THE INFLUENCE OF PES AND TRIBLOCK COPOLYMER ON THE PROCESSING AND PROPERTIES OF HIGHLY CROSSLINKED EPOXY MATRICES

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Abstract

This paper focuses on toughening of a highly cross-linked epoxy system with reactive and nonreactive PES and reactive block copolymer (BCP) toughening agents. The neat resin and toughened resins were characterised by dynamic-mechanical (DMTA) and fracture testing to determine T_g, density, full width half maximum (FWHM) of tan δ, and fracture toughness (K_{IC}). Carbon fibre reinforced composites were manufactured with selected systems by resin film infusion and studied by DMTA and interlaminar fracture testing. Results show that addition of toughening agents did not significantly influence T_g. Nonreactive PES showed phase separation resulting in higher K_{IC}. Whereas the phase separation of reactive PES was dependent on both molar mass and the addition level. Overall, the BCP exhibited the highest toughening effect.

1 Introduction

Aerospace composites are required to exhibit high heat resistance in order to maintain their mechanical properties at high operating temperatures. The heat resistance of an epoxy-resin matrix can be improved by increasing the cross-link density of the system; however this leads to a more brittle matrix. Therefore a second phase can be introduced to a highly cross-linked network to improve the facture toughness whilst maintaining the other favourable properties of the matrix. A significant number of studies have been carried out on polyethersulfone (PES) toughening and related these results to toughening with rubber particles, for example [1-5], whereas relatively few studies have been done on block copolymer (BCP) toughening and related that to PES toughening. Most studies involved BCP toughening of difunctional epoxy resins, [6-8]; whereas no studies have been conducted on toughening of high functionality (trifunctional and tetrafunctional) epoxy system with block copolymers. Moreover, no evidence was found on the effect of reactivity and molecular weight of PES on highly cross-linked epoxy systems. This study is an attempt to cover some of these gaps in the field. This paper presents structure development in epoxy systems based on mixtures of tetraglycidyldiaminodiphenylmethane and triglycidyl-aminophenol cured with 4, 4'diaminodiphenyl sulphone and toughened with reactive low molecular weight PES, reactive high molecular weight PES, non-reactive medium molecular weight PES and reactive tri-block copolymer. The effect of different tougheners on the resin system and the CFRP composite thermal and mechanical properties are investigated.

2 Materials and testing methods

2.1 Materials

The epoxy resins used in this study were triglycidylaminophenol; TGAP (Araldite® MY0510, Huntsman) and tetraglycidyl-4,4'-diaminodiphenylmethane; TGDDM (Araldite® MY721, Huntsman) and the hardener was 4,4'-diaminophenyl sulfone; DDS (Aradur® 976-1, Huntsman). The thermoplastic modifiers used were polyethersulfone (PES); reactive high molecular weight (RHMW), reactive low molecular weight (RLMW) and non-reactive medium molecular weight (NRMMW)(respectively Virantage® VW10200 RFP, Virantage® VW10700 RFP and Virantage® VW10300 FP, Solvay) and triblock co-polymer modifier; reactive block copolymer (RBCP) (Nanostrength® M52N NP, Arkema) both in powder form. Their structures are given in Fig. 1.
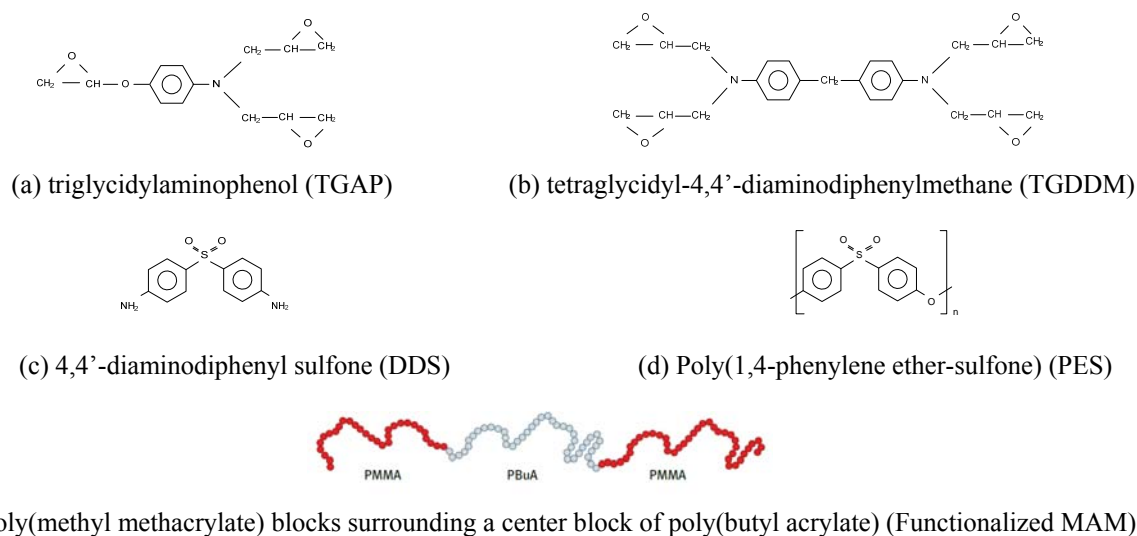

(a) triglycidylaminophenol (TGAP)   (b) tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM)

(c) 4,4'-diaminodiphenyl sulfone (DDS)   (d) Poly(1,4-phenylene ether-sulfone) (PES)

(e) poly(methyl methacrylate) blocks surrounding a center block of poly(butyl acrylate) (Functionalized MAM)

Figure 1. Structures of chemicals used in this study.

Carbon fibre reinforced composite panels were manufactured with the formulated resins and the reinforcement, a unidirectional carbon fibre fabric, which was supplied by Sigmatex, UK. 6 k carbon tows were bound with a fine glass fibre yarn in a distance of approximately 6 mm giving a fabric of 445 gm^{-2}.

2.2 Sample Preparation and Characterisation

The base epoxy system and the toughened systems were prepared by melt mixing. The toughening agents were dissolved in the epoxy blend prior to the hardener addition. PES was dissolved at 130 °C and the BCP at 160 °C for 2 hr followed by DDS dispersion at 80 °C for 1 hr. Samples were prepared containing 0, 5, 10 and 15% (w/w) of RHMW PES, 5, 10, 15 and 20% (w/w) of RLMW PES, 10% (w/w) NRMMW PES and 2.5, 5 and 7.5 % (w/w) RBCP to the overall mixture.

The polymer blends were degassed at 130 °C for 1 hr and then cured at 130 °C, 165 °C and 200 °C for 2 hr at each temperature. Composite laminates were manufactured by resin film infusion (RFI). Resin films were degassed at 130 °C for 1 hr and then were immediately frozen. The infusion setup is presented in Fig. 2. The laminates were cured in an oven under vacuum for the infusion to take place. The cure cycle was same as for the polymer blends. The manufactured laminates contained 0 and 10 % (w/w) RHMW PES, 10 % (w/w) NRMMW PES and 5 % (w/w) RBCP to the overall mixture of the matrix. A 20 μm release

film was inserted in the centre of the fabric stack between two resin films to create the required initial crack in order to perform the mode I interlaminar fracture toughness test.
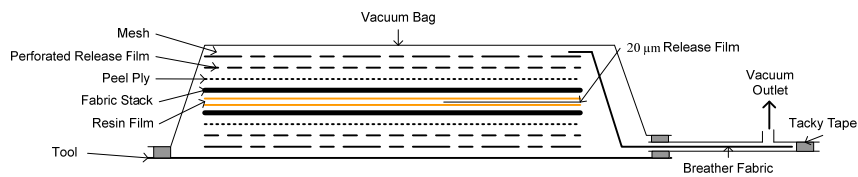
Figure 2. Resin Film Infusion setup.

2.2.2 Dynamic Mechanical Thermal Analysis (DMTA)

The dynamic mechanical properties of the polymer systems and the composites were determined using a PerkinElmer DMA8000 in dual cantilever beam mode. Rectangular specimens (40 mm x 10 mm x 3 mm) were scanned from 30 °C to 350 °C at 5 °C/min and 1 Hz frequency. The values of T_g were taken at the maximum of the α peak in the *tan δ* vs. *T* curve.

The density of the cured systems were measured by water displacement using a Mettler Toledo XP205 Delta Range® electronic balance with a density measurement kit.

2.2.2 Measurement of Plane-Strain Fracture Toughness

Fracture toughness test was carried out according to ASTM D5045, [9] using an Instron 4411 testing machine. Specimen dimensions (44 mm x 10 mm x 5 mm) were measured prior to the test and a natural crack was produced by inserting a fresh razor blade into the machined notch and tapping it with a jeweller's hammer. The specimen was placed into a rig shown in Fig. 3 and was tested at 10 mm/min crosshead speed. After the test the crack length, *a* (machine notch + natural crack) was measured using a travelling microscope. A minimum of ten specimens were tested to calculate the final fracture toughness for each formulation. The fracture toughness in terms of critical stress intensity factor, K_{1C} was calculated using:

$$K_{1C} = \left(\frac{P}{BW^{1/2}} \right) f(x) \tag{1}$$

where *P* is the maximum load from the load-deflection curve, *B* is the thickness and *W* is the width of the specimen. $f(x)$ is a function of *a/W* which is calculated according to ASTM D5045, [9].
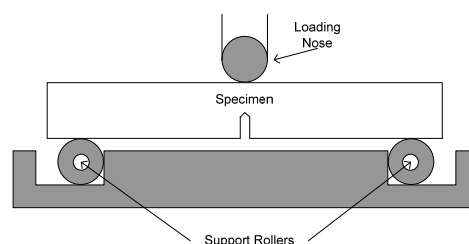
Figure 3. Single Edge Notch Bending (SENB) test rig.

2.2.3 Mode I Interlaminar Fracture Toughness

Mode I testing was carried out according to ASTM D5528, [10] using an Instron 8862 H2007. Metal piano hinges were bonded to the end of each specimen for loading and both edges of the specimen were marked with 1 mm vertical lines to measure the crack growth (Fig. 4). A 0.75 mm/min crosshead speed was used and crack growth was followed using a magnifying glass. During loading the onset of crack growth was observed on the edge of the specimen and was recorded on the load-displacement data values. Loading was stopped and the specimen was unloaded after the first 5 mm crack growth. The crack tip was marked on the both edges of the specimen, and then the specimen was then reloaded (at 0.75 mm/min crosshead speed) and crack growth was observed from the new crack tip. For the first 5 mm every 1 mm increment of crack growth was noted in the data. Afterwards, every 5 mm was noted upto 35 mm and for the last 5 mm (*i.e.* to 40 mm) 1 mm increments were again noted. A minimum of 5 specimens were tested for each formulation. The mode I interlaminar toughness in terms of modified beam theory was calculated using:

$$G_I = \left(\frac{3P\delta}{2b(a + |\Delta|)} \right) \tag{2}$$

Where G_I is the mode I interlaminar fracture toughness, P is the applied load, δ is load point deflection, b is the width of specimen, a is the crack length and Δ is a crack extension to correct for rotation of the beam arms.
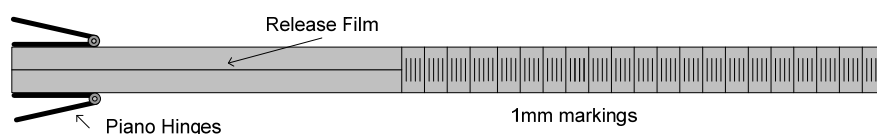

Figure 4. Specimen geometry for mode I interlaminar fracture toughness test.

3 Results and Discussion

3.1 Dynamic Mechanical Thermal Analysis (DMTA)

The DMTA results show that the lower levels of toughening additive do not have a significant effect on the T_g (Table 1). However at 20 % addition of RLMW PES the T_g dropped by 8 °C compared to the base system. An interesting observation is the change in T_g of the cured laminates (Table 2). It shows that the composite with unmodified resin has a T_g about 22 °C lower than the cured neat resin. This shows the effect of the reinforcement on curing of the composite which results in lower T_g than the matrix.

Addition of PES gradually increases the density of the system whereas the block co-polymer has the opposite effect. The full width half maximum (FWHM) of *tan δ* graphs increases with the increase of toughener content for RLMW PES and RBCP. It can be noted that at lower level of RHMW PES the FWHM remain similar to the neat resin value. However at 15 % addition the FWHM has increased despite the fact that it has a *β* peak (Fig. 5). The *β* peak is indicative of a phase separated morphology, however the increase in FWHM is indicative of a homogeneous phase morphology. Therefore a partially phase separated morphology can be expected. The NRMMW PES α peak has similar FWHM to the neat resin and has a clear *β* peak (Fig. 5), indicating a complete phase separated morphology.

Additive	Additive wt %	T_g °C	Density g/cm³	Full width half maximum of *tan δ* °C
Neat Resin	0	273.4 ± 0.3	1.295 ± 0.001	26.9 ± 0.2
RLMW PES	5	270.8 ± 0.3	1.297 ± 0.001	28.9 ± 0.4
	10	271.2 ± 1.0	1.303 ± 0.001	29.7 ± 0.8
	15	269.4 ± 0.3	1.306 ± 0.001	34.2 ± 0.8
	20	265.3 ± 0.8	1.306 ± 0.001	35.9 ± 1.5
RHMW PES	5	273.4 ± 0.2	1.297 ± 0.000	27.0 ± 0.3
	10	273.1 ± 0.5	1.303 ± 0.001	27.2 ± 0.2
	15	271.9 ± 0.6	1.307 ± 0.001	30.2 ± 0.5
NRMMW PES	10	274.1 ± 0.6	1.303 ± 0.001	27.6 ± 0.8
RBCP	2.5	271.5 ± 0.1	1.286 ± 0.000	33.0 ± 2.0
	5	269.4 ± 0.7	1.279 ± 0.001	39.0 ± 0.1
	7.5	270.0 ± 0.4	1.271 ± 0.001	42.6 ± 1.6

Table 1. DMTA results of the neat resin and the toughened systems.

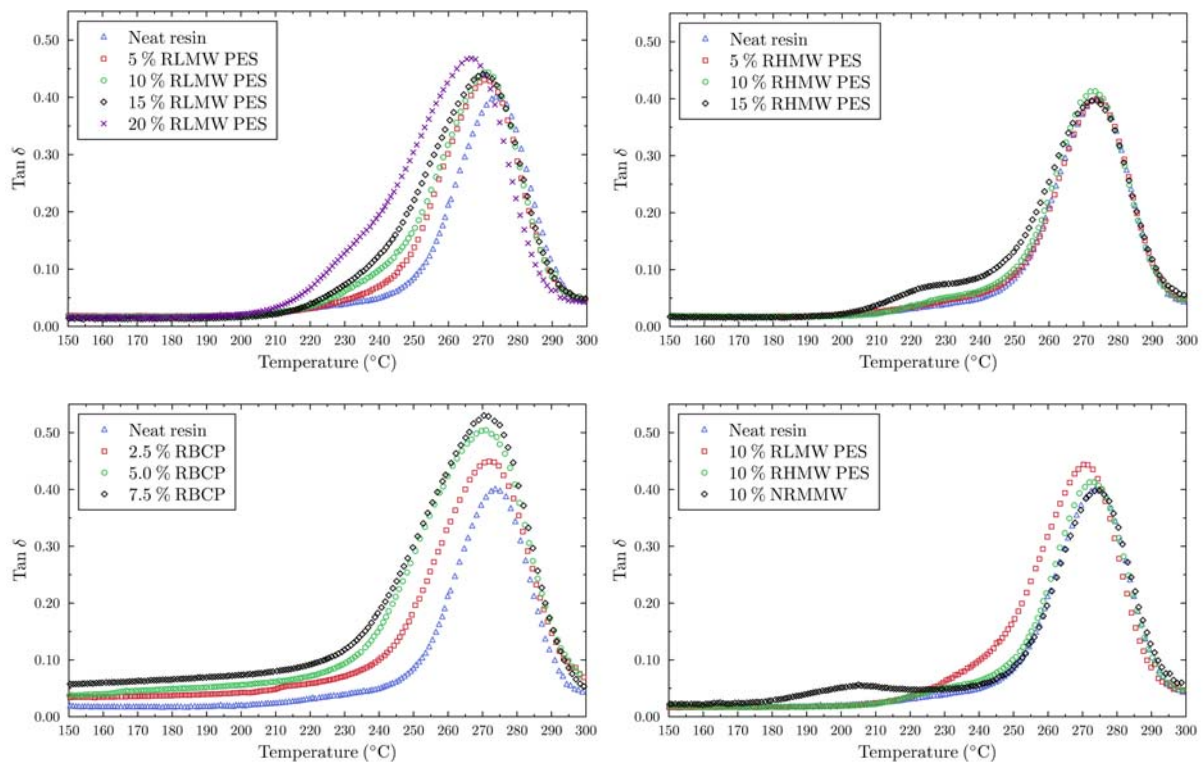| Laminates with	Additive wt %	T_g °C
Neat Resin	0	251.0 ± 0.7
RHMW PES	10	254.8 ± 0.4
NRMMW PES	10	259.5 ± 0.2
RBCP	5	261.3 ± 0.4

Table 2. T_g of manufactured laminates.

Figure 5. *Tan δ* vs. temperature curves of the neat resin and the toughened systems.

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The *tan δ* graphs obtained from DMTA shown in Fig. 5 show no evidence of phase separation of the RLMW PES and RBCP from the epoxy resin matrix. According to the supplier's information RLMW PES has a 216 °C T_g. Thus the *tan δ* graph shifts to lower temperature with the increasing amount of RLMW PES in the system. The RHMW PES data indicates that the system becomes increasingly immiscible as the additive content increases. At 15 % RHMW PES a significant *β* transition can be seen at about 223 °C. According to the supplier the T_g of RHMW PES is 220 °C, thus it can be assumed this transition is due to the PES content and is therefore indicative of a phase separated morphology. NRMMW PES *β* transition peak is at about 207 °C. The T_g of the NRMMW PES is 220 °C according to the supplier's information. However it should be noted that the T_g of all the PES supplied were measured using differential scanning calorimetry (DSC).

3.2 Plane-Strain Fracture Toughness -K_{IC}

The K_{IC} data for all the systems are presented in Fig. 6. It can be seen that the BCP toughener has the greatest effect. The highest toughening effect achieved with BCP was about 50 % increase in toughness. The results show that with the increase of molecular weight of PES the toughening effect increases. The RLMW PES results suggest that with higher PES content K_{IC} may reach a plateau. According to the presented data it can be expected that with higher addition of RHMW PES and RBCP, K_{IC} will keep on increasing. At 10 % addition of NRMMW PES shows the greatest effect to 10 % addition of RLMW and RHMW PES, which is 40 % increase in toughness compared to the neat resin. This is due to the non-reactivity of the system and the higher molecular weight. The DMTA results indicate a phase separated morphology resulting in higher fracture toughness. Note the difference in size between the error bars for the BCP and PES samples. Cured PES containing resins are transparent where as BCP containing resins are opaque. The poor visibility through the samples made it difficult to observe when a natural crack had began to propagate. This resulted in higher error on the BCP toughened systems. Only one NRMMW PES system was studies as a comparison point. However, for the rest of the systems the maximum amount of toughener was added to the neat resin until it became too viscous to process.
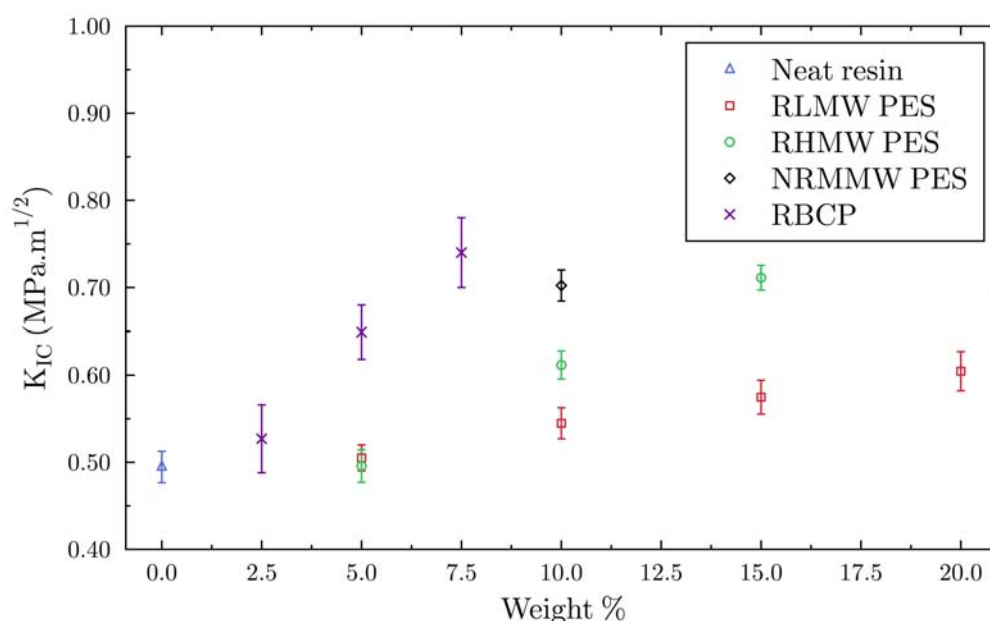

Figure 6. Plot of fracture toughness vs. toughener content.

3.3 Mode I Interlaminar Fracture Toughness- G_{1C}

Fig 7. shows the relationship between applied load and crack opening displacement (COD) for CFRP laminates. The laminates with neat resin and PES toughened resin give a similar gradient whereas the laminate with BCP has a higher gradient. This could be due to higher resin volume fraction in the composite. From the G_{1C} vs. increment of crack length graphs (Fig. 8) it can be seen initially that all three toughened systems increase the fracture toughness. However towards the end of the test, both unmodified and modified systems exhibit similar fracture toughness.
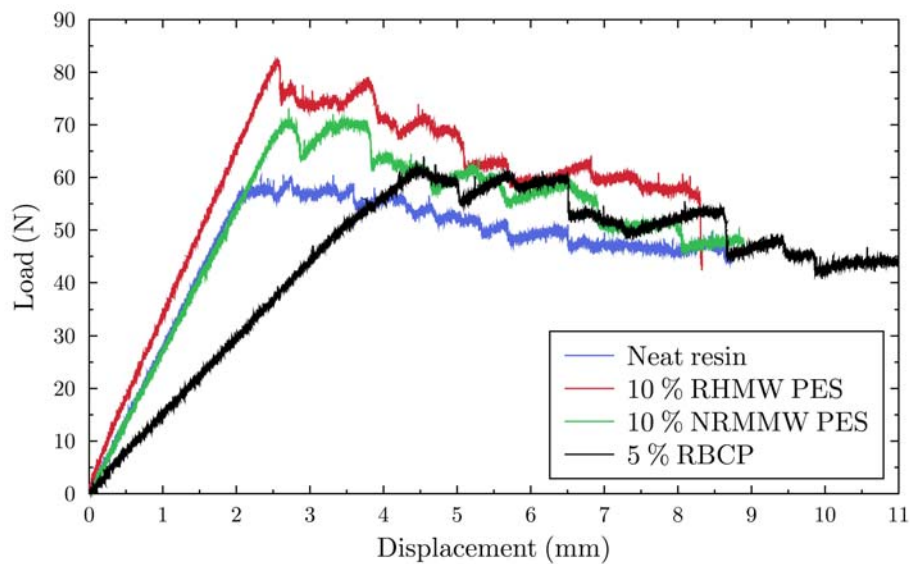

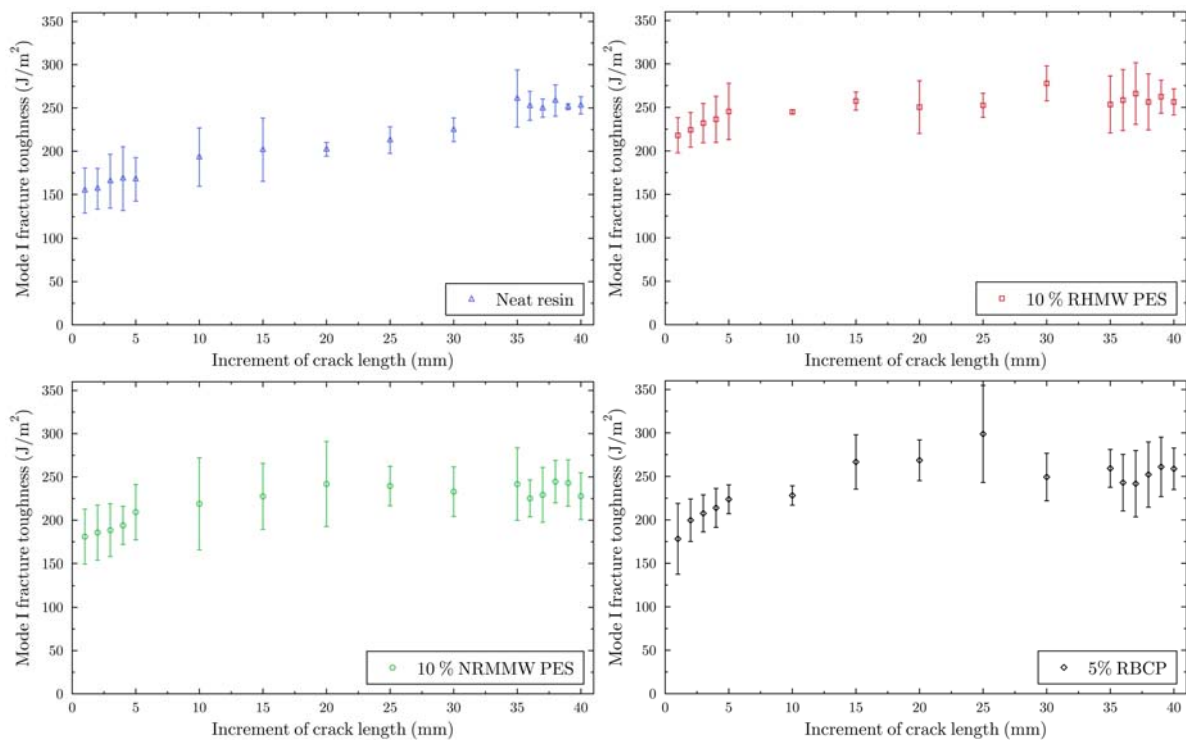**Figure 7.** Applied load vs. crack opening displacement for CFRP composites.

Figure 8. Mode I fracture toughness vs. increment of crack length for CFRP composites.

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4. Conclusion

PES and BCP have little effect on the neat resin T_g at the studied toughener content levels. The T_g of the composite is lower than the T_g of the purely cured resin as a results of the heat conductivity of the carbon fibres.

Reactive end groups of PES inhibit the phase separation. However there is a higher tendency for partial phase separation as the molecular weight of PES increases, resulting in higher fracture toughness. Even at lower BCP content there is a higher effect on the toughness compared to PES systems.

Acknowledgement

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