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GRADIENT INTERPHASES BETWEEN HIGH-T$_G$ EPOXY AND POLYETHERIMIDE FOR ADVANCED JOINING PROCESSES

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Keywords: thermoset, thermoplastic, welding, solubility, interphase, phase separation.

Abstract

Adhesive joining of carbon fibre reinforced polymer (CFRP) is cumbersome due to the careful surface preparation required and multiple validation steps to certify adhesion quality. Further these joints are often supplemented by mechanical fastenings add weight whilst also localising bearing stress. As an alternative technique, CFRP parts can be functionalized with thermoplastic surfaces during manufacture to enable cost-effective welding of composite structures. In the process of manufacturing the CFRP, curing an epoxy resin in the presence of the functionalising thermoplastic polymer can lead to local dissolution of the latter in the epoxy, followed by a reaction-induced phase separation. This results in a thermosetting-thermoplastic interphase featuring gradient concentrations and a multiphase morphology, which promotes load transfer between the thermosetting matrix and the thermoplastic joint. The aim of the work presented in this paper was to investigate interphase formation between high-T$_g$ epoxy and polyetherimide (PEI) at different curing temperatures. The morphology was characterised using scanning electron microscopy and the composition of the interphase was quantified through Raman spectroscopy. The curing experiments indicated that temperature has a significant effect on the interphase morphology and led to two different biphasic morphologies which generally increased in size with increasing curing temperature. This suggests that the size of the gradient interphase can be tailored through the curing process, which is as a fundamental step in optimising the structural performance of welded joints with PEI-functionalized epoxy-based CFRPs.

1. Introduction

Carbon fibre reinforced polymers (CFRPs) exhibit outstanding mechanical properties combined with low weight and are increasingly used in automotive or aerospace industries. Most CFRPs are manufactured with epoxy thermosetting matrix for their high performance at low cost and ease of processing. Thermosetting CFRP structures are typically assembled by a combination of (i) riveted joints and/or (ii) by adhesives. Both require either substantial machining or surface preparation and inspection which is labour intensive. Thermoplastic welding, on the other hand is a cost-efficient structural joining technique because joining can be achieved in short times and is robust. Being able to functionalise thermoset CFRPs with thermoplastic surfaces allows thermoset CFRPs to be joined using well established thermoplastic welding methods [1]. A strong connection between the thermoset CFRP and the thermoplastic functional layer is a necessary requirement to enable high-performance welded joints.

The interaction between thermoplastic polymers and reactive epoxy systems has been well studied due to the brittle nature of epoxies with a focus on the thermoplastic toughening of epoxy resins [2]. Some thermoplastic polymers, such as polyetherimide (PEI), are known to be soluble in a number of epoxy precursors and to subsequently undergo phase separation as the curing reaction progresses [3]. The reaction-induced phase separation results in different multiphase morphologies depending on the relative concentration of thermoplastic. The improvement achieved on the fracture, mechanical or thermal properties of the resulting resin system are sensitive to the nature of the thermoplastic-epoxy morphology [2][4]. In order to enable subsequent thermoplastic welding processes, when a PEI film is added to the surface of an uncured epoxy-based CFRP laminate, solution and phase separation during the curing process result in a micron-size PEI-epoxy interphase with gradient composition and complex morphology [1][3]. The size and characteristics of that interphase are dependent on the curing cycle and can be expected to affect the final strength of the welded joints [5].

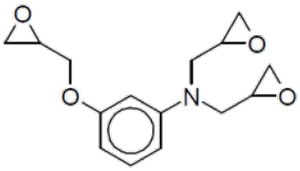
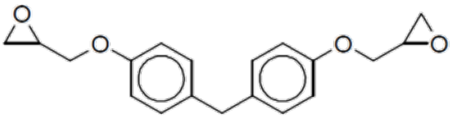
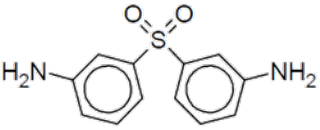
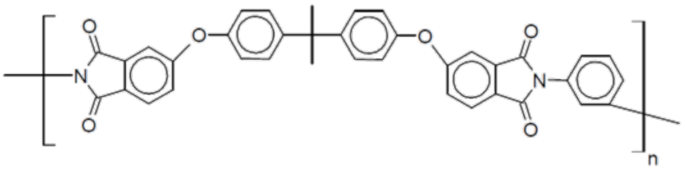
The research work presented in this paper studies the effect of cure temperature and time on interphase formation between a high T_g epoxy systems (such as those in aerospace prepregs) and PEI. To that end, isothermal curing experiments were carried out between 120- and 180°C. Different stages during the formation of the interphase as well as relevant interphase dimensions were identified through time-lapse hot-stage microscopy and they were subsequently related to the degree of cure through the use of a cure kinetics model. The morphologies present at the interphase were observed through scanning electron microscopy of etched samples and the composition of the interphase was quantified through Raman spectroscopy.

2. Materials and methods

2.1. Materials

Table 1 shows the chemical structure and relevant information about the different materials used in this study. It must be noted that the epoxy system is representative of typical high-performance aerospace prepreg epoxy systems with 180°C curing temperature.

Table 1. Chemical structures and relevant information about the epoxide and diamine precursors and of the thermoplastic used in this work.

Epoxide and diamine precursors	
	Triglycidized meta-aminophenol, TGMAP (Huntsman, Switzerland)
	Diglycidyl Ether of Bisphenol F, DGEBF (Huntsman, Switzerland)
	3,3'-Diaminodiphenyl sulfone, DDS (Huntsman, Switzerland)
Thermoplastic polymer	
	Polyetherimide (PEI) Ultem 1000, molecular weight 55000 g/mol, n≈90, Tg 217°C (SABIC, Saudi Arabia)

2.2. Curing experiments

The experimental setup schematically shown in Figure 1 was used to observe the isothermal PEI-epoxy interphase formation at different curing temperatures. The setup consisted of a single-use 60 µm PEI film with a 2-3 mm wide central slit sandwiched in between two cover glasses and placed on a temperature controlled microscope stage (Linkham Scientific, UK). The slit in the PEI film was filled with a liquid reactive epoxy. The room temperature resin drop was placed the edge of the slit and heated upon contact to the stage temperature. The almost instantaneous increasing temperature resulted in a reduction of viscosity and capillary driven spontaneously filling of the gap, as shown in Fig. 3. Time-lapse optical microscopy (Keyence VHX-2000) was used to observe and record any visual changes in the vicinity of a PEI-epoxy interface.

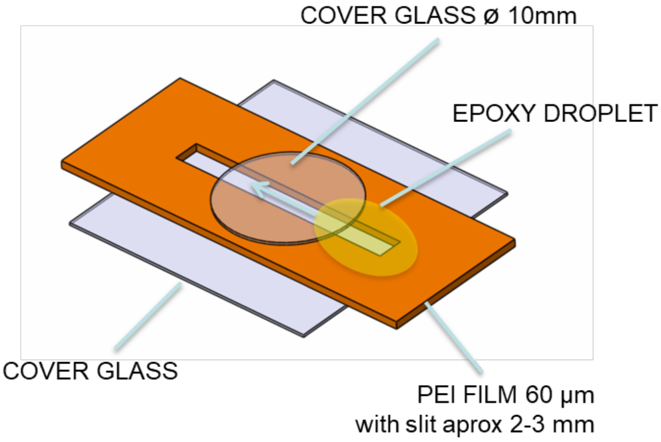


Figure 1. Schematic of the experimental setup to observe interphase formation during the epoxy curing reaction.

2.3. Cure kinetics model

The Kamal Sourour model [6] was used to predict the time-dependant evolution of the degree of cure of the epoxy resin, α, at different curing temperatures, T:

$$\frac{d\alpha}{dt} = \left(k_1 \cdot e^{-\left(\frac{E_1}{T}\right)} + k_2 \cdot e^{-\left(\frac{E_2}{T}\right)} \cdot \alpha^m\right) \cdot (\alpha_{max}(T) - \alpha)^n \tag{1}$$

where the non-dimensional constants k_1, k_2, E_1, E_2, m and n were determined through differential scanning calorimetry (DSC) experiments using a Perkin Elmer calorimeter (Pyris Sapphire), using the resulting in the values listed in Table 2.

Table 2. Experimental values for the non-dimensional constants in the Kamal-Sourour model (Eq. 1)

Constant	Value
k_1	9.1556e-4
k_2	2.9659e+3
E_1	8.3209e+3
E_2	6.0487e+3
m	0.9
n	1.3

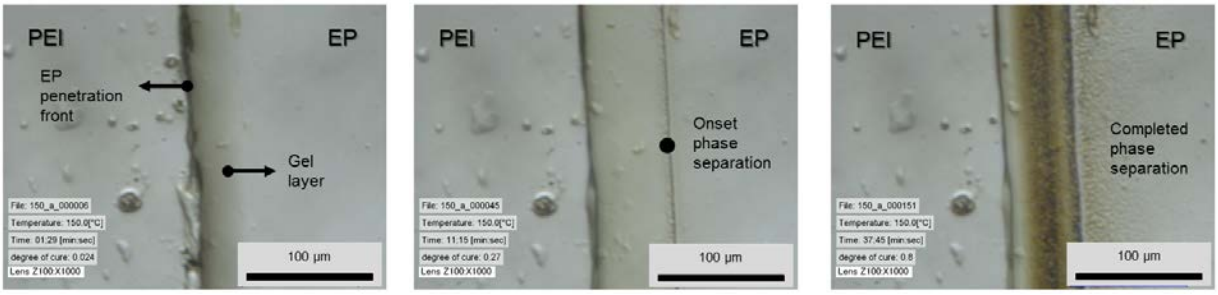
2.4. Analysis

Raman spectroscopy combined with confocal laser microscopy (Renishaw in Via Raman microscope) using a 785 nm laser was used for semi-quantitative analysis of the composition across the interphase [7] after the curing experiments described in section 2.2. This analysis was based on peak amplitude normalization using the peaks at 1004 cm^{-1} and 987 cm^{-1} wavelengths for PEI and the cured epoxy system, respectively. Scanning electron microscopy (SEM) analysis was used on polished samples etched with NMP (N-Methyl-2-pyrrolidone) following the procedure explained in [1] for qualitative observation of the interphase morphologies.

3. Results and discussion

3.1. Interphase formation and dimensions

Fig. 2 displays optical micrographs of a sample subjected to 150°C curing temperature. Note that the images were taken at the same location during the curing process. The first image (Fig. 2a) shows a distinct penetration front of the epoxy precursors in the PEI film, also known as infiltration layer [3]. Behind this epoxy penetration front, a darker band could be observed which was identified as the gel transition zone or gel layer. The gel layer is composed of swollen PEI in a rubberlike state by the dissolution action of the epoxy precursors [3]. As the process progressed (Fig. 2b), the penetration front moved deeper into the pure PEI whilst the opposite boundary of the gel layer moved towards the pure epoxy system, gradually increasing the thickness of the gel layer. At a certain moment in the curing process a sharp interface between gel layer and epoxy appeared (Fig. 2b), indicating the onset of phase separation. With increasing time, the size of the gel layer remained constant, however the textural morphology of the gel layer and epoxy gradually evolved into the final state shown in Fig. 4c. It should be noted that a certain spinodal decomposition texture already visible in Fig. 4b and especially clear in Fig. 4c could be observed beyond the gel layer and towards the pure epoxy system. This texture can be related to dissolved PEI molecules de-mixing from the gel layer that diffused deep into the reactive epoxy before the dissolution process stopped, referred to as liquid layer in literature [3]. The PEI-epoxy interphase was delimited by the penetration front on the one side and the end of the liquid layer on the other side [3].



(a) (b) (c)

Figure 2. Optical micrographs from the same sample area subjected to 150°C curing temperature (EP: epoxy). Images taken at: (a) 89 s, (b) 675 s and (c) 2,265 s from the beginning of the experiment.

Micrographs at the onset of phase separation (Fig. 2b) were used to measure the thickness of the gel layer at different curing temperatures. The thickness of the gel layer was considered as a relevant dimension to describe the formed interphase. The evolution of the thickness of the gel layer as a function of the temperature is shown in Fig. 3. As shown in this figure, the minimum curing temperature at which interphase formation was 120°C. The thickness of the gel layer formed at 120°C was approximately 10 µm and it was found to increase with increasing curing temperature until reaching a maximum of about 75 µm at 170 °C. Saturation in the thickness of the gel layer seemed to occur at 180°C. Two main competing factors are believed to have an influence on the size of the size of the gel layer and on that of the total interphase, namely epoxy diffusivity and epoxy reactivity. Both of these competing factors increase with higher temperature. Given the results shown in Fig. 3, increased diffusivity with increasing temperature is the dominant factor in the system studied, causing an overall increase of the gel layer thickness with increasing curing temperature up to 170°C. An increased reactivity at very high temperatures could be the cause for the slight thickness drop at 180°C [8], limiting the diffusion time, however more experimental data would be necessary to confirm such trend.

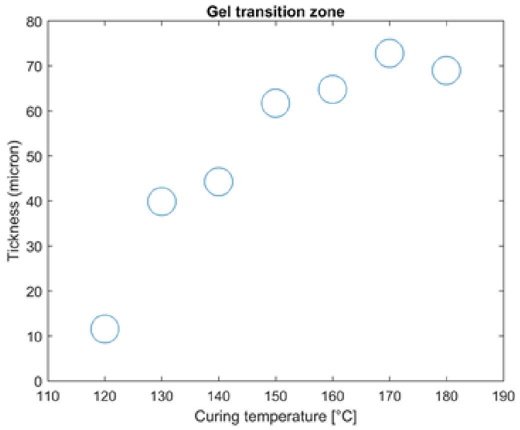


Figure 3. Gel layer thickness versus curing temperature. Data circles indicate measurement uncertainty.

The combination of the cure kinetics model in Eq. 1 and the times at which the onset of phase separation was observed to occur (time-lapse microscopy), allowed us to establish a relationship between the degree of cure at the onset of epoxy-PEI phase separation as a function of the curing temperature shown (Fig. 4). As a general rule, at higher curing temperatures, phase separation was initiated at a higher degree of cure, which is consistent with the expected increased solubility at increased temperature. Finally, Fig. 3 and Fig. 4 combined results into a processing map shown in Fig. 5. The processing map shows the onset of phase separation as well as the gel layer thickness as functions of the degree of cure and time for each curing temperature. Such a map could serve as a basis to design a cure cycle to result in a certain desired gel layer thickness.

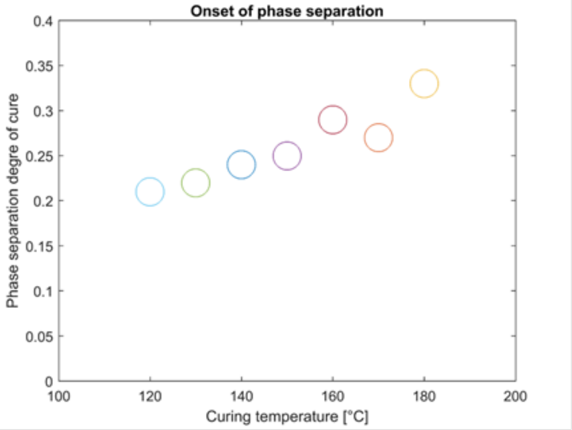


Figure 4. Degree of cure at onset of phase separation as a function of the curing temperature. Data circles indicate measurement uncertainty.

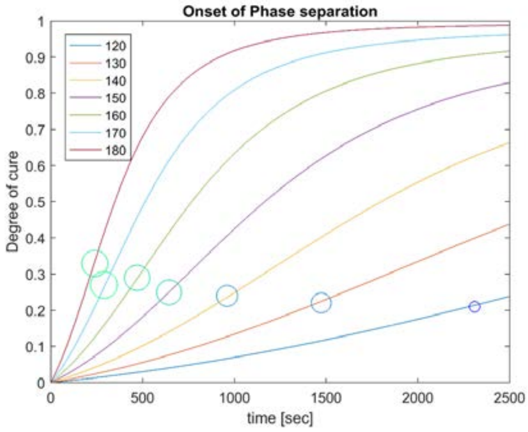


Figure 5. Onset of phase separation and gel line thickness as a function of degree of cure, curing time and temperature. Diameter of the data points indicates gel layer thickness.

3.2. Interphase morphology and composition

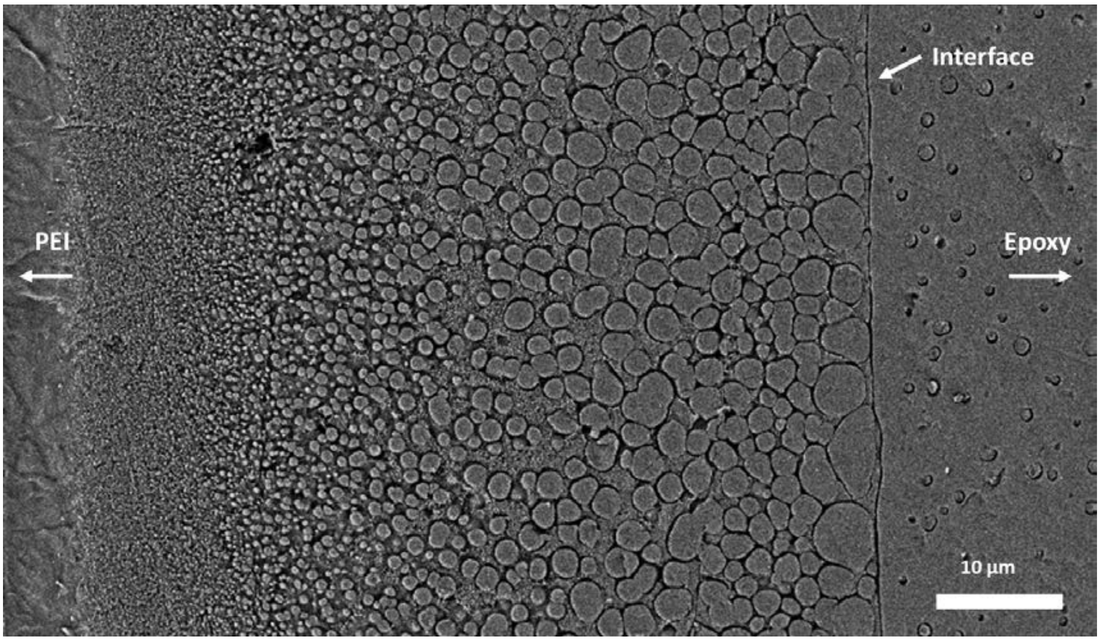


Figure 6. SEM micrograph showing morphology of a PEI-epoxy interphase obtained at 180°C cure temperature.

The SEM micrograph in Fig. 6 corresponds to a sample cured at 180°C. It shows two PEI-epoxy biphasic regions separated by a sharp straight interface. To the left of this interface, i.e. towards the pure PEI, the PEI-epoxy biphasic morphology was characterized by epoxy-rich particles densely dispersed in a continuous PEI-rich matrix, known as a phase-inverted morphology [3]. The size of the epoxy-rich particles gradually decreased towards the pure PEI area. To the right of the interface, i.e. towards the pure epoxy area, the PEI-epoxy biphasic morphology was characterized by scattered PEI-rich particles in a continuous epoxy-rich matrix. The sharp interface observed in Fig. 6 could be related hence to the right boundary of the gel layer, i.e the boundary between the gel and the liquid layer, in Figs. 2b and 2c. Correspondingly, the size of the biphasic region with a continuous PEI-rich matrix (approximately 65 µm, as measured on Fig. 6) was similar to the gel layer thickness values measured at 180°C cure temperature (Fig. 3).

Fig. 7 shows the results of Raman spectroscopic analysis of a sample cured at 180°C. From left to right, a decrease of the PEI content from 100% to just above 0% was observed over the 80 µm span. The epoxy content follow the inverse correlation of initially increasing steeply to 20% content, then a near linear region followed by a locally rich region of PEI close to the epoxy interface. The similarities between this epoxy concentration profile (Fig. 7) and the generic profile proposed by Lestriez et al. in [3] (Fig. 8) provide validation of the experimental observations.

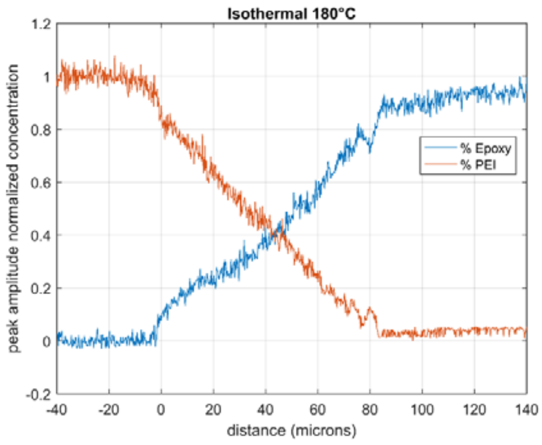


Figure 7. Relative PEI and epoxy concentrations across the interphase for a sample subjected to 180°C cure temperature based on Raman peak intensity at 1004 cm^{-1} (PEI) and 987 cm^{-1} (epoxy) wavelengths.

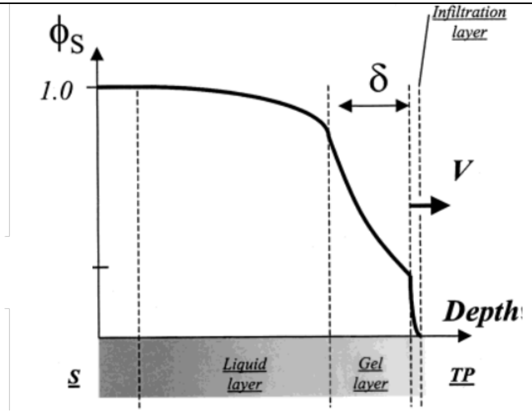


Figure 8. Generic solvent concentration (ϕ_S) profile as proposed by Lestriez et al. [3]. S: solvent (epoxy in the present study), TP: thermoplastic (PEI, in the present study), δ: thickness of the gel layer, V: direction of the penetration front.

4. Conclusions

The research work presented in this paper aimed at characterising the effect of cure temperature and time on interphase formation between a high T_g aerospace epoxy prepgreg systems and PEI. The main conclusions drawn from the results obtained were:

- Optical and scanning electron microscopy allowed identifying the three main regions in the PEI-epoxy phase-separation interphase, i.e. infiltration layer, gel layer and liquid layer. Time-lapse optical microscopy during hot-stage isothermal curing allowed clear identification of the formation, translation and growth of the infiltration and gel layers. Scanning electron microscopy of etched samples allowed resolving of the morphology of the gel and liquid layers.
- Gradual variation of the epoxy and PEI composition across the interphase was confirmed through Raman spectroscopy.
- The thickness of the gel layer was found to generally increase with increasing curing temperature. Likewise the onset of phase separation occurred at a higher degree of cure for increasing curing temperature. These observed trends were believed to result from increased diffusivity and solubility with increasing temperature, respectively.
- A processing map relating the onset of phase separation and gel line thickness to cure temperature and time was defined with the results from this study. Such a phase diagram guideline provides the processing knowledge necessary for optimal functionalisation of epoxy-based CFRPs with PEI surfaces for welding.

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