STRENGTH OF LAMINATES WITH SURFACE MODIFIED POLYMER/MWCNTS NANO-COMPOSITE INTERLAYERS

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Keywords: *laminated composites, electrospun nanofiber, interlayer, delamination resistance*

1 Introduction

Intra and interlaminar resistance to failure in laminated composite materials is an active and constantly growing research field. The improvement is typically sought altering the constituent properties, introducing effective sub-phases and reinforcement without significant weight penalty. Other than traditional laminate stitching and z-pinning applications, matrix toughening and interlayer toughening [1] emerged to increase delamination resistance. The innovative works byRenekeret.al[2] showed the ability of electrospun nano-fibers as potential bulk toughening elements. In line with Reneker's work, Dzenis et. al[3,4] pioneered the idea of using electrospun nano-fibers as interlayer toughening elements. This idea is also applied to several composite systems and tested under various testing conditions.[5-7] which were thoroughly reviewed and put together by Zuchelliet.al [8]. By sharing the same aim several studies offered the use of carbon nano-tubes as toughening elements to increase ply by ply sticking and delamination resistance[9].
Chasing the effective use of electrospun nanofibers in structural composites, our previous efforts [10] revealed that polystyrene-co-glycidyl methacrylate P(St-*co*-GMA) is a promising base polymer for nano-fiber production due to its chemical compatibility with the surrounding crosslinking epoxy systems. Also, we have demonstrated that P(St-co-GMA) has an aromatic ring that would assist in dispersion and long term stabilization of MWCNTs in polymer solution during nanofiber formation.[11]

This study is focused on the application of our P(St-co-GMA) based nanofibers tailored for epoxy crosslinking and multi walled carbon nanotube (MWCNT) reinforced P(St-co-GMA)
Hybrid nanofibers as interlayer toughening elements in carbon/epoxy composites. It also reports the importance of curing temperature on nano-fiber morphology and consecutive effects on flexural performance. Resistance against delamination was measured in mode II,by End Notched flexure (ENF) tests whereas the interlaminar shear strength was measured by Double Notched Shear(DNS) testing. Additionally, the matrix toughening due to the nano-fibers were investigated by transverse impact testing.

2. Experimental Procedure and Testing

2. 1 Electrospinning of P(St-co-GMA)/MWCNT solution

Polymer solutions containing 30wt.% of P(St-co-GMA) copolymer and 1wt% of MWCNT were electrospun directly onto uncured prepreg layers so that one face of the prepreg layers was totally covered with polymer nano-fibrous layer. During electrospinning the applied voltage was adjusted to 15kV and the pre-cut uncured prepreg sheets were placed on the grounded collector 10cm away from the syringe needle. A syringe pump (NewEra NE-1000 Syringe Pump) was used to maintain a solution flow rate at 30 μL/h.

2.2 *Laminate Fabrication*

Carbon fiber/epoxy prepregs by TCR Composite Ltd. (Zoltek standard modulus PX-35-50K-11 carbon fibers embedded in UF3325-100 thermosetting

epoxy) were with an average fiber volume fraction of 63% and had a standard ply thickness of 0.6mm. Both interleaved and reference laminates with and without electrospun fibrous layers, respectively, were vacuum bagged and cured. The curing cycle was set to consolidate laminates for 48 hours at 100°C in order to avoid adverse thermal effects on the structural integrity of the nano-fibers. An alternativecycle at 125°C for 6 hour was also usedfor an additional set of three-point bending specimens so that the elevated cure temperature and glass transition temperature (T_g) effects on the mechanical performance can be observed.

2.3 Mechanical Testing

2.3.1 Three Point Bending Tests

Laminates with two different lay-up 0/0/0 and 90/0/90 were used for three point bending test specimens. Moreover, interlayered laminates had the stacking sequence as 0/I/0/I/0, and 90/I/0/I/90, where "I" stands for the interlayers either formed of MWCNT reinforced poly(St-co-GMA) hybrid fibers or unreinforced poly(St-co-GMA) nano fibers. Test specimen dimensions are of L= 75 mm length, b=12.5 mm width and d=1.8 mmthickness per ASTM D790 test standard [12] . Also the span length between two supports was fixed at32 mm. Bending tests were done at a constant crosshead speed of 8mm/min. Applied load vs. crosshead displacement values were recorded and the corresponding flexural strength (σ_f) and flexural modulus (E_B) values were calculated.

2.3.2 End Notched Flexure(ENF) Tests

Mode II critical strain energy release rate (G_{IIc})of the composite laminates was studied with ENF tests under three-point bending load. Non-interlayered, P(St-co-GMA) nano-fiber interlayered and P(St-co-GMA)/MWCNT hybrid nano-fiber interlayered laminates, with [0/0/I/0/0] lamination sequence were manufactured. The total thickness of the laminates were approximately 2.4 mm. Fig.1 shows the detailed specimen dimensions where the half-span length was 50mm. Pre-crack of length 30mm was introduced by using a non-sticking teflon layer with a thickness of 30µm. Tests were done with a constant displacement rate of 1mm/min.Mode II critical strain energy release rate was calculated via direct beam theory. [13]

2.3.3 Double Notched Shear(DNS) Test

Interlaminar shear strength and the role of the nano-fibrous interlayers were also tested with DNS tests. (Fig.2.)The inherent problem of out of plane deformation during tensile loading due to the asymmetric geometry[14] of the DNS specimen was attempted to reduce by allowing small grip-to-grip separation (110mm). Maximum tensile load for non-interlayered and P(St-co-GMA) nanofiber interlayers were determined, with a constant crosshead speed of 1mm/min.

2.3.4 Transverse Impact Testing

Transverse impact tests with Charpy impact configuration were done according to ASTM D6110 standard. An impact hammer of 4 joule energy capacity was used with 150° release angle. Energy absorbed upon transverse impact was measured for specimens of neat epoxy ply-to-ply interfaces, P(St-co-GMA) interlayered, and P(St-co-GMA)/MWCNT) interlayered specimens .

2.4 Microscopic Investigation

Cross section and fracture surface analysis of the composite laminates were carried out using scanning electron microscopy(SEM LEO 1530VP) containing field emission gun using secondary electron detector at 2 kV. All of the specimen surfaces were carbon coated before microscopic analyses in order to have a good conduction. The distribution of MWNTs within the polymer matrix was studied with transmission electron microscopy (TEM).

3. Results and Discussion

3.1 Effect of Cure Temperature on Nanofiber Morphology and Flexural Performance

3.1.1 Nanofiber Morphology

Previous work of the team revealed that the glass transition temperature of P(St-co-GMA) nano-fibers was around 96°C [13]. Fig.3a and Fig.3b

corresponds to the SEM images of the P(St-co-GMA)/MWCNT hybrid interlayers at room temperature and at T_g respectively. In addition fig.3c and fig.3d corresponds to their zoomed-in views. The average fiber diameter is observed to be between 200-450nm. A clear transitionwas observed: from continuous and relatively loose collection of fibersto a moreinter-connectedand network like structure with large nodal polymer beads. Note that the bead structure seen in fig.3c is quite different than the typical bead on fiber formation observed and reported in many of the electrospinning applications where the beads are relatively smaller and considered to be defects in the internal structure[17]. However, the bead like structures herein were formed of several individual fibers which clustered presumably upon viscosity decrease with increasing temperature. Despite the transition, high surface area of the interlayers were preserved and the beads can work as anchors to those fibers. Overall the structure ressembles a porous network which may be expected to work well against crack propagation.[18]
At temperatures well above T_g, the polymer will pass to the rubbery state, then the fibrous structure network may disintegrate completely which is undesirable in terms of mechanical performance. The extent of morphologic transition near T_g is crucial for the application of low T_g polymeric fibers as toughening elements and leverages the upper temperature limit for composite curing. The T_g associated constraint has been further investigated by three-point bending tests.

3.1.2 Flexural Performance by three-point bending test

Fig. 4shows the flexural strength values observed for nano-fibrous interlayered and non-interlayered composite laminates subjected to different curing cycles. The results suggest that the use of interlayers significantly increases the flexural strength of the laminates cured below the T_g of the P(St-co-GMA) nanofibers. Also it is clearly seen that increase in the strength was elevated by the addition of MWCNT. Closer look into the fracture modes(fig5) suggested that, laminatesfailed by resin cracking and subsequent delamination, the detailed analysis of tested specimens and enhanced strength showed that the addition of interlayers were also effective in crack and delamination resistance as claimed by Sihn et. al. [5] The authors think that electropun fibrous mat is infused by the epoxy from the prepreg and forming a toughened interlayer during the curing process. As a result, the resistance against microcrack induced delamination increases compared to traditional neat epoxy ply-to-ply interface. This toughening effect can also be demonstrated more clearly with ENF and transverse impact testing as reported in the following sections.

3.2 Mode II Strain Energy Release Rate by End-Notched Flexure (ENF) tests

Effect of the interlayers on G_{IIc}values from the ENF tests are shown in fig.6. Toughening due to the fibrous interlayer is evident. Increase in G_{IIc} relative to the neat epoxy ply-to-ply interface was %55 and %70 with P(St-co-GMA) and P(St-co-GMA)/MWCNT nanofibers, respectively. Further increase in G_{IIc} by the addition of %1 MWCNT indicates the toughening is well correlated with the properties of the interlayer as well as morphology within. Moreover, fig 7 compares the fracture surfaces of a non-interlayered and interlayered specimens. The hackle markings and failure along fiber matrix interface seem to be consistent with ENF tested brittle composite materials.[7] However for the interlayered specimens the formation of the hackled pattern was locally altered and the exposure of the fibers diminished. The absence of on fiber-hackle patterns can be attributed to the presence of severe microcracking in front of the main crack which propagated through the interlayer rather than fiber-matrix interface[19]. Bumpy looking failure surface also suggest the crack propagated inside the interlayer as it is seen at figure 7b. That is the failure appear to be cohesive like.

3.3 Interlaminar Shear Strength with Double Notched Shear (DNS) tests
On the contrary to the substantial increase in mode II performance by the nanofibrous interlayer, DNS test results revealed that the fibrous interlayer addition decreased the double-notched shear strength of the laminates by 10%. This is attributed to the fact that design of the DNS specimen cannot totally eliminate the mixed-mode loading on the test region.This was evident in the tensile tests by the observed rotation of the DNS specimen's mid section. That is, the

bonding line by the interlayer is not only subject to the shear mode, but also openingmode. This result necessitates additional look into the performance also in opening mode and double cantilever beam (DCB) tests are currently being planned.Consistent with the expectation herein, earlier studies [20-22] reported negligible effect or reduction in DCB opening mode strength despite increase in pure shear resistance. The failure surface images from DNS test specimens are shown in Fig.8. They show the mode of failure was altered by the existence of the interlayer.

3.4 Impact Energy Absorbance with Transverse Charpy Impact Test

The effect of interlayers against the transverse microcracking was reported by preliminary three point bending results. Further demonstration of the toughening effect was sought by charpy impact tests where unidirectional composite specimen was subject to transversal impact (impact head to hit against the specimen side wall rather than its surface). Fig.9 shows the amount of energy absorbance for the neat epoxy ply-to-ply interface (non-interlayered), P(St-co-GMA) interlayered and P(St-co-GMA)/MWCNT interlayered. An increase up to 20% was recorded for interlayered specimens. The increase in energy absorbance is attributed to toughening due to the electrospun nanofibrous interlayers.

3.5 MWCNT in P(St-co-GMA) nanofibers

The mechanical test results, throughout the article suggested that the addition of MWCNT to the fibrous structure introduced stiffening effect. The visual evidence of MWCNT presence is presented by TEM analysis of the fibrous structures obtained after electrospinning. The straight MWCNTs embedded into the electrospun fibrous structure can be clearly seen from fig 10.a Parallel to that the distribution of MWCNT inside of the polymeric fiber surface is seen at fig 10.b which all together suggests that the MWCNT were successfully introduced into the polymeric structure during electrospinning.

4. Conclusion

This study presented a demonstration of the toughening by nano-fibrous interlayers. Specifically, the epoxy cross-linking P(St-co-GMA) and P(St-co-GMA)/MWCNT electrospun nano-fibers were applied on conventional carbon/epoxy prepreg plies prior to curing under vacuum. It was shown that Tg of the polymeric fibers limits the curing temperature to gain from the fibrous interlayer.Strain energy release rate under shear (ENF tests) loading was enhanced by more than %50. The reduction in strength (%10) in DNS tests was attributed to the shear-opening mixed-mode loading. DCB tests are underway to further show the effect of the mode I, i.e. opening. Finally transversal impact tests also provided evidence for toughness increase (about %20) by the nano-fibrous interlayers. Overall the experimental results herein suggest there is a significant potential by the nano-fibrous interlayers chemically tailored for the matrix to increase the delamination resistance of the laminated composites with almost no weight penalty.

Acknowledgement

The Scientific and Technological Research Council of Turkey(TUBİTAK) for their grant # 109M65.

5.References

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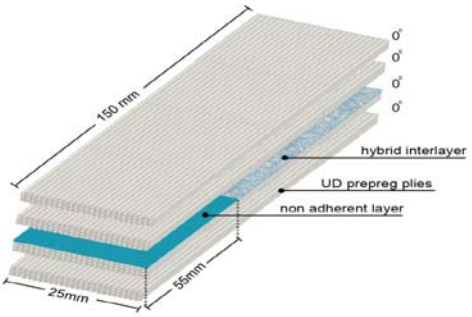

Fig.1. ENF test specimen dimensions

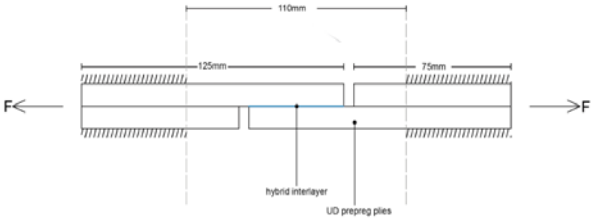

Fig.2. DNS test specimen dimensions

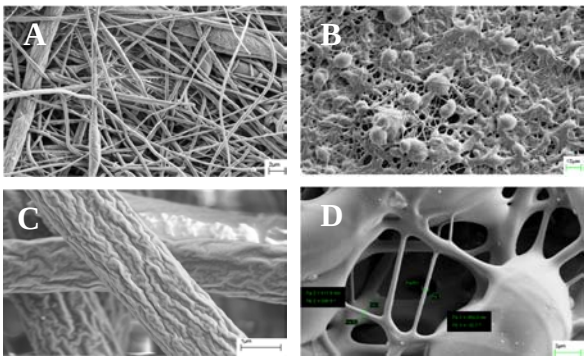

Fig.3a,Fig.3c. Hybrid interlayers at room temperature, Fig3.b,3.d. Hybrid interlayers at T_g

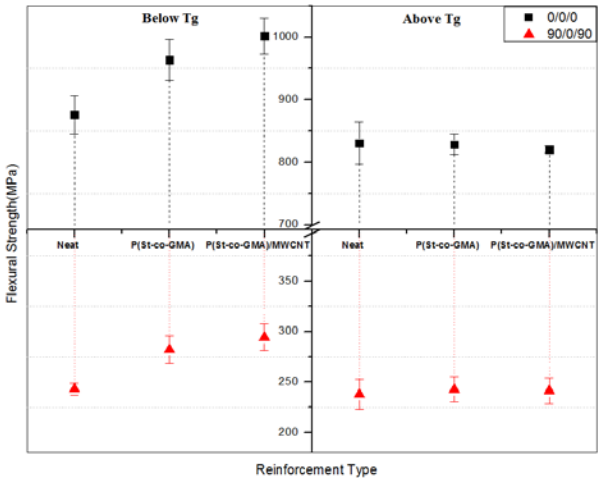

Fig.4. Flexural strength variation by the curing cycle and reinforcement type

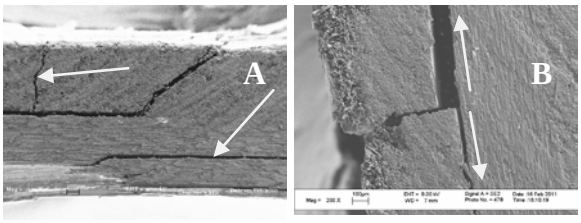

Fig.5.a. Resin cracking and delamination for 0/0/0 specimen Fig 5.b. Interlaminar damage for 90/0/90 specimen

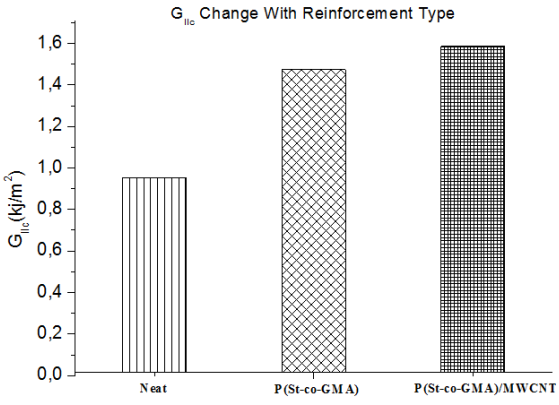

Fig.6. G_{IIc} with respect to the reinforcement type

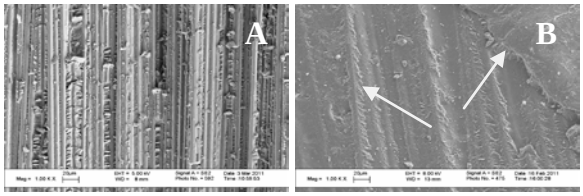

Fig.7.a. Fracture surface of a ENF tested ,non-interlayered specimen with hackle markings 7.b. Absence of usual hackle markings for the interlayered specimen due to severe microcracking

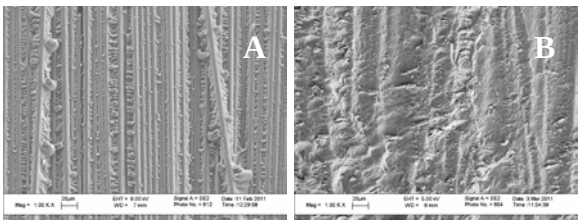

Fig.8.a. Failure surface at non-interlayered and. 8.b at interlayered DNS test specimens

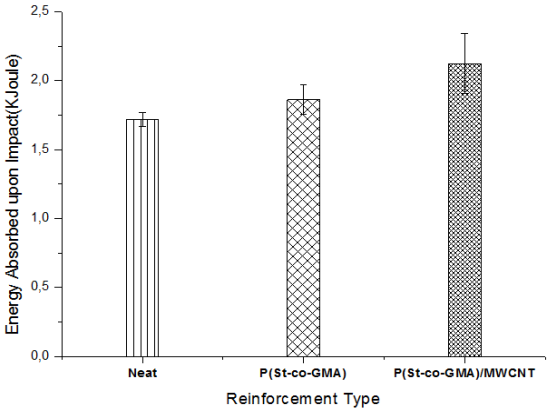

Fig. 9 Energy absorbance with respect to reinforcement type

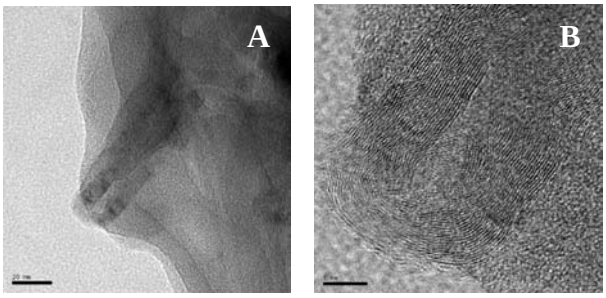

Fig.10.a. Side sectional view of a P(St-co-GMA) nanofiber 10.b. Surface of a P(St-co-GMA) nanofiber