IMPROVEMENT OF INTERLAMINAR FRACTURE TOUGHNESS IN CARBON FIBER/EPOXY COMPOSITES WITH CARBON NANOTUBES/POLYSULFONE INTERLEAVES

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ABSTRACT

Carbon fiber/epoxy (CF/EP) composites have been widely used as structural materials in many aerospace applications owing to their superior specific strength and specific elastic modulus. However, interlaminar delamination, the most common failure mode of these composite materials, often occurs due to the inherent brittleness of the epoxy matrix. In this study, a vacuum filtration method was used to fabricate sandwiched carbon nanotubes/polysulfone nanofiber (CNTs/PSF) paper as an interleaf to improve the interlaminar fracture toughness of CF/EP composite laminates. During curing of the epoxy resin, the PSF nanofibers were first dissolved and then phase separated from the continuous epoxy matrix to form microspheres while the CNTs were dispersed homogeneously in the epoxy. It was found that interleaving the laminates with the sandwiched paper increased both mode I and mode II interlaminar toughness. Also, the CNTs/PSF interleaved laminates displayed an increase in flexural strength and flexural modulus owing to the reinforcing effect of the CNTs. DMA tests confirmed that better compatibility between PSF and epoxy could be achieved by adding CNTs. The mechanisms for the simultaneous improvements of toughness and flexural properties were analysed.

Keywords: A. Carbon nanotubes, Polymer matrix composites (PMCs); B. Delamination, Fracture toughness; C. Dynamic mechanical thermal analysis (DMTA)

1. INTRODUCTION

With high specific strength and elastic modulus, carbon fibre/epoxy (CF/EP) composites have been widely used as structural materials for aerospace applications [1,2]. However, the inherent brittleness of the epoxy matrix has limited their wider applications and interlaminar delamination is the predominant failure mode of these high performance composite laminates [3,4]. Many strategies have been developed to overcome this problem, and one of the most popular methods is interleaving, whereby a discrete interlayer (either thermoset or thermoplastic) is inserted between adjacent plies. The interleaves facilitate the formation of mechanical linkages between crack interfaces and tortuous crack paths, increasing both mode I and mode II delamination fracture toughness of the composite laminates [5]. Many kinds of interleaves exist which include particles [6], films [7,8] and nanofibrous membranes [9] used in CF/EP composites. Electrospun nanofiber mat is a good candidate because of its unique properties, such as high specific surface area and large porosity, which facilitate easy diffusion of epoxy resin in processing the interleaved composite laminates.

Electrospun nanofibrous mats as interleaves to toughen composite laminates were patented first by Dzenis *et al.* [10]. In their work, non-woven electrospun fabrics of polybenzimidazole (PBI) were used and the mode I fracture toughness was increased by ~15%. Subsequently, many kinds of nanofibrous membranes were used for interlaminar toughening of composite laminates, e.g., nanofibers based on polyamide [9,11], polyacrylonitrile (PAN) [12,13], polycarbonate (PC) [14], polyetherketone cardo (PEK-C) [15] and polycaprolactone (PCL) [16]. Although nanofiber-based interleaves can increase the fracture toughness, the lack of compatibility and strong interaction between nanofibers and epoxy introduces processing

difficulties. Hence, those polymer nanofibers compatible with epoxy resin, like polysulfone (PSF) [17,18], have been used to increase the fracture toughness of CF/EP composites. Generally, PSF is dissolved first in epoxy and then phase separated into microspheres with decreasing miscibility during curing of epoxy. In delamination, the crack spreads in a zig-zag fashion as it approaches and leaves the PSF microspheres [19,20], dissipating higher fracture energy. However, PSF toughening also brings loss of flexural strength [21].

To improve the toughness and retain the in-plane properties of composite laminates, Li *et al.* [22] fabricated CNT/PSF nanofibers as interleaves since CNTs have superior mechanical properties such as high elastic modulus and tensile strength [23-27]. In their work, PSF solution containing a certain amount of CNTs was prepared for electrospinning, and the hybrid nanofiber mat obtained was then used as interleaves in CF/EP composite laminates. Compared to neat PSF nanofibers toughened CF/EP, the mode II fracture toughness G_{IIC} was increased by 48.4% when the CNT loading was 10 wt.%. However, when CNTs exceeded 10 wt.%, G_{IIC} was slightly decreased. Although CNTs could be incorporated into PSF nanofibers, the preparation of a uniform CNTs/PSF solution, especially at a high CNT loading, was difficult. At relatively high CNT loadings, the solution viscosity could be dramatically increased and electrospinning would become much harder. Also, even at low loadings, CNTs tend to aggregate within the polymer matrix due to their high van der Waals forces and their long and entangled structure. Consequently, CNTs agglomerate rather than individual nanotubes occur in the nanofibers, which can limit the increase in or even deteriorate the mechanical performance of CF/EP laminates. Another issue for CNT/PSF nano-fibers as interleaves is that

most CNTs are enveloped inside the PSF microspheres after phase separation from the epoxy. Hence, the CNTs cannot significantly enhance the toughness of the composite laminates.

Based on the discussion above, it is desirable that CNTs can be homogeneously dispersed in epoxy matrix rather than inside the PSF microspheres. This is because their high aspect ratio yields a large interfacial interaction area with epoxy and they can act as nano-bridges in the crack-wake, thus increasing the fracture toughness [28]. Besides, when the crack propagates along the interlaminar region, CNTs in the crack paths will cause crack deflection or CNT pull-out from the epoxy matrix [5,29]. More importantly, the incorporation of CNTs in composite laminates could retain or even increase the in-plane properties simultaneously.

In this work, CNTs were uniformly deposited on both sides of the electrospun PSF nanofibrous membranes, forming a sandwich composite. The as-prepared sandwiched CNTs/PSF papers were then used as interleaves in CF/EP laminates. After curing, PSF was phase separated from the continuous epoxy resin to form microspheres, while the CNTs were homogeneously dispersed in epoxy and at the PSF/epoxy interface. Results of double-cantilever-beams (DCB) and three-point end notched flexure (ENF) tests demonstrate that the combination of CNTs and thermoplastic PSF contributes to the large increase in interlaminar mode I and mode II fracture toughness of CF/EP composite laminates. The toughening mechanisms activated by the interleaves were studied based on SEM examination of the delaminated surfaces. The flexural properties of the CNT/PSF interleaved laminates were also investigated.

2. EXPERIMENTAL

2.1. Materials

Carboxyl multiwall carbon nanotubes (purity: 95%, diameter: 20-30 nm, length: 10-30 μm , -COOH content: 1.23 wt.%) were supplied by Chengdu Organic Chemistry Co. Ltd., China. Polyvinyl-pyrrolidone (PVP), polysulfone (PSF, $M_w=35000$), N,N-dimethyl acetamide (DMAc), and acetone were purchased from Sigma-Aldrich Co., Australia. The plain woven CF fabric was provided by Inter-Turbine Advanced Logistics Pty Ltd. The matrix system was Araldite-F (diglycidyl ether of bisphenol A, Huntsman) and piperidine (Sigma-Aldrich) in a weight ratio of 100:5.

2.2. Preparation of PSF nanofibrous membrane and CNTs/polysulfone interleaves

The nanofiber electrospinning unit (NEU) from Kato Tech Co., Ltd, Japan was used to process polysulfone (PSF) nanofibers. The PSF solution was first prepared by dissolving 5.3 g PSF pellets in pre-determined proportions of N,N-dimethylacetamide (DMAc)/acetone (9:1w/w) to maintain a 25 wt.% concentration. After stirring for 4 h at 55 $^{\circ}\text{C}$, the PSF solution was placed in a 20 ml syringe with a stainless steel needle. The PSF nanofibrous membrane was electrospun at a flow rate of 1.5 ml/h and a voltage of 15 kV onto an aluminum foil collector electrode. Then, the PSF nanofiber membrane was used as the “filter paper” to deposit the MWNTs, (which were prepared by dispersing 0.5 wt.% CNTs in distilled water with 1% PVP as surfactant by ultra-sonication for 1 h), onto the two surfaces of the membrane, one at a time, by the method of vacuum filtration. Distilled water from the CNT solution could easily go through the interconnected pores inside the PSF membrane, while the CNTs were captured

on the nanofiber surfaces. The amount of CNTs on the PSF nanofibers membrane was controlled to 5 wt.% and 10 wt.% of PSF.

2.3. Preparation of CF/EP composite laminates

CF/EP laminates for DCB and ENF tests were made of sixteen plies of plain woven CF fabric and Araldite F/piperidine by hand lay-up. A 25- μ m thick PTFE film was inserted in the mid-plane of the laminates between the 8th and 9th plies as the initial crack. Simultaneously, 5% and 10% CNTs/PSF nanofibrous paper, respectively, as interleaf was also placed in the mid-plane. The interleaved composite laminates were then sealed in a vacuum bag, vacuumed for 0.75 h and followed by curing in a hot-press at 120 °C for 16 h under a pressure of 200 kPa. The volume percentage of carbon fibers in the composite laminates was 60%, and that of PSF in epoxy of the middle layer was calculated to be ~17%, while the CNT contents in the middle interleaf layer are 0.5 and 1.0 vol.%, respectively, for the two sandwiched CNTs/PSF paper interleaved laminates. For comparison, composite laminates with the same loading of PSF nanofiber mat (i.e., ~17 vol.%) as interleaf and no interleaf were also prepared. Hereafter, we will refer to these 4 types of CF/EP laminates as: 5%CNTs/PSF-ICL, 10%CNTs/PSF-ICL, PSF-ICL and Control, respectively. ICL stands for “interleaved composite laminate”.

2.4. Characterization

The morphology and microstructures of the composite laminates were studied by scanning electron microscopy (Zeiss ULTRA Plus) and FTIR (Bruker Vertex 80v spectrometer). Mode I and mode II interlaminar fracture toughness values were measured by DCB and ENF samples on an Instron 5567 machine based on ASTM D5528 for mode I interlaminar fracture toughness tests [30] and ESIS protocol for mode II interlaminar fracture

toughness tests [31], respectively. For the mode I DCB delamination tests, the crack mouth opening displacement rate was 2 mm/min and the initial crack length was 50 mm. The mid-plane deflection of the ENF sample was controlled by a crosshead rate of 2 mm/min and the initial crack length was 25 mm. At least three samples were tested for each of the 4 types of composite laminates. Dynamic mechanical analysis was performed on a TA Instrument DMA model 2980 by dual cantilever mode at a fixed frequency of 1 Hz and an oscillation amplitude of 20 μm . The temperature range was varied from 50 to 180 $^{\circ}\text{C}$ with a heating rate of 3 $^{\circ}\text{C}/\text{min}$. The flexural properties of these four types of composite laminates were measured by three-point bending tests with 2 mm/min crosshead speed on an Instron 5567 machine according to ASTM D790. The DMA and flexural specimens were made of three plies of plain woven CF fabric interleaved with two plies of PSF or CNTs/PSF paper in an alternating assembly. Specimens with no interleaves were also used as controls.

3. RESULTS AND DISCUSSION

3.1. Morphology of PSF nanofibrous membrane and CNTs/polysulfone interleaf

Fig. 1(a) shows how a CNT/PSF/CNT sandwich composite is prepared. Electrospun polysulfone (PSF) nanofibers, whose diameters range from 150 nm to 500 nm, have a relatively smooth surface (see Fig. 1(b)). Many interconnected pores existed inside the PSF membrane and they can promote epoxy infusion during fabrication of the CF/EP laminates. CNTs were homogeneously dispersed in water with the assistance of PVP, which acted as a surfactant, and remained so after a week (see Fig. 1(c)). The PSF nanofiber membrane served as the filter paper, and CNTs were then deposited onto both surfaces of the membrane by vacuum filtration.

Fig. 1(d) shows an as-prepared sandwich CNTs/PSF paper displaying good flexibility. After CNT deposition, the surface of the nanofiber membrane turned from white to completely black, indicating the nano-fibrous membrane surfaces were fully covered by CNTs (see Fig. 1(e)). Fig. 1(f) shows the cross-section of the CNTs/PSF membrane exhibiting two thin CNT layers $\sim 10\ \mu\text{m}$ with a PSF nanofiber core $\sim 170\ \mu\text{m}$. CNT distribution on the nanofiber surface is revealed in Fig. 1(g) and it can be seen that the PSF nanofibers are densely decorated with uniformly dispersed CNTs which are several μm in length.

Fig. 1. (a) Schematic showing preparation of CNTs/PSF sandwich paper; (b) SEM image of electro-spun polysulfone (PSF) nanofibers; (c) photo of CNTs-PVP solution in a bottle after a week; (d,e) digital photos of CNTs/PSF sandwich paper; and (f,g) SEM images of cross-section and top surface of CNTs/PSF sandwich paper, respectively; large spherical particles in (f) are beads formed on the PSF fibre mat.

3.2. Morphology and distribution of polysulfone and CNTs in CF/EP laminate

The morphology and distribution of CNTs and PSF microspheres in CF/EP laminates are important to understand the toughening mechanisms. Fig. 2 shows the fracture surfaces of composite laminates with the sandwich paper interleaf. No carbon fibres can be found except pulled out CNTs (blue arrows in Fig. 2), debonded PSF microspheres (yellow arrows in Fig. 2) and cavities (red arrows in Fig. 2(a)), indicating that cohesive failure has occurred in the interleaf. EDS spectrum for the CNT-rich area in Fig. 2(b) detects no sulfur element implying that the CNTs are embedded within the epoxy. Also, EDS spectrum of the microsphere in Fig. 2(c) identifies sulphur, suggesting it is the PSF microsphere formed by phase separation of PSF during curing of epoxy.

Fig. 2. (a) SEM image of fracture surfaces of laminates with CNTs/PSF interleave; and (b,c) EDS spectra of CNT-rich area and selected microsphere, respectively.

From the thermodynamics viewpoint, the distribution of CNTs in a two-phase polymer system can be predicted using the interfacial free energy theory [32]. There usually exists a selective distribution of fillers in polymer blends due to the different interfacial interactions between the filler particles and the polymer components [33]. Fowkes proposed the interfacial energy between two phases, A (EP) and B (PSF), could be described by [34]:

$$\gamma_{AB} = \gamma_A + \gamma_B - 2(\gamma_A^d \gamma_B^d)^{1/2} - 2(\gamma_A^p \gamma_B^p)^{1/2} \quad (1)$$

where γ^d and γ^p are the dispersion and polar components of the surface energy γ , respectively. The distribution of CNTs in CNT/PSF/EP [28] can be determined from the wetting coefficient W_a value, which is given by:

$$W_a = (\gamma_{\text{PSF-CNT}} - \gamma_{\text{EP-CNT}}) / \gamma_{\text{PSF-EP}} \quad (2)$$

where $\gamma_{\text{PSF-CNT}}$, $\gamma_{\text{EP-CNT}}$ and $\gamma_{\text{PSF-EP}}$ are interfacial energies between (PSF-CNT), (EP-CNT) and (PSF-EP), respectively. When $W_a > 1$, i.e., $\gamma_{\text{PSF-CNT}} > \gamma_{\text{EP-CNT}} + \gamma_{\text{PSF-EP}}$, CNTs distribute within the EP phase to achieve the minimum interfacial free energy of the system; however, CNTs are selectively distributed within the PSF phase when $W_a < -1$; and CNTs are located at the interface between PSF and EP when $-1 < W_a < 1$. The surface energies γ of PSF [35], EP [36], and CNT [37], including the dispersive and polar components, are summarized in Table 1. Hence, based on Eq. (1), $\gamma_{\text{PSF-CNT}}$, $\gamma_{\text{PSF-EP}}$ and $\gamma_{\text{EP-CNT}}$ are 4.54, 3.9 and 7.76 mJ/m², respectively. From Eq. (2), W_a is -0.83, indicating that CNTs should be selectively located at the interface between epoxy and the PSF phase.

However, in our experiments, the CNTs/PSF interleaf was located in the mid-plane of the composite laminates, and the epoxy monomer first wetted the thin CNT layer deposited on the PSF nanofiber surfaces, and then diffused inwards into the PSF nanofiber mat. Subsequently, the PSF nanofibers were gradually dissolved in the epoxy, forming a PSF-EP blend solution, during which inter-diffusion between CNT/epoxy and PSF/epoxy would occur caused by the relatively low viscosity of the yet uncured epoxy. But, as curing continued, PSF began to phase separate from epoxy and the viscosity of epoxy matrix was gradually increased. Both would, to some extent, prevent the CNTs moving to the interface between the EP matrix and the PSF

phase. Hence, some CNTs were located at the interface but most of them remained in the epoxy phase of the interleaf as shown in Fig. 2.

Table 1. Surface energy of EP, PSF and CNT

Material	γ_s (mJ/m ²)	γ_s^d (mJ/m ²)	γ_s^p (mJ/m ²)
EP	50.6	39.6	11
PSF	28.10	18.77	9.34
CNT	45.3	18.4	26.9

3.3 FTIR spectra of CNTs/PSF interleaf in CF/EP laminate

The FTIR spectra of EP, PSF, PSF-ICL and 10%CNTs/PSF-ICL are shown in Fig. 3. For EP, the characteristic peak of epoxide ring appears at 829 cm⁻¹; the absorption bands attributed to asymmetric and symmetric stretching vibration of C=O=C group can be observed at 1242 and 1036 cm⁻¹; the peaks at 1509 and 1609 cm⁻¹ are due to the skeletal vibration of the aromatic hydrocarbons. These characteristic peaks can also be found in PSF due to their similar molecular structures. Specifically, the absorption bands of epoxide ring, ether linkage and aromatic hydrocarbons for PSF are located at 834, 1242, 1488 and 1586 cm⁻¹. Besides, the peaks at 1150 and 1242 cm⁻¹ are also found which are assigned to the symmetric and asymmetric O=S=O stretching of the sulfone group.

As shown in Fig. 3, after the incorporation of the PSF nanofiber mat and 10%CNTs/PSF sandwich paper into the CF/EP laminates, no significant peak variations were observed compared to pure epoxy. Conversely, the intensity of the characteristic peak of O=S=O group

is much lower than that of PSF, which might be caused by the low content of PSF in the middle layer of the laminate. These results indicate that there are no inter-reactions between CNTs/PSF interleaf and epoxy during the curing of epoxy and the phase separation of PSF [38].

Fig. 3. FT-IR spectra of epoxy, PSF, PSF-ICL and 10%CNTs/PSF-ICL.

3.4 Mode I interlaminar fracture toughness (G_{IC}) of composite laminates

Fig. 4(a) shows mode I interlaminar fracture toughness, G_{IC} , with increasing crack length a for the Control, PSF-ICL, 5%CNTs/PSF-ICL and 10%CNTs/PSF-ICL laminates. G_{IC} is generally independent of crack length a for a given laminate; however, it can be appreciably increased by the interleaves. Thus, as shown in Fig. 4(b), G_{IC} for the Control is 0.49 kJ/m², while the interleaved composites are 0.60 kJ/m², 0.69 kJ/m² and 0.75 kJ/m² for PSF-ICL, 5%CNTs/PSF-ICL and 10%CNTs/PSF-ICL, respectively. Compared to the Control laminate, G_{IC} of PSF-ICL is enhanced by 23%, and G_{IC} increases of 41% and 53% are obtained for the other two CNT/PSF interleaved laminates.

Fig. 4. (a) Relationship between fracture toughness G_{IC} and crack length a of the composite laminates; and (b) G_{IC} values for Control, PSF-ICL, 5%CNTs/PSF-ICL and 10%CNTs/PSF-ICL.

The failure mechanisms of the Control and interleaved laminates are mainly governed by their microstructures. Fig. 5(a,b) show SEM images of the fracture surface of the Control laminate. Carbon fibres are debonded cleanly from the epoxy matrix showing poor adhesion. Brittle fracture of epoxy between adjacent carbon fibre bundles is also displayed. Clearly, these observations explain the low G_{IC} value of 0.49 kJ/m² obtained from the experiments.

Typical fracture surface features of PSF-ICL are revealed in Fig. 5(c,d) reflecting the influence of the morphology of this laminate. Different to the Control, the fracture is mainly cohesive through the interleaf exhibiting a highly deformed epoxy matrix (see Fig. 5(c)) containing many exposed PSF microspheres still embedded in epoxy and cavities owing to the debonded and pulled out PSF particles (see Fig. 5(d)). Local matrix plastic deformation can also be seen near the PSF particles (see yellow arrows in Fig. 5(d)). All these failure features give rise to a higher G_{IC} of 0.60 kJ/m².

To understand the toughening mechanism of CNTs/PSF paper interleaved laminates, the fracture surfaces of 10%CNTs/PSF-ICL are displayed. A considerably rougher fracture surface

compared to that of PSF-ICL is shown in Fig. 5(e). The fracture is cohesive (see also Fig. 2) through the interleaf with intense deformation of the epoxy matrix decorated with PSF microspheres and cavities similar to PSF-ICL. In addition, many CNTs are found pulled out from the epoxy matrix, dissipating extra work (see red arrows in Fig. 5(f)). These CNTs along with those few much longer CNTs (see yellow arrows in Fig. 5(f)) may have provided some bridging effect to the advancing crack front before being pulled out. Crack deflection, and hence surface roughness, due to the CNTs, which are much smaller than the PSF particles, cannot be very efficient. However, the presence of CNTs in the interleaf has further increased the delamination toughness of the 10%CNTs/PSF-ICL laminates to G_{IC} of 0.75 kJ/m².

Fig. 5. SEM images of mode I fracture surfaces of composite laminates for (a,b) Control, (c,d) PSF-ICL, and (e,f) 10%CNTs/PSF-ICL.

3.5 Mode II interlaminar fracture toughness (G_{IIC}) of composite laminates

The G_{IIC} data for the four types of CF/EP laminates are shown in Fig. 6. The average values are 1.40, 1.65, 1.75 and 1.87 kJ/m² for the Control, PSF-ICL, 5%CNTs/PSF-ICL and

10% CNTs/PSF-ICL, respectively. The PSF interleaved laminate exhibits a 17% increase in G_{IIC} , and the 5% CNTs/PSF and 10% CNTs/PSF interleaved laminates show nearly 25% and 34% increases in G_{IIC} compared to the Control laminates.

Fig. 6. Comparison of fracture energies, G_{IIC} , of the four types of specimens.

The fracture surfaces of ENF specimens after mode II shear tests are shown in Fig. 7(a-f). For the Control laminate, Fig. 7(a, b) shows smooth fiber surfaces which indicate significant interfacial failure has occurred. Moreover, characteristic shear hackles parallel to crack growth direction can be found between the carbon fibres. Similar to the mode I fracture surfaces, many PSF microspheres and cavities after PSF debonding are visible in PSF-ICL (Fig. 7(c, d)), which consume extra energy during crack growth due to the shear induced deformations. Especially, the PSF microspheres may act as “pins” when the crack passes through them. Although the PSF interleaved laminates possess better adhesion between CFs and matrix, it can be seen (Fig.

7c) that the fracture surface is largely adhesive (giving clean CFs) and partly cohesive (crack spreads through the PSF-toughened matrix). For the 10% CNTs/PSF-ICL, the fracture surface is primarily characterised by cohesive failure displaying the best interfacial adhesion compared to the Control and PSF-ICL giving subsequently large shear deformation of the CNT and PSF toughened epoxy (Fig. 7e). In addition, many CNTs can be found on the fracture surface of the epoxy matrix besides the much larger PSF particles (Fig. 7f). These CNTs also serve as “pins” to deter the shear crack but are dragged out when the crack passes them though the effectiveness is not as good as in mode I.

Fig. 7. SEM micrographs of mode II fracture surfaces of laminates with (a,b) untoughened, (c,d) toughened by PSF interleaves, (e,f) toughened by 10% CNTs/PSF interleaves. Red arrows indicate crack growth direction.

3.6. Flexural properties of CF/EP composite laminate

The flexural properties of the un-toughened composite and toughened composites by PSF, 5% and 10% CNTs/PSF interleaves are given in Table 2. The flexural strength and modulus of the Control are 1069.40 MPa and 92.77 GPa. With the PSF interleaf, the flexural strength and

modulus of the laminates are slightly decreased to 1007.26 MPa and 84.31GPa. Although PSF have a higher modulus than epoxy, the relatively poor interfacial adhesion (Fig. 7d) between the PSF microspheres and epoxy matrix after phase separation may lead to the slight reductions in flexural strength and modulus. After the incorporation of 5%CNTs, the flexural strength and modulus of laminates improved to 1269.83 MPa and 100.32 GPa. When the loading of CNTs is increased to 10 wt.% in PSF, the composites show a large increase of 27% and 29% for the average flexural strength and flexural modulus compared with the Control, which should be attributed to the reinforcing effect of CNTs that are located within the epoxy matrix of the CF plies by diffusion during curing with subsequent effective load transfer between CNTs and matrix.

Table 2. Flexural properties of Control, PSF-ICL, 5%CNTs/PSF-ICL and 10%CNTs/PSF-ICL

Sample	Flexural strength [MPa]	Flexural modulus [GPa]
Control	1069.40±97.4	92.77±4.2
PSF-ICL	1007.26±62.5	84.31±6.1
5%CNTs/PSF-ICL	1269.83±78.8	100.32±5.1
10%CNTs/PSF-ICL	1356.61±90.3	119.62±5.5

3.7. Dynamic mechanical thermal properties of composite laminates

The effect of CNTs/PSF interleaves on the dynamic thermal mechanical behaviors of the composite laminates is investigated based on the **DMTA** results. Fig. 8 shows variations of the

storage modulus E' and loss peak $\tan \delta$ for the three composite laminates (Control, PSF-ICL and 10%CNTs/PSF-ICL) from 60 to 180 °C. The storage modulus values at 60 °C (Fig. 8a) are consistent with the corresponding flexural modulus values shown in Table 2. For the $\tan \delta$ results (Fig. 8b), there is one sharp peak at 100.5 °C for the Control, corresponding to the glass transition temperature (T_g) of epoxy. However, for PSF-ICL and 10%CNTs/PSF-ICL, they are two transition peaks, indicating the occurrence of phase separation during the epoxy curing process. Compared to the Control laminate, T_g of the epoxy-rich phase for PSF-ICL is decreased from 100.5 to 98.9 °C, However, it is increased to 101.8 °C for 10%CNTs/PSF-ICL due to the CNTs in the interleaf which have restricted the mobility of the epoxy chains through interfacial interactions, consistent with the stiffening effect of the CNTs. As for the PSF rich phase, T_g for 10%CNTs/PSF-ICL is dramatically shifted from 143.2 to 137.9 °C towards T_g of the epoxy-rich phase. The approach of these two transition peaks may be caused by the fact that the addition of CNTs could, to some extent, limit phase separation between epoxy and PSF, and the compatibility between these two phases is hence improved.

Fig. 8. Storage modulus (E') and $\tan \delta$ spectra of Control, PSF-ICL and 10%CNTs/PSF-ICL.

4. CONCLUSION

In this work, CNTs/PSF sandwich paper was prepared by depositing CNTs on both sides of the PSF nanofiber mat by vacuum filtration. The as-prepared paper had good flexibility and its surfaces were fully covered by CNTs. 5% and 10% CNTs/PSF paper were used as interleaves to study the delamination toughening effect on CF/EP composite laminates. In the laminates prepared for the toughness tests, PSF was phase separated into microspheres and CNTs were uniformly distributed in the epoxy phase.

DCB tests showed the mode I toughness (G_{IC}) for PSF interleaved laminates increased by 23% due to the generation of PSF micro-particles. G_{IC} of 5% and 10% CNTs/PSF interleaved laminates were 41% and 53% higher than that of Control due to the intense deformation of the epoxy matrix promoted by the PSF micro-particles and pull-out of CNTs. Similarly, PSF, 5% and 10% CNTs/PSF interleaved laminates also produced 17%, 25% and 34% increases in G_{IIC} from the ENF tests. DMA results of 10% CNTs/PSF-ICL confirmed that better compatibility between epoxy and PSF could be achieved by adding CNTs.

More importantly, PSF-ICL decreased the flexural properties of laminates. But integration of 10% CNTs/PSF interleaves into CF/EP laminates improved the flexural strength (27%) and flexural modulus (29%) compared to the Control owing to the reinforcing effect of the CNTs. Therefore, our method can be regarded as promising which can *simultaneously improve the interlaminar toughness and in-plane properties of the CF/EP composite laminates*.

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