Effects of bromination on the viscoelastic response of vinyl ester nanocomposites

A. Almagableh^{1*}, P. R. Mantena², A. Alostaz³, W. Liu⁴, L. T. Drzal⁴

¹University of Mississippi, PO. Box 3967, MS 38677, USA

²University of Mississippi, 201 D Carrier Hall, MS 38677, USA

³University of Mississippi, 202 Carrier Hall, MS 38677, USA

⁴Composite Materials and Structures Center, Michigan State University, 2100 Engineering Bldg, East Lansing, MI 48824, USA

Received 25 May 2009; accepted in revised form 1 September 2009

Abstract. Fire, smoke and toxicity are of significant concern for composite materials used in marine applications. Bromination of vinyl ester resin imparts fire retardancy as manifested by a reduction in the amount of smoke, carbon monoxide, and corrosive combustion products. In this research, the viscoelastic properties, modulus (stiffness) and damping (energy dissipation), of 1.25 and 2.5 wt. percent nanoclay and exfoliated graphite nanoplatelet (xGnP) reinforced non-brominated and 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: 0.01, 0.1, 1 and 10 Hz, and temperature range from 30–150°C at a step rate of 4°C per minute. Master curves were generated by time-temperature superposing the experimental data at a reference temperature. The nano reinforced composites showed a drop in initial 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. 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

Thermoset vinyl ester matrices are becoming increasingly important in industrial applications due to their enhanced mechanical properties. They exhibit characteristics similar to epoxy resins, as well as unsaturated polyester resins. Advantages include high tensile strength and stiffness, low cost, process versatility and good chemical resistance. However, vinyl ester still has some challenges like poor resistance to crack propagation, brittleness and large shrinkage that occurs during polymeriza-

tion. Therefore, introducing good interfacial bonding between nanofillers and the resin is often used to alleviate volume shrinkage, void formation and improving surface dispersion along with toughness. Methods of incorporating nanoparticles into polymer matrices could be *ex-situ*, like dispersion of the synthesized nanoparticles into resin solution, or *in-situ* monomer polymerization process in the presence of the nanoparticles [1]. The interaction between the nanoparticles and matrix for the *ex-situ* fabricated composites are normally van der Waals

*Corresponding author, e-mail: amalmag1@olemiss.edu
© BME-PT

forces, steric interaction. However, the *in-situ* synthesis methods may create strong chemical bonding within the composite.

Optical and mechanical properties of vinyl ester polymer reinforced with ZnO nanoparticles, functionalized with a bi-functional coupling agent methacryloxypropyl-trimethoxysilane (MPS) were investigated by Guo *et al.* [2]. The existence of MPS at the interface between the matrix and particles results in improved interfacial interaction which in turn improves UV shielding, modulus and strength significantly.

The physical properties of vinyl ester reinforced with unmodified CuO nanoparticles and those functionalized with a bi-functional coupling agent methacryloxypropyl-trimethoxysilane (MPS) were studied by Guo *et al.* [3]. Increase in both thermal stability and mechanical properties were attributed to good nanoparticles dispersion at the interface and the resulting chemical bonding between the functionalized nanoparticles and the matrix.

Vinyl ester thermosetting nanocomposites reinforced with iron oxide nanoparticles were prepared and characterized by Guo *et al.* [4]. Iron oxide nanoparticles functionalized with a bi-functional coupling agent was observed to increase the adhesion and dispersion of the nano filler into the matrix resulting in increased thermal stability, lower curing temperature and improved mechanical properties. The nanocomposites became also magnetically stronger and were independent of particles functionalization.

Schroeder *et al.* [5] analyzed morphologically thermoset materials obtained from styrene/vinyl ester resins of different molecular weights modified with polymethyl methacrylate (PMMA). It was found that different morphologies including dispersion 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 affecting both volume shrinkage reduction and the thermal-mechanical properties of the modified thermosets.

Recent interest in the use of organic-matrix composite materials in US Navy submarines and ships has generated the requirement for significant improvement in the flammability performance of

these materials including reduction in the amount of smoke, carbon monoxide, and corrosive combustion products. New fire retardant approaches for organic-matrix composite materials are needed to address the smoke issues and to further reduce the flammability of these composites. 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. The US Navy is currently using brominated vinyl ester matrix resin with glass reinforcement for composite applications in topside surface ship structures [6]. 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 retardancy as manifested by flame spread and lower heat release rates. However, this fire-retardant system functions primarily in the gas phase causing incomplete combustion. As such, brominated resins produce dense smoke, an increase in the yield of carbon monoxide, and hydrogen bromide.

The work reported here is an extension of previous work [7] on the viscoelastic behavior of non-brominated vinyl ester nanocomposites. DMA measurements are usually 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 [8]. 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 exfoliated graphite nanoplatelets (xGnP) 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) [8]. 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 shifting mechanism used to shift a set of data upon a reference curve follows WLF [8] model. This model assumes that the fractional free volume increases linearly with respect to temperature in the transition region, and when the free volume increases, its viscosity decreases. In this model, the degree of shifting was calculated according to Equation (1);

$$\log a_T = \frac{-C_1(T-T_0)}{C_2 + (T-T_0)} \quad (1)$$

For both resin systems (with and without bromination), C_1 and C_2 were found to be around 103.9 and 399 K, respectively. Relationship between the shifting factor (a_T) versus T is plotted in Figure 1 for pure and brominated vinyl ester.

Figure 1. Relationship between shifting factor (a_T) and temperature for pure and brominated vinyl ester based on the WLF model

3. Experimental

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. Stress and strain with the single-cantilever clamp used in

model Q800 DMA are calculated with Equations (2) and (3), respectively [8], assuming linear viscoelastic behavior.

$$\sigma_x = \frac{6PL}{wt^2} \quad (2)$$

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

where L – clamp span length
 t – sample thickness
 w – width of the specimen
 ν – Poisson's ratio
 F_c – clamping correction factor
 σ_x – stress
 ϵ_x – strain
 P – applied force
 δ – amplitude of deformation

3.2. Test description

The 1.25 and 2.5 wt. percent nanocaly and xGnP 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 35×10×1.6 mm were subjected to frequencies of: 0.01, 0.1, 1 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 μm) 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 to generate the master curves.

3.3. Materials and sample preparations

The polymeric matrix used was a vinyl ester resin (manufactured and supplied by Ashland specialty chemical, Division of Ashland INC (Columbus, OH)). DERA KANE 411-350-(non-brominated) is a mixture of 45 wt.% styrene and 55 wt.% vinyl ester. Styrene allows the chain extension because of its single unsaturated carbon-carbon double bond, while the vinyl ester resin with two reactive vinyl

Figure 2. Morphology of xGnP using (a) edge view (TEM), and (b) Lateral view (SEM)

end groups enables the crosslinking for network. DERAKANE 510A-40 (brominated) vinyl ester resin is a brominated bisphenol-A based vinyl ester consisting of 38 wt.% styrene, and modified to produce the maximum degree of fire retardancy combined with enhanced chemical resistance and toughness. These additives are Butanone peroxide, N,N-Dimethylaniline, Cobalt Naphthenate, and 2-4-Pentanedione, all supplied from Sigma Aldrich (St. Louis, Mo).

Exfoliated graphite nanoplatelets (xGnP) were produced according to the method described in [9]. The nanoclay was Cloisite 30B from Southern Clay Products, Inc (Gonzales, TX). Figures 2a and 2b show a morphology using TEM and SEM for both edge and lateral views of xGnP inside a polymer. These xGnP nanocomposites have exfoliated and dispersed graphite platelets with 1 nm thickness and several hundred nanometers widths. Distance between layers is in the range of 10~30 Å and size of the layered graphite extends from several hundred nanometers to several microns.

The samples were prepared by dispersing about 3000 g of epoxy vinyl ester resin solution with different percentages of nanoclay or nanographite in a 1 gal container for 4 hours, followed by 4 passes through a flow cell connected to a 100 W sonicator. 1% Butanone peroxide, 0.2% of 2-4 Pentanedione, 0.1% N,N-Dimethylaniline, and 0.2% Cobalt Naphthenate were added to the mixed vinyl ester resin solution in order and mixed for 10 min. The above mixed resin solution was mixed for 2 min with FlackTek speed mixer at 3000 RPM. The well-mixed vinyl ester resin solution with nanoclay or nanographite was poured into a 13×13×0.4” mold, let stand for 30 minutes at room temperature

and then was post cured at 80°C for 3 hours. Prismatic samples with nominal dimension of 35×10×1.6 mm size were prepared from these plates and tested in a DMA using the single-cantilever clamp fixture.

4. Results and discussion

4.1. Densities

As shown in Figure 3, 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 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 3. Densities of non-brominated (411-350) and brominated (510A-40) vinyl ester nanocomposites

4.2. 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 density. Crosslink density, typically given as the average molecular weight between crosslinks (M_c), is an important factor governing the physical properties of cured thermoset resins. Moreover, it can be changed by adjusting the styrene content in the resins, molecular weight of vinyl ester oligomers, altering the state of conversion, and control of the cure conditions [10]. Crosslinking densities of the two resin systems (non-brominated and brominated) resulting from different styrene contents were calculated [10] as 1116 and 597 mol/m³, respectively, based on Equation (4):

$$V = \frac{G_0^n}{RT} \quad (4)$$

where V – crosslinking density

R – gas constant

G_0^n – plateau modulus from master curve of the shear modulus versus frequency.

Calculation of crosslinking density for nanocomposites using this equation is invalid, because contribution of nanoparticles in the crosslinking mechanism is unknown.

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 [11]. Figure 4 shows initial storage modulus (30°C) for vinyl ester nanocomposites, with and without bromination. Initial modulus was observed to increase with addition of nanoparticles in the non-brominated system. On the other hand, bromination resulted in a reduction of the initial storage modulus with addition of nanoparticles. Among the brominated specimens, gain in glassy (initial) modulus was observed with xGnP reinforcement, and a loss in glassy modulus was associated with the addition of nanoclay particles. Loss in storage moduli with the brominated nanoclay composites could be due to weak interfacial bonding between the nanoclay particles and brominated resin. However, the 1.25 wt.% xGnP appears to be bonding better with the brominated

Figure 4. Initial storage modulus for non-brominated and brominated nanocomposites at 1 Hz frequency

resin resulting in higher storage modulus compared to pure brominated vinyl ester.

Figures 5–7 show the storage modulus (E') evolution with temperature for some of the vinyl ester nanocomposites, with and without bromination. Bromination effect modifies the dynamic mechanical behavior for VE and its nanocomposites. Drop

Figure 5. Storage modulus for pure vinyl ester with and without bromination

Figure 6. Storage modulus for 2.5 wt. percent nanoclay reinforced vinyl ester with and without bromination

Figure 7. Storage modulus for 1.25 wt. percent xGnP reinforced vinyl ester with and without bromination

in modulus in the transition region is shifted to higher temperature. It is interesting to note that no major variation appears in the value of the rubbery modulus in both systems (brominated and non-brominated) with the addition of nanoparticles. This indicates that the crosslinking density of both networks has not been significantly affected with the addition of nanoparticles.

4.3. Damping

Tan δ , defined as the ratio of loss modulus to storage modulus, is a measure of the inherent material damping. Peak of tan δ 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. 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 (Figures 8–10). Two relaxations were observed for non-brominated vinyl ester, one

Figure 8. Tan δ curves for pure vinyl ester, with and without bromination

Figure 9. Tan δ curves for vinyl ester reinforced with 2.5 wt.% xGnP, with and without bromination

at around 60°C and another between 110–120°C, which corresponds to the transition of St-resin rich phase at higher temperature. Varying the nanoclay concentration from 0 to 2.5 wt. percent produced a significant increment in the height of the corresponding loss factor peak (Figure not shown). However, significant drop of tan δ peak was associated with the addition of 2.5 wt.% xGnP to brominated resin. The greater amount of xGnP added to the brominated resin, more brittle material behavior was observed.

Area under tan δ curve (with units of °C) over the temperature range (30–150°C) was also calculated, as it is another good indicator of the total energy absorbed by the material [12]. The higher the area under tan δ curve, the greater the degree of molecular rearrangement, which enables the material to better absorb and dissipate energy. Brominated nanocomposites in general exhibited higher area under tan δ curves compared to the non-brominated

Figure 10. Tan δ peak for brominated and non-brominated vinyl ester nanocomposites at 1 Hz frequency

Figure 11. Area under $\tan\delta$ curves for brominated and non-brominated vinyl ester nanocomposites at 1 Hz frequency

samples (Figure 11). From Figure 10, the higher $\tan\delta$ peak value observed with the addition of 2.5 wt. percent nanoclay compared to 2.5 wt. percent graphite for brominated specimens, indicates greater molecular mobility in nanoclay brominated composites. Besides, the greatest loss in storage modulus along with the superior $\tan\delta$ peak associated with the addition of nanoclay particles to brominated resin indicates that this reinforcement may be adversely affecting the interfacial bonding. Consequently, graphite nanoplatelets appear to form better interfacial bonding with brominated resin than nanoclay reinforcements.

4.4. Glass transition temperature, T_g

Figure 12 shows the loss modulus curves for the pure and brominated vinyl ester, as a function of frequency. Bromination system produced network

Figure 12. Loss modulus for pure vinyl ester, with and without bromination, as a function of frequency

with higher glass transition temperature (temperature corresponding to peak of loss modulus) than the non-brominated case. For example, T_g , for pure vinyl ester increased by about 80% with bromination. Glass transition temperature for the non-brominated vinyl ester nanocomposite system increased with increasing content of nanoparticles. Whereas in case of brominated vinyl ester nanocomposite system, it did not change with addition of nanoparticles. Furthermore, the glass transition temperature of the brominated samples for both pure resin and the nanocomposites was still higher than that of the non-brominated samples.

The significant increase in, T_g , achieved with bromination is probably due to higher initial density (molecular weight). 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 [13].

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 master curves for the 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 [8]. Figure 13 shows the generated master curves of storage modulus over an extended period of time. From Figure 13a, the brominated 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 xGnP reinforced specimens exhibit superior average modulus of 2.7 GPa over 321.5 years (Figure 13b). 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 13c) for the first 10^8 sec (3.2 years) only.

Figure 13. Master curves of storage modulus at a reference temperature of 50°C as a function of log time for a) pure vinyl ester, b) 1.25 wt. percent and c) 2.5 wt. percent nanoparticles

5. Conclusions

Bromination of vinyl ester resin imparts fire retardancy as manifested by a reduction in the amount of smoke, carbon monoxide, and corrosive combustion products. 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 nanoplatelets was investigated with a DMA. Frequency sweep across three decades: 0.01, 0.1, 1 and 10 Hz was

performed over temperature range from 30 to 150°C at a step 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.

Initial modulus was observed to increase with addition of nanoparticles in the non-brominated system. However, bromination resulted in a reduction of initial storage modulus with the addition of nanoparticles. Among the brominated specimens, gain in glassy (initial) modulus was observed with xGnP reinforcement, and a loss in glassy modulus was associated with the addition of nanoclay particles. Both the pure vinyl ester and nanocomposites with bromination exhibited higher $\tan\delta$ peak values and larger areas under the $\tan\delta$ curves. From the storage modulus and damping results, it is surmised that graphite platelets appear to form better interfacial bonding with the brominated resin than the nanoclay reinforcements. Bromination was also found to significantly increase the glass transition temperature for both pure vinyl ester (up to 80%) and the nanocomposites. The brominated vinyl ester reinforced with 1.25 wt. percent graphite platelets exhibited the best viscoelastic response with high damping and glass transition temperature, along with superior storage modulus over a longer time period.

Acknowledgements

The authors would like to acknowledge the support received from the Department of Civil Engineering at the University of Mississippi, and funding received under a subcontract from the Department of Homeland Security-sponsored Southeast Region Research Initiative (SERRI) at the Department of Energy's Oak Ridge National Laboratory. Support for this research by ONR Grant # N00014-07-1-1010, Office of Naval Research, Solid Mechanics Program (Dr. Yapa D.S. Rajapakse, Program Manager) is also acknowledged.

References

- [1] Schroeder W. F., Borrajo J., Aranguren M. I.: Poly (methyl methacrylate)-modified vinylester thermosets: Morphology, volume shrinkage and mechanical properties. *Journal of Applied Polymer Science*, **106**, 4007–4017 (2007). DOI: [10.1002/app.27006](https://doi.org/10.1002/app.27006)

- [2] Guo Z., Wei S., Shedd B., Scaffaro R., Pereira T., Hahn H. T.: Particle surface engineering effect on the mechanical, optical and photoluminescent properties of ZnO/vinyl-ester resin nanocomposites. *Materials Chemistry*, **17**, 806–813 (2007).
DOI: [10.1039/b613286c](https://doi.org/10.1039/b613286c)
- [3] Guo Z., Liang X., Scaffaro R., Pereira T., Hahn H. T.: CuO nanoparticle filled vinyl-ester resin nanocomposites: Fabrication, characterization and property analysis. *Composites Science and Technology*, **67**, 2036–2044 (2007).
DOI: [10.1016/j.compscitech.2006.11.017](https://doi.org/10.1016/j.compscitech.2006.11.017)
- [4] Guo Z., Lei K., Li Y., Wai Ng H., Prikhodko S., Hahn H. T.: Fabrication and characterization of iron oxide nanoparticles reinforced vinyl-ester resin nanocomposites. *Composites Science and Technology*, **68**, 1513–1520 (2008).
DOI: [10.1016/j.compscitech.2007.10.018](https://doi.org/10.1016/j.compscitech.2007.10.018)
- [5] Schroeder W. F., Auad M. L., Vico M. A. B., Borrajo J., Aranguren M. I.: Thermodynamic, morphological, mechanical and fracture properties of poly(methyl methacrylate)(PMMA) modified divinylester(DVE)/styrene(St) thermosets. *Polymer*, **46**, 2306–2319 (2005).
DOI: [10.1016/j.polymer.2005.01.019](https://doi.org/10.1016/j.polymer.2005.01.019)
- [6] Sorathia U., Ness J., Blum M.: Fire safety of composites in the US Navy. *Composites Part A: Applied Science and Manufacturing*, **30**, 707–713 (1999).
DOI: [10.1016/S1359-835X\(98\)00112-2](https://doi.org/10.1016/S1359-835X(98)00112-2)
- [7] Almagableh A., Gupta S., Mantena P. R., Alostaz A.: Dynamic mechanical analysis of graphite platelet and nanoclay reinforced vinyl ester, and MWCNT reinforced nylon 6,6 nanocomposites. in 'Proceeding of SAMPE Fall Technical Conference, Memphis, USA', M034 p.19 (2008).
- [8] TA Instruments.: Thermal analysis application brief, 144: Application of time-temperature superposition principles to DMA. TA Instruments, Newcastle (2004).
- [9] Drzal L. T., Fukushima H.: Expanded graphite products produced therefrom. US Patent 7550529, USA (2009).
- [10] Li H., Burts E., Bears K., Ji Q., Lesko J. J., Dillard D. A., Riffle J. S., Puckett P. M.: Network structure and properties of dimethacrylate-styrene matrix materials. *Journal of Composite Materials*, **34**, 1512–1528 (2000).
DOI: [10.1106/Q064-0U44-FWDJ-9LET](https://doi.org/10.1106/Q064-0U44-FWDJ-9LET)
- [11] Kuzak S. G., Shanmugam A.: Dynamic mechanical analysis of fiber-reinforced phenolic. *Journal of Applied Polymer Science*, **73**, 649–658 (1999).
DOI: [10.1002/\(SICI\)1097-4628\(19990801\)73:5<649::AID-APP5>3.0.CO;2-B](https://doi.org/10.1002/(SICI)1097-4628(19990801)73:5<649::AID-APP5>3.0.CO;2-B)
- [12] Gupta S., Mantena P. R., Al-Ostaz A.: Dynamic mechanical and impact property correlation of nanoclay and graphite platelet reinforced vinyl ester nanocomposites. *Journal of Reinforced Plastics and Composites*, in press, (2009).
DOI: [10.1177/0731684409341762](https://doi.org/10.1177/0731684409341762)
- [13] Hertzberg W. R.: Deformation and fracture mechanics of engineering materials. Wiley, New York (1989).