Abstract

The transverse cracking behavior was investigated experimentally for two systems of glass fiber reinforced epoxy composites: with carbon nanotubes (CNTs) and without CNTs. An experimental campaign which involves 4 and 8 layers cross-ply [90/0]_ns laminates were conducted in this study. A manufacturing process using vacuum infusion technique followed by hot pressing techniques was used to produce glass fibre-reinforced laminates with the epoxy matrix and with the CNT based epoxy matrix. The cure condition was 80°C for 15 hours followed by a post cure of 180°C for 6 hrs. The identification is carried out for basic tests like monotonic tensile test on cross-ply [90/0]_ns laminates. Experimental results indicates that the presence of CNTs suppress the matrix cracking of the specimen. This article has also been reported the effect of CNTs in laminates through thermo-mechanical studies.

Keywords: damage, cracking, Multiwalls carbon nanotubes (MWCNTs), composite, laminate

1 Introduction

Composite materials containing carbon fibers/glass fibers are widely used in applications ranging from aerospace to sport equipments due to their good mechanical properties comparable to those of the best metal alloys but with low density. Nevertheless, the relatively poor mechanical properties of the matrix and fibers/matrix interfacial bonds lead to their damage through numerous modes at various scales, namely: diffuse intra laminar damage (fiber/matrix debonding), fiber breaking, diffuse interlaminar damage, transverse cracking and macroscopic delamination. Advanced models based on micromechanics or mesoscale damage mechanics are well established and provide a reasonable prediction for classical laminated composites [1,2,3].

Yet, as the use of composite materials in modern applications is increasing, these materials are now extensively used in primary parts of aeronautical applications and are submitted to more and more severe mechanical loadings. Consequently, classical laminates are reaching their limit. Introducing an additional scale through nano reinforcement of the matrix is a potential solution to improve their mechanical properties. As far as many studies have been achieved on nanocomposites [4, 5], only few investigations were conducted on truly multiscale composites including both classical fibers and nanoreinforcements [6]. This study pointed out the effect of nano reinforcements on main damage mechanisms in laminates. The modification of transverse cracking kinetics through multi-cracking experiments on nano reinforced cross ply laminates were tackled to determine their effect on classical damage evolution laws. This provides some inputs on how nano scale enhancement of fiber reinforced composite influences classical models available in the literature.

In this study, transverse matrix cracking was investigated for two systems of glass fiber reinforced epoxy composites: with MWCNTs and without MWCNTs. In our experimental campaign for transverse cracking identification, we considered...
cross-ply laminates \([90/0]_{m}\) with different number of plies. These were tested to get the transverse cracking kinetics and to determine the thickness effect in these materials.

2 Experimental

2.1 Material system: Due to the atomically non-reactive surface of nanotubes, nanotubes are show limited reinforcement role. These problems can be overcome by functionalization of CNTs wall and cap with such groups that will form some kind of bonds with the matrix phase, such as van der Waals bonds, hydrogen bonds, chemical bonds, etc. In this work, COOH functionalized (f)-MWCNTs (COOH-MWNTs) was used and supplied by Cheap Tubes.com. According to the supplier's specifications, the raw powder has over 95% MWCNT content with 2.56% COOH groups and 1.5% ash. The announced dimensions \((d = 8-15\text{nm and length (l): } 10-50\text{ µm})\) have been checked and confirmed by TEM observations (Fig 1). Fig 2 shows the Raman spectrum of MWNT in the regions of 200-3500 cm\(^{-1}\). In this figure, the D-band, G-band and G' band are observed at 1350, 1580 and 2710 cm\(^{-1}\). The ratio between the intensity of D band \((I_D)\) and intensity of G band \((I_G)\) is a good indicator of the quality of the crystalline order in the nanotubes wall. Here, it has been observed that the value of \(I_D/I_G\) ratio and intensity value of G' band is higher due to the presence of defect and functional groups in the nanotube walls [7, 8].

![Fig.1. HR-TEM image of MWCNTs.](image1)

Unidirectional (UD) glass fibers (HEXTS92145) from P-D Interglas Technologies Ltd., have been used as reinforcing material. The surface density of the fabric was 220 g/m\(^2\) and its thickness is 0.18 mm. Average diameter of the fibers is estimated to 10 µm.

Epoxy resin EPOLAM 2063, a low viscosity \((\text{viscosity: } 100 \text{ mPa}.\text{S at } 80^\circ\text{C})\) and the compatible hardener (EPOLAM group) used as the matrix were obtained from AXSON Technologies.

2.1 Preparation:

Step 1: Dispersion:

In the first step, the epoxy resin was placed in a glass beaker, which was heated to 80°C to lower its viscosity. Then, the CNTs were added into the epoxy in such a way that the final material was 0.1 wt% of CNT by wt% in epoxy. Next, this mixture was ultrasonicated by using ultrasonicator (model: CPX500, frequency: 20kHz, Cole-Parmer Instruments) as well as stirred using magnetic stirrer for 2 hr at 80°C. After this step, the required amount of hardener was added into the mixture (ratio of 5 : 5.35 by weight). It was thoroughly stirred for 15 minutes at 80°C to make a homogeneous mixture.

Step 2: Lamination and Curing

The vacuum infusion technique is used to introduce the resin into the glass fiber lay-up and remove air from glass fiber-resin preform. This technique mainly consist of steel mold, peel ply, perforated and non-perforated film, breather, vacuum bag etc.
as shown in Fig.3(a). Four layers and eight layers (30 x 30 cm) UD glass fibers were stacked together and kept on peel ply covered steel mold. Then it was covered with a peel ply, a perforated film, and a breather. Spiral plastic tube with hole in same distance was kept one side of steel mold, which was connected with resin supply tube and the other tube was placed on the breather, which is connected with the vacuum pump. It was introduced in the vacuum bag. Then, the vacuum bag was sealed by vacuum tape to maintain the vacuum inside the bag. Next, the whole system was placed in a hydraulic press preheated at 80°C. Fig. 3(b) shows the vacuum applied before introducing resin. When vacuum is applied, resin or CNT modified resin is flow from one side of the glass fabric to other side, as shown in Fig.3(c). Vacuum was maintained at pressure 0.2 bar until the end of curing of epoxy resin. A pressure of 3 bar was also applied to the laminates using hot press with vacuum pressure. The mold was kept at 80°C for 15 hr to obtain curing of the resin. The cured sample was removed from the vacuum bag and placed in an oven for 6 hrs at temperature of 180°C for post curing.

Fig.3. (a) material for vacuum infusion set-up (b) vacuum applied before introducing resin and (c) vacuum applied after introducing resin

3 Results and Discussion

Fig.4 (a) and (b) show optical micrographs of the cross-section of the 4-layers and 8-layers cross-ply laminates. It has been observed that there is no any clear void in the surface of laminates.

Fig.4. Optical micrograph of cross-ply laminates (a) 4-layers and (b) 8-layers

Thermo-gravimetric Analysis (TGA) is used to evaluate the volume fraction of glass fiber and matrix. Fig. 5 shows the TGA graphs of 4 plies and 8 plies cross-ply laminates. Both samples started to decomposed at around 280°C and epoxy are completely decompose at about 500°C. From the graph, we obtained 70 wt% (51 volume %) of glass fiber in both 4 and 8 plies laminates.

Fig.5. TGA graph of cross-ply laminates (a) 4-layers and (b) 8- layers

Fig.6. shows the stress-strain responses from monotonic tensile tests conducted on the 4 layers glass fiber-epoxy cross-ply laminates with and without CNTs. The elastic modulus of glass fiber-epoxy laminate with 0.1 wt% CNTs is higher than that of glass fiber epoxy laminate. The tensile modulus and stress to failure of the glass fiber-epoxy laminate was 18 GPa and 244 Mpa, respectively. These values are increased by 28% and 17% to 25 GPa and 294 MPa, respectively for laminates containing 0.1 wt% MWNTs. Young’s modulus, stress to failure and strain to failure are listed in Table-1. It is worth mentioning that the deformation in presence of CNTs is very slow compared to the pure glass fiber-epoxy laminates.
In order to link to transverse cracks with the applied stress, we captured in-situ pictures of the loaded sample during mechanical testing. Concerning transverse cracking observations on cross-ply laminates, it seems that the MWCNTs are efficient fillers to delay the degradation. Fig. 7(a) shows the optical image of transverse cracks as seen in 90° ply without MWCNT, where Fig. 7(b) shows the optical image of transverse cracks in 90° ply in the presence of MWCNTs. At the same loading level, less number of matrix cracks was observed in the MWCNT reinforced laminates. The crack counting was performed using Avizo® software, which enhances crack features by using the contrast gradient. Fig. 8 shows an example of enhanced image by using this software. Fig. 8(a) is the original picture. In Fig. 8(b), the red lines indicates the transverse cracking.

Table 1: Young’s modulus, stress to failure and strain to failure of the examined material

<table>
<thead>
<tr>
<th>% of MWCNT</th>
<th>Young Modulus</th>
<th>Stress to failure</th>
<th>Strain to failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 plies laminate</td>
<td>0%</td>
<td>18 GPa</td>
<td>244 MPa</td>
</tr>
<tr>
<td>4 plies laminate</td>
<td>0.1 at.%</td>
<td>25 GPa</td>
<td>294 MPa</td>
</tr>
</tbody>
</table>

The storage moduli (E’) of glass fiber reinforced epoxy cross-ply laminate with and without CNTs are presented in Fig. 9. In this figure, it has been observed that the cross-ply laminate without CNTs shows a lower storage modulus than cross-ply laminate with CNTs over the entire range of temperatures, except at lower temperature range.
The modulus is increased due to the presence of CNTs. In addition to this, the improvement is also due to the good interaction between the CNTs and matrix. It is well known that the peak temperature of TanD curve is glass transition temperature (T_g). From the TanD curves, as shown in Fig. 10., the T_g of the laminate without and with CNTs are observed at 166°C and 169°C, respectively. The T_g is shifted slightly to the higher temperatures in presence of CNTs, because, the movement of polymer backbone is restricted by CNTs.

References


4 Conclusions

The influence of CNTs in cross-ply laminates has been studied using DMA and mechanical testing, etc. The young’s modulus and storage modulus of cross-ply laminates is enhanced due to the presence of high modulus CNTs. Experimental results indicated that the matrix cracking was inhibited due to the presence of CNTs. Due to the restriction of polymer chain in presence of CNTs; the T_g is shifted to higher temperature.