HYBRID NANO-ADDITIVES WITH IMPROVED DISPERSIVE, THERMAL AND REINFORCING PROPERTIES FOR EPOXY, POLYESTER AND VINYL ESTER MATRICES

Bhishma R. Sedai[1], Kevin Keith[1], Lynsey Baxter[3], Frank D. Blum[2] and Ranji Vaidyanathan[3]

[1]MITO Material Solutions, LLC; 1414 S Sangre Rd, Stillwater, OK 74074

[2]Oklahoma State University, Department of Chemistry, Henry Bellmon Research Center, Stillwater, OK 74078

[3]School of Materials Science and Engineering, Helmerich Research Center, Oklahoma State University, Tulsa, OK 74106

ABSTRACT

Hybrid nano-additives based on graphene oxide (GO) and polyhedral silsesquioxane (POSS) with improved dispersive, thermal and reinforcing characteristics have been prepared using a novel approach. Hybrid additives were characterized using Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM) and thermogravimetric analyzer (TGA). Dispersion of the additives in different amounts (mg/mL) were tested in most common industrial solvents. Additionally, hybrid additives and resin composites of 0.1%, 0.5% and 2% compositions were prepared by mixing it with common industrial resins. Dynamic mechanical analysis (DMA) of epoxy, vinyl ester and polyester resins and hybrid nano-additives composites of 0.1 and 0.5% compositions showed significant shift in Tan δ peaks and increases in storage moduli were observed for vinyl ester and polyester composites. Epoxy and nano-additive composites (0.1%), showed 4 °C increase in glass transition temperature compared to neat resins. Polyester and hybrid additives composites (0.1%) showed 8 °C shift in Tan δ peak compared to neat resin. Similarly, vinyl ester and hybrid additives composites showed 12 °C increase in glass transition temperature compared to neat resin at the same composition (0.1%). Differential scanning calorimetry (DSC) results of the composites with 0.5% hybrid additives also showed increases in glass transition temperatures compared to neat resins. Thermogravimetric analysis of composites with 2 to 10% hybrid additives showed increased thermal stability of the composites compared to neat resins.

1. INTRODUCTION

Epoxy, vinyl ester and polyester resins are well-known thermosetting polymers which are widely used for making composite structures in automotive, aerospace and marine industries. Fiber reinforced composites prepared with epoxy resins are mostly used to make aircraft and automobile parts. Vinyl ester resins composites are generally used in swimming pools, sewer pipes and solvent storage tanks [1]. Polyester resin composites are used in various industries such as coating, construction, transportation, storage tanks, and piping. Polyester resins reinforced with fiberglass so-called fiberglass reinforced plastic (FRP) are used in marine industries, restaurants, kitchens, restrooms and other areas that require washable low-maintenance walls [2].

1.1 Epoxy resins

Epoxy resin generally possesses two or more epoxide rings which participate in a chemical reaction with a curing agent and forms crosslinks which provide superior mechanical properties. Due to its inherent brittleness, poor thermal and electrical conductivity, a lot of efforts have been made to improve their properties with the addition of nanoparticles such as carbon nanotubes (CNT's) [3], graphene [4], POSS [5], nanoclay [6] and carbon nanofibers [7] etc. Nanoparticles are more efficient than micron sized particles because of their high surface area to volume ratio and high aspect ratio. Hence very low filler content is required to achieve desired properties. Recently, graphene and graphene oxide have been a filler choice owing to its high surface to volume ratio, higher reactivity and lower manufacturing costs when compared to CNT's [8].

1.2 Vinyl ester resins

Vinyl ester resins are prepared by the copolymerization of styrene monomer and a dimethacrylate monomer based on the diglycidyl ether of bisphenol-A. Among engineering materials, vinyl ester resin is a relatively less expensive than other polymers of its class and possesses properties that are intermediate between epoxy resin and polyester resin. Vinyl ester and polyester resins are most valuable industrial polymers because they occupy approximately 3/4 of the market share. Therefore, improvement in their properties without sacrificing the basic properties of the resins is highly desirable. Several reports are available to enhance the properties of vinyl ester resin by incorporating carbon nano-materials such as single and multiple walled carbon nanotubes (CNT) [9-11]. Recent studies have shown that the presence of graphene and graphene oxide in polymer nanocomposite tends to improve the mechanical properties of the polymers. Such nano-modified polymeric materials may find enormous applications in areas such as adhesives for wind turbine blades, electromagnetic interference shielding, corrosion resistant, and fire resistant coatings etc. [12].

1.3 Polyester resins

Polyester resins are unsaturated synthetic resins formed by the reaction of dibasic organic acids and polyhydric alcohols. Maleic Anhydride is one of the common raw material with diacid functionality. Polyester resins have a short storage life because they will set or 'gel' on their own over a long period of time. Small quantities of inhibitor are added during the resin manufacture to slow this gelling action. Tensile strength and stiffness of the polyester resins are lower than those of epoxy resin. Different fillers like clay, layered silicates, carbon fiber, and CNTs have been used to improve properties of polyester composites [13-15]. Various other reports are available to improve thermal, mechanical, electrical and rheological behavior of polyester and fillers or nanomaterials [16-19].

1.4 Graphene nanomaterials including graphene oxide (GO)

Graphene is a one-atom thick sheet consists of a hexagonal array of carbon atoms. GO is obtained from oxidation and exfoliation of graphite and it contains several oxygens containing functional groups such as carbonyl, hydroxyl and epoxy. The presence of these functional groups in GO imparts several advantages to the graphene such as a) flexibility of further modification b) excellent dispersion in polymer matrices and solvents c) facilitates interfacial interaction between the functional groups and the polymer matrix [20, 21]. Several studies have recently shown improved quasi-static [22], fatigue [23] and electrical properties [24] for graphene-based polymer composites. Numerous reviews on the graphene and polymer composites have also become available [25, 26]. Some debates have arisen over the appropriate graphene structure for use in polymer composites, for example, GO or a reduced form containing fewer surface and edge oxygen groups. Although promising results have been reported by several groups working with reduced forms of graphene in epoxy matrices, e.g., Rafiee et al., [27, 28], it appears that from the most recent literature [29] the oxide form may be more advantageous for composite synthesis and future scale-up operations. The “wrinkled” surface of reduced graphene is often credited as a favorable medium for creating a robust interface able to locally interlock with the matrix. At the same time, the atomically smooth surface has been shown to effect low interfacial strength [30] in strain-dependent Raman spectroscopy measurements. Furthermore, restacking of the sheets following chemical or thermal reduction due to their instability in popular solvents used in polymer processing can hinder performance, similar to the consequences of agglomeration in CNT composites. The latter concern however has been partially alleviated through the use of surfactants [31] or polymer blending prior to reduction [24]. The functional groups (epoxide, hydroxyl, carboxyl, and carbonyl) present on the basal planes and edges of GO facilitate dispersion in water or protic solvents. Moreover, the groups may further improve matrix affinity and allow for additional surface chemistry tailoring if desired. GO is preferred over other expensive fillers like CNT due to its higher aspect ratio and extraordinary mechanical and thermal properties [32,33].

1.5 Polyhedral oligomeric silsesquioxanes (POSS)

Polyhedral oligomeric silsesquixanes (POSS) are a class of nanomaterials with unique cage structures. POSS consist of both organic and inorganic moieties. The silsesquioxane unit is represented by the formula of $RSiO_{1.5}$. In a POSS unit, each silicon atom is connected to three oxygen atoms and an organic group and form a unique organic/inorganic hybrid molecule. The siloxane (Si-O-Si), the inorganic moiety in POSS, imparts thermal stability, chemical resistance, rigidity and flame-retardant properties. The organic groups can be either inert or reactive depending on its use. The organic moiety imparts reactivity, processability, and ductility to POSS. A wide range of properties could be introduced to POSS by altering the organic groups. POSS has been widely used for the polymer composite applications owing to its hybrid nature [34-36]. This hybrid property of POSS could be used to react with a molecule such as GO to create nanoparticles that could disperse well in resin matrices due to their possible ability to repel each other.

1.6 Graphene oxide and POSS hybrid

Researchers have tried to graft POSS with GO to enhance the dispersion of GO and to make it useable in various applications. Xue and coworkers have mentioned the reaction between Aminopropylisobutyl POSS and GO and its application as liquid marbles [37]. They have mentioned that POSS-g-GO product can be used to fabricate superhydrophobic surfaces with contact angle as high as 157°. Wang et al. reported the fire retardancy of Octaaminophenyl POSS grafted GO in epoxy resins [38]. It was an effective way to reduce GO over the extensive and complex conventional reduction methods. They have mentioned that the onset degradation temperature at 5% weight loss of pure epoxy composites was improved by 24 °C and 43 °C after reinforcing with POSS (2 wt%) and POSS-Graphene (2 wt%) respectively. The superior fire-retardant property of POSS-graphene is considered due to a) formation of a more stable form of graphene while compared to neat GO and b) improved char yield because of the silica layers on the surface. In one of the study, Vaidyanathan research group reacted GO with Octaammonium POSS (OAM POSS) in water as a reaction medium. The effect of the POSS-g-GO and GO was evaluated by incorporating OAM POSS-g-GO and GO in the epoxy matrix at different filler loadings. The performance of OAM POSS-g-GO was evaluated against the neat GO in terms of mechanical and thermal properties [39]. Wang, X., et al., did simultaneous reduction and surface functionalization of GO by simple refluxing of GO with octa-aminophenyl polyhedral oligomeric silsesquioxanes (OapPOSS) without the use of any reducing agents [40]. Valentini, L., et al., reacted amino-funtionalized polyhedral oligomeric silsesquioxanes (POSS-NH_2) with GO sheets to graft POSS-NH_2 onto a GO layer immobilszed onto a layer of (3-aminopropuyl)triethoxysilane, self-assembled onto Si subtrate [41]. Luca, V., et al. developed a nanomaterial that consists of graphene sheets decorated with silsesquioxane molecules. Aminopropyl-silsesquioxane (POSS-NH_2) has been employed to functionalize GO sheets. When exposed to visible light the hybrid showed a photoconductivity response [42, 43]. Yu, W., et al. functionalized GO with octa-aminophenyl polyhedral oligomeric silsesquioxanes (OapPOSS) and reported a new application of OapPOSS-g-GO. They showed improvement in thermal stability of OapPOSS-g-GO. They also found that with the incorporation of only 0.2 wt% OapPOSS-g-GO, at 10^4 Hz the dielectric constant and dielectric loss of OapPOSS-g-GO/epoxy composites dropped by 9% and 49% compared to the neat epoxy composites [44]. Potsi, G., et al. mentioned the synthesis and properties of carbon nanostructures containing organic-inorganic cage-like polyhedral oligomeric silsesquioxane (POSS) nanoparticles. They reported the physical and chemical functionalization of carbon nanomaterials such as graphene, graphene oxide, carbon nanotubes, and fullerenes with POSS towards the development of novel hybrid nanostructures [45].

However, to the best of our knowledge, only few works have been reported in the literature based on POSS-w-GO and epoxy, vinyl ester and polyester composite. The present work focuses on grafting least expensive and most common POSS molecules with GO (POSS-w-GO) and investigating its effect on mechanical and thermal properties of resins matrices. Although other researchers have shown the grafting of POSS with GO, there is a need for a simple and scalable technique. There is also a need to use POSS molecules that have good compatibility with resins matrices, such as those with epoxy functional groups and double bonds present in the GO. In this work, we have reported a simple method of preparation of GO and POSS based hybrid nano-additives using the least expensive and most common POSS molecules. The dispersion of POSS-w-GO in organic solvents has been observed using transmission electron microscope. Polymer composites of different compositions have been prepared using epoxy, vinyl ester and polyester resins. The effect of POSS-w-GO hybrid additives on thermal and mechanical properties of epoxy, vinyl ester and polyester resins has been investigated. This new type of hybrid nano-additive has shown very good and stable dispersion in organic solvents and has been found compatible with epoxy, vinyl ester and polyester resins.

2. EXPERIMENTATION

2.1 Materials

Graphene oxide dispersion (0.4%) in water was purchased from Graphenea Inc. (Cambridge, MA). Ethylene diamine (99%) and Aluminum trifluoromethanesulfonate (99%) was purchased from Alfa Aesar (Tewksbury, MA). POSS with epoxy functionality was purchased from Hybridplastics (Hattiesburg, MS). Epon 862 and Epicure 3274 were purchased from Hexion LLC (Columbus, OH). Polyester laminating resin NOVOC 8050 and vinyl ester resin SCP-4982 LVW-25 with initiators were obtained from Andara, LLC (Sheboyyan, WI). Tetrahydrofuran and ethyl alcohol (190 proof) ACS grade was purchased from Pharmco-Aaper (Brookfield, CT). Acetone and isopropyl alcohol ACS grade were purchased from BDH VWR analytical (Radnor, PA).

2.2 Methods

2.2.1 Preparation of GO-amine

Approximately 4g of graphene oxide was reacted with 12 gram of ethylene diamine. The mixture was then filtered and washed. After complete filtration, the residue was collected for next step reaction. The GO-amine product was dried and characterized by Fourier transform infrared spectroscopy.

2.2.2 Reaction of GO-amine with POSS

GO-amine (~4.0 g) dispersed in 1000 mL of tetrahydrofuran and mixed with shear mixer for 30 minutes. Then, the dispersion was transferred to 2 L round bottom flask. The dispersion of GO-amine was stirred with magnetic stirrer for 15 minutes. Approximately 6.0 g of POSS with epoxy functionality was added and refluxed for 5 hours in the presence of a catalyst, aluminum triflate. The reaction mixture was concentrated and dried at room temperature. The dried product was characterized by FTIR, TGA and TEM.

2.2.3 Dispersion of MITO additives in solvents

For the preparation of dispersions with different amount of hybrid additives, desired amount of GO-g-POSS additives were measured and mixed with solvents. Hybrid additives were dispersed in different organic solvents (acetone, ethanol, isopropanol and tetrahydrofuran) by grinding with a three roll mill. Thus resulted dispersions were sonicated for 30 minutes and left undisturbed at room temperature.

2.2.4 Preparation of POSS-w-GO and resins composites

For making composites, approximately 100.0 g of vinyl ester or polyester resin was taken in a plastic container and 0.1 and 0.5 g of POSS-w-GO was added in to it and mixed in speed mixed at 3500 rpm for 5 minutes and sonicated for 2 h. Then 2% of initiator was added in to the mixture and again mixed in speed mixture for 5 minutes at 3500 rpm. The mixture was poured in to silicon rubber mold to get samples for DMA and DSC test. After 24 h curing at room temperature, samples were post cured at 200 ^{0}F for 2 h.

For making epoxy composites, approximately 40.0 g of epicure 3274 was taken in a plastic container and 0.1 and 0.5 g of POSS-w-GO was added in to it. It was mixed in speed mixture for 5 minutes at 3500 rpm. The resulting mixture was sonicated for 2 h. After that 60.0 g of epon 862 resin was added in to it and mixed in speed mixture for 5 minutes at 3500 rpm. The resulting mixture was poured into silicon rubber mold and left for overnight at room temperature for curing. The samples were taken out and again post cured at 120 °C for 6 h.

2.3 Characterization

2.3.1 FTIR

To confirm the reaction of GO-amine with POSS, experiments were performed using Fourier transform infrared spectroscopy in attenuated total reflection (ATR) mode. The IR spectra of samples were collected using a Nicolet iS50 Spectrometer Thermo Scientific Inc. (Waltham, MA) equipped with a deuterated triglycine sulfate detector and a diamond crystal (45° angle) as an ATR accessory. Each sample was run using 64 scans versus the background that was also collected using 64 scans to generate a single beam spectrum at 4 cm^{-1} resolution in the range of 500 to 4000 cm^{-1}.

2.3.2 TGA

The compositions of GO and modified GO were analyzed by high-resolution thermogravimetric analyzer (TA Q-50, TA instruments, New Castle, DE). The samples were heated with a rate of 20 °C/min from room temperature to 950 °C under 40 mL/min with continuous air flow.

2.3.3 TEM

The transmission electron microscope, JEM-2100, with an integrated PC system from Jeol USA, Inc. (Peabody, MA) was used to study the dispersion and composition of hybrid nano-additives. Diluted hybrid nano-additives samples in ethanol was mixed well and a drop of sample was dried in a carbon grid. Sample thus prepared was observed under transmission electron microscope in different magnification.

2.3.4 DMA

A dual cantilever clamp of the dynamic mechanical analyzer, DMA Q800 (TA Instruments) was used for dynamic mechanic analysis. The specimen dimension used was 50 x 12 x 3 mm^3. The temperature range over which these properties measured were 25-200 °C at a heating rate of 5 °C /min. The tests were carried out at frequencies of 1 Hz under custom mode.

2.3.5 DSC

Differential scanning calorimetry (DSC) experiments of neat and composites samples were performed to observe the thermal transitions. DSC Q2000 from TA instruments was used to conduct those experiments. For DSC experiment, approximately 5 mg of samples were used. Samples were heated in standard mode from 0 to 200 °C in a heating rate of 10 °C/minutes under N_2 gas atmosphere. Second cycle (cooling) was chosen for thermal analysis. Similar results were observed in three different DSC experiments for each composition.

3. RESULTS

3.1 FTIR of modified GO

Fourier transform infrared spectroscopy was performed to observe the reaction of graphene oxide with ethylene diamine and graphene amine with POSS molecules. FITR spectra of ethylene diamine, GO and GO modified with amine (GO-amine) is shown in Figure 1. In the spectrum of GO sample, broad signal for –OH group was observed from 3000 to 3600 cm^{-1}. Similarly, C=O stretching for -COOH and C-O-C stretching vibrations were seen at 1715 and 1046 cm^{-1} frequencies. In GO-amine, a new peaks around 1615 and 1534 cm^{-1} were observed which corresponds to C=O and -NH stretching vibrations in GO-amine. Appearance of these new resonances (at 1615 and 1534 cm^{-1} which are not present in GO samples' FTIR spectrum) in GO-amine suggested the reaction of GO and ethylene diamine.

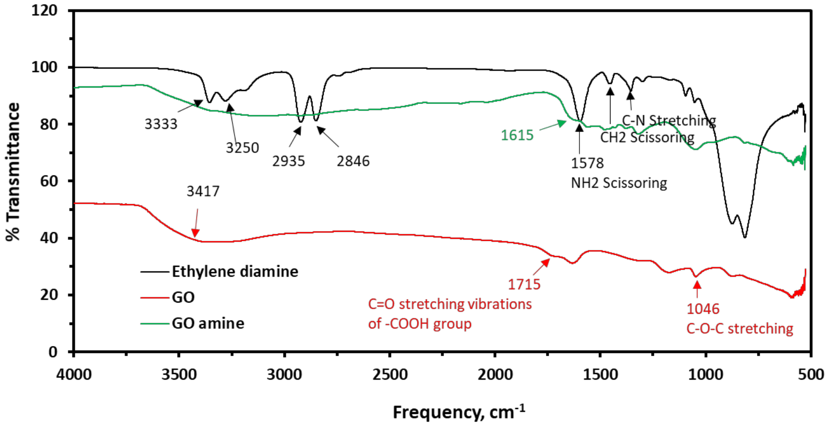


Figure. 1. FTIR spectra of ethylene diamine, GO and GO-amine

To observe the reaction of GO-amine with POSS with epoxy functionalities, FTIR spectra of POSS, GO-amine and POSS-w-GO (POSS with GO) were taken Figure 2. New resonances observed after reaction. New –OH stretch was observed around 3200 - 3600 cm^{-1}. Epoxy –CH stretches shifted from 3012 cm^{-1} to 2935 cm^{-1}. More distinct amide C=O resonance was observed at 1641 cm^{-1}. Decrease in peaks intensities due to epoxide groups around 907, 849, and 704 cm^{-1} were observed in hybrid additives. Appearances of new resonances at 1641 cm^{-1}, shifts of epoxy –CH stretches, and decrease in peak intensities of epoxy groups suggested the reaction between GO-amine and POSS.

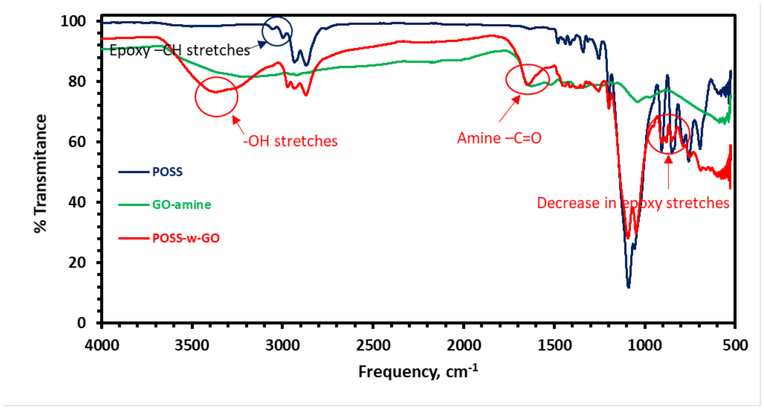
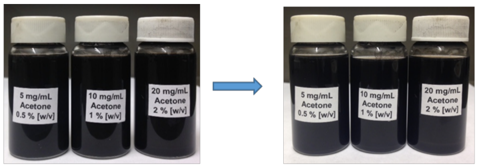


Figure. 2. FTIR spectra of POSS, GO-amine and POSS-w-GO

3.2 Dispersion of hybrid nano-additives in solvents

POSS-w-GO hybrid additives were dispersed in different organic solvents, acetone, alcohols and



Just after dispersion

After 5 days

Figure. 3. Stability of hybrid additives dispersion tetrahydrofuran. Thus prepared samples were left undisturbed for several weeks. Figure 3 shows the dispersion of hybrid additives in acetone and the dispersion was stable after 5 days of standing. Such dispersions prepared in acetone and ethanol were found to be stable for several weeks.

3.3 Transmission electron microscopy of POSS-w-GO dispersion

Transmission electron microscopy of POSS-w-GO hybrid additives was conducted to observe the dispersion and structure of nano-additives. TEM image of POSS-w-GO in alcohol dispersion in Figure 4 showed the presence of POSS molecules with graphene oxide layers. Black spots of POSS molecules were found to be distributed on GO sheets. GO sheets were transparent. So, it is assumed that POSS molecules might be inside of graphene oxide sheets. POSS molecules were found to be dispersed on the surfaces of transparent graphene oxide layers. No separation of solvent layers in POSS-w-GO dispersion in solvents and separated dots like structure of POSS molecules in TEM images indicated the formation of very good dispersion of POSS-w-GO additives in organic solvents like acetone and alcohols. Acetone and alcohol are the most commonly used industrial solvents during composite fabrication.

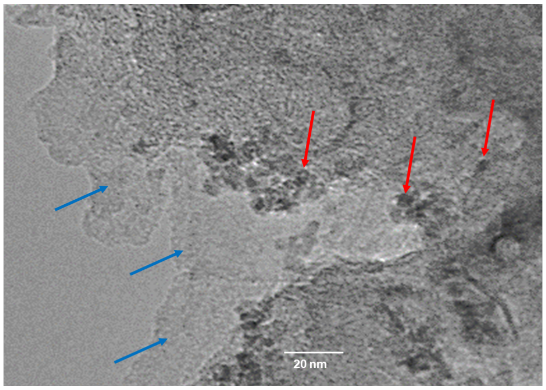


Figure. 4. TEM image of POSS-w-GO dispersion in ethanol; black dots (pointed by red arrows) were POSS molecules; transparent layers (pointed by blue arrows) were GO sheets. The scale bar was 20 nm.

3.4 Thermogravimetric analysis

3.4.1 TGA of GO and modified GO

Thermogravimetric analysis of the GO and modified GO was carried out to know the effect of chemical modification on thermal degradation of GO. The thermal plots of GO, GO-amine, POSS and POSS-w-GO are shown in Figure 5. The thermal plots in Figure 5 clearly showed that chemical modification of GO with ethylene diamine and POSS significantly increased the degradation temperature of GO. The plot of GO-amine sample (green curve) showed that it can tolerate higher temperature than GO samples from the starting of heat. It may be due to the absence of functional groups like –COOH, -epoxy, -C=O etc in

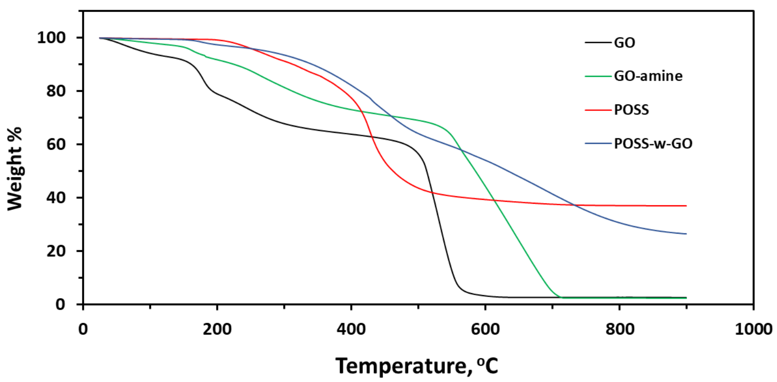


Figure. 5. Thermogravimetric analysis of GO, GO-amine, POSS and POSS-w-GO

GO-amine which are more volatile and come off at low temperature (<200 °C). Such functional groups are absent in GO-amine because of the reaction of such functional groups with amine. Modification of GO with POSS increased the thermal degradation temperature even more (blue curve). POSS-w-GO sample showed very small loss in mass up to 150 °C and after 150 °C there was very slow mass loss and the POSS modified sample was only degraded to 50% at 600 °C. These results clearly indicated that the variation of POSS amount will affect the thermal stability of resins when these additives are added.

3.4.2 TGA of neat resin and composites

Thermogravimetric analysis of neat epoxy resin and composites of epoxy resin with hybrid nano-additives were performed to observed the effect of heat. Composites with 0.5, 2.0, 5.0 and 10.0 % were chosen for thermogravimetric analysis. The thermal plots in Figure 6 showed that addition of hybrid nano additives increased the thermal degradation temperature of composites. Results showed that incorporation of larger amount of additives has made the composites thermally more stable. The results confirmed that the thermal stability of the composites samples increased with addition of hybrid nano-additives. The increase in thermal stability of composites was due to the formation siloxane layer in degraded samples after heating the samples at larger temperature.

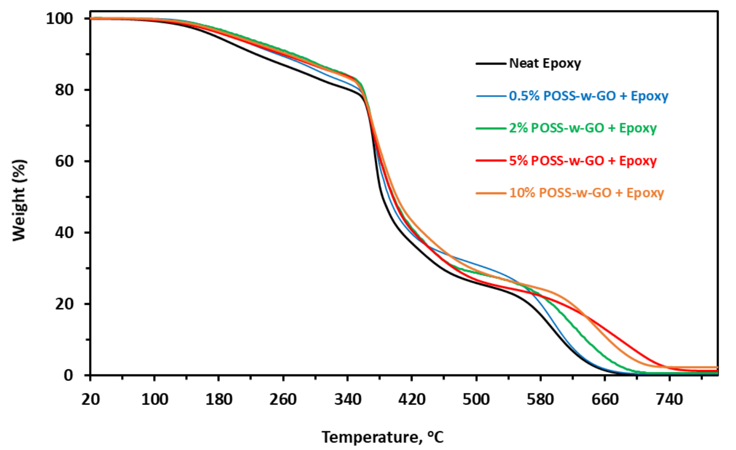


Figure. 6. Thermogravimetric analysis of neat epoxy and composites

3.5 Mechanical Properties

3.5.1 Dynamic Mechanical Analysis

The effect of hybrid nano filler on the damping properties of vinyl ester, polyester and epoxy matrices were studied by using dynamic mechanical analysis. The effects of hybrid nano filler as a function of temperature on the tan δ values of bulk polymer matrices and hybrid nano-additive resins composites at 1 Hz frequency are shown in Figure 7. The tan δ values decreased with addition of filler. The plots indicate that the incorporation of fillers in the matrix has considerably decreased the damping property of the matrix.

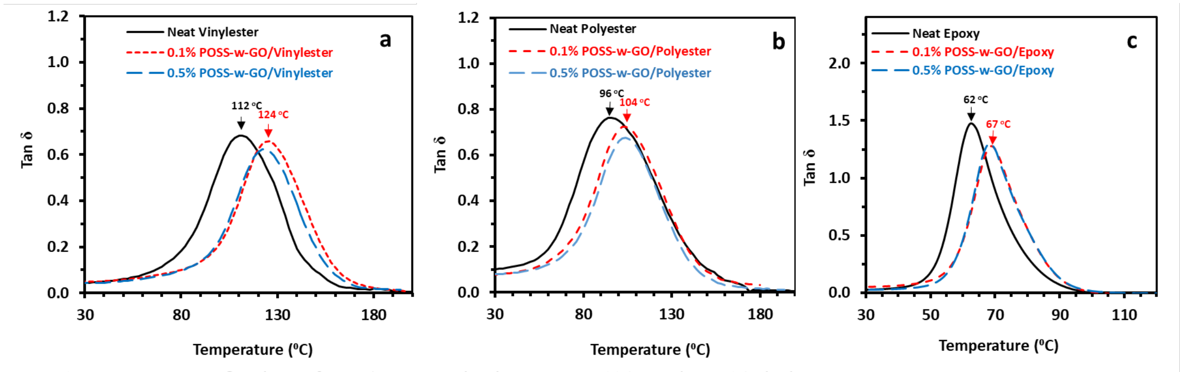


Figure. 7. Tan δ plots for: a) neat vinyl ester, 0.1% and 0.5% hybrid nano-additives and vinyl ester composites; b) neat polyester, 0.1% and 0.5% hybrid nano-additives and polyester composites; c) neat epoxy, 0.1% and 0.5% hybrid nano-additives and epoxy composites

Three samples for neat resins and hybrid nano-additives resins composites were run at 1 Hz frequency to determine the storage moduli. The average values of storage moduli were taken for neat resins and hybrid nano-additive resin composites. Average storage moduli of all composites were larger than that of neat resins. The storage moduli values of hybrid nano filler and resin composites increased as compared to neat resins.

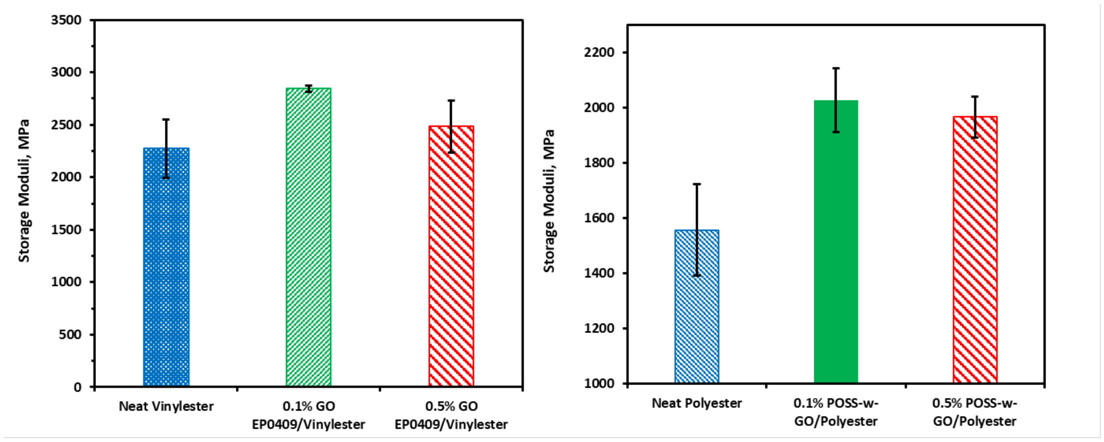


Figure. 8. Average storage moduli plots for: a) neat vinyl ester, 0.1% and 0.5% hybrid nano-additive and vinyl ester compsites; b) neat polyester, 0.1% and 0.5% hybrid nao-additive and polyester composites.

These increases in storage moduli of hybrid nano-fillers and resins composites are expected due to better filler/matrix adhesion and greater degree of stress transfer at the interface. Incorporation of filler in the resins matrix has increased the stiffness of the matrix with the reinforcing effect.

The glass transition temperature of neat resins and hybrid nano-filler resins composites were determined for each measurement from the mechanical data. Average values of the three measurements were taken. A plot of average glass transition temperature for neat resins and vinyl ester/polyester composites are shown in Figure 9.

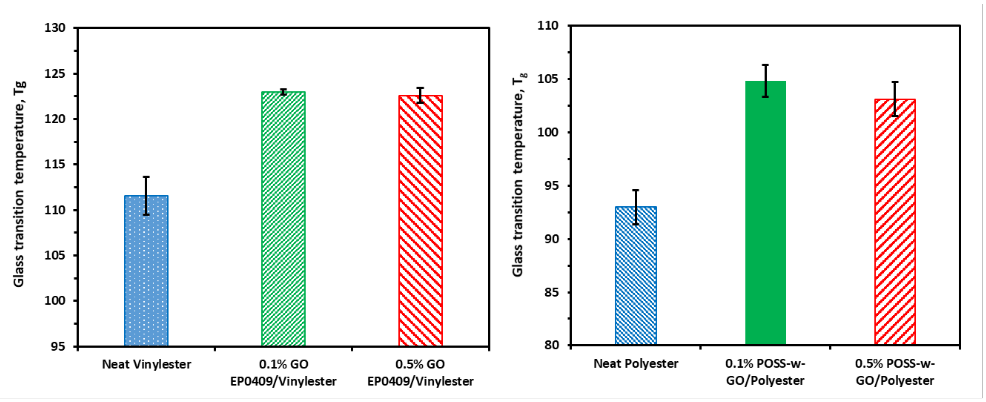
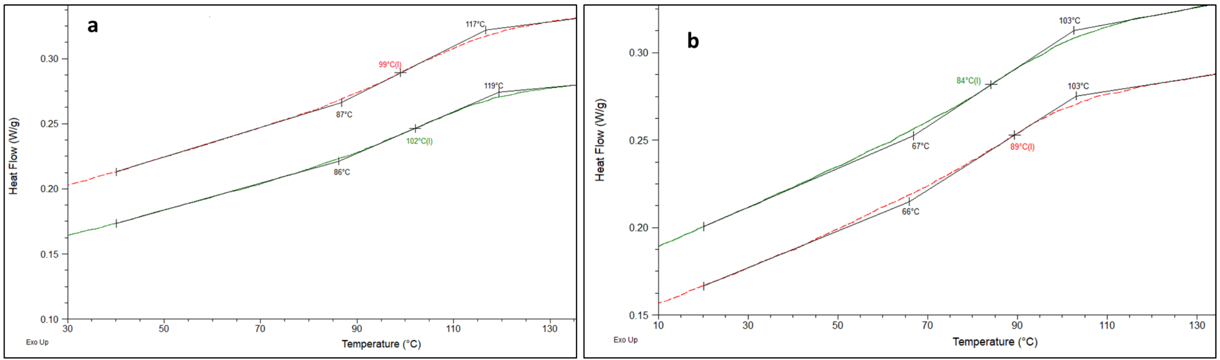


Figure. 9. Average glass transition temperatures of: a) neat vinyl ester, 0.1% and 0.5% hybrid nano-additives and vinyl ester composites; b) neat polyester, 0.1% and 0.5% hybrid nano-additives and polyester composites.

The plot of average glass transition temperature (T_g) values of neat resins and hybrid additives resins composites in Figure 9 showed that T_g of composites were larger than the T_g of neat resins. This indicated that there was the good filler/matrix interface in all hybrid additive and resins composites.

3.6 Differential scanning calorimetry

DSC scans of the pure resins and hybrid nano filler resins composites were taken in standard mode at ramp rate of 10 °C/min under N_2 atmosphere. A typical plot of DSC scan results for neat resins and hybrid nano-additives resins composites is shown in Figure 10.



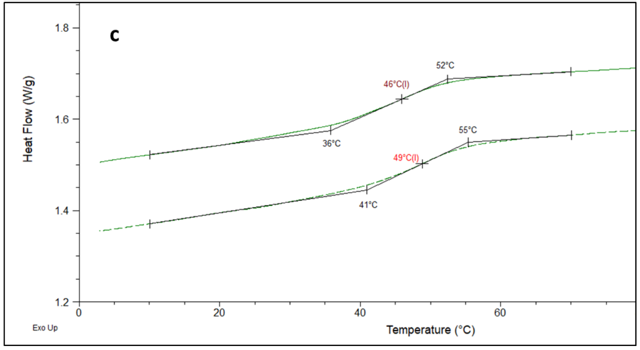


Figure. 10. DSC scans of: a) neat vinyl ester and 0.5% hybrid nano-additive and vinyl ester composites; b) neat polyester and 0.5% hybrid nano-additive and polyester composites; c) neat epoxy and 0.5% hybrid nano-additive and epoxy composites

The DSC plots in Figure 10 showed the larger glass transition temperatures for composite with hybrid nano filler resins compared to neat resins. The increase in glass transition temperatures of hybrid additives and resins composites suggested good filler and resins matrices interaction.

GO modified with POSS additive was found to be compatible with vinyl ester, polyester and epoxy resins. Larger glass transition in resins and additive samples were due to the good dispersion of additives in to the polymer matrices and good nano-filler and polymer matrices interaction. Scale up synthesis of hybrid additives, understanding the effects of hybrid nano-filler in mechanical properties composites like interlamiar fracture toughness and further investigation to understand the reinforcing nature of hydrid nano-filler is undergoing.

4. CONCLUSIONS

GO was successfully modified with POSS and characterized by FTIR, TGA and TEM. The FTIR results confirmed the chemical modification of GO with ethylenediamine and POSS. POSS-w-GO additives dispersions in organic solvents like acetone were found to be stable for more than a month. The thermogravimetric analysis results showed that chemical modification of GO increased its thermal stability and the incorporation such hybrid additives increased the thermal stability of epoxy resins. POSS-w-GO hybrid nano-additives were compatible with epoxy, vinyl ester and polyester resins. The addition of hybrid additives in all resins showed increase in glass transition temperature as well as storage moduli. Vinyl ester composites with 0.1% hybrid nano additives showed ~12 °C increase in glass transition temperature. Polyester composites with 0.1% of hybrid nano additives exhibited ~8 °C increase in glass transition temperature. Similarly, epon 862 epoxy composites with 0.1% hydrid nano-filler amounts showed ~5 °C increase in glass transition temperature. In vinyl ester and polyester resins composites with 0.1% hybrid additives, increase in storage moduli were observed. New type of GO and epoxy POSS based hybrid additives showed improved dispersive and reinforcing properties in vinyl ester, polyester and epoxy resins. This low cost and scalable hybrid additive is expected to be potential future additive substitute for improving vinyl ester, polyester and epoxy composites reinforcing properties.

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