Introduction

Fiber reinforced polymer-matrix laminated composite materials have been used successfully in many industries, due to their high specific strength and stiffness, excellent abilities of corrosion and crack-extending resistant, and fatigue properties. Meanwhile, with quick growth of the composite application, higher properties of the composites are required for purpose of light-weight structure design. However, the interlaminar shear strength (ILSS) of the fiber reinforced composites is usually a limiting design characteristic since conventional manufacturing techniques do not produce reinforcing fibers oriented in the thickness direction to sustain transverse load [1]. To improve ILSS, many approaches have been tried in the fiber reinforced composite field, for example, stitching along the thickness or even weaving fibers to form three dimensional preform of reinforcement [2-4]. Indeed, these efforts produce higher ILSS. However, in-plane properties weakened because of the damage in fiber bundles during stitching or weaving. On the other hand, due to the limit of the volume fraction of the fibers embedded in the matrix, the part of the fiber volume fraction for the in-plane is relatively low. These techniques are usually labor intensive and require additional manufacturing processes that can greatly increase the cost of the resulting components.

And at the microscopic level, the fiber composites are generally inhomogeneous. The mechanism of damage and failure under applied loadings are complex and random. The combination of the multi-modes of damage and the defects makes the properties of the composites more complicated, scattered and hard to predict. Considering this fact, the allowed stress of the composite structures is usually lower than the ultimate stress. Especially for primary structures, the safety factor is quite high. Therefore, the saving weight of the composite structures is not as expected so far. This becomes the barrier for the composite structures to apply for the primary engineering structures in present days and near future.

Carbon nanotubes (CNTs) have been considered as an ideal filler for polymer composites owing to their outstanding mechanical properties as well as high aspect ratio [5]. Kim et al. [6] found that by adding multi-walled carbon nanotubes (MWNTs) into carbon fiber reinforced epoxy composites, the material showed enhanced fracture toughness and low crack density at the cryogenic temperature. Zhou et al. [7] found that adding 2 wt% carbon nanofibers (CNFs) into glass fiber reinforced epoxy composites increased the ILSS by 22.3%. Gojny et al. [8] gained 20% improvement in ILSS by adding 0.3 wt% double-walled carbon nanotubes (DWNTs) into fiber reinforced epoxy composites. Wichmann et al. [9] also got similar enhancement of ILSS. Besides the improvement in ILSS, Yokozeki et al. [10] found that carbon fiber reinforced composites can benefit from dispersion of cup-stacked carbon nanotubes (CSCNTs) between fiber mats and that these can delay the onset of matrix cracking, resulting in fracture toughness improvement and residual thermal strain decrease. Siddiqi et al. [11] found that adding nanoparticles increases both crack growth resistance and fracture toughness in carbon fiber reinforced polymer composites.

Hence, we hypothesizes that the adding of a small amount of CNTs into the matrix may not affect the traditional manufacturing technology, but improve the mechanical properties and decrease the scattering of mechanical properties by increasing the fracture toughness of matrix and improving the interfacial stress transfer between fiber and matrix. To test this hypothesis, we fabricated carbon fiber (CF) reinforced epoxy composites with multi-walled CNTs (MWNTs) dispersed in the matrix by laying up process. The MWNTs were introduced into the matrix without changing the conventional manufacturing process since they are small in quantity as well as size.
2 Experimental

The resin used in this research was bisphenol A epoxy (E-51), and the curing agent was Ethylamine Boron Trifluoride (EBT), both purchased from Balin Petrochemical Company, Inc. The Toray T700 CF produced in Japan was used. The MWNT diameters range from 10 to 30 nm and the tube lengths range from 1 to 5 μm.

The hybrid MWNT/CF/epoxy composites were fabricated by laying up process. First, the epoxy was dissolved in acetone with a weight ratio of 1:1, and proper amount of EBT was added. The MWNTs were dispersed separately in acetone by high-intensity ultrasonic. The epoxy solution and MWNT suspension were subsequently mixed in a bath ultrasonic for 30 min. The weight ratio of E-51, EBT and MWNTs was 100:3:1. Then the prepreg layer was manufactured by filament wind process. Lastly, the prepreg layer was removed from the wind mould and dried for several hours before laying up into a flat mould for curing process. The cured panel was machined for mechanical testing. Composites without MWNTs were fabricated using the same method.

Mechanical properties were measured with a universal testing machine (MTS810). In order to get more reasonable results, more than five specimens for each sample were cut from both neat and nanophased laminates. Typical specimen dimensions were 250 mm in length, 14 mm in width, 2.0 mm in thickness for tensile tests, 25 mm in length, 7.0 mm in width, 2.0 mm in thickness for ILSS tests, and 140 mm in length, 12 mm in width, 2.0 mm in thickness for compressive tests. Images of the samples for mechanical tests are shown in Fig. 3.

Fracture surfaces of the composites were investigated using scanning electron microscopy (SEM) (KYKY-2800, 25 kV and FEI Quanta-200, 25kV).

3 Results and Discussion

3.1 ILSS, Tensile and Compressive Properties

ILSS, tensile and compressive properties along the axial direction of the composites with and without MWNTs are summarized in Table 1.

As shown in Table 1, when 1.0 wt.% MWNTs is added, the mean ILSS of the composites increases by 6.16%. A possible reason for the improvement of ILSS is that the MWNTs oriented in the thickness direction increase the crack propagation resistance by bridging the composite layers [1]. And this can also explain that why the mean compressive strength and ultimate strain of the composites with MWNTs increase by 11.18% and 15.78%. It also can be seen that the mean strength at fracture and ultimate strain of the composites with MWNTs increase by 7.53% and 8.20%. The improvement of tensile properties may caused mainly by the MWNTs that oriented in the axial direction increase the crack propagation resistance of matrix and the interfacial stress transfer between CF and matrix.

Another important fact shown by the above data is that the data scattering of ILSS, tensile strength and ultimate strain are much smaller for the composites with MWNTs compared to the composites without MWNTs. A possible reason is that the MWNTs can efficiently delay the onset of matrix cracking and increase the fracture toughness [10] due to their high aspect ratio and strong interface bonding [5]. As a result, the homogenously dispersed MWNTs in the matrix minimize the influence of the defects and reduce the stress concentration. All these lead to the decrease of scattering of the ILSS, tensile strength and ultimate strain of the composites.

It can be also noticed that the scattering of the compressive strength and ultimate strain of the nanophased composites are larger compared to the neat composites. One main reason for this is that the fracture modes during compressive tests are more complicated than that during shear ply and tensile tests. Another possible reason for this is that the MWNTs are tend to agglomerate when dispersed in the matrix and bulks of MWNTs may be produced during the processing of manufacturing the CF/epoxy composites.

3.2 Fracture Surfaces of the Composites

SEM images of fracture surfaces show that the MWNTs tend to align and bridge the crack as shown in Fig.1. More fracture energy will be consumed when the bridging MWNTs break or pulled out of the matrix. And what’s more, they can also minimize the influence of the defects and reduce the stress concentration. As a result, the MWNTs can efficiently delay the onset of matrix cracking and increase the fracture toughness. To understand the MWNTs network influence on the mechanical properties of the composites, composite fracture surfaces of the composites with and without MWNTs after tensile tests were compared (shown in Fig. 2). Fracture surface of the composites without MWNTs shows multi-modes of damage, while fracture surface of the composites with MWNTs is
rough and even, indicating a more homogeneous structure.

4 Conclusions

Hybrid MWNT/CF/epoxy laminated composites were fabricated by traditional laying up process since the concentration of MWNTs in the epoxy was low (1.0 wt.%). MWNTs were well dispersed in the epoxy by the technique of high-intensity ultrasonic agitation. Distribution and orientation of the MWNTs embedded in the matrix were random and isotropic. The introduction of MWNTs led to an obvious improvement of ILSS, tensile properties and compressive properties of the composites. Furthermore, with high aspect ratio and strong interface bonding, MWNTs can efficiently delay the onset of matrix cracking and increase the fracture toughness resulting in the minimization of influence of defects and the reduction of stress concentration. All these lead to the decrease of scattering of the ILSS, tensile strength and ultimate strain of the composites with MWNTs.

Fig. 1. MWNTs tend to align and bridge the crack.

(a) Fracture surface of the neat composites
(b) Fracture surface of the nanophased composites

Fig. 2. Fracture micrographics of the CF/epoxy composites

References


Table 1 Mechanical properties of the composites with and without MWNTs

<table>
<thead>
<tr>
<th>Mechanical properties</th>
<th>ILSS (MPa)</th>
<th>Tensile properties</th>
<th>Compressive properties</th>
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<tbody>
<tr>
<td></td>
<td>Strength (GPa)</td>
<td>Strain (%)</td>
<td>Modulus (GPa)</td>
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<tr>
<td>Mean</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Without MWNTs</td>
<td>50.47</td>
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<td>1.83</td>
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<tr>
<td>With MWNTs</td>
<td>53.58</td>
<td>2.57</td>
<td>1.98</td>
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<td>Scattering</td>
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<tr>
<td>Without MWNTs</td>
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<td>-17.15%/-+7.95%</td>
<td>14.21%/-+8.74%</td>
</tr>
<tr>
<td>With MWNTs</td>
<td>-2.30%/-+4.54%</td>
<td>-5.45%/-+7.39%</td>
<td>-6.57%/-+5.56%</td>
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