Summary

In this work, a new type of carbon fibre reinforced polymer (CFRP) composite, based on a multiphase epoxy based matrix has been prepared and characterized with respect to the mechanical properties and fracture behavior. Structuring the matrix at micro-scale using a deformable and crystallizable thermoplastic phase is believed to modify the stress distribution and hence damage behavior of the matrix as well as the resulting CFRP composite. In the present study, reaction induced phase separating (RIPS) Polyoxymethylene (POM) micro-phases, were found to be able to improve the fracture properties of the neat epoxy matrix as well as the resulting epoxy based carbon fibre reinforced (CFRP) composites. Microstructural analysis of the fracture surfaces of the two phase matrix systems revealed that the phase separated POM micro-particles are able to significantly deform during the crack growth, hence improving the fracture toughness of the matrix system. As it is shown in this study, as a result of RIPS, POM micro-particles can homogeneously be formed in between fibres. This is believed to improve the tensile properties of the resulting modified CFRP in terms of tensile strength and ultimate strain, by affecting matrix dominant failure mechanisms.

2 Materials and methods

The epoxy resin used in this study (Epikote 828 LVELL) was a diglycidyl ether of bisphenol A (DGEBA). This was cured with 4,4′-Methylenebis(3-chloro-2,6-diethylaniline) (MCDEA) as hardener which was added to the resin at 51.3 phr (parts per hundred resin). The thermoplastic phase was Polyoxymethylene (POM) from Hostaform. A woven twill 2×2 carbon fabric (HEXTOW AS4C GP 6K) from Hexcel was utilized as textile reinforcement. Thermoplastic (TP) modified resin was prepared by melt-mixing the epoxy resin and POM at 180 °C until a homogeneous mixture is attained. CFRP composite samples were then prepared by vacuum assisted resin infusion of carbon fibre plies under hot-press, at a curing temperature of 200 °C for one hour followed by a postcuring step at 225 °C for two hours. Carbon fibres, the mold as well as tubular connections were kept above the melting temperature of the thermoplastic (~170°C) to avoid preliminary crystallization induced phase separation of POM [1]. Crystallization induced phase separation can hinder the formation of individual particles, in case the entire system is not homogenously heated above the crystallization temperature of the thermoplastic. It’s worth mentioning that prior to this method, hand-layup technique followed by autoclave curing was employed to prepare the composite specimens. However, microscopic investigation of the resulting composite specimens, revealed nonhomogeneous distribution of irregular POM rich domains, which have been apparently phase inverted (Fig. 1a). On the other hand, the specimens made using vacuum infusion under hot-press seem to be quite homogenous and flawless (Fig. 1b). Therefore, the latter method was employed in this study to produce composite samples. Rheological characterization of the matrix was carried out using an AR2000 rheometer, equipped with a 2° cone and plate geometry of 200 mm diameter. Shear viscosity curves were obtained by sweeping the shear rate from 0 to 50 s⁻¹ at different temperatures from room up to 175°C. A three-point bending setup was used in order to measure the mode I fracture toughness of the the phase separated epoxy/POM matrix specimens using
Instron 5567 tensile machine. 5 samples per each system were initially notched using a saw machine, followed by implementing a pre-crack (natural crack) by sliding a sharp razor blade into the saw slot in the specimen, according to ASTM D5045. A 5kN load cell was installed on the machine in order to apply a displacement rate of 10 mm/min, as demanded by the standard. Figure 2 shows a schematic of the test specimens.

The stress concentration factor, $K_{IC}$, is then calculated based on following relationship:

$$K_{IC} = \left( \frac{P_0}{BW^2} \right) f(x)$$

Where $(0<x<1)$:

$$f(x) = 6x^{1/2} \left[ 1.99 - x(1-x)(2.15 - 3.93x + 2.7x^2) \right]$$

$$(1 + 2x)(1 - x)^{3/2}$$

With $x=\alpha/W$, $P_0$ is load already determined in kN, and $B$, $W$ and $a$, thickness, width and crack length, respectively, in cm.

The critical strain energy release rate $G_{IC}$ is then obtained from $K_{IC}$, using this relationship:

$$G_{IC} = \frac{(1 - v^2)K_{IC}^2}{E}$$

Where $E$ and $v$ are elastic modulus and Poisson’s ratio of the sample, which can be determined from the tensile test.

CFRP composite samples were characterized under quasi-static tensile loading in the fiber direction, according to ASTM D3039. The tests were performed using a 4505 Instron tensile machine, equipped with a 100 kN load cell. The tensile tests were carried out at a cross-head speed of 2 mm/min. Test specimens with a dimension of 250 mm×25 mm, were cut from the CFRP composite plates using a diamond saw. In order to minimize the stress concentrations induced by the grips during the experiments, glass-fibre end-tabs of 40 mm×25 mm were glued to the specimens using an epoxy glue (Araldite 2011). Full-field strain maps were obtained during the experiments through digital image correlation (DIC) technique. Subsequent images were registered from the samples under loading using a digital camera and vic-snap acquisition software (LIMESS Messtechnik und Software GmbH). Speckle patterns were created on the surface of the samples by spraying black and white paints, prior to the testing. Image correlation was performed later on using VIC-2D software in order to calculate the strain values based on the obtained displacements. The tensile set-up was also combined with Acoustic Emission (AE) registration set-up, so as to record the strain energy waves (events) while microcracks are formed and propagate in the specimen during loading. Two sensors V5375-M (Vallen Systems) are placed on the surface of the specimen to detect these waves. The signals received during microcrack formation are filtered and amplified. Irrelevant lower energy events are filtered out when a threshold of 40 dB is set. More details on this technique have been published in another paper [2].

3 Results and discussion

3.1 Rheological properties of the resin

The flow curves (shear viscosity vs shear rate) of the reference (epoxy/hardener) and the POM containing resin systems at different temperatures are compared in Fig. 3. The POM modified resin exhibits a significant shear thinning effect; whereas, the reference material shows a Newtonian behaviour. This implies that that POM phase could be successfully incorporated into the epoxy resin, leading to a homogeneous single phase solution.

3.2 Morphology and fracture toughness investigation of the matrix

Upon curing reaction, the molar mass of the epoxy resin increases. As a result, the entropy of the system is decreased which in turn, due to an increase in the Gibbs free energy ($\Delta G_m$) of the curing blend (equation 1) the thermoplastic/epoxy resin blend becomes thermodynamically unstable and finally undergoes a phase separation, when $\Delta G_m$ becomes positive.

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

This phenomenon is known as reaction-induced phase separation (RIPS). Fig. 4a and 4b compare the morphology of the neat epoxy and epoxy/POM. Phase separated thermoplastic particles can be readily observed in the fracture surface of the modified system. Investigations of the fracture surfaces of the above mentioned matrices revealed that phase separated POM particles, can alter the fracture behavior of epoxy through a number of different mechanisms, such as crack path deflection,
crack pinning, cavitation, and particle deformation. It has been shown that curing reaction of the epoxy blends including smaller quantities of POM (< 15 wt%) will result in the formation of particulate morphologies where thermoplastic particles are dispersed in the continuous epoxy phase [2]. These particles are able to exhibit ductile behaviour due to the relatively low glass transition temperature of POM (~ -83 °C). Figure 5 shows SEM micrograph of the fracture surface of the POM/epoxy bi-phase matrix. Phase separated thermoplastic micro-particles significantly are deformed during the crack growth, thereby dissipating considerable amounts of energy. This together with a number of other failure mechanisms observed in this system (such as debonding of particles, crack path deflection, crack pinning, cavitation of the particles) can explain the two fold increase in the fracture toughness of the neat epoxy matrix, following addition of the thermoplastic phase. This can mainly be attributed to the relatively low glass transition temperature ($T_g$) of POM (~-83 °C), due to which, plastic deformation at the initial stages of the crack propagation is possible.

3.3 Morphology of the CFRP composites

SEM micrographs of the TP modified fibre reinforced composite specimens shown in Figure 6 indicates that POM has been phase separated in between the carbon fibres during the curing process. However it seems that phase separation occurs more easily in resin rich zones between fibre bundles. This is somehow expected since thermoplastic chains in the curing blend, have more limited mobility in the small space within the fibre bundles. Moreover, it is noteworthy that in comparison with the matrix blend, in POM modified CFRP composites the uniformity in size distribution is lost to some extent. This can be due to the fact that thermoplastic phase in the CFRP doesn’t have the same chance for phase separation in all locations within the matrix.

3.4 Tensile properties and microstructure of the CFRP composite samples

Figure 7, shows a representative stress strain curve including the AE events registered during the tensile testing. However it should be noted that the final part of the curve is not shown, since the AE sensors were removed before final failure of the sample. The red dots show the AE events corresponding to the crack formation in the sample. Tensile testing of the CFRP composite samples, revealed an approximately 16% increase in tensile strength as well as 9% improvement in strain at break of the modified composite in comparison with the unmodified reinforced CFRP (Figure 7). This can be related to the fracture toughness improvements observed in the modified matrix which was discussed in the previous section. The enhanced ductility of the modified matrix has possibly delayed fibre breakage by limiting micro-delaminations and transverse cracks. This effect seems to be more pronounced due to the presence of fibre undulations. Our ongoing research on the microstructural analysis and transverse properties of the modified and unmodified CFRP composites will provide more evidence in the future that can support these hypotheses.

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References


Fig. 1. Optical micrograph of the specimens made through a) hand-layout/autoclaving and b) vacuum infusion under hot press.

Fig. 2. Schematic representation of the mode I fracture toughness specimens made according to ASTM D-5045.

Fig. 3. Shear viscosity vs shear rate of the a) neat epoxy/hardener b) POM modified epoxy/hardener.
Fig. 4. SEM micrograph of the fracture surface of a) neat epoxy and b) POM modified epoxy matrices.

Fig. 5. Fracture surface of the POM modified epoxy matrix.

Fig. 6. SEM micrographs of the modified CFRP composite cross section.

Fig. 7. Representative stress–strain curve (black) with AE events (red dots) and cumulative AE energy (blue) plotted against strain for a CFRP specimen based on the matrix modified with POM.
Fig. 7. Comparison of the tensile strength and the strain at break of the modified and unmodified CFRP composites.