POLYMERIC NANOCOMPOSITES WITH BINARY NANOPARTICLE REINFORCEMENTS AND HYBRID COMPOSITES FOR MARINE APPLICATIONS

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Abstract

In this study, graphene nanoplatelets (GNP), hexagonal boron nitride (hBN) and montmorillonite nanoclay (MMT) were considered as reinforcing agents in polymer matrix. Montmorillonite nanoclay Nanomer® I.30E (MMT) and hexagonal boron nitride (hBN) were combined at different concentrations with 0.1 wt. % amino-functionalized graphene nanoplatelets (GNP) into two binary systems; (a) 5 wt. % hBN and 0.1 wt. % GNP; and (b) 3 wt. % MMT and 0.1 wt. % GNP. Effect of each binary system on mechanical, viscoelastic and thermal properties of SC-780 epoxy composite was studied. While the results of viscoelastic properties showed modest improvements, there was significant improvement in flexural modulus values for binary nanocomposites. Hybrid FRPC samples include Profiles 1: (2G-9C-2G); 2: (G-C-G - alternating sheets) and 3: (5C-3G-5C), which showed average enhancements of 25, 47 and 103% in flexural strength and 19, 58 and 94% in flexural modulus respectively, when compared to E-glass/epoxy samples. Similarly, viscoelastic properties showed -10, 8 and 21 % changes in storage moduli at 30^{o} C for profile 1, 2 and 3, respectively compared to E-glass composites.

1. Introduction

In recent years, there has been substantial increase in the use of fiber reinforced polymer composites (FRPC) in different applications due to numerous advantages they have over traditional engineering materials [1, 2]. Despite desirable properties of FRPC such as resistance to chemical and other environmental attacks, they are sensitive to temperature and prone to moisture absorption [3, 4]. In marine applications, prolonged exposure to seawater causes moisture aging, which induces physico-chemical changes in FRPC leading to poor performance [5]. Chemical affinity of matrix to moisture, temperature and FRPC thickness have also shown to influence the rate of seawater diffusion leading to increased deterioration in material properties [6]. Several research attempts have reported minimizing impacts of moisture on properties of FRPC by use of nanoparticles as matrix reinforcements to slow down the moisture ingress. Others have employed the use of hybrid fiber reinforced polymer composites for various applications [3, 5]. In many of these FRPs, fiber lay-up and the interlocking interactions between constituents minimize environmental attacks, resulting in enhanced durability [1, 7]. Synergy between service environments and loading type are also critical factors to FRPC survivability during service, and therefore requires serious attention during designing. Montmorillonite nanoclays (MMT) have been widely used in this regard, exploiting their sheet-like morphology to block UV radiation and moisture ingress, while enhancing mechanical and thermomechanical properties, among others [8]. Hexagonal boron nitride (*h*BN), another nanoplatelet with morphology similar to that of MMT has also been explored [9-10].

In recent years, binary nanoparticles systems have gained significant research attention, where desirable properties of individual nanoparticles are harnessed through interactions with each other, and the host polymer matrix [11]. Graphene nanoplatelets (GNP) have been combined with nanoclay to enhance various properties of polymer composites [12]. Hence, in this study *h*BN, GNP and MMT were explored as binary reinforcements at different concentrations to enhance properties of SC-780 epoxy composites. Epoxy samples were fabricated using individual nanoparticles and binary consisting of 3 wt. % MMT/0.1 wt. % GNP (MMT/GNP) and 5 wt. % *h*BN/0.1 wt. % GNP (*h*BN/MMT) respectively. Mechanical and thermal properties were characterized using three-point bend flexure tests, dynamic mechanical analyses (DMA). Properties of binary systems were compared to those of unmodified and modified epoxy composites loaded with individual nanoparticles.

A separate study was conducted to understand the influence of hybridization on seawater absorption characteristics of FRPC and its effect on durability. FRPC laminates were fabricated using epoxy SC-780 reinforced with E-glass, carbon and hybridized carbon/E-glass consisting of Profiles 1: (2G-9C-2G); 2: (G-C-G - alternating sheets), and 3: (5C-3G-5C). Moisture absorption characteristics of all samples was studied by determining weight gain of each sample, while corresponding degradation in mechanical properties were characterized using three-point bending flexure tests as function of duration of seawater exposure time. Influence of hybridization and seawater absorption on viscoelastic properties was studied using dynamic mechanical analysis (DMA), and results characterized as function of exposure duration.

2. Experimentation

2.1 Materials

Materials used in the study were two part diglycidyl ether of bisphenol A epoxy SC-780(part A) and an amine based curing agent (part B) acquired from Applied Poleramic Inc. Nanoparticle reinforcements used were amine functionalized graphene nanoplatelets (GNP), montmorillonite nanoclay, I.30E (MMT) and hexagonal boron nitride (*h*BN). GNP was acquired from Cheap Tubes Inc., while MMT and *h*BN were acquired from Sigma Aldrich and Skysprings Nanomaterials Inc., respectively. Surface of MMT has been modified with 25-35 wt. % octadecylamine. Dimensions of these nanoplatelets were a few nanometers between platelets with average particles sizes for *h*BN and MMT being 100 nm and between 2-10 nm; and density of 2.3 and 0.41 g/cm^3 respectively, while thickness of GNP was less than 2 nm. Carbon fabric used as reinforcement was, 8” harness satin (HS) weave with a density of 0.3 kg/m^2, 3k tow size and thickness of 0.46 mm, supplied by US Composites Inc. E-glass fabric was obtained Fiberglassite.com. Sizing material used in carbon fibers is unknown, however silane compound was used in E-glass fibers to promote adhesion between the fibers and the matrix. Other material used for conditioning includes industrial seawater, purchased from Doctors Fosters and Smith with a pH of 8.5 and specific gravity of 1.027.

2.2 Sample Fabrication

Fabrication of unmodified and modified epoxy composites using different loadings of various nanoparticles was done by first dispersing these nanoparticles into part A of epoxy resin. Samples were fabricated with 0.2 wt. % GNP, 3 wt. % MMT; 5 wt. % *h*BN, and binary 1 - MMT/GNP, and binary 2 - hBN/GNP. Binary 1 consists of 0.1 wt. % GNP and 3 wt. % MMT; and binary 2 consists of 0.1 wt. % and GNP 5 wt. % *h*BN. Prior to fabricating MMT samples, measured amount was dried in a vacuum oven at temperature 50° C for two hours, due to hydrophilic nature of organoclay. MMT/SC780 mix was magnetically stirred at 400 rpm for 24 hours at room temperature. Calculated amount of GNP was mixed in the epoxy resin, stirred manually followed by ultrasonication for 1 hour. Similarly, measured amounts of *h*BN and epoxy resin were mixed, stirred together and sonicated for 1.5 hours. Sonication parameters used were pulse rate of 20 sec on and 30 sec off using 45 % amplitude, while maintaining the mixture in a cooling bath set at 40º C for both GNP and *h*BN samples respectively. Sonicated mixtures of *h*BN/SC-780 and GNP/SC-780 were magnetically stirred to further disperse each corresponding nanoparticle for about six hours at 400 rpm. GNP/SC780 mixture was further processed using three-roll shear mixer with gap between the rollers set at 15, 10 and 5 µm with speed of rollers at 120 rpm for three passes. For binary nanocomposite fabrications, measured amount of resin was divided into two unequal parts in beakers. Calculated amount of dried nanoclay was mixed and magnetically stirred in the larger portion for 15 hours. *h*BN was also dispersed in the larger portion using sonication process discussed earlier. Determined amount of GNP nanoparticles for each binary system were dispersed in the other part of resin and sonicated at the same conditions discussed earlier. Each GNP/resin mixture was added to nanoclay mixed resin solution and *h*BN/SC780 solutions respectively, and combined mixture was subsequently processed through three-roll shear mixer using parameters discussed earlier followed by magnetic stirring for six hours. SC-780-part B was added to nanoparticle dispersed part A, mechanically stirred and degasified using "Thinky" vacuum mixer for 15 minutes, at 1500 rpm.

For fabricating FRPCs desiccated, unmodified epoxy resin was applied to completely wet individual layers of fabrics, stacked sequentially by hand, placed in a Wabash Hot press compression molding, and allowed to cure for 24 hours under 1-ton pressure. Targeted thickness of each FRPC sample was 4.5±0.5mm, hence different number of layers were used for each type of fabric based on density including hybrid composites. Fabricated FRPC samples were E-glass, carbon and carbon/E-glass hybridized composites indicated as profiles 1, 2 and 3. Various test coupons were machined from each composite laminate according to ASTM standards for characterization and comparison of properties.

2.3 Characterization

2.3.1 Dynamic Mechanical Analysis (DMA)

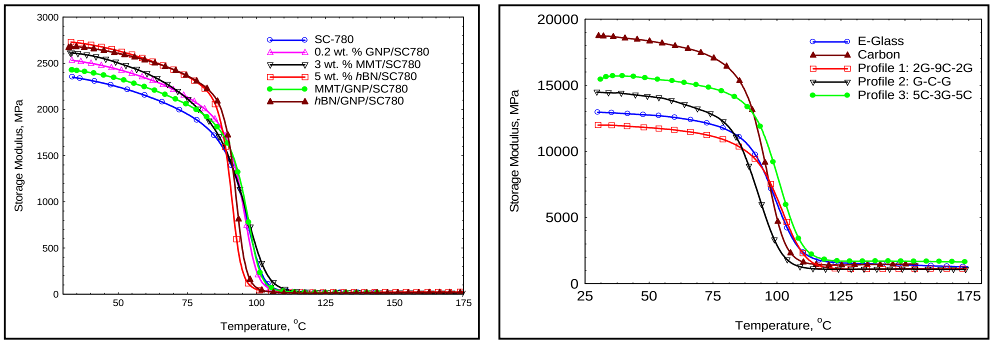
Viscoelastic properties of SC-780 epoxy composites and various FRPC samples were investigated using dynamic mechanical analysis (DMA) using TA Instruments' Q800 in dual cantilever mode at oscillating frequency and amplitude of 1 Hz and 50 µm respectively. DMA samples were scanned from 30-180 °C at 5 °C/min according to ASTM D4065. Rectangular shaped samples of size 54 x 12.5 x 3.5mm were used. Storage modulus (G'), loss modulus (G'') and damping coefficient (Tan Delta) were recorded as function of temperature for each sample. Glass transition temperature (Tg) was determined using the peak of loss modulus curves and reported as function of nanoparticle infusion and seawater exposure time. Five samples were tested and average data are presented for comparison.

2.3.2 Flexural Characterization

Influence of different nanoparticles on flexural properties of SC-780 epoxy composites and various FRPC samples was investigated using three-point bend flexure tests. Tests were conducted in displacement mode with crosshead speed of 2.0 mm/min according to ASTM D790-10 standard. Epoxy samples were tested using Zwick Roell Z25 test setup. FRPC samples were tested using a servohydraulic MTS 809 testing equipment. Both systems are equipped with data acquisition software. Five samples were tested from each type of composites including conditioned and unconditioned ones.

2.3.4 Seawater Conditioning

FRPC test coupons were completely submerged in industrial grade seawater for marine environmental conditioning at room temperature. Representative samples were identified and their respective weight recorded prior to complete immersion into seawater. Weight of each representative sample was recorded every seven days during conditioning. For that, samples weare removed, patted with dry paper towel to remove dripping seawater, weighed and placed back into the conditioning container. Samples would be conditioned up to 240 days and various properties characterized every sixty days, to study the effects of conditioning on each sample. Weight gained by each samples would be used to characterize moisture absorption in composite properties.



(a) (b)

Figure 1. Representative Storage Modulus of (a) unmodified and modified epoxy composites and (b) Carbon, E-glass and Hybrid FRPC.

3. Results and Discussion

3.1 Viscoelastic Characterization

Characteristic DMA storage and loss moduli thermographs obtained from representative unmodified and nanoparticle modified SC-780 epoxy and FRPC composites are shown in Fig. 1 (a, b) respectively. Results from DMA showed slight improvements in storage modulus at 30° C by 10, 8, 10, -1 and 9% for 0.2 wt. % GNP, 3 wt. % MMT, 5 wt. % *h*BN, MMT/GNP and hBN/GNP nanocomposites, respectively when compared to unmodified SC-780 counterpart. On the other hand, glass transition temperature (Tg) determined from peak of the loss modulus curve decreased across the board due to nucleating effects of nanoparticles. Interactions between nanoparticles and epoxy molecules results in a bridging effect, which subsequently prevents the relaxation and flow of epoxy molecules during heating. Bridging of these reinforcements restricts mobility of molecular chain movements during glass transition phase.

In FRPC samples, interactions between different fibers and epoxy led to enhanced storage moduli values in all three-hybrid profiles compared to E-glass FRPC. Carbon/epoxy composites as expected showed superior properties compared to the other samples with storage modulus at 30° C approximately 38% higher than that of E-glass/epoxy samples. Carbon/epoxy samples also showed approximately 54, 28 and 14% enhanced storage modulus values when compared to hybrid reinforcements in Profile 1, 2 and 3 respectively. Effect of hybridization on viscoelastic properties of

FRPCs, especially in profile 2 and 3 showed enhanced performances compared to E-glass. Comparison of storage modulus data at 30 °C between hybridized FRPs and E-glass showed approximately 8 and 21% improvements for profiles 2 and 3 respectively. This indicates that there was strong interlocking dynamics between carbon/E-glass hybrid fibers and epoxy molecules compared to that between E-glass/epoxy molecules. Furthermore, segmental mobility of polymer molecules during glass transition was slightly restricted by the intertwined fiber weave patterns between the two fabric types, especially in Profile 3.

3.3 **Absorption Characteristics**

Seawater absorption characteristics of selected FRPC samples from each composite laminate during conditioning were monitored through weight changes. Plots of percent mass changes monitored through absorption behavior of FRPC samples during conditioning as function of square root of time is shown in Figure 2. An initial spike in rate of seawater absorption was recorded in all samples, a phenomenon often associated with both Fickian and non-Fickian absorption behavior in polymers [7]. Data from the study revealed different degrees dictated by interaction between individual components of each FRPC and seawater molecules. This resulted in a disparity in initial percent weight of absorbed seawater in FRPC samples, and at different times during conditioning [9]. The initial high rate of absorption is driven by internal and external interactions between constituents of each FRPC and conditioning environment [7, 13].

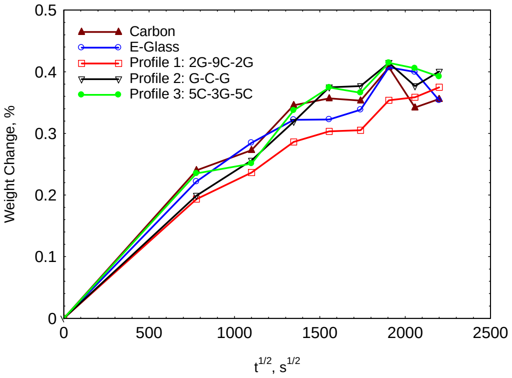
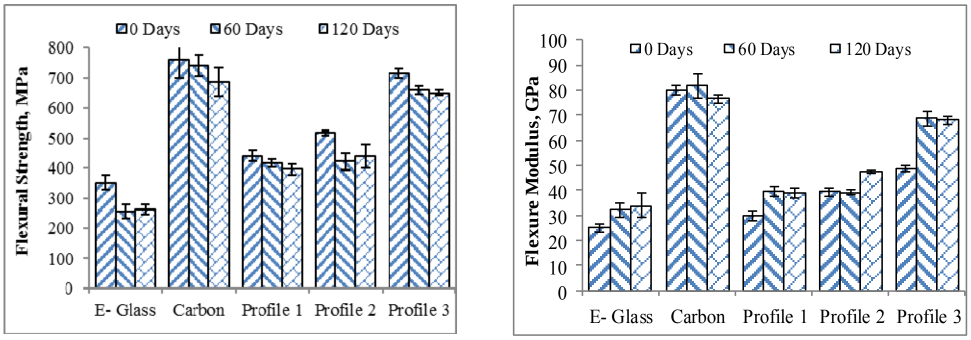


Figure 1. Percent weight change versus as function of $t^{1/2}$.

Flexural Characterization

Data from the flexural study showed a relative increase in flexural strength in all nanocomposites, except samples with 3 wt. % MMT loading which showed the lowest value among all samples including neat. The increase in flexural properties was attributed to enhance adhesive strength between nanoparticles and epoxy molecules, due to interfacial interaction causing a bridging effect between polymer molecules. This bridging effect by nanoparticles on polymer chains was more pronounced in 0.2 wt. % GNP due to increased bonding, resulting in 8% and 35% enhancement in strength and modulus compared to unmodified. Increased interfacial stiffness enhances the ease of load transfer from the matrix to the fillers, thereby improving load-bearing capability. Interestingly, samples with 5 wt. % loading *h*BN showed nominal flexural properties compared to other nano-infused samples, however strain to failure was significantly high. The higher strain to failure is indicative of molecular chain movement under flexural stress, and this may be caused by weak bond formation between the nanoparticles and polymer chains. Another factor that can instigate this behavior is lower crosslinking density due to incomplete polymerization, causing the sheet-like morphology to slide past each other under flexural stress. Hence different nanoparticle system may require different cure parameters. This may also be responsible for the relative nominal improvements in flexural strength of all nanocomposites compared to unmodified. Thus, inefficient transfer of load between nanoparticles and polymer molecules in response to applied external load may lead to material strength comparable or lower than that of unmodified composite. Combinations of MMT and *h*BN with GNP in binary system yielded significant increase in flexural modulus compared to other samples. Samples with *h*BN/GNP showed nearly 80% enhancements in modulus, while MMT/GNP reported approximately 63%, which was attributed to better interactions leading to increased bridging and restrictive mobility. As a result, strain at failure significantly decreased in binary nanocomposites compared to others. There was statistically no change in overall strength in both binary nanocomposites, possibly due to reasons mentioned earlier.

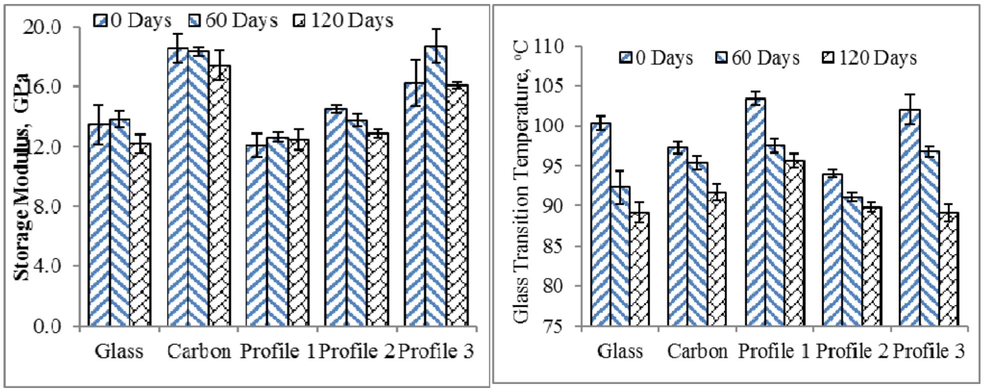
In FRPC samples, properties of various combinations of carbon and E-glass hybrid composites were between that of carbon and E-glass, with profile 1 showing the least and Profile 3 exhibiting the most properties respectively amongst the hybrid FRPC. Comparison between hybrids and E-glass FRPC showed an increase in flexural strength by approximately 25, 47 and 103% for profiles 1, 2 and 3 respectively. Similarly, there was also an observed increase in flexural modulus by approximately 19, 58 and 94% for profiles 1, 2 and 3 respectively. Thus, hybridization resulted in significant enhancements in flexural properties of FRPC when compared to E-glass samples. Compared to carbon samples, flexure strength of FRPC decreased by 54, 42, 31and 6% E-glass and Profiles 1-3 hybrids respectively. By comparison, Profile 3 showed the minimum disparity in flexure properties among the hybrids with respect to carbon, while exhibiting the highest properties among the hybrids and E-glass. Carbon fibers have excellent tensile stiffness and strength, but poor compressive strength due to lack of ductility, while E-glass is known for great toughness and lower stiffness compared to carbon fibers. Thus, carbon fibers used in the outer layers enhanced the flexural stiffness while glass fibers in the core-enhanced ductility, resulting in improved toughness of Profile 3 samples compared to rest of the samples.



(a) (b)

Figure 3. Effect of Seawater absorption on Flexural (a) Strength and (b) Modulus of all FRPC Samples.

Effect of seawater conditioning on flexure property retention of all samples was characterized and results presented as function of duration of exposure. The goal was to observe potential defects that may affect the rate of deterioration in material's property as duration of exposure increases. Such defects include interlaminar delamination due to plasticization of the matrix in each FRPC, and the effectiveness of hybridized fibers in minimizing such effect as noted by Mourad et al. [6]. Seawater exposure to glass/epoxy composites is reported to increase the ductility in such materials due to plasticized matrix, hence it is expected that hybridized fibers minimize such an effect. Figures 3 (a, b) show comparison of experimental data from flexure test results of FRPC samples, depicting the effect of seawater aging on flexural strength and modulus properties, respectively, for all samples. Results of the tests indicated an overall decrease in flexure strength in all samples compared to their respective unconditioned counterpart. Rate of deterioration significantly varied among different samples, with E-glass and Profile 2 deteriorating the most by approximately 27 and 18% respectively after the first 60 days of exposure. At the end of the study, flexural strength of the same slightly increased after 60 days, which constitutes a decline by approximately 26 and 23% respectively compared to respective baseline data. Among all the samples, these two exhibited a slight increase in flexure properties after 120 days of exposure, while the rest showed steady decline. Outer layers of Profile 2 were E-glass fibers; however, the presence of carbon in the core enhanced the ability to resist bending during flexure testing leading to slight improvement in the observed results.



(a) (b)

Figure 4. Effect of Seawater Conditioning on (a) Storage modulus and (b) glass transition temperature of all FRPC Samples.

Figure 4 shows comparison of the effect of seawater exposure on storage modulus of each FRPC after 60 and 120 days. Results from the test showed slight improvements in storage modulus for E-glass, Profile 1 and 3, while carbon and Profile 2 showed steady degradation over the duration of the study. The effect of seawater conditioning was noticeable immediately after 60 days, and it continued to decline until the end of the study for all samples. The decreased in Tg values across the board was attributed to onset of damaging effect of absorbed seawater, leading to increased mobility of segmental molecular polymer chains during DMA test. Presence of different salts in seawater degrades matrix-dominated properties in FRPC through the gaps between fiber and matrix interface.

4. Conclusions

Influence of combined hBN and MMT with GNP on mechanical and viscoelastic properties of epoxy SC780 composites was studied. Results from the study showed sufficient synergy between MMT/GNP; and hBN/GNP binary nanocomposites resulting in relatively better dimensional stability at elevated temperatures compared to neat system. Addition of binary nanoparticles resulted in significant enhancement in flexural modulus compared to neat and other nanoparticle loaded samples. Processing of binary nanoparticles in SC-780 can be optimized to harness full potential. Effect of seawater conditioning on flexural and viscoelastic properties of E-glass, carbon and hybrid FRPC are presented in this study. E-glass, carbon and various configurations of hybrid fiber composites were subjected to seawater for 120 days and properties characterized. E-glass absorbed the most seawater during the study, while carbon composites absorbed the least amount. Dynamics of seawater absorption in hybrids samples were independent of the type of fiber on the outer layer, hence no pattern was observed. Profile 3 with carbon outer layers absorbed the most while profile 1 with E-glass outer layers absorbed the least. Glass transition temperatures decreased steadily as duration of exposure increased due to seawater ingress. Flexural strength decreased with increasing exposure time. However, a slight increase in flexural modulus of all samples except carbon/epoxy composites was noticed over the duration of the study. Overall, profile 3 showed best mechanical and viscoelastic properties before and after conditioning among all hybridized samples. Mode of failure after seawater exposure was mainly fiber debonding, matrix cracking and delamination due to plasticization of the matrix.

Acknowledgments

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