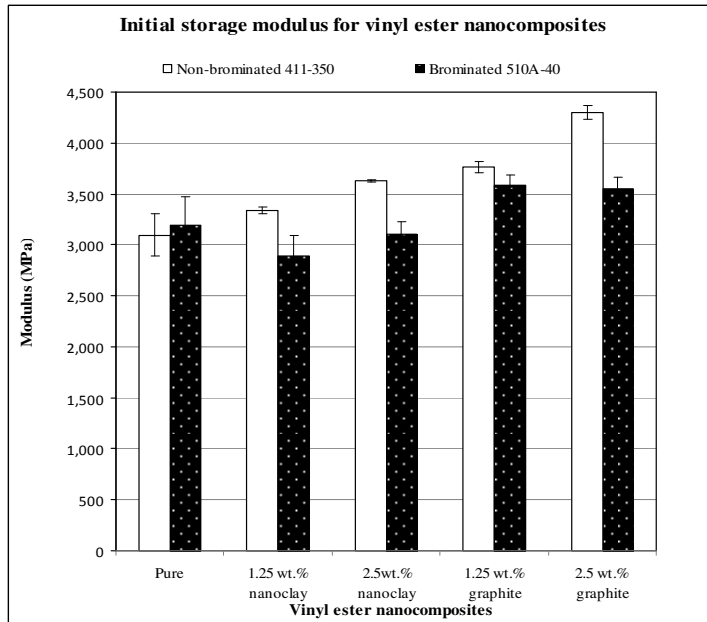


Figure 5. Initial storage modulus for brominated and non-brominated nanocomposites at 1 Hz frequency.

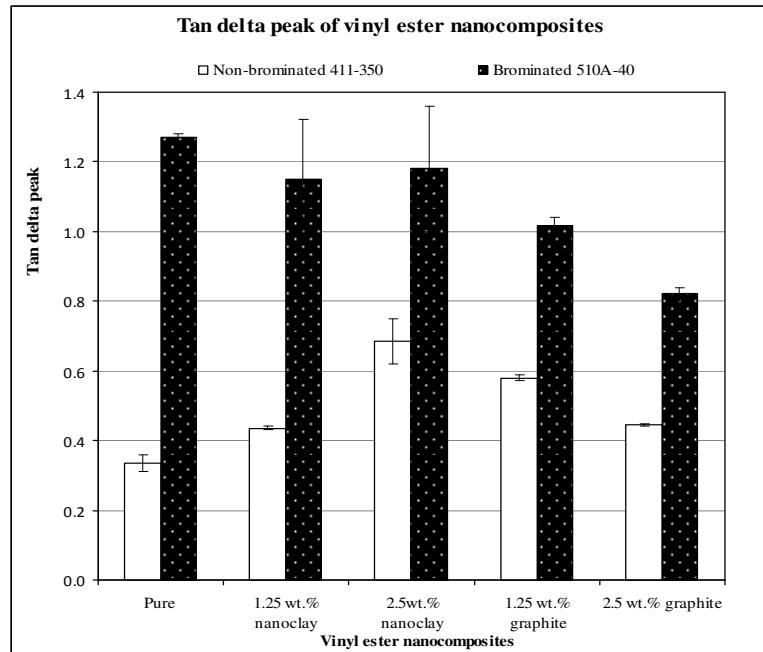


Figure 6. Peaks of Tan  $\delta$  for brominated and non-brominated vinyl ester nanocomposites at 1 Hz frequency.

### 4.3. Damping

Tan  $\delta$ , defined as the ratio of loss modulus to storage modulus, is a measure of the material damping. Peak of Tan  $\delta$  is the region over which the material experiences a transition from glassy to a leathery behavior, associated with the onset of short range molecular segments motion, of which all are initially fixed. Materials with high Tan delta have the tendency to flow more and are found to be better in resisting impact energy [9]. Bromination in general resulted in greater Tan  $\delta$  peak values for all the nano reinforcements including pure vinyl ester, which showed a 300% increase in damping (Figure 6). The 2.5 wt. percent graphite platelet reinforced vinyl ester had the lowest Tan  $\delta$  peak among all brominated specimens.

The area under Tan  $\delta$  curve is another good indicator of the total energy absorbed by the material [10]. Higher the area under Tan  $\delta$  curve, the greater the degree of molecular rearrangement, which enables the material to better absorb and dissipate energy. Similar Tan  $\delta$  peak trend shown in Figure 6 was also observed in area under Tan  $\delta$  curves (Figure 7). Brominated

nanocomposites in general exhibited higher area under  $\text{Tan } \delta$  curves compared to the non-brominated samples at 1 Hz frequency (Figure 7). Again, the 2.5 wt. percent graphite reinforced vinyl ester showed the lowest (area under  $\text{Tan } \delta$ ) among all brominated specimens.

The higher  $\text{Tan } \delta$  peak value observed in Figure 6 with 2.5 wt. percent nanoclay reinforcement compared to 2.5 wt. percent graphite for brominated specimens, indicates greater molecular mobility in nanoclay brominated composites. The greatest loss in storage modulus along with the superior  $\text{Tan } \delta$  peak associated with the addition of nanoclay reinforcement (Figures 5 and 6) to brominated vinyl ester indicates that this reinforcement may be adversely affecting the interfacial bonding. The graphite platelets appear to form better interfacial bonding with brominated resin than nanoclay reinforcements.

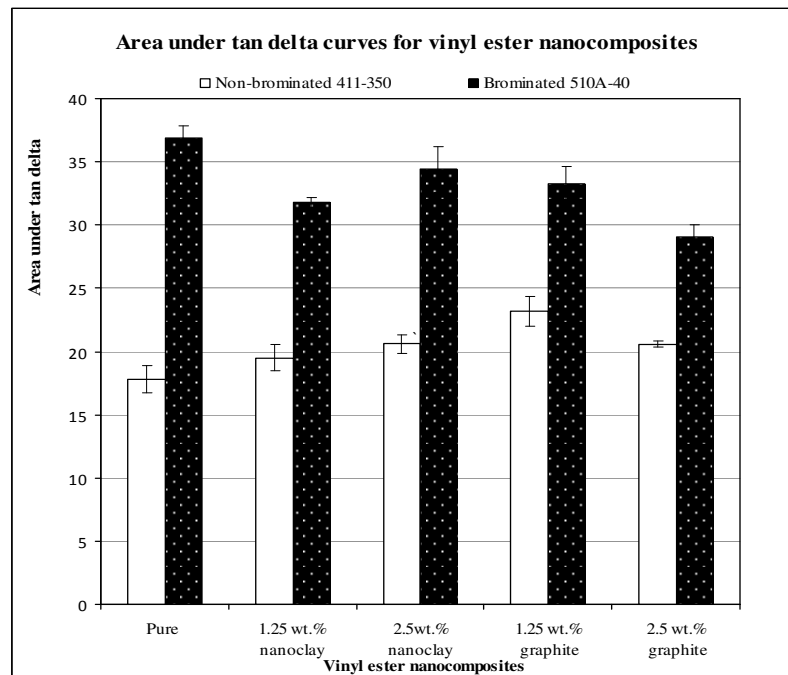


Figure 7. Area under  $\text{Tan } \delta$  curves for brominated and non-brominated vinyl ester nanocomposites at 1 Hz frequency.

#### **4.4. Glass transition temperature, $T_g$**

Figures 8 to 10 show the loss modulus curves for the pure and 2.5 wt. percent nanoclay and graphite platelet reinforced vinyl ester, with and without bromination, as a function of frequency. Glass transition temperature reported here is the temperature corresponding to the peak of loss modulus curves. Referring to Figure 11, bromination had a significant effect in increasing the glass transition temperatures for all specimens. For example,  $T_g$ , for pure vinyl ester increased by about 80% with bromination at 1 Hz frequency. However, all the brominated nanocomposites have almost the same glass transition temperatures at a given frequency. Moreover, the glass transition temperatures shifted marginally higher with increasing frequency. The significant increase in,  $T_g$ , achieved with bromination is probably due to the molecular weight effect. As molecular weight increases with bromination, the glass transition region is displaced to longer time or temperature, because chain movement is expected to suppress when molecular entanglement is increased [11]. Based on this phenomenon, the almost constant,  $T_g$ , was expected for all brominated nanocomposites, because of minor changes in weight with addition of nano-reinforcement.

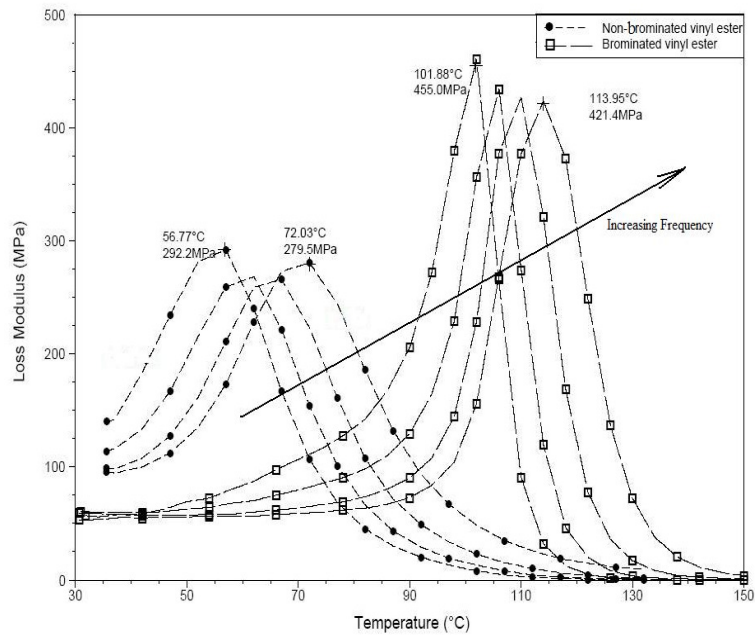


Figure 8. Loss modulus for pure vinyl ester, with and without bromination, as a function of frequency.

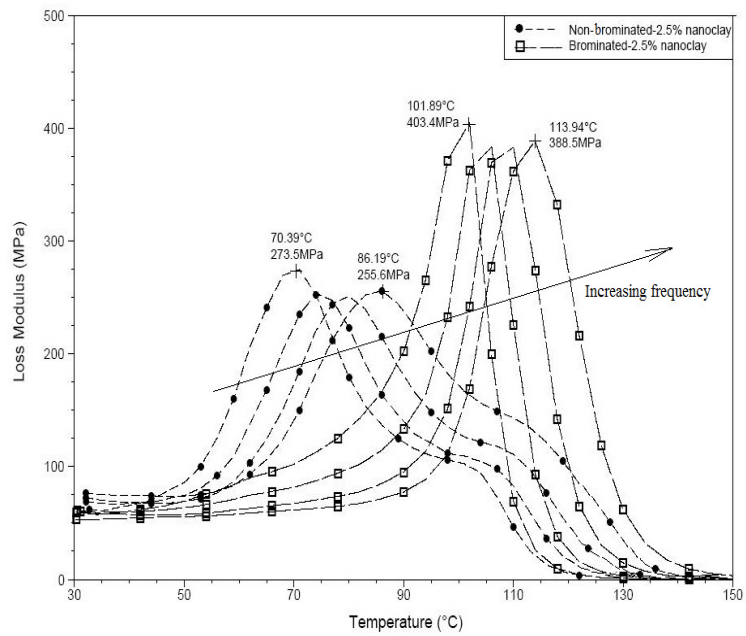


Figure 9. Loss modulus for 2.5 wt. percent nanoclay reinforced vinyl ester, with and without bromination, as a function of frequency.

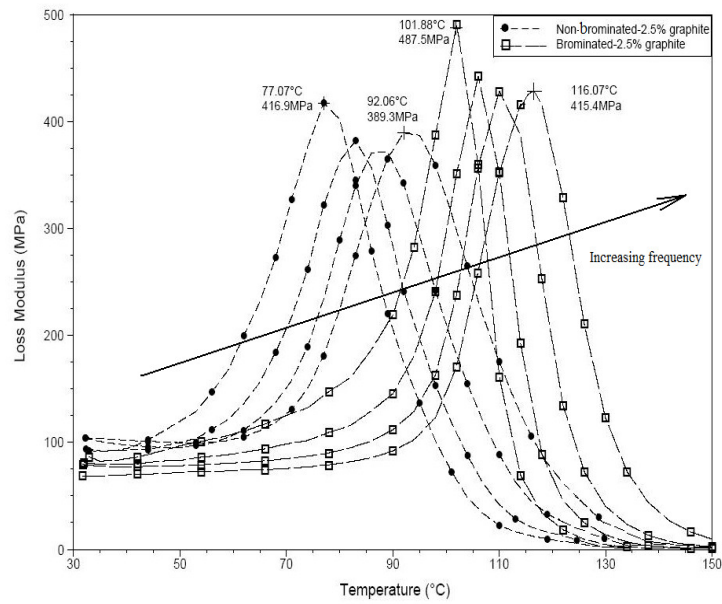
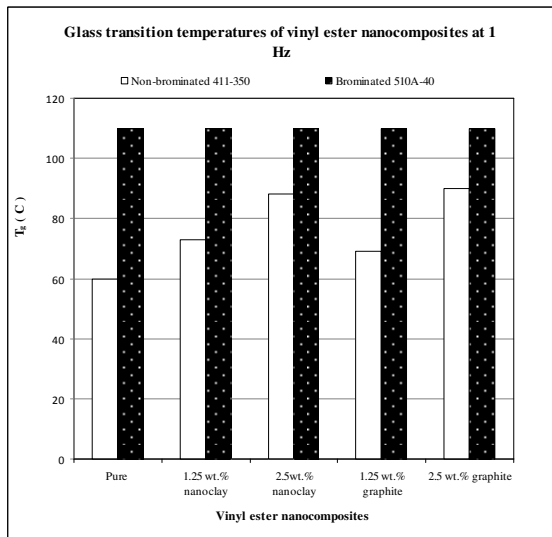
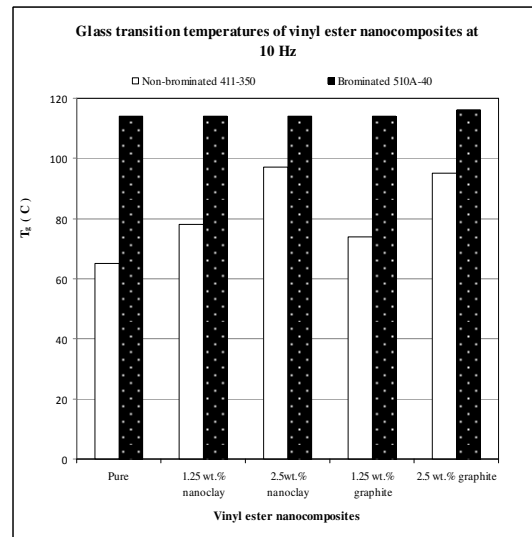


Figure 10. Loss modulus for 2.5 wt. percent graphite platelet reinforced vinyl ester, with and without bromination, as a function of frequency.



(a)

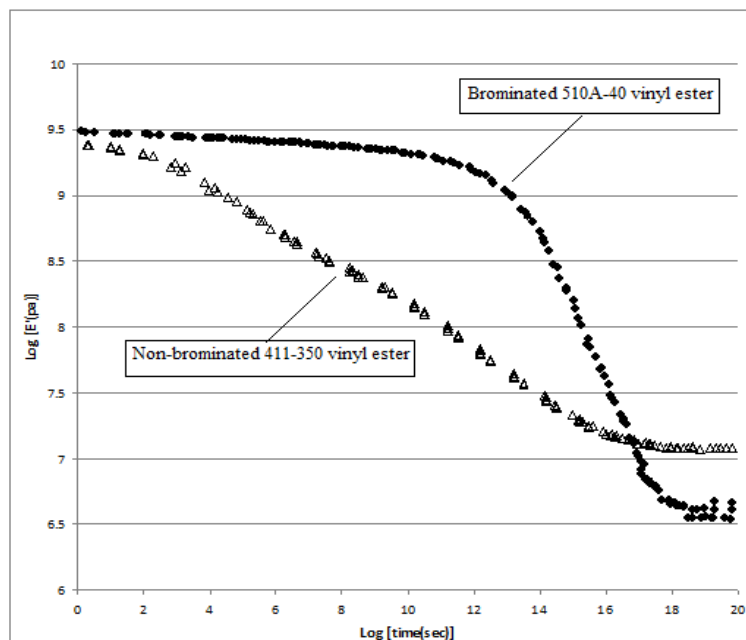


(b)

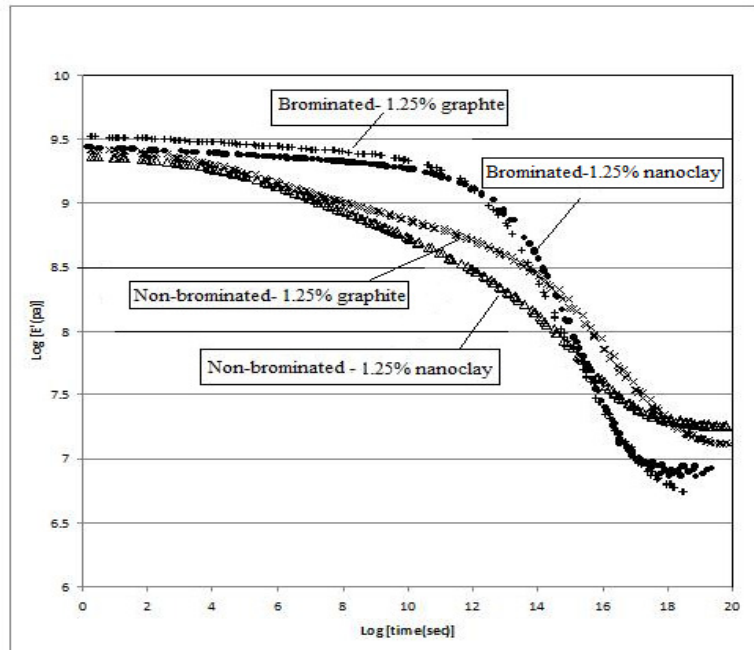
Figure 11.  $T_g$  (°C) for vinyl ester nanocomposites, with and without bromination at (a) 1 Hz, and (b) 10 Hz.

#### 4.5. Time-Temperature Superposition

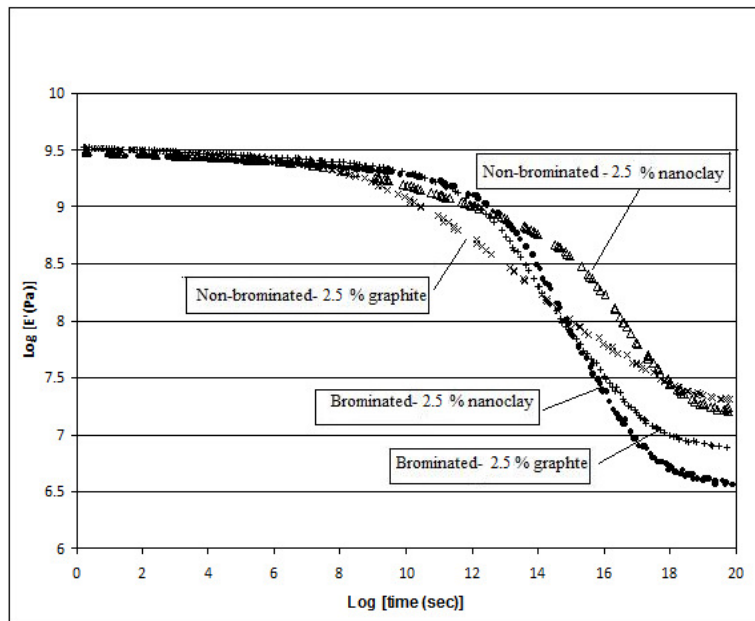
Since the glass transition temperature for nanocomposites with and without bromination is found to be varying, for this work a reference temperature of 50 C was chosen to generate the master curves for storage modulus. To perform this, data from higher temperature experiments in the lower portion of the plot are shifted to the left (lower frequencies) and curves corresponding to the temperatures lower than 50 C are shifted to the right. Figure 12 shows the generated master curves of storage modulus over an extended period of time. From Figure 12-a, the brominated pure vinyl ester is observed to maintain its rigidity (at 50 C) with an average dynamic storage modulus of (2.5 GPa) over a period of  $10^{10}$  secs (321.5 years), where as the non-brominated vinyl ester starts to loose it's stiffness gradually just after  $10^3$  secs (17 minutes). This is a significant improvement on the long term behavior of vinyl ester with bromination. Similarly, the brominated 1.25 wt. percent graphite platelet reinforced specimens exhibit superior average modulus of 2.7 GPa over 321.5 years (Figure 12-b). In contrast, all the specimens with 2.5 wt. percent nanoreinforcement, both with and without bromination, show a stable dynamic response with an average storage modulus of 2.5 GPa (Figure 12-c) for the first  $10^8$  sec (3.2 years) only.



(a)



(b)



(c)

Figure 12. Master curves of storage modulus (at 50 C) as a function of log time for (a) pure vinyl ester, (b) 1.25 wt. percent and (c) 2.5 wt. percent nano-reinforcements.

## 5. Conclusions

In this article, the effect of bromination on the viscoelastic behavior of Derakane 411-350 (non-brominated) vinyl ester reinforced with 1.25 and 2.5 wt. percent nanoclay and graphite platelets was investigated with a DMA. Frequency sweep across three decades (0.01-10 Hz) was performed over temperature steps from 30 C to 150 C at a rate of 4 C/min. The time-temperature superposition principle was applied to create master curves of dynamic storage modulus at a reference temperature of 50 C.

The brominated nanocomposites showed an initial drop in storage modulus with nano-reinforcements. The 1.25 and 2.5 wt. percent graphite, however, had the highest storage modulus among brominated specimens. Both the pure vinyl ester and nanocomposites exhibited better  $\text{Tan } \delta$  peak values and a larger area under the  $\text{Tan } \delta$  curves with bromination. Lowest damping ( $\text{Tan } \delta$  peak) was observed with the 2.5 wt. percent graphite platelet nano reinforcement among all brominated specimens. From the storage modulus and damping results, it is concluded that graphite platelets appear to form better interfacial bonding with the brominated resin than the nanoclay reinforcements. Bromination was found to significantly increase the glass transition temperature for both pure vinyl ester (up to 80 %) and the nanocomposites. This amount of increase is probably due to the molecular weight effect. The glass transition temperatures also shifted marginally higher with increasing frequency. The brominated vinyl ester reinforced with 1.25 wt. percent graphite platelet exhibited the best viscoelastic response with high damping and glass transition temperature, along with superior storage modulus over a longer time period.

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