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Bromination Effects on theDynamicBehavior of Graphite Platelet and CTBN Vinyl Ester Reinforced Nanocomposites

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Abstract

Derakane 411-350 grade of Vinyl ester has been generallyemployed as a matrixin nanoparticle reinforced glass/carbon polymeric based composites, after which new class has been developed, namely (510A-40) brominated vinyl ester resin.This matrix resin was selected due to its good corrosion resistance and toughness and recently, this brominated version has been modified with an unreactive liquid carboxy terminated butadiene nitrile (CTBN) rubber to promote interfacial properties and impact mitigation. Two classes or generations of vinyl ester resin have been Visco-elastically analyzed after reinforcing with different amount of graphite platelets. In this research, the dynamic responseof DERAKANE 411-350 vinyl ester thermoset is studied against DERAKANE 510A-40 vinyl ester resin modified with 10 weight percent Carboxy Terminated Butadiene Nitrile (CTBN). Both systems are reinforced with 1.25 and 2.5 wt. % exfoliated graphite nanoplatelets (xGnP). Investigation is made over a range of temperature and frequency. Effects of frequency on the dynamic behavior were investigated using a Dynamic Mechanical Analyzer (DMA) by sweeping the frequency over : 0.01 to 10 Hz, and temperature range from room temperature to140°C at a step rate of 4 oC/min. The nano reinforced composites showed a drop in initial dynamic modulus with bromination. Brominated nanocomposites with 1.25 and 2.5 wt. percent graphite had the highest storage modulus among all specimens.

Keywords: Bromination, Vinyl ester, Nanocomposites, Graphite, viscoelastic.

Nomenclature

Parameter Notation	**Parameter definition**
XGnP	Exfoliated graphite nano-platelet
CTBN	Carboxy Terminated Butadiene Nitrile
L	Clamp span length
t	Sample thickness
w	Width of the specimen
ν	Poisson’s ratio
F_c	Clamping correction factor
M	Bending moment
σ_x	Bending stress
ε_x	Axial strain
P	Applied force
δ	Amplitude of deformation
V	Crosslinking density
R	Universal Gas Constant
G_0^n	Plateau modulus from the shear modulus curve
T_g	Glass Transition Temperature

1. Introduction

Classical composite materials are no longer sufficient for demanding requirements of materials with enhanced chemical and thermal properties, nor can they be engineered to control properties at atomic/nano scale. The need of such control in properties has come from the fact that the bulk mechanical properties of materials under impact load or temperature are dictated by their molecular level orientation. Eventually, nano systems could be built at the molecular level to create large structures with primarily novel molecular organizations. The emphasis is on light-weight nanoparticle reinforced glass/carbon polymeric composites and structural foams for blast, shockwave and impact mitigation [1-3]. The ideal flexural rigidity, vibrational damping and enhanced energy absorption capability of vinyl ester-based composite are investigated in this research.

Thermoset vinyl ester polymeris are becoming increasingly crucial in industrial applications due to their enriched properties. They show characteristics like epoxy resins, as well as unsaturated polyester resins. Benefits include high tensile strength and stiffness, low cost, process versatility and stable chemical response. However, vinyl ester still has some challenges like inadequate resistance to crack propagation, brittleness, and high shrinkage during polymerization process. To improve their fracture resistance or toughness, they are usually blended with different additives or modifiers, which normallycreateanother dispersed phase. The most frequently used modifiers are liquid rubbers.

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Interfacial interaction between fillers and thermoset resin is oftencontrolled to alleviate volume shrinkage, void formation and improving surface dispersion along with impact toughness.Understanding stress transfer tool and interfacial adhesion across multi layers inclusions and developing accurate material models will help in establishing upcoming design criteria in the engineering of polymer based composites [4]. Means of incorporating nanoparticles into polymer could be *ex-situ*, like dispersion of the synthesized nanoparticles into polymer solution, or *insitu* monomer polymerization process in the presence of the nanoparticles [5]. The bonding between the nanoparticles and matrix for the *ex-situ* fabricated composites are Van der Waals forces, steric interaction. However, the *in-situ* synthesis technique may form strong chemical bonding within the composite.

Mechanical response of vinyl ester resin healed with styrene and treated with liquid rubber (CTBN) has been studied by Auad et.al [6]. A noticeable drop in density causing unfavorable fracture toughness was observed in higher CTBN content. Balakrishnan *et al.* [7] inspected the fracture response of rubber dispersed epoxy and conditional cavitations, yielding, plastic distortion of matrix, crack diversion and energy dissipation caused by rubber elements which enhancesthe ductility of epoxy nanocomposites.

Frohlich *et al.* [8] suggested compatibility matching as the key to novel phase-separated nanocomposites with significantly improved toughness. Schroeder *et al.* [9] characterized morphologically thermoset styrene/vinyl ester resins of different molecular weights modified with polymethyl methacrylate (PMMA). It was found that different morphologies including distribution of thermoplastic rich particles in a thermoset resin, continuity of network structure were highly dependent on molecular weight of vinyl ester, curing temperature and concentration of the PMMA additives. The addition of the thermoplastic PMMA increased the fracture resistance without significantly influencing both volume shrinkage reduction and the thermal-mechanical properties of the built thermosets.

The focus of ongoing research is on developing stronger, safer and more cost-effective structures for the new generation ships; especially nanoparticle reinforced glass/carbonthermoset-polymeric composites and structural foams for blast/shock/impact mitigation [10]. Fire, smoke and toxicity are of significant concern in ship and marine structures[11]. This article presents recent results on processing of brominated vinyl ester structural composites with nanoreinforcement for marine composite applications [12]. Instead of using the commercial Derakane 411-350 vinyl ester resin, a510A-40 brominated bisphenol-A-based vinyl ester consisting of 38 wt. % styrene was developed and modified to produce the maximum level of fire retardancy along with enhanced chemical stability and toughness. This matrix resin was selected due to its good corrosion resistance and toughness. Bromine is an effective flame retardant, especially when combined with antimony oxide. Bromination of vinyl ester resin imparts fire retardancyas manifested by flame spread and lower heat release rates. However, this brominated vinyl ester resin itself is typically brittle. To improve their fracture resistance or toughness, they are usually blended or reacted with different additives and modifiers, which generally forms a second dispersed phase. The most frequently used modifiers are liquid rubbers. The brominated version has been treated with an unreactive liquid carboxy terminated butadiene nitrile (CTBN) rubber to promote interfacial properties. These two classes or generations of vinyl ester have been viscoelastically analyzed after reinforcing with graphite platelets (xGnP). The aim of this paper is to characterize the dynamic behavior of 510 A-40 vinyl ester reinforced with xGnP treated with an unreactive liquid carboxy terminated butadiene nitrile (CTBN) rubber versus DEREKANE 411-350 vinyl ester reinforced with xGnP only. The viscoelastic response of the two material systems was studied using dynamic mechanical analyzer (DMA). Multi-frequency sweep loading was performed over a wide range of temperatures.

2. Experimental

2.1. *Dynamic Mechanical Analyzer (DMA)*

Dynamic measurements were conducted using the TA Instrument model Q800 as demonstrated in Figure 1 [13].Prismatic specimens are deformed in a single cantilever clamping mode, with a span length of 0.7 inch. Stress and strain with the single-cantilever clamp used in model Q800 DMA are calculated as per Equations (1) and (2), respectively [14]

$$\sigma = \frac{M \cdot (t\,/\,2)}{\left(\frac{wt^3}{12}\right)} \qquad (1)$$

$$\epsilon_x = \frac{3\,(\delta.t.F_c)}{L^2\left[1+2.4(1+\nu).\left(\frac{t}{L}\right)^2\right]} \qquad (2)$$

The 1.25 and 2.5 wt. percent xGnP reinforced411-350 vinylester along with 510A-40 vinyl ester reinforced with same content of xGnP having 10wt.% CTBN were characterized by performing a multi-frequency isothermal mode, in which the sample is equilibrated at selected temperatures and subjected to a series of frequencies [15].Specimens with dimensions of 1.4×0.4×0.06 inch were subjected to loading frequencies of 0.01, 0.1, 1 and10 Hz with a temperature step rate of 4°C perminute starting from 30°C to 150°C.

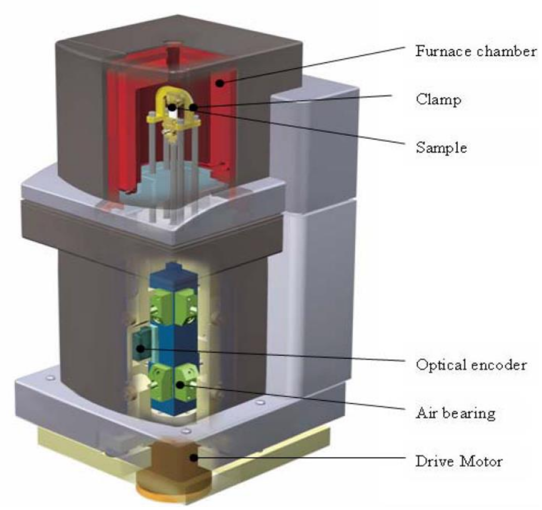
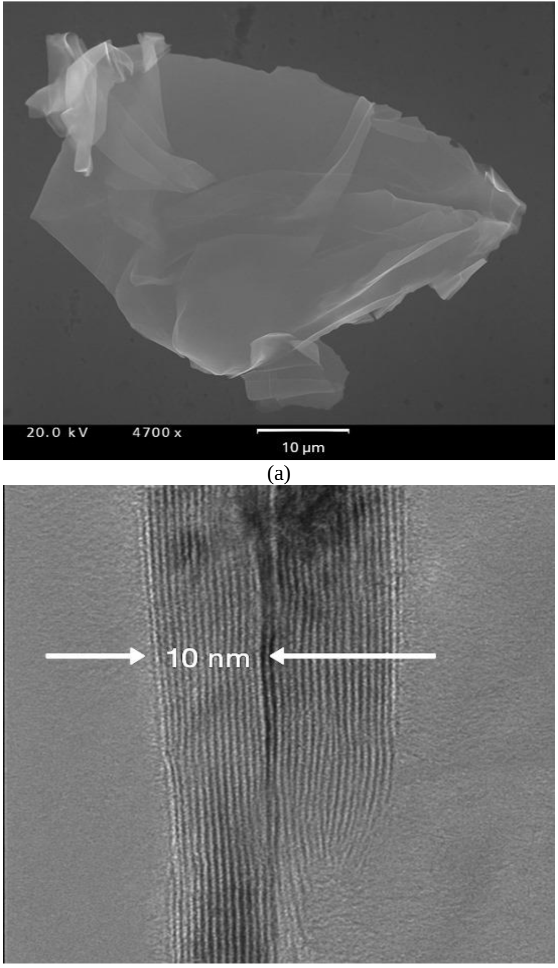


Figure 1. Schematic of TA instruments model Q800 DMA [13]

2.2. Materials and sample preparations

Two classes of vinyl ester resin matrix were used here. The first class is DERAKANE 411-350 which isa mixture of 45 wt.% styrene and 55 wt.% vinylester. Styrene allows the chain extension because of its single unsaturated carbon-carbon double bond,while the vinyl ester resin with two reactive vinyl end groups enables the crosslinking for network.

The second class of material is DERAKANE 510A-40 vinyl ester resin which is a brominated bisphenol-A based vinyl esterconsisting of 38 wt.% styrene and modified with liquid rubber (CTBN).Some additives were added to the brominated resin such as Butanone peroxide, N,N-Dimethylaniline, Cobalt Naphthenate, and 2-4Pentanedione.Figures2a and 2bshow a morphology using TEM and SEM for bothedge and lateral views ofgraphite platelets (xGnP) inside vinyl ester.Blending of vinyl ester resin solution with different amount of graphite platelets was accomplished in a glass beaker, stirring for couple of hours. Then the mixture was constantly sonicated with 100-watt output for about half an hour. 1 wt.% butanone peroxide, 0.1 wt.% 2-4-Pentanedione, 0.1 wt.% N, N-Dimethylaniline, and 0.2% Cobalt Naphthenate were insertedinto the mixed vinyl ester solution in order for 10 min. The above blended resin solution was stirred for 2 min using a Speed mixer. The resin solution was cured at 80^{o}C for 3 hours and post-cured at 120^{o}C.



(a)

(b)

Figure 2. Morphology of graphite platelet xGnP within vinyl ester (a) lateral view (SEM) of xGnP, (b) edge view (TEM) of xGnP.

3. Results and discussion

3.1. Densities

As shown in Figure 3, densities of 510A-40 brominated vinyl ester and its nanocomposites are greater than that of the baseline (411-350)/ non brominated samples. Bromine in nature has quite high molecular weight and it exists as a molecule consists of four bonded atoms, which results in density being higher for brominated specimens. Specific gravity of 510A-40 brominated vinyl ester is around 1.23 while that of the non-brominated version 411-350 is 1.046.

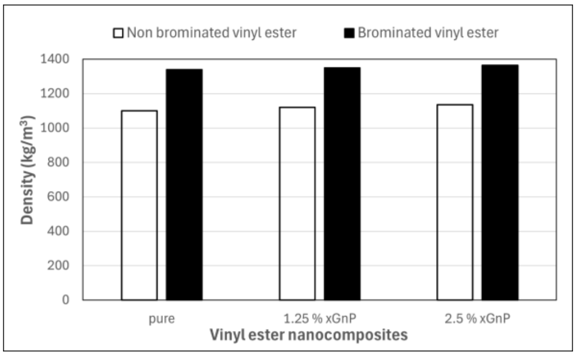


Figure 3. Densities of baseline (411-350) and brominated (510A-40) vinyl ester reinforced nanocomposites.

3.2. Dynamic modulus

The dynamic modulus versus temperature curve offers respected information about the stiffness of a material as a function of temperature, and it is related to structural changes such as molecular weight, interfacialbonding, and level ofcrosslinking density. Crosslink density, typically measures the average molecular weight betweencrosslinks, is a vital factor controlling the physical properties of cured thermoset polymer.

Moreover, it can be altered by regulating the styrene content in the resins, changing the state of conversion, molecular weight ofvinyl ester oligomers, and adjusting curing conditions. Therefore, Crosslinking densities of the two vinyl ester systems(baseline and brominated) having different styrene contents were determined as1116 and 597 mol/m^3, respectively, using the following Equation.[16]

$$V = \frac{G_0^n}{RT} \qquad (3)$$

Applying Equation (3) in calculating crosslinking density for nanocompositesis worthless, because roleof nanoparticles in the crosslinkingprocess is unknown.

Figure 4 shows the dynamic modulus versus temperature for baseline and brominated treated nanocomposites at single frequency; one can notice that addition of 2.5 wt.% xGnP to brominated treated samples show best dynamic profile versus temperature under 1 Hz loading frequency.

Figures 5 and 6 investigate the effect of varying frequency on dynamic modulus for baseline and brominated treated nanocomposites with 1.25 % and 2.5 %, respectively.The treated brominated samples in general show stable stiffness function at high loading frequency over broad range of temperatures. Moreover, these brominated samples exhibit the highest initial dynamic modulus as compared to others which in general can be attributed to good fiber/matrix bonding (cross linking), or higher initial molecular weight [17].

Among the non-brominated samples, gain in rubbery modulus (modulus at highest temperature) was observed extensively with xGnP reinforcement, and marginal increase in glassy modulus was associated with xGnP content. On the other hand, brominated treated samples show higher rubbery modulus than that for baseline ones, however, the rubbery modulusof this class of materials was insensitive to xGnPaddition. This indicates that the crosslinking density of brominated (CTBN) resin has not been significantly affected withthe addition of xGnP nanoparticles.

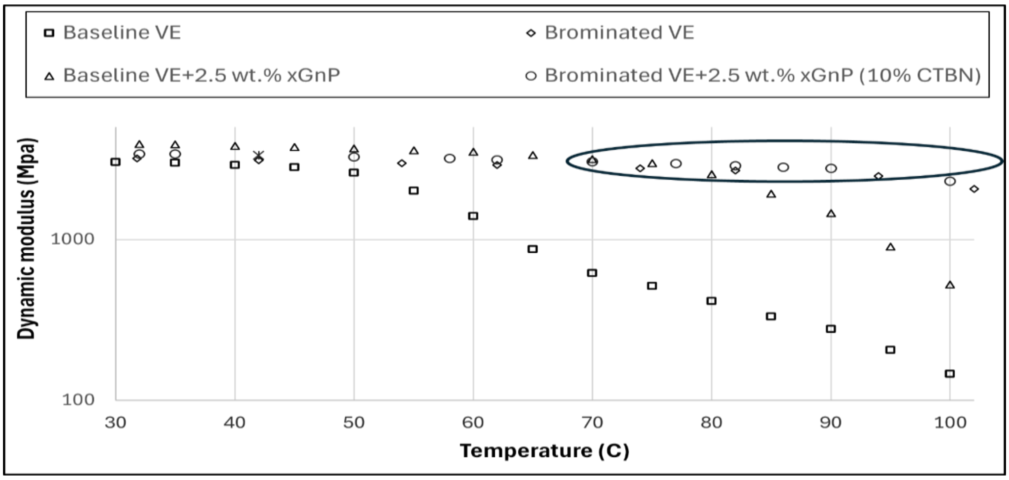


Figure 4. Dynamic modulus for baseline and brominated/(CTBN) treated vinyl ester nano- samples at 1 Hz frequency.

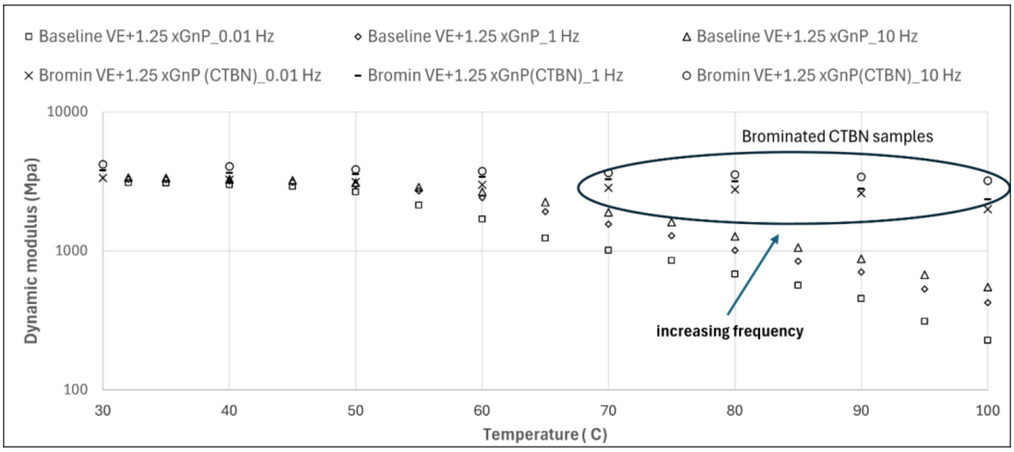


Figure 5. Effect of loading frequency on dynamic modulus of 1.25 wt. % xGnP, both baseline and brominated (CTBN)/ vinyl ester samples.

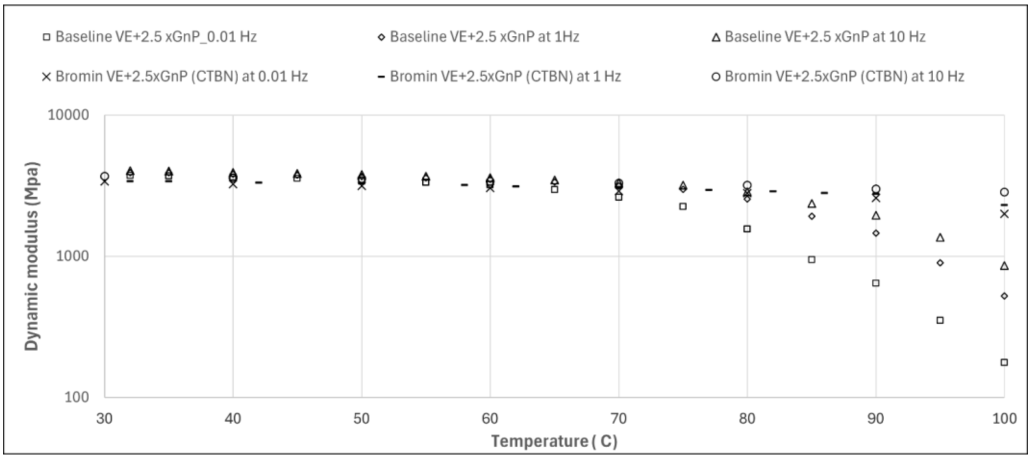


Figure 6. Effect of loading frequency on dynamic modulus of 2.5 wt. % xGnP, both baseline and brominated (CTBN)/ vinyl estersamples.

Figure7 shows the loss factor variation with temperature for baseline and brominated (CTBN) vinyl ester nanocomposites at 1 Hz frequency. Lossfactor in general measures the material plasticity mode behavior. Loss factor increases at higher temperature as shown in the Figure where the material becomes softer. Brominated nano-samples show low loss factor response as compared to the baseline ones. For example, the maximum value of damping has been recorded for baseline VE with 2.5 wt.% xGnP at 100 C. On the contrary, brominated (CTBN) samples with 2.5 wt.% have shown the lowest values of loss factoramong allsamples.

Another important quantity is the peak of Tan δ. Tan-delta, defined as the ratio of loss modulus to storage modulus, is another measure of inherent material damping. Peak of Tan-delta is the region over which material experiences a transition from glassy to leathery behavior, associated with the onset of short-range molecular segments motion, of which all are initially frozen [18]. Bromination in general resulted in greater value of tan δ peak for all the nano reinforcements including pure vinyl ester (300% increase) suggesting that more material is involved in the relaxation. CTBN addition into brominated resin resulted also in greater value of Tan δ peak showing more inherent material damping as shown in Figure 8 which indicates the possibility of higher energy absorption.

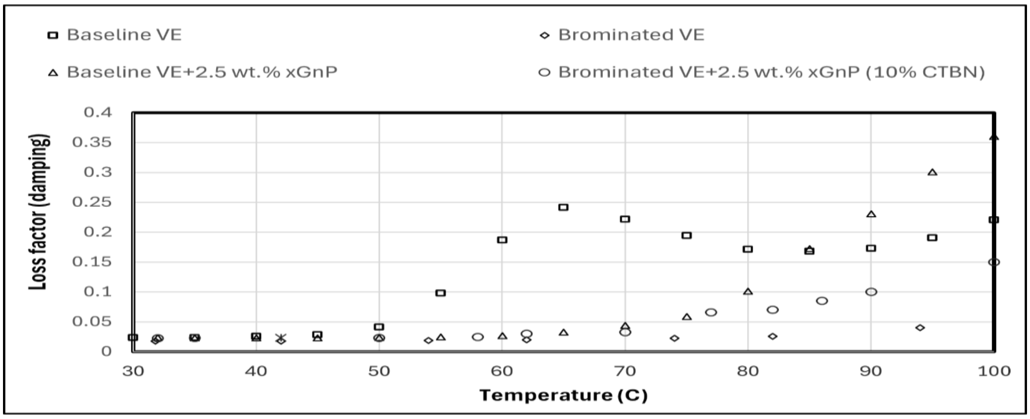


Figure 7. Loss factor for baseline and brominated (CTBN) vinyl ester nanocomposites at single frequencyof 1Hz.

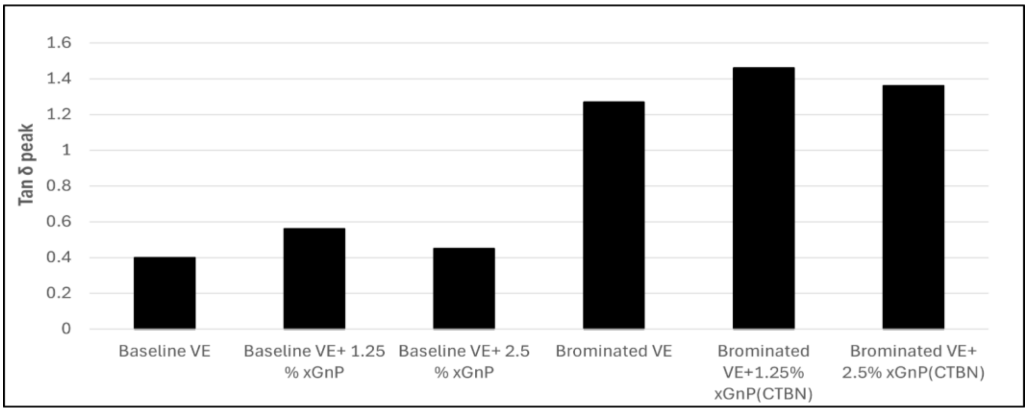


Figure 8: Tan-δ peaks for baseline and brominated (CTBN) vinyl ester nano-composites.

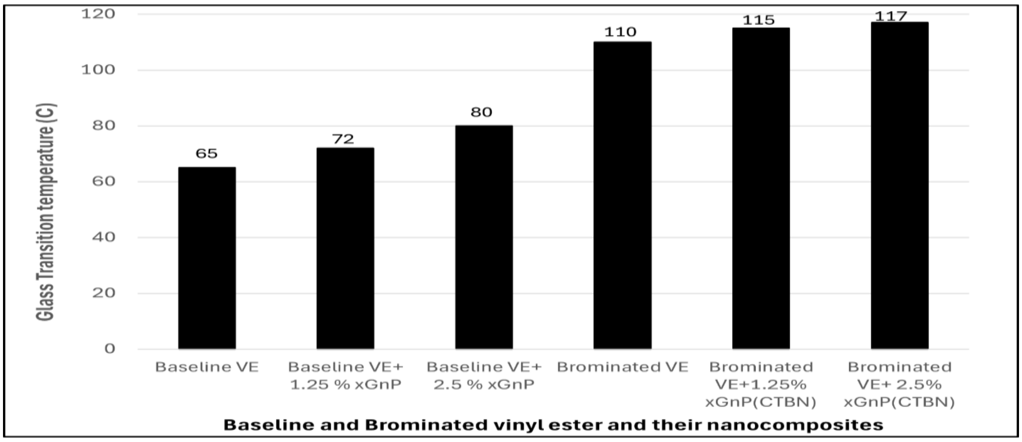


Figure 9. Glass transition temperature for Baseline and Brominated (CTBN) treated nano-samples.

Figure 9 shows the glass transition temperature for the baseline and brominated (CTBN) vinyl ester nanocomposites. Brominating system produced network with higher glass transition temperature (temperature corresponding to peak of loss modulus) than the non-brominated case. For example, *Tg*, for pure vinyl ester increased by about 80% with bromination.

Glass transition temperature for the baseline vinyl ester nanocomposite system significantly increases with increasing nanoparticles. Whereas in case of brominated treated vinyl ester

system, it did not change much with adding nanoparticles. However, the glass transition temperature of the brominated system for both pure VE and the nanocomposites was still greater than that of the baseline system. The substantial gain in, *Tg*, accomplished with bromination is due to the highinitial density (molecular weight) of the resin itself. As molecular weight grows with bromination, the glass transition territory is extended to longer time or higher temperature, because chain mobility is expected to suppress when molecular entanglement is increased.

4. Conclusions

Bromination of vinyl ester resin treated with an unreactive liquid carboxy terminated butadiene nitrile (CTBN) imparts interfacial adhesion and fire retardancy as manifested by a reduction in the amountof smoke, carbon monoxide, and corrosive combustion products. The dynamic response of DERAKANE 411-350 vinyl ester thermoset reinforced with 1.25 and 2.5 wt. % exfoliated graphite nanoplatelets (xGnP) is studied versus DERAKANE 510A-40 vinyl ester resin with 1.25 and 2.5 weight percent exfoliated graphite nanoplatelet (xGnP) treated with 10 weight percent Carboxy Terminated Butadiene Nitrile (CTBN). Frequency sweepacross three decades: 0.01, 0.1, 1 and 10 Hz was performed over temperature range from room temperature to150°C at a step rate of 4°C/min. Initial modulus was observed to increase with additionof nanoparticles in the non-brominated (baseline) system.

However, brominated treated samples show reduction of initial dynamic modulus with the addition of xGnP nanoparticles. As opposed to the brominated samples, the non-brominated samples show gain in rubbery modulus associated with xGnP loading.

CTBN addition into brominated resin resulted in greater value of Tan δ peak (damping) suggesting that more material participates in the relaxation and indicates the possibility of higher energy absorption. Both the pure vinyl ester and treated (CTBN) nanocomposites with bromination exhibited higher tanδ peak values.

Bromination was also foundto significantly increase the glass transition temperaturefor both pure vinyl ester (up to 80%) and the (CTBN) nanocomposites. Glass transition temperature for the baseline vinyl ester nanocomposite system significantly increases with increasing nanoparticles. Whereas in case of brominated treated vinyl ester system, it did not change much with adding nanoparticles. However, the glass transition temperature of the brominated system for both pure VE and the nanocomposites was still greater than that of the baseline system. The 510A-40 vinyl ester (brominated) reinforcedwith 1.25 wt. percent graphite plateletsadded to 10% (CTBN) exhibited the excellent viscoelastic response with highdamping level and high glass transition temperature, alongwith superior dynamic modulus over a wider temperature range and longer time.

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