Thermal mending in E-glass reinforced Poly(ϵ -caprolactone)/epoxy blends

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Abstract. Blends of difunctional epoxy monomer with a 4,4'-diaminodiphenylsulfone hardener and poly(ϵ -caprolactone) (PCL) were used as a self-healing matrix in woven glass fibre-reinforced polymer composites (FRPs). FRPs with these blends (containing 0, 25 and 37vol% of PCL in the blend) were manufactured through Vacuum Assisted Resin Infusion Moulding at high temperature and the matrix, resulting from polymerization induced phase separation, consisted of interconnected epoxy particles embedded in PCL. With 25vol% PCL in the matrix, similar storage modulus and interfacial shear strength as compared to unmodified systems have been observed, however toughness was decreased by 40%. Up to 45% toughness recovery and over 100% stiffness recovery were observed over several cycles when the blend matrix composite samples were re-tested after a thermal cycle at 150°C for 30 minutes. These composites can thus provide efficient crack healing, but remain more sensitive to initial crack propagation due to confinement of the thermoplastic phase.

Keywords: A. Smart materials; B. Delamination; B. Fracture toughness; E. Vacuum infusion

1. Introduction

The field of self-healing thermoset materials has been widely investigated over the past 25 years. Considerable effort has been carried out to impart a self-healing functionality to polymeric thermosets, so that internal damage can be repaired autonomously. Self-healing approaches include the incorporation of capsules or vascular systems that release, upon rupture, a healing agent (reactive monomers or solvents) which is able to fill the damage volume, polymerise or trigger a polymerisation reaction [1,2]. Extrinsic systems, under the form of capsules, have been integrated into fibre reinforced polymers (FRPs), but demonstrated poor healing and loss in structural properties [3,4]. Another strategy is to confer an intrinsic

healing ability to the matrix. Intrinsic healing systems have been studied both on neat resins [2,5] and when integrated to FRPs [6,7]. In particular, one approach consisted of creating a miscible [8,9] or immiscible [10–13] blend between a thermoset matrix and a low melting point semicrystalline thermoplastic. For immiscible blends, the healing phenomenon is related to the following concurrent mechanisms, provided that the crack propagates through (or at the interface of) the thermoplastic material [10]: (i) melting and subsequent volume expansion of the thermoplastic phase, (ii) flow of the melt into the damage volume, (iii) characteristic physical or chemical phenomena taking place at the molecular level. This last mechanism can consist, depending on the approach, in either chain re-entanglement of the thermoplastic melt, based on the thermally enhanced chain mobility, or presence of reversible non-covalent (e.g. hydrogen or ionic) bonds in the thermoplastic phase, triggered by UV radiation or temperature. This healing approach is repeatable and latent, since it is inherent to the stable chemical structure of the thermoplastic phase. However, external activation such as heat or light is required to trigger repair.

Immiscible thermoplastic/thermoset blends usually present two limiting morphologies depending on the constituent concentrations: (i) a particulate thermoset phase embedded in a thermoplastic matrix (*e.g.* [10,11]) or (ii) a particulate thermoplastic phase embedded in a thermoset matrix (*e.g.* [12]). The former type of morphology is usually obtained by polymerisation-induced phase separation (PIPS) processes (this can take place under certain conditions with certain crosslinkers and has been demonstrated for example with the following thermoplastics: polycaprolactone (PCL) [14], poly(ether sulfone) [15], polyetherimide [16], poly(methyl methacrylate) [17] and polystyrene [17]); while the latter type of morphology can be achieved either by simple mixing of the thermoplastic material within the thermoset or by the PIPS process. If there is no miscibility of the constituents in the liquid phase, clustering of thermoplastic segments takes place, as in the case of the ionomeric copolymer polyethylene-co-methacrylic acid (EMAA) [12,18]. In case of initial miscibility, the PIPS process leads to morphology (i) or (ii) for respectively high and low thermoplastic concentrations [10,11]. In addition to these two morphologies, the PIPS process can give rise, at intermediate compositions, to a range of co-continuous morphologies [10]. The mechanical properties of these morphologies can significantly differ depending on the stiffness and strength of the continuous phase as well as on the mechanisms of energy dissipation over crack propagation, such as crack bridging, pinning or deflection.

Systems consisting of a particulate thermoplastic phase embedded in a thermoset matrix have been studied for thermal healing applications in neat resins [12,18], as well as integrated into FRPs [13][19]. These mainly concern the ionomeric copolymer EMAA blend with epoxy. The interest of this ionomeric copolymer reside in (i) the strong adhesion between epoxy and EMAA as covalent bonds are formed during curing [20]; and (ii) the thermal expansion of EMAA that is seven times higher than that of epoxy [12]. Meure *et al.* [12] showed that by inserting 15vol% EMAA particles into an epoxy resin, the strong adhesion between the two components increased the load to failure, measured in Mode I crack opening, by up to 25%. After thermal healing of the cracked samples at 150°C for 30 minutes, they further demonstrated recovery in fracture toughness of up to 85%. This amount of recovery was achieved thanks to the high expansion ability of EMAA, which in addition reacts during healing with epoxy and creates air bubbles, allowing EMAA to flow and fill the cracks. Those systems were further integrated into FRPs made by hand lay-up [13]. Mode I Double Cantilever Beam (DCB) testing demonstrated, as compared to a relatively brittle epoxy composite, a 63% improvement in fracture toughness for EMAA modified systems as well as the ability to recover this property by 156% after thermal healing. The potential of EMAA for thermal healing in FRPs has been further demonstrated when integrated under the form of layers [21] or stitches [22].

Systems consisting of a particulate thermoset phase embedded in a thermoplastic matrix have been also studied for thermal healing applications in neat resins [10,11], however not yet integrated into FRPs. In these systems, the thermoset resin forms a network of interconnected particles, whose interstices contain a continuous thermoplastic phase having a significant self-diffusion (reptation) at moderate temperatures, but adequate thermal stability under service conditions. Luo *et al.* [11] first proposed to create an epoxy-PCL biphasic morphology by using 4,4'-diaminodiphenylsulfone (DDS) as cross-linker and by the PIPS process. At a PCL content of 15.5 wt% in the matrix, the microstructure consisted of a PCL matrix with particulated epoxy. Epoxy particles were thus interconnected and acted as “bricks” for load bearing, and PCL expands at least 10 times more than epoxy when the temperature is raised, which allows, as for blends with EMAA, a differential expansive bleeding mechanism. In a recent study, we investigated a similar system over a wider range of compositions, devoting attention to the resulting materials properties in terms of PIPS morphology, strength, stiffness and toughness, but also using a relatively mild healing temperature (below epoxy glass transition temperature) in order to keep the system integrity [10]. Mechanical performance (both strength and toughness) was shown to decrease with increasing PCL

content; this was attributed to the confinement of the ductile PCL within the system. Mode I crack opening and subsequent healing at 150 °C for 30 min (this healing temperature allows the PCL to expand by 14% [23]) showed an increased (up to full) recovery with the increase of PCL content. In particular, blends with 25vol% PCL exhibited a healing efficiency in excess of 70%, while retaining suitable room-temperature mechanical properties, as shown in Table 1 and were concluded to be promising candidates to be integrated as matrix for healing in FRPs.

In the present work, we extend the application of phase separated epoxy-PCL blends to a matrix material in FRPs, bringing the possibility to thermally mend the material. In particular, we manufactured FRPs with these blends (as well as with pure epoxy for comparison) through Vacuum Assisted Resin Infusion Moulding (VARIM) at high temperature. The influence of the fibres on phase separation kinetics as well as on interfacial shear strength between blends and fibres was investigated. Interlaminar toughness of the produced composites was assessed through Mode I DCB experiments. The samples were then subjected to a thermal cycle at 150 °C for 30 minutes to investigate their self-healing capacity.

2. Materials and methods

2.1. Materials

*Epon*TM 828EL (*Momentive*), a widely available diglycidyl ether bisphenol A (DGEBA) resin with a molar mass of 340.41 g/mol and a molar mass per epoxide group of 185-192 g/eq was blended with different amounts of PCL (number average molar mass, $M_n \approx 45000$ g/mol, *Sigma Aldrich*) and then cured with DDS (4,4' DDS 98%, *ABCR*, molar mass = 248.3 g/mol, 2:1 molar ratio with respect to the epoxy). The different amounts of PCL initially mixed with the epoxy monomer are given in Table 2 as the mass ratios of the two components ($m_{\text{epoxy}}:m_{\text{PCL}}$), and the volume fractions of PCL determined after addition of the DDS, ϕ_{PCL} . This last is in each case given for the liquid blends, assuming a density of 1.145 g/cm³ for the PCL and a density of 1.34 g/cm³ for the epoxy-DDS. These blends were then used for composite production. The glass fibre reinforcement was a woven twill 2x2 E-glass fabric, with a nominal areal weight of 390 g/m², 6 end/cm for warp fibres and 6.7 picks/cm for weft fibres, fibre diameter of 9 µm, yarn thickness of 0.45 mm, warp tex of 68x5 and weft tex of 272, from *Suter-Kunststoffe AG*. The obtained fibre volume fractions within each composite are also given in Table 2. Finally, glass lamellae (*Assistent*) made of soda lime glass were used as bulk glass for nanoindentation tests.

2.2. Samples preparation and processing

The three types of composite plates were processed by Vacuum Assisted Resin Infusion Moulding (VARIM). Sixteen layers of fibre reinforcement were cut in 210x180 mm rectangles and stacked with a sequence of $[(+45/-45)/(0/90)_2/(+45/-45)]_4$. A target fibre volume fraction (V_f) of 50 vol% and a final plate thickness of 5 mm were sought. The preforms to be infused were prepared following the lay-out as depicted in Figure 1. A release film (Cytec, 15 μm , non-perforated) was placed between the two central plies to form the crack which was the starting point for the delamination in Mode I (DCB) samples. The used design was already determined in our previous study [4] as optimum for the VARIM process considering that the film is resin proof and therefore confines the flow of resin.

Blends of epoxy and PCL were prepared with the compositions indicated in Table 2 and following a similar procedure to that of *Luo et al.* [11] and our previous study [10]. The liquid epoxy and the PCL pellets were first melt-mixed at 120 °C for 1h by stirring mechanically (100 rpm) with a four-blade propeller. After 1 hour, the temperature and stirring rate were increased to 140 °C and 400 rpm respectively, before slowly adding the DDS (in powder form) to the mixture. When the mixture became transparent, it was degassed at 120 °C for 20 min and infused into the composite in an oven set to 140°C, which ensured a viscosity below 1 Pa·s for the blend containing the highest PCL content (determined by a plate rheometer AR 2000 from *TA Instrument*). The plates then underwent a curing treatment at 180°C for 3h, which previously showed full resin polymerization [10]. DCB samples were cut out of the plates (following the dimensions shown in Figure 1) using a *Maïco* saw equipped with a diamond blade. For each sample, the weight was recorded, the thickness measured in 3 points, averaged and the fibre volume fraction calculated.

2.3. Morphological characterization

In situ observations of the morphology during cure were performed using a transmission optical microscope (*Olympus BX-60*) equipped with a hot-stage held at 180 °C (*Linkam THMS600/Linkam TMS92*) on drops of the as-prepared blends, containing few glass fibres and inserted between two glass cover-slides immediately after degassing. The assembly was placed directly onto the hot-stage and images were taken every 20 seconds until complete reaction. Transverse cuts of the cured composite specimen were embedded in *Epofix* Resin, polished until 1 μm size diamond disc polishing, and observed

with a reflexion optical microscope (*Olympus BH-2*). Fracture surface of the DCB specimens, coated with 10 nm of gold, were also observed by scanning electron microscopy (SEM, *Philips XLF-30 FEG*).

2.4. Thermomechanical characterization

2.4.1. Differential scanning calorimetry (DSC)

From the cured composite specimens, 5-10 mg samples were extracted and subjected to DSC (*TA Q100, TA Instruments*) heating scans from -90 to 300 °C at 10 °C/min followed by cooling to 0 °C at the same rate.

2.4.2. Dynamic mechanical analysis (DMA)

35×12.5 mm² rectangles were cut from the cured composite specimens to perform the DMA measurements in single-cantilever mode (*TA Q800, TA Instruments*). The temperature was ramped from -150 to 300 °C at 6 °C/min, using a frequency of 1 Hz, a displacement amplitude of 15 µm and assuming a Poisson's ratio, ν , of 0.4 in calculating E' from the bending stiffness.

2.4.3. Flexural tests

Three point bending tests, following the ASTM standard D790 [24], were performed on *Plain* and *PCL(25)* samples at room temperature only, using 96×13 mm² coupons cut from the cured composite specimens. Tests were performed using a Universal Testing Machine (UTM, Walter & Bai AG, Switzerland) equipped with a 10 kN load cell. A span-to-depth ratio of 16:1 was used, corresponding to a span of 80 mm and a cross-head speed of 2 mm/min. At least 8 samples were tested per system. Notice that 2 samples were cut larger in order to reach a span-to-depth ratio of 32:1 and confirm the validity of the results.

2.5. Interfacial Characterisation

Interfacial shear strength on the previously polished specimens was determined by means of nanoindentation tests (Nanoindentation Tester NHT², *Anton Paar*) with a Berkovich diamond indenter ($\alpha=65.3^\circ \pm -0.3$) at fibre locations. Loading and unloading rates were set to 200 mN/min with a pause of 5 s whereas the maximum load was set to 100 mN. This maximum load was sufficient to ensure entire debonding of the largest fibres (determined through increasing load step tests). At least 50 measurements were performed per sample. The data reduction scheme for interfacial shear strength determination followed the procedure developed by Kharrat *et al.* [25] and Zidi *et al.* [26] assuming that the

displacement during the indentation test, u , is the sum of two independent contributions: (i) the displacement u_{ep} due to the elasto-plastic indentation of the fibre surface by the indenter (this component is determined from the indentation behaviour in a bulk material having the same composition as the fibre, i.e. soda lime glass in the present work); (ii) the displacement u_0 of the fibre surface due to the fibre compression into the matrix and the matrix deflexion. Interfacial shear strength between the fibre and the matrix is therefore found from the curve of indentation stress versus $u_0 = u - u_{ep}$, which can be fitted with the two following equations:

$$u_0 = \frac{\sigma_0}{nE_f} \quad \text{when } \sigma_0 \leq \sigma_d \quad (1)$$

$$u_0 = \frac{1}{2nE_f} \left(\frac{\sigma_0^2}{\sigma_d} + \sigma_d \right) \quad \text{when } \sigma_0 > \sigma_d \quad (2)$$

where σ_0 is the stress on the fibre, σ_d the stress at debonding, n the packing parameter and E_f the fibre Young's modulus. Knowing the radius of the indented fibre, r_f , the load P_0 at each displacement u_0 and E_f , n can be determined from Eq. (1). By using then Eq. (2), σ_d and therefore the load at debonding, P_d , can be determined and used to finally calculate the interfacial shear strength:

$$\tau_s = \frac{nP_d}{2\pi r_f^2} \quad (3)$$

The packing parameter can also be theoretically evaluated, using the analysis proposed by Desaegeer [27]:

$$n^2 = \frac{2E_m}{E_f(1 + \nu_m) \ln \left(\frac{2\pi}{\sqrt{3}V_f} \right) \pi r_f^2} \quad (4)$$

where E_m is the Young's modulus of the matrix, ν_m the Poisson's ratio of the matrix and V_f the local fibre volume fraction. Notice that we consider here only the indentation loading portion, which is sufficient in the interfacial shear strength determination (further details on the unloading portion fitting are provided in [26]).

An example (for a *Plain* sample) of this approach is provided in Figure 2 where Eqs. (1) and (2) demonstrated appropriate fitting of this system. Notice that the load at debonding (P_d) can also be defined as the deviation between the linear and non-linear part of the reduced curve (but its determination was

here performed through Eq. (2)). Also shown on this figure is the corresponding indented fibre image (taken through optical microscopy) where the black circle around the fibre demonstrates its debonding.

2.6. Mode I Double Cantilever Beam Testing

The fracture behaviour of the prepared samples was assessed in Mode I Double Cantilever Beam (DCB) following the ASTM standard D5528 [28] and using the UTM, equipped with a 10 kN load cell. The stacking sequence was $[(+45/-45)/(0/90)_2/(+45/-45)]_4$, different from the ASTM standard in order to test a 45° interface, but keeping similar stress and strain intensities as required in the standard. For load introduction, aluminium blocks were glued on each side of the samples using Spabond resin cured with Spabond adhesive non-pigmented hardener purchased from *Gurit* (5 minutes curing at room temperature). Each sample underwent four loading-unloading cycles, the first one corresponded to the test of the *virgin* specimen, whereas the three others applied to the *healed* specimens each after a thermal mending cycle of 30 minutes at 150°C , i.e. the healing ability was tested three consecutive times. In each cycle, loading was performed until displacement reached 30 mm before unloading at the same speed of 4 mm/min until the load reached zero. At least 7 tests were performed for each batch. During thermal mending, samples were left as unloaded, with only the crack faces imposed to be in contact at the location of the loading blocks, leading to a maximum crack thickness of nearly 100 μm .

A typical load-displacement curve with the loading-unloading cycles of the *virgin* and *healed* specimens is depicted in Figure 3. Healing efficiency was first estimated by comparing the slope during loading of the *healed* specimen ($\text{slope}_{\text{load,healed}}$, after thermal mending) to the slope during loading ($\text{slope}_{\text{load, virgin}}$, 100% efficiency) and unloading ($\text{slope}_{\text{unload, virgin}}$, 0% efficiency) of the *virgin* specimen. The efficiency was therefore defined, in this stiffness based calculation, as:

$$\eta = \frac{\text{slope}_{\text{load,healed}} - \text{slope}_{\text{unload, virgin}}}{\text{slope}_{\text{load, virgin}} - \text{slope}_{\text{unload, virgin}}} \quad (5)$$

In addition, interlaminar fracture toughness, G_{IC} , was calculated based on crack length measurements (Modified Beam Theory) [28] and therefore a second way of characterising healing efficiency was defined as:

$$\eta = \frac{G_{IC, \text{healed}}}{G_{IC, \text{virgin}}} \quad (6)$$

3. Results and Discussion

3.1. Microstructural development in the blends

Microstructural development of the composites during curing was assessed by hot-stage microscopy observations. Figure 4 shows typical images for *PCL(25)* at a nominal temperature of 180°C and for different times until complete polymerization of the structure. White lines are fibres whereas the black circle is a bubble trapped in between the glass slides. Even though the fibres seemed to serve as nucleation sites for the particles during cure (see Figure 4 at 22 minutes, where a layer of epoxy phase forms preferentially around the fibres), phase separation upon polymerization of epoxy-PCL blends (i.e. particle distribution) was overall not influenced by the presence of fibres in the cured state (see Figure 4 at 46 minutes). At full cure (46 minutes), a thin layer of epoxy could be observed around the glass fibres. This behaviour, explained previously by *Turmel and Partridge* [29] in similar systems, is attributed to preferential wetting of the epoxy on the fibres, and therefore prevented the creation of an interface between the glass fibres and the continuous PCL phase. Notice that the range in particle diameters was similar to what was observed in our previous study [10].

The phase-separated microstructure was further assessed in presence of high fibre volume content. Transverse cuts of the cured samples are shown on Figure 5, and for each image, the corresponding schematic structure is shown on the right. The quality of the composite through the VARIM process can be first highlighted as no porosities were observed (notice that the black regions in the composites with epoxy-PCL blends (Figure 5 (b) and (c)) were due to polishing artefacts, corresponding to the removal of softer PCL regions). In the *PCL(25)* composition (Figure 5 (b)), the matrix showed a two phase structure (epoxy particles with a surrounding matrix) only where larger spaces existed in the composite, i.e. in between the plies in the resin rich regions. In these fibre-reinforced composites, phase separation was thus limited within the fibre tows, leading to a different structure between (phase separated) and within (continuous epoxy phase) tows. This behaviour was confirmed by the measurement of epoxy particle diameters, which were of $12.60 \pm 3.66 \mu\text{m}$ in the resin rich region, greater than the distance between two fibres within a tow. This measured diameter was smaller than what has been measured in our previous study [10] for neat resin systems ($20.14 \pm 4.75 \mu\text{m}$), indicating that phase separation started later due to the presence of fibres, even though these served as nucleation sites. Indeed, as the fibres were covered by a layer of epoxy, the blend equilibrium in the resin rich region might have been shifted, which delayed the

start of phase separation due to the curved shape of the spinodal curve on the system phase diagram [10]. This statement is further confirmed by the variability in particle sizes and the higher concentration of small particles at the edges of the resin rich region, close to the glass fibres. In the *PCL(37)* composition (Figure 5 (c)) however, phase separation could be observed between and within tows of the composite. As epoxy particle diameters were $3.55 \pm 1.05 \mu\text{m}$ in this case, particles could fit between fibres within tows. Notice again that this mean diameter was slightly smaller than what has been measured in neat resin systems ($7.36 \pm 1.58 \mu\text{m}$), therefore confirming the later start of phase separation in presence of fibres. Even though phase separation was present within tows of the *PCL(37)* composition, a continuous epoxy layer could be observed around the glass fibres, demonstrating again preferential wetting of the epoxy phase [29]. Overall, the matrix phase separation, albeit constrained by the fibres, proceeded similarly to neat resins [10,11], leading to similar morphological developments.

3.2. Thermomechanical properties

Figure 6 shows DSC heating scans for the different samples after cure. Two characteristic transitions were highlighted: (i) the endothermic peak at about 54°C corresponded to the PCL melting (not present for the *Plain* sample); (ii) the small enthalpy peak at about 197°C was associated with the epoxy glass transition. These transition temperatures were similar to those of the pure PCL and pure epoxy (see our previous study on neat systems [10]), indicating a high degree of phase purity. Notice also that the lack of exothermic reaction indicated that the obtained composites were in a fully cured state. The presence of fibres therefore did not induce changes in the required curing schedules of the matrix blends determined in our previous study [10].

Traces of the bending storage modulus, E' , and the loss tangent, $\tan \delta$, as determined by DMA experiments, are shown as a function of temperature on Figure 7. Again, the characteristic transition temperatures (PCL glass transition and melt as well as epoxy glass transition) are invariant for the three assessed samples, indicating high degree of phase purity. More interesting are the obtained properties at room temperature and at the targeted healing temperature, 150°C . At room temperature, a decrease in E' from 6.6 to close to 6.3 GPa was observed as the PCL content varied from 0 to 25vol% in the matrix, indicating a nearly constant modulus between these two compositions thanks to the interconnectivity of the epoxy particles, as previously observed in neat resins [10]. Increasing further the PCL content (to 37vol% in the matrix) led however to a higher modulus decrease, down to 4.6 GPa, because at higher

PCL content, the particle size and interconnectivity are lowered as already stated in our previous study [10]. At 150 °C, E' decreased from about 5.5 GPa for the *Plain* sample to about 3.7 GPa for *PCL(25)* and about 1.5 GPa for *PCL(37)*, reflecting the molten state of the PCL. However, at that temperature, the composite samples behaved globally as stiff elastic solids with no significant dimensional instabilities, indicating that the contacts between the epoxy particles were sufficient to maintain structural integrity, even at the healing temperature. DMA measurements are however not fully sufficient to quantify bending stiffness and strength of the tested samples. Three point bending tests were thus performed on *Plain* and *PCL(25)* samples at room temperature only. These tests revealed bending moduli of 15.99 ± 1.24 GPa and 15.30 ± 0.63 GPa for respectively *Plain* and *PCL(25)* samples, and flexural strengths of respectively 389.68 ± 31.75 MPa and 349.89 ± 26.74 MPa. At room temperature, stiffness and strength for *PCL(25)* are thus almost similar to *Plain*, again demonstrating the preservation of structural integrity while using such modified composites relevant load cases.

3.3. Interfacial Shear Strength determination

Interfacial shear strength (IFSS) between fibres and matrix of the assessed composites (Figure 8) has been determined by means of nanoindentation tests. *Plain* samples exhibited a mean IFSS value of 95 MPa, consistent with values reported in literature for similar systems [25–27,30]. While adding PCL to the matrix, the IFSS value decreased to 81 MPa and 76 MPa for *PCL(25)* and *PCL(37)* respectively, indicating lower interfacial properties when PCL was added to the system. As stated in §3.1, the continuous PCL phase in the two phase morphology did not cover the fibres due to preferential wetting of the epoxy phase on glass fibres. Therefore, interfacial shear strength in blend systems was measured between a fibre and its surrounding epoxy phase; the decrease in IFSS values when the PCL content increased originated from the surrounding softer environment taken into account by the n parameter of the data reduction scheme (see Eqs. (1) and (2)). n values being in the present case for *Plain*, *PCL(25)* and *PCL(37)* compositions respectively of 107, 96 and 88 mm^{-1} , the previous statement is confirmed from Eq. (4) and the direct proportionality between E_m and n . The results show relatively large standard deviations, even though the data reduction procedure over more than 50 samples reduces this scatter [26], for two main reasons: (i) the variation in fibre diameters ranged from 8 to 14 μm for the present case; (ii) the precision in centring the indenter with each fibre (if the indentation mark was not enough centred (on visual assessment) or if it ran over the fibre diameter, the test was discarded). Notice also that even if the

surrounding fibre environment is taken into account in the model, care was taken in testing fibres in a nearly close packed arrangement, as shown in Figure 2 (b), to avoid further data scatter.

3.4. Mode I Double Cantilever Beam Testing

3.4.1. Fracture properties in the virgin state

Figure 9 shows fracture toughness mean values for the three types of composites. Even though a $\pm 45^\circ$ interface was tested, the toughness value obtained for the *Plain* system (1135 J/m²) was similar to what was measured in previous studies [4]. As compared to this *Plain* system, a decrease of 40% and 58% in fracture toughness was observed for respectively *PCL(25)* and *PCL(37)* systems. This behaviour was directly related to (i) the decrease in IFSS values when increasing the PCL content as the matrix becomes less stiff and more ductile and interfacial debonding between the fibres and the matrix is made easier (see 3.4.3) and (ii) the intrinsic toughness behaviour of the blends where the PCL, which exists as a confined layer between epoxy particles, governs the system's strength, as determined in our previous study [10]. Notice that the dashed line drawn between *Plain* and *PCL(25)* system values may not represent the expected behaviour, because at low PCL contents, the morphology consists of PCL particles embedded into an epoxy matrix, which could probably locally increase fracture toughness [31,32].

3.4.2. Healing efficiency assessment

Multiple healing efficiencies were first determined in terms of stiffness, based on Eq. (5) and are shown for *PCL(25)* and *PCL(37)* on Figure 10 for three healing cycles. Efficiencies for *Plain* samples are not depicted as their value was null, as expected. Notice first that the scatter was relatively high due to the difficulty in crack faces alignment while unloading the sample. Both *PCL(25)* and *PCL(37)* exhibited high potential for recovery in stiffness after thermal healing. After one healing cycle, *PCL(25)* recovered its stiffness by 82% whereas full recovery was observed for *PCL(37)*. Recovery in properties was higher for higher PCL contents, due to the higher expansion capability as more volume of PCL was present. Stiffness recovery was further improved over multiple testing and healing cycles, again due to the expansion capability of the PCL. Efficiencies above 100% could be observed because a propagating crack broke the interconnected particulate morphology which created a new and tougher PCL interface after healing (see section 3.4.3 for evidence of this behaviour on the fracture surface observations).

Multiple healing efficiencies were then determined in terms of toughness, based on Eq. (6) and are shown for *PCL(25)* and *PCL(37)* on Figure 11 for three healing cycles. Efficiencies for *Plain* samples are not

depicted as their value was null, as expected. Both *PCL(25)* and *PCL(37)* exhibited moderate recovery in toughness after thermal healing. Notice first that the scatter was relatively high due to the difficulties in (i) crack faces alignment while unloading the sample and (ii) properly determining the advancement of the crack in the healed state (the thermoplastic often did not wet the entire sample surface). Similar behaviour as for stiffness based calculations could be observed even if the values did not reach 100%. The co-continuous epoxy-PCL morphology was broken during the virgin cycle, which created an interface of only PCL during healing. This PCL interface provided the same initial stiffness but not the same strength and therefore toughness, as concluded in our previous study [10]. Incomplete recovery in fracture toughness could be further understood by comparing the R-curve behaviour during the test with the sample crack thickness during thermal healing (i.e. with the crack faces imposed to be in contact at the location of the loading blocks) (see Figure 12). The R-curve behaviour showed a two-step shape with two values of steady state fracture toughness, not expected from conventional FRPs [33]. A first plateau was observed at low toughness values (50 J/m^2) whereas a second plateau existed at around 250 J/m^2 until reaching again the fracture toughness of the virgin specimen if the crack was further propagated. The crack thickness having been measured after test while leaving the specimen in its healing conditions, it represents the gap to heal within the damaged sample. From the study of Rodgers [23], it was possible to measure the PCL expansion capacity for the used healing temperature (14% at 150°C), and therefore determine the maximum thickness the PCL could fill considering the geometry and PCL content. For the present case, the PCL had the ability to fill a crack of $36 \mu\text{m}$ (for a *PCL(37)* sample, this value was $53 \mu\text{m}$), which corresponded to the value where the second steady state fracture toughness was observed. This second plateau was therefore representative of the toughness after healing, and lead to the conclusion that incomplete crack filling occurred in the present case. The fact that crack filling was not complete therefore decreased the obtained steady state fracture toughness due to different stress states as compared to samples where crack filling would be complete.

3.4.3. Fracture surface considerations

Fracture surface analysis was performed on the modified composites in the damaged state after 1, 2 and 4 testing cycles. The fracture surface for a *PCL(25)* specimen (Figure 13 (a)) after the first fracture testing cycle (*virgin*) indicated that failure has been dominated by interfacial debonding between the fibres and the matrix. This mechanism of delamination between fibre bundles and their surrounding matrix has been observed previously in many cases [3,4,34] for woven composites. Even though the matrix consisted of

epoxy particles surrounded by a PCL matrix, there was evidence of epoxy interfacial debonding in addition to PCL cohesive failure (indicated by the arrows on Figure 13 (a)). As demonstrated in section 3.1, glass fibres were covered by a thin layer of epoxy due to preferential wetting during microstructural development, thus this interface ruptured during crack opening. Figure 13 (b) depicts the fracture surface of a *PCL(25)* specimen, after one healing cycle. Observations were performed in the resin rich regions, characterised by the presence of the phase separated particulate morphology (at the intersection of fibre bundles). Whereas interfacial debonding could be observed (in the central region of Figure 13 (b)), as in the case after a *virgin* cycle (Figure 13 (a)), the surface shows evidence of PCL bleeding with partial coverage, thus explaining healing of the mechanical properties discussed in section 3.4.2. In addition to this central interfacial debonding, three regions, explaining the healing process, could be highlighted (shown with arrows on Figure 13 (b)): (i) *PCL bleeding* showed glass fibres recovered by PCL, (ii) *Trace of virgin fracture* showed epoxy interfacial debonding created during the *virgin* cycle but now covered by PCL that bled during healing, (iii) *PCL cohesive failure* showed evidence of PCL fracture after having healed the surface. These three regions thus highlighted evidence of PCL bleeding and surface coverage, however, as PCL cohesive failure could be observed only partially on the surface, PCL crack bridging could not proceed on the entire fracture surface (due to the limited PCL expansion capacity), explaining the partial toughness recovery observed in section 3.4.2. While in the first fracture testing cycle (Figure 13 (a)) epoxy interfacial debonding was dominant, PCL cohesive failure was dominant after the second fracture testing cycle (Figure 13 (b)) which could explain efficiencies higher than 100% observed in the stiffness based calculation as the crack has been propagated on an interface consisting now only of PCL. Figure 13 (c) finally shows the fracture surface of *PCL(37)* after three healing cycles. The higher PCL content for this sample, but also the three performed healing cycles, led to higher PCL coverage on the surface (this evidence is provided by the arrows on the figure showing PCL bleeding as well as large areas of PCL cohesive failure) as well as to smaller particles as compared to Figure 13 (b). In addition, the dispersion in epoxy particle sizes due to the influence of fibres on the phase separation process could be observed, as for optical microscopy shown in Figure 5. The higher coverage in PCL for this case also explained the higher efficiencies in terms of stiffness as well as toughness based calculations.

4. Conclusion

Glass fibre reinforced epoxy-PCL composites with fibre volume fractions around 50vol% were successfully processed through Vacuum Assisted Resin Infusion Moulding at elevated temperature. Due

to preferential wetting of the epoxy on the glass fibres, these were recovered by a small layer of epoxy, and not by the expected PCL phase. While phase separation and development of the epoxy particulate morphology could happen in the resin rich regions of the reinforcement, it was completely prevented within the fibre tows due to space constraints when epoxy particle diameters were higher than the mean distance between two fibres within tows. These space constraints were observed as less critical for higher PCL contents as diameters of the epoxy particles were smaller, which allowed particles to be inserted within fibre tows. Even though each individual fibre was surrounded by a thin epoxy layer, interfacial shear strength decreased with the increase in PCL content because of the surrounding softer environment in the phase separated epoxy-PCL matrices.

The presence of PCL in the composites did not lead to a significant difference in room temperature storage modulus, flexural modulus and strength, as compared to *Plain* systems, whereas Mode I DCB tests revealed a large decrease in toughness when PCL was added to the system. This decrease was attributed to the decrease in interfacial shear strength values and by the intrinsic fracture toughness of the blends where the PCL is present as a confined layer in between the epoxy particles, as determined in our previous study [10]. Mode I DCB testing further allowed the determination of the healing efficiencies in terms of stiffness and toughness over several cycles. For both composites modified by PCL, higher efficiencies were observed for higher PCL contents as well as for a higher number of healing cycles due to the higher PCL coverage (thanks to its ability to bleed and expand within the crack) on the samples fracture surface during healing. In terms of toughness, efficiencies obtained were lower due to incomplete crack filling affecting the R-curve behaviour.

Even though phase separation was affected by the presence of fibres in composites, it can be concluded from the present findings that 25vol% of PCL within the matrix provides suitable healing efficiencies without any deterioration in modulus or strength of the composite. However, toughness is considerably decreased by the presence of PCL due to its lower intrinsic strength. This model system thus demonstrates the feasibility and interest of processing self-healing composites based on this concept. When high toughness in virgin state is required for a given application, a thermoplastic phase with higher strength would be more suitable, provided that it can also create a phase separated morphology and has the ability to provide healing of a crack within fibre reinforced polymer composites, using moderate healing temperatures. Finally, this model system, providing that its strength competes with reference epoxy

systems, is promising for healing damage events such as low energy impacts where matrix cracks dominate.

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6. References

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Figure 1: Schematic top view of the VARIM lay-out, including the fibre preform (grey), the flow medium (grey mesh), the release film (blue), the inlet and outlet lines. Note that the release film lies on the eighth ply, but is shown at the top for clarity. The geometry of DCB samples is also showed. Dimensions are in mm. Adapted from [4].

Figure 2: Indentation test on a *Plain* sample: (a) Determination of the reduced curve from the initial indentation curve and that in a soda lime glass, fitted with Eq. (1) for the linear part and Eq. (2) for the non-linear part. Unloading portions of the tests are not shown for clarity; (b) corresponding indentation imprint on the fibre.

Figure 3: Typical loading and unloading cycles for a DCB test in the virgin state and in the healed state (here shown for a specimen in the PCL(37) batch).

Figure 4: Evolution of the microstructure of *PCL(25)* in presence of glass fibres as a function of cure time at a nominal temperature of 180 °C.

Figure 5: Transverse cut of the three assessed samples: (a) *Plain*; (b) *PCL(25)*; (c) *PCL(37)*. A schematic of the structure is drawn on the right of each image.

Figure 6: DSC heating scans for the different samples after cure.

Figure 7: E' and $\tan \delta$ as a function of temperature for the three assessed samples: *Plain*, *PCL(25)* and *PCL(37)*.

Figure 8: Interfacial shear strength for the three assessed systems.

Figure 9: Fracture toughness as a function of the PCL volume fraction in the matrix.

Figure 10: Multiple healing assessment in terms of stiffness based calculation for *PCL(25)* and *PCL(37)*.

Figure 11: Multiple healing assessment in terms of toughness based calculation for *PCL(25)* and *PCL(37)*.

Figure 12: Crack thickness as a function of the crack length during healing of a *PCL(25)* sample, superimposed with its R-curve behaviour in the healed state.

Figure 13: SEM image of a DCB fracture surface for (a) *PCL(25)* specimen after a virgin cycle; (b) *PCL(25)* after one healing cycle and (c) *PCL(37)* after three healing cycles.

Table 1: Mechanical properties of pure epoxy and of its blend with 25 vol% of PCL, both cured with DDS [10]. Notice that 150°C is the system healing temperature. Numbers in brackets show standard deviations.

Material	E' [GPa] at 25°C	Drop in E' at 150 °C [%]	$\sigma_{\max}$ [MPa] at 25°C	K_{IC} [MPa·m ^{1/2}] at 25 °C
Pure epoxy	2.59 (0.01)	30.50	78.89 (14.06)	1.45 (0.38)
Epoxy-PCL(25vol%)	1.58 (0.07)	80.38	16.02 (1.15)	0.70 (0.25)

Table 2: Specimen designations and the corresponding mass ratios of epoxy resin to PCL, and the overall PCL volume fractions after addition of the DDS. Fibre volume fraction obtained after composite production is also given.

Specimen	epoxy to PCL	PCL volume fraction in matrix [%]	Fibre volume fraction in sample [%]
	$m_{\text{epoxy}}:m_{\text{PCL}}$	ϕ_{PCL}	V_f
Plain	100:0	0	47.1±0.6
PCL(25)	72:28	25.0	50.1±0.2
PCL(37)	59.5:40.5	36.9	48.1±1.8