EFFECT OF CARBON NANOFIBERS ON COMPRESSION PROPERTIES OF POLYESTER

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ABSTRACT
In the present investigation, a high intensity ultrasonic liquid processor was used to obtain a homogeneous mixture of polyester resin and vapor grown carbon nanofiber (CNF). The CNFs were infused into the polyester through sonic cavitations and then mixed with catalyst using a high speed mechanical agitator. To investigate dispersion effect on mechanical properties of CNF/polyester, sonication dispersion were performed at 20 minutes, 40 minutes, 60 minutes and compared with mechanical mixing method. Experimental results show that sonication time has no effect on mechanical properties of neat polyester, but significantly improve dispersion of CNF. Experimental results also show that, at the same processing conditions, 0.2% CNF/polyester provides maximum enhancement in strength. Higher than 0.2%, strength of nanocomposites decreased with increasing CNF content caused by agglomeration of CNFs.

Keywords: CNF, Polyester, Mechanical Properties

INTRODUCTION
Due to their high specific strength and specific stiffness, fiber-reinforced composites have become attractive structural materials not only in the weight-sensitive aerospace industry, but also in the marine, armor, automobile, railway, civil engineering structures, and sporting goods industries. Generally, the in-plane tensile properties of a fiber/polymer composite are defined by the fiber properties, while the compression properties and properties along the thickness dimension are defined by the characteristics of the matrix resin. Polyester resin is the polymer matrix used most often with reinforcing fibers for advanced composites applications. The resins of this class have good stiffness, specific strength, and chemical resistance with low cost. Using an additional phase (e.g. inorganic fillers) to strengthen the properties of polyester resins has become a common practice [1-2]. The use of these fillers has been proven to improve the material properties. Based on the fact that micro scale fillers have successfully been synthesized with polyester resin, nano-scaled materials are now being considered as filler material to produce high performance composite structures with further enhanced properties. Improvements in mechanical, electrical, and chemical properties have resulted in major interests in nanocomposite materials in numerous automotive and aerospace applications [3-5]. Vapor grown carbon nano fibers (CNFs) due to their high tensile strength, modulus and relatively low cost are drawing significant attention for its potential applications in nano-scale polymer reinforcement. It is synthesized
from pyrolysis of hydrocarbons or carbon monoxide in the gaseous state, in the presence of a catalyst [6-7]. Vapor grown CNFs distinguish themselves from other types of nano fibers, such as polyacrylonitrile or mesophase pitch-based carbon fiber, in its method of production, physical properties and structure. Thermoplastic such as polypropylene [8-13], polycarbonate [14-18], nylon [19], thermosets such as epoxy [20] as well as thermoplastic elastomers such as butadiene-styrene diblock copolymer [21] have been reinforced with carbon nano fibers. The purpose of this paper is to show the effect of carbon nanofiber on compression properties of polyester. An ultrasonicator was used to process the CNT-polyester nanocomposite. Compression tests were performed to evaluate mechanical performances. Microscopic approaches were used to investigate the material’s fracture behavior and mechanisms.

MATERIALS
The resin used in this study is commercially available B-440 polyester resin. It contains two-part i.e. part-A (polyester resin) and hardener part-B (MEKP- methyl ethyl ketone peroxide). This resin is a low viscosity resin and mainly used for laminating, layup, repair or construction. Because it allows a longer working, time than other polyester resins and will allow maximum flow and workability up until the final stages of gelling. The PR-24 carbon nanofibers were obtained from Applied Science, Inc. In PR-24, the fiber diameter ranges from 60 to 200 nm, and the fiber length ranges from 30 to 100 nm.

Figure 1A and 1B show the pictures of as-received carbon nanofibers at different magnifications. High specific surface area and cotton-like entanglement cause the formation of agglomerates. Agglomerates of CNFs, called nanoropes, are difficult to separate and infiltrate with matrix. For polymer matrix nanocomposites, the high power dispersion methods, such as ultrasonic and high speed shearing, are the simplest and most convenient methods to improve the dispersion of nanosized fillers in a polymer matrix. In this study, the components were mixed using a high intensity ultrasonic processor. The CNF and polyester were first mixed in a glass beaker. The mixing was carried out in pulse mode (50 sec. on/ 25 sec. off)
using a high intensity ultrasonic irradiation (Ti-horn, 20 kHz Sonics Vibra Cell, Sonics Mandmaterials, Inc, USA). The mixing times were 20 minutes, 40 minutes, and 60 minutes. To avoid temperature rise during the sonication process, external cooling was employed by submerging the beaker in an ice-bath. Once the irradiation was complete, 1wt% catalyst was mixed with the CNF-filled polyester using a high-speed mechanical stirrer for about 10 minutes. The intense mixing of polyester and catalyst produced highly reactive volatile vapor bubbles at the initial stages of the reaction, which could detrimentally affect the properties of the final product by creating voids. To reduce the void formation, high vacuum was applied using Brand Tech Vacuum system for about 30 minutes. In parallel, neat polyester samples were fabricated by using the same method to compare it with the nanophased system.

**TESTING**

Compression tests were performed according to ASTM D695. The tests were conducted in a 10 KN servo hydraulic testing machine (MTS) equipped with Test Ware data acquisition system. The machine was run under displacement control mode at a cross head speed of 2.0 mm/min, and all the tests were performed at room temperature. Test samples were in 12.5 mm in diameter and 25 mm in length. Five replicate specimens from all different materials were prepared for static tests.

Thermo gravimetric Analysis (TGA) was conducted with a TA Instruments TGA2950 at a heat rate of 10°C/min from ambient to 600°C. The TGA samples were cut into small pieces using ISOMET Cutter and were machined using the mechanical grinder to maintain the sample weight of about 5-20 mg range. These samples were sealed in aluminum crucibles and placed inside the apparatus. The real time characteristic curves were generated by Universal Analysis 2000-TA Instruments Inc., data acquisition system.

**RESULTS AND DISCUSSION**

Effect of sonication time on mechanical properties of nanocomposite was studied on 0.1 wt% system. Figure 2 shows compression stress strain curves of 0.1% CNF/polyester with different sonication time. Stress strain curves are nonlinear. There is a maximum point on each curve, which is yield strength of materials. After yielding, stress firstly decreased with increasing of strain, then after 10% deformation stress increased with strain again. During compression procedure, test was stopped at about 15% strain since non-uniform deformation occurred.

![Figure 2. Stress strain curves of neat and nanophased polyester.](image-url)
Table 1. Compression properties of neat and nanophased polyester with different processing conditions

<table>
<thead>
<tr>
<th></th>
<th>Modulus (GPa)</th>
<th>Yield Strength (MPa)</th>
<th>Yield Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat</td>
<td>2.13</td>
<td>71.4</td>
<td>4.62</td>
</tr>
<tr>
<td>20 minutes sonication</td>
<td>2.19</td>
<td>80.1</td>
<td>4.99</td>
</tr>
<tr>
<td>40 minutes sonication</td>
<td>2.22</td>
<td>82.3</td>
<td>5.02</td>
</tr>
<tr>
<td>60 minutes sonication</td>
<td>2.55</td>
<td>92.0</td>
<td>4.80</td>
</tr>
<tr>
<td>Mechanical mixing</td>
<td>2.12</td>
<td>69.4</td>
<td>4.25</td>
</tr>
</tbody>
</table>

In Figure 2, mechanical mixing method has little effect in the yield strength of nanocomposite compared with neat polyester. However, sonication procedure can significantly enhance performance. Yield strength of nanocomposite increased with increasing of sonication time. 28.7% increase in yield strength and 19.8% increase in modulus were found in 0.1% system after 60 minutes sonication. The average properties obtained from these tests are listed in Table 2. Figure 3 shows the relationship between mechanical properties at sonication time. The following equations were found to fit the modulus and tensile strength data of the composite.

\[ E = E_0 + m_1 t \]  
\[ \sigma_y = \sigma_{y0} + m_2 t \]

where, \( E_0 \) and \( \sigma_{y0} \) are reference elastic modulus and reference yield strength, and \( t \) is the sonication time. Two other parameters, \( m_1 \) and \( m_2 \) appearing in Equations. (1) and (2) represent time strengthening coefficients for modulus and yield strength, respectively. Mathematically, they are defined as

\[ m_{1,2} = \frac{\partial(E, \sigma_y)}{\partial t} \]

Using the least squares method, the \( m \) values of the composite were calculated as following:

\[ E = 2.07960 + 0.00648w_f (GPa) \]
\[ \sigma_y = 71.863 + 0.31915t (MPa) \]

There are two possible reasons caused improvement in strength of nanocomposite. The first one is sonication procedure changed properties of polyester matrix. The other one is sonication improved dispersion of CNF. To better understand enhancement mechanism, compression tests on neat polyester with the same sonication time were performed as shown in Figure 4.

All stress strain curves of neat polyester are overlap and sonication procedure does not change properties of matrix. Dispersion of CNF in polyester was comparatively examined by using SEM.
Table 2. Compression properties of neat and nanophased polyester with different fiber weight fraction.

<table>
<thead>
<tr>
<th></th>
<th>Modulus (GPa)</th>
<th>Yield Strength (MPa)</th>
<th>Yield Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat</td>
<td>2.13</td>
<td>71.4</td>
<td>4.62</td>
</tr>
<tr>
<td>0.1wt% CNF</td>
<td>2.55</td>
<td>92.0</td>
<td>4.80</td>
</tr>
<tr>
<td>0.2wt% CNF</td>
<td>2.73</td>
<td>107.1</td>
<td>5.08</td>
</tr>
<tr>
<td>0.3wt% CNF</td>
<td>2.59</td>
<td>100.3</td>
<td>4.98</td>
</tr>
<tr>
<td>0.4wt% CNF</td>
<td>2.27</td>
<td>82.43</td>
<td>4.87</td>
</tr>
</tbody>
</table>

Figure 4. Effect of sonication time on stress strain curves of neat polyester.

It can be seen in Figure 5A that neat resin exhibits a relatively smooth fracture surface and river pattern in Figure 5B indicates a typical cleavage fractures, thus accounting for the low fracture toughness of the unfilled polyester. For CNF/polyester composite with mechanical mixing, large size particles are found (Figure 6A). These large size particles are agglomerated CNF (Figure 6B), and were formed before mechanical mixing. In some location, no polyester resin can be found between the space of individual CNFs. These results indicate that traditional mechanical mixing method cannot achieve a uniform dispersion of CNF, which dose not enhances properties of polyester. Compared to the case of neat epoxy and CNF/epoxy with mechanical mixing method, the SEM picture of the nanocomposites with sonication dispersion showed considerably different features (Figure 7A). A much rougher fracture surface is seen upon adding CNF into the polyester matrix. The increased surface roughness implies that the path of the crack tip is distorted because of the carbon nano fiber, making crack propagation more difficult. Agglomerated CNFs were un-tangled and distributed in matrix separately (Figure 7B).
Since optimal processing conditions were determined, 0.1wt%, 0.2wt%, 0.3wt% and 0.4wt% CNF were infused into polyester by using the same sonication mixing method to determined optimal weight fraction of CNF in nanocomposite. Typical composite stress strain behavior from the polyester with different CNF weight fraction is shown in Figure 8. Five specimens were tested for each condition. The average
properties obtained from these tests are listed in Table 2.

Figure 10. Agglomeration of CNFs in 0.4% system.

It is observed in Table 2 and Fig. 8 that the optimal loading of CNF at this processing condition was 0.2 wt. %. And an improvement of about 24.4% in modulus and 53.5% in yield strength were observed. Beyond 0.2%, modulus and yield strength begins to degrade. The relationship between modulus, yield strength, and CNF weight fraction was plotted in Fig. 9.

Figure 10a shows the SEM picture of 0.4wt% CNF reinforced polyester. A large particle with size of 30um was found in nanocomposite. Higher magnification SEM picture (Figure 10b) indicate that is an agglomerated CNFs. At higher weight (or volume) fraction, current processing procedure cannot separate all agglomerated CNFs. Once agglomerated particles remain in composite, yield strength will decrease because of strength concentration effect.

CONCLUSIONS
1: Sonication processing has no effect of compression properties of neat polyester.
2: Dispersion of CNF in polyester has been improved by extending sonication time, which resulting in improvement of mechanical properties.
3: Optimal weight fraction of CNF in polyester is about 0.2% by using sonication mixing method. Maximum 24.4% in modulus and 53.5% in yield strength were observed.

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REFERENCES


