Fabrication and Thermo-Mechanical Characterization of CNF-Filled Polyester and E-glass/Polyester Nanophased Composites

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ABSTRACT

A high intensity ultrasonic liquid processor was used to infuse CNFs into the polyester matrix which was then mixed with catalyst using a high speed mechanical agitator. Results showed the significant improvement of mechanical properties in the dispersion of CNFs in sonication over the mechanical mixing, magnetic stirring and thinky mixing methods. Flexure tests performed on the neat polyester (NP), 0.1wt.%, 0.2 wt.%, 0.3 wt.% and 0.4 wt.% CNF-filled polyester (CNF-FP) showed 86% and 16% increase in flexural strength and modulus, respectively, compared to the unfilled polyester with increasing loading percentage of CNFs up to 0.2%. Both conventional and nanophased glass reinforced polyester composites (GRPC) were fabricated using vacuum assisted resin transfer molding (VARTM). Similar increasing trend in the mechanical properties was observed in these nanophased GRPC. Dynamic mechanical analysis (DMA) studies indicated an increase of about 35% and 92% in the storage modulus, and slight increasing trend of glass-transition-temperature (T_g) in the CNF-FP and CNF-filled-GRPC (CNF-GRPC), respectively, as compared to the conventional ones. Thermo-gravimetric analysis (TGA) results showed the insignificant improvement in the decomposition temperature with addition of CNFs in these materials systems. Thermo-mechanical Analysis (TMA) of this new material system studied, and results of which illustrated the coefficient of thermal expansion (CTE) of polyester decreased with an infusion of CNFs into the polyester.

Keywords: Polyester, CNFs, VARTM, Nanophashed composites, Thermo-mechanical properties.

1   INTRODUCTION

Fiber reinforced polymer matrix composites due to their high specific strength and specific stiffness to weight ratios have become attractive structural materials in aerospace industry, marine, armor, automobile, railways, civil engineering structures, sport goods etc. [1]. Extensive research are currently underway to develop the nanophased fiber reinforced polymer matrix composites. Hence, it is very important to have a sound knowledge on the thermal and mechanical behavior of these advanced materials tailored with nanoparticles, such as carbon nanotubes (CNTs), carbon nanofibers (CNFs), clay nanoplatelets, and other nanoparticles. Hayes et al. [2] have shown the ability to incorporate nanosized alumina structures in the matrix and interlayer regions of prepreg based carbon/epoxy composites. Contribution made by the interphase modification adding low nanofiller provides possibilities to enhance performances of GRPC. It was documented that a small percentage of strong fillers can significantly improve the mechanical, thermal, and barrier properties of the pure polymer matrix [3].

Timmerman et al. [4] studied the influence of nanoclay on the carbon fiber/matrix composites under thermal cyclic loading and reported that the transverse cracking in symmetric carbon fiber/epoxy laminates was significantly reduced when nanoparticle fillers were used. Pervin et al. [5] evaluated the thermal and mechanical properties of carbon nanofiber reinforced SC-15 epoxy and documented the significant improvement in the thermal and mechanical properties of the material system. Mahfuz et al. [6] found the higher tensile strength and modulus by about 15–17% and increased thermal stability and crystallinity of the carbon nanoparticles/whiskers reinforced polyethylene system as compared to the neat polyethylene control samples. Chowdhury et al. [7] investigated the flexural and thermo-mechanical properties of woven carbon/nanoclay-epoxy laminates and noticed improvement in the thermal properties including glass transition temperature and storage modulus. Pramoda et al. [8] showed a good dispersion of graphite throughout the PMMA matrix and the addition of graphite into the matrix led to the significant improvement in the thermal stability and the storage modulus of the PMMA nanocomposites. The coefficient of thermal expansion (CTE) of the PMMA/GNCs decreases with an increase in the graphite content. Tognana et al. [9] summarized the coefficient of thermal expansion (CTE) experimental results of epoxy matrix particulate composite

as a function of filler content in both glassy and rubbery state. Morales et al. [10] used high speed dispersion mixer to disperse CNFs into matrix and observed improvement in flexural and tensile strengths with addition of 1 wt. % CNFs in the glass/polyester composite.

In this study, nanophased polyester and glass/polyester composites were fabricated tailoring with 0.1wt.%, 0.2 wt.%, 0.3 wt.% and 0.4 wt.% CNFs. Flexure results showed enhanced properties in nanophased composites compared to the conventional ones. Both nanophased polyester and glass/polyester composites were characterized using dynamic mechanical analysis (DMA), thermo-gravimetric analysis (TGA), and thermo-mechanical Analysis (TMA).

2 EXPERIMENTAL

2.1 Materials Selection

Commercially available B-440 premium polyester resin and styrene from US Composite, heat treated PR-24 CNFs from Pyrograf Inc., and woven E-glass fiber from fiberglasssite.com were selected as matrix, nanoparticle, and reinforcement, respectively, in this current study because of their good property values and low cost. Polyester resin contains two-part: part-A (polyester resin) and accelerator part-B (MEKP- methyl ethyl ketone peroxide).

2.2 Resin Preparation

Ultrasonic cavitation technique is one of the most efficient means to disperse nanoparticles into a polymer [11]. In this study, sonication was performed using a high intensity ultrasonic irradiation (Ti-horn, 20 kHz Sonics Vibra Cell, Sonics Mandmaterials, Inc, USA) for 60, 90, and 120 minutes, respectively, adding 0.1, 0.2, 0.3, and 0.4 wt.% CNFs with corresponding percent polyester resin and 10 wt.% styrene in a glass beaker. The mixing process was carried out in a pulse mode of 30 sec. on/15 sec. off at amplitude of 50%. Continuous external cooling was employed by submerging the beaker in an ice-bath to avoid temperature rise during the sonication process. To remove the bubbles, high vacuum was applied using Brand Tech Vacuum system for about 90-120 minutes. Once the bubbles were completely removed from the mixer, 0.7 wt.% catalyst was mixed with the mixer using a high-speed mechanical stirrer for about 2-3 minutes and vacuum was again applied for about 6-8 minutes to degasify the bubbles produced during the accelerator mixing. The whole mixing system is shown in Figure 1.
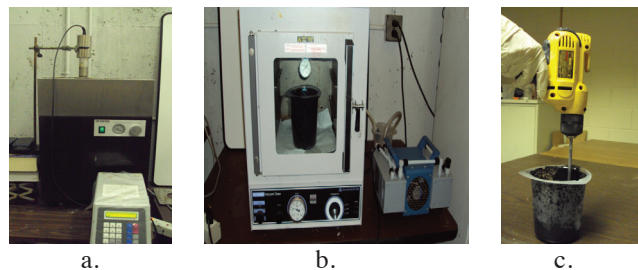

Figure 1: a. Sonication, b. Degasification, c. Mechanical mixing

2.3 Composite Fabrication

Both conventional GRPC and CNF-GRPC were manufactured by VARTM method. The panel was cured for about 12-15 hours at room temperature. The room temperature cured material was taken out from the vacuum bagging and trimmed, and test samples were machined according to ASTM standard. They were thermally post cured at 110 °C for 3 hours in a mechanical convection oven.

2.4 Test Procedure

Flexural tests under three-point bend configuration were performed on the Zwick Roell testing unit according to ASTM D790-02 to determine the ultimate strength and young modulus of the polymer nanocomposites and its laminates. The machine was run under the displacement control mode at a crosshead speed of 2.0 mm/min [5] and tests were performed at room temperature.

Storage modulus, glass transition temperature (T_g), and loss factor, tanδ, of the fully cured samples were obtained from a TA instruments Q 800 operating in the dual cantilever mode at a heating rate of 5 °C/min from 30 °C to 175 °C and an oscillation frequency of 1 Hz. The specimens were cut by a diamond cutter in the form of rectangular bars of nominal dimensions 3 mm×60 mm×12 mm. The test was carried out according to ASTM D4065-01 [12]. Thermo-gravimetric analysis (TGA) was conducted with a TA Instruments Q 500, which was fitted to a nitrogen purge gas. The temperature was increased from ambient to 600 °C at a rate of 10 °C/min. The coefficient of thermal expansion (CTE) were obtained from a TA instruments Q 400 operating in the expansion mode at a heating rate of 5 °C/min from 30 to 175 °C. The nominal thickness of these samples was 3.5 mm.

3 RESULTS AND DISCUSSIONS
3.1 Flexural Properties

Flexure tests were performed on the NP, 0.1, 0.2, 0.3, and o.4 wt.% CNF-FP nanocomposites and its laminates to evaluate their bulk stiffness and strength. Their typical stress-strain behaviors are shown in Figure 2. It is clear

from these stress-strain curves that all the samples of CNF-FP composites failed immediately reaching to their maximum values showing significant improvement in the mechanical properties up to 0.2 wt.% of CNFs loading, beyond that there was a decreasing trend. Similar trend was found for the CNF-GRPC showing considerable nonlinearity before reaching the maximum stress. However, more or less ductility was observed in each type of laminate sample but no obvious yield point was found.
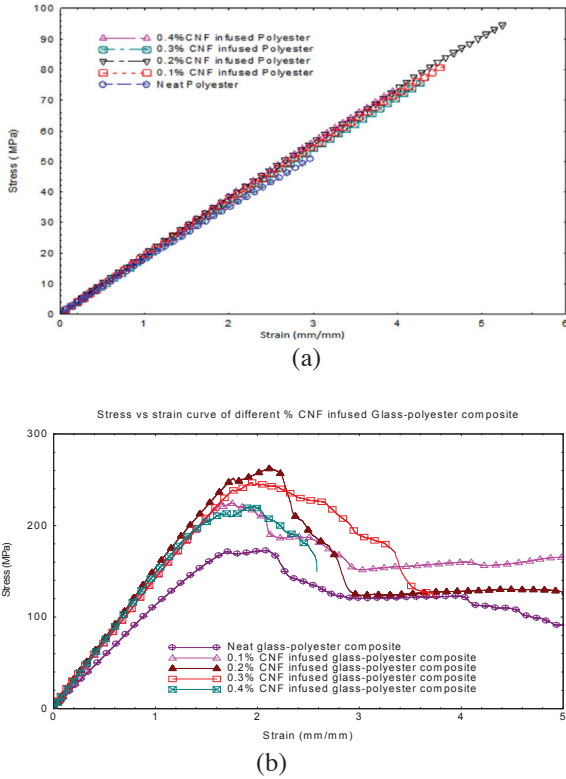

(a)

(b)

Figure 2: Stress-strain curves of (a) NP & CNF-FP (b) GRPC and CNF-GRPC

Five samples were tested for each condition and the average properties obtained from these tests. It is evident that for 0.2 wt.% loading the flexural strength and modulus were increased by about 86% and 16%, respectively, as compared to the NP samples. Similar trend was observed for the CNF-GRPC.

3.2   Dynamic Mechanical Analysis (DMA)

The storage modulus and loss factor, tan δ, of polyester and CNF-FP plotted as a function of temperature from DMA are shown in Figures 3 and 4, respectively. It is observed from the analysis that the storage modulus was increased and peak height of the loss factor was decreased with the addition of CNFs. The addition of 0.2 wt.% of CNFs infused polyester showed the maximum improvement of 35% in the storage modulus at room temperature and increasing trend on T_g of this material.
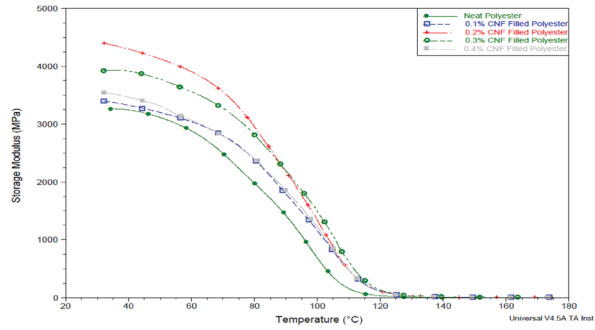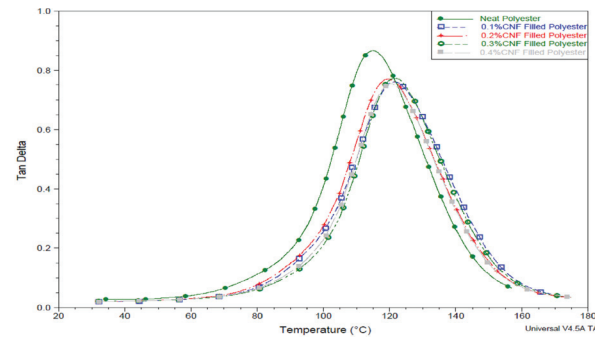

Figure 3: Storage modulus-temparature curve

Figure 4: Loss factor-temperature curve

In case of glass/polyester composites it is observed that the addition of 0.2 wt.% of CNFs infused glass/polyester showed the maximum improvement of 92 % in the storage modulus at room temperature and also increasing trend of T_g. The DMA results are given in Table 1.

Type of Composites	Storage Modulus (MPa)	% Change	Glass Transition Temp.(°C)
GRPC	22067 ± 1375	-------	116.4 ± 0.21
0.1%	32550 ± 1245	47.5	118.4 ± 0.8
0.2%	42393 ± 1074	92.1	118.6 ± 0.2
0.3%	31942 ± 1023	44.8	119.1 ± 0.2
0.4%	25780 ± 1336	16.8	119.0 ± 0.3

Table 1: DMA results for GRPC and CNF-GRPC

3.3   TGA Results

TGA responses of GRPC and CNF-GRPC have been shown in Figure 5 as a function of temperature. It is clear from the plots that the decomposition temperature was slightly improved and overall weight loss was less for the 0.2 wt.% CNF-FP sample compared to all other samples.
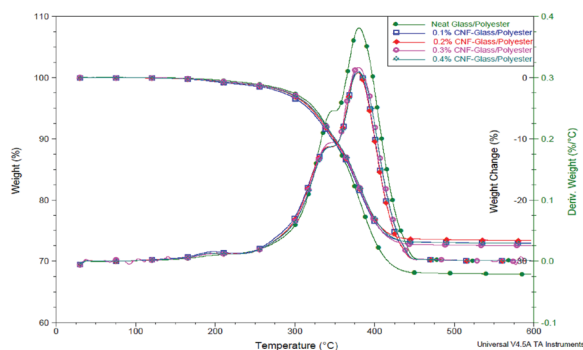
Figure 5: TGA of GRPC and CNF-GRPC

3.4 TMA Results

The coefficient of thermal expansion (CTE) of polyester decreased with an infusion of CNFs into polyester. This result agreed well with the DMA and also TGA results. The TMA results of NP and CNF-FP showed in Figure 6 and Table 2, respectively.
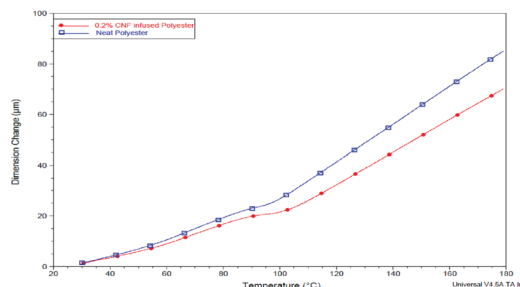

Figure 6: Dimension change with temperature both NP and CNF-FP

Type	Coefficient of Thermal Expansion	
	Below T_g (40--80°C)	Above T_g (120--170°C)
NP	106 μm/(m°C)	201 μm/(m°C)
0.2% CNF-FP	104 μm/(m°C)	196 μm/(m°C)

Table 2: CTE of NP and CNF-FP

The reduction of CTE was observed in the CNF-FP due to the better dispersion of CNFs in the polyester and the reduced segmental motion of the polyester matrix. [13]

4 CONCLUSIONS

A significant improvement in the properties of engineering structural polymeric composite materials can be made by tailoring a small amount of organic or inorganic fillers at a nanoscale level. Carbon nanofibers (CNFs) fillers have been shown to be effective reinforcements in the neat polyester resin to enhance the flexure behavior of this resin system. The neat, CNF-filled polyester, conventional and nanophased composites samples were manufactured and tested under the flexural and thermo-mechanical loading conditions. The significant conclusions drawn from the investigation are given below.

1. 0.2 wt.% CNFs and 90 minutes sonication showed the maximum 86 and 16% improvement in the flexural strength and modulus, respectively, over the mechanical mixing method.
2. 0.2 wt.% CNF-GRPC exhibited the 49 and 31% improvement in the flexural strength and modulus, respectively.
3. DMA results illustrated an increase of 35% in the storage modulus and insignificant improvement in the T_g of 0.2 wt.% CNF-FP.
4. DMA evaluation indicated the 92% improvement in the storage modulus and insignificant effect on the T_g of the 0.2 wt.% CNF-GRPC.
5. TGA analysis showed that addition of CNFs has insignificant effect in the decomposition temperature.
6. The CTE of polyester decreased with addition of CNFs into polyester.

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