Thermal mending in immiscible Poly(ϵ -caprolactone)/epoxy blends

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Abstract. Blends of commercial epoxy monomer with a 4,4'-diaminodiphenylsulfone hardener and poly(ϵ -caprolactone) (PCL) were evaluated for their potential as a self-healing matrix for fiber-reinforced composites, based on their room temperature toughness and stiffness and their capacity for healing when subjected to a moderate heating cycle. Analysis of the microstructure and thermal properties of the blends indicated three types of morphology to result from polymerization-induced phase separation during cure, depending on the PCL content, including an interconnected particulate epoxy phase and a co-continuous PCL phase above 23vol% PCL. While the mechanical performance diminished with increasing PCL content, toughness recovery after healing at 150 °C for 30 min strongly increased. Blends with 25vol% PCL showed a healing efficiency in excess of 70 %, while retaining suitable room-temperature mechanical properties (a tensile modulus of 1.5 GPa and a tensile strength of about 20 MPa), and were concluded to be promising candidates for self-healing composites.

Keywords: self-healing materials, PCL, toughness, stiffness, phase separation, phase diagram

1. Introduction

Considerable effort has been made over the last 25 years to integrate self-healing functionality into thermoset polymers for the autonomous repair of sub-critical damage. Many current approaches to self-healing are based on incorporation of capsules or vascular systems that release a healing agent in the presence of a crack. The healing agent may be a reactive monomer that polymerizes on contact with a catalyst present in the polymer, for example, thus healing the crack, or a solvent capable of activating residual reactive groups within the polymer itself [1,2]. An alternative strategy is to prepare a miscible [3,4] or immiscible [5–7] blend between the thermoset and a low melting point semicrystalline thermoplastic. For immiscible blends in particular, healing involves the following concurrent mechanisms, whose effectiveness requires damage to propagate through the thermoplastic phase or along the interface between the thermoplastic and the thermoset:

- melting and consequent volume expansion of the thermoplastic;
- flow of the thermoplastic melt into the damage zone;
- physical or chemical healing at the molecular level.

The precise nature of the healing mechanism depends on the system in question and may involve either thermally activated re-establishment of entanglements across the crack faces or the re-establishment of reversible

non-covalent (e.g. hydrogen- or ionic) bonds. This type of healing is repeatable and latent, in so far as it implies the recovery of thermodynamic equilibrium in the thermoplastic phase. However, it is also possible in some cases to achieve thermal mending through reversible covalent bonding in modified thermoset matrices, as first demonstrated by Chen et al. [8].

Immiscible thermoplastic-thermoset blends generally show two limiting morphologies depending on their respective concentrations: (i) a particulate thermoset phase embedded in a thermoplastic matrix (e.g. [5]) or (ii) a particulate thermoplastic phase embedded in a thermoset matrix (e.g. [6,7,9]). Morphology (i) is usually obtained by polymerization-induced phase separation (PIPS) from an initially miscible blend of a thermoplastic and the uncured thermoset resin, while morphology (ii) is typically associated with mechanical mixing of a fully immiscible system, in which the thermoplastic is the minority component. However, PIPS may also give rise to a range of co-continuous morphologies at intermediate compositions, particularly in the vicinity of the critical point (see section 3.1.2) [10]. It follows that the mechanical properties may vary significantly for a given overall composition, depending on the relative stiffness and strength of the continuous and discrete phases, and the mechanisms of energy dissipation during crack propagation.

Of particular interest for thermal healing are blends in which the thermoset resin forms a network of interconnected particles, whose interstices contain a continuous thermoplastic phase that shows significant self-diffusion (reptation) at moderate temperatures, but adequate thermal stability under service conditions. Thermoplastics that have been demonstrated to show this type of morphology when combined with epoxy thermoset resins include polycaprolactone (PCL) [5,11–20], poly(ether sulfone) [21–23], polyetherimide [24–27], poly(methyl methacrylate) [28–30] and polystyrene [28–30]. The potential of PCL for the thermal healing of epoxies stems from its low melting temperature (55 °C) and high degree of thermal expansion (an increase in volume by up to 14 % between room temperature and 150 °C [31]), and it has also been demonstrated to be of interest for shape-memory assisted self-healing [32,33].

The phase behavior of epoxy-PCL blends has been widely reported in the literature. It is known, for example, that PCL becomes immiscible with certain anhydride-cured epoxy resins during polymerization, but typically remains fully miscible with amine-cured epoxy resins up to full conversion of these latter. This difference in miscibility is attributed to the presence of hydroxyl groups in the amine-cured epoxy, which are capable of forming hydrogen bonds with the ester groups of the PCL [11,12]. PIPS has nevertheless been observed in epoxy-PCL blends cured with the diamines diethyltoluenediamine (DETDA) and 4,4'-diaminodiphenyl sulfone (DDS), and the dependence of the morphology of DDS-cured epoxy-PCL blends on composition and cure temperature has been described in some detail by Chen and Chang [13,14].

The self-healing of phase-separated DDS-cured epoxy-PCL blends was evaluated by Luo *et al.* [5], who obtained an interconnected epoxy-rich particulate phase at PCL contents at and above 15.5 wt%. The interconnected epoxy particles were considered to act as “bricks” for load bearing, while the thermoplastic PCL “mortar” present in the interstices enabled thermally actuated self-healing of fractured specimens. However, although these authors investigated morphological and thermomechanical properties over a relatively wide range of compositions, they only considered self-healing in blends containing 15.5 wt% PCL. The extent of healing was assessed using single edge-notched beam (SENB) specimens fractured in three-point bending. The crack faces

were held together for 8 min at 190 °C, in some cases using an axial compressive load to promote crack closure. The healing efficiency was defined as the ratio of either (i) the maximum load or (ii) the area under the load-displacement curve up to the maximum load, measured in bending tests on the healed specimens, to the respective values obtained from bending tests on the virgin specimens. It was found that healing efficiencies of more than 100 % could be achieved on application of the axial compressive load, and scanning electron microscopy (SEM) indicated that this was due to “differential expansive bleeding” of the PCL during heating, i.e. bleeding of molten PCL from the fracture surface, owing to its high degree of thermal expansion relative to that of the cured epoxy. The self-healing behavior of PCL has been further combined by Wei *et al.* [34] with an epoxy based shape memory polymer, which enabled to fully close cracks during healing. Finally, to improve mechanical properties of epoxy-blends, Zhang *et al.* [35] introduced vapor-grown carbon nanofibres which increased tensile strength and toughness by respectively 2.15 and 1.38 times for the targeted healing epoxy-PCL composition while keeping 78% recovery in bending strength.

In the present study we have investigated phase separation, mechanical properties and the self-healing capacity of immiscible PCL blends with a commercial DDS-cured epoxy over a relatively wide range of PCL contents compared with previous studies, and using a relatively mild healing temperature. Because our ultimate aim is to use such blends as a matrix for self-healing fiber-reinforced composites, it was considered important to choose a reference epoxy formulation and cure conditions leading to an optimum combination of toughness and stiffness. Using such blends as a matrix in fiber-reinforced composites is believed to: (i) provide autonomous healing functionality (thanks to PCL expansion within the cracks) that is absent in many intrinsically self-healing systems; (ii) provide similar stiffness and toughness to conventional epoxy formulations; (iii) allow the use of a relatively low healing temperature so that the overall mechanical integrity of the system is maintained during the healing cycle. The influence of PCL content and phase morphology on the mechanical performance of the epoxy was assessed through static and dynamic tests on un-notched specimens, and static fracture tests using the tapered double cantilever beam (TDCB) geometry. TDCB specimens were then used to investigate the self-healing capacity of the blends after thermal cycling to 150 °C for 30 min.

2. Materials and methods

2.1. Materials

Epon™ 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 used throughout the present work unless specific reference is made to comparative tests using DGEBA (Sigma Aldrich) with the same molar mass but a reduced molar mass per epoxide group (172-176 g/eq, as in reference [5]). The resin was blended with different amounts of PCL (number average molar mass, $M_n \approx 45,000$ g/mol, Sigma Aldrich) (Table 1) 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 (see section 2.2 below) are given in Table 1 as the mass ratios of the two components ($m_{\text{epoxy}}:m_{\text{PCL}}$), and the weight and volume fractions of PCL determined after addition of the DDS (m_{PCL} and ϕ_{PCL}). ϕ_{PCL} 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.

Table 1: Specimen designations and the corresponding mass ratios of epoxy resin to PCL, and the overall PCL weight and volume fractions after addition of the DDS.

Specimen	epoxy to PCL	PCL weight fraction [%]	PCL volume fraction [%]
	$m_{\text{epoxy}}:m_{\text{PCL}}$	m_{PCL}	ϕ_{PCL}
Epoxy-PCL(0)	100:0	0	0
Epoxy-PCL(1.7)	98:2	1.5	1.7
Epoxy-PCL(8.7)	90:10	7.5	8.7
Epoxy-PCL(13.1)	85:15	11.5	13.1
Epoxy-PCL(17.7)	80:20	15.5	17.7
Epoxy-PCL(19.5)	78:22	17.1	19.5
Epoxy-PCL(21.3)	76:24	18.8	21.3
Epoxy-PCL(23.2)	74:26	20.5	23.2
Epoxy-PCL(25.0)	72:28	22.2	25.0
Epoxy-PCL(26.9)	70:30	23.9	26.9
Epoxy-PCL(46.2)	50:50	42.3	46.2
Epoxy-PCL(66.7)	30:70	63.1	66.7
Epoxy-PCL(100)	0:100	100	100

2.2. Preparation of the blends

Blends of PCL and epoxy were prepared with the compositions indicated in Table 1 following a similar procedure to that of Luo *et al.* [5]. The liquid epoxy and the PCL pellets were first melt-mixed in glass jars at 120 °C by mechanical stirring at 100 rpm for 1 h with a three-blade propeller (Caframo, Canada, 1", 5/16" bore). After 1 h, the temperature was increased to 140 °C, the stirring rate was increased to 400 rpm, and DDS (in powder form) was slowly added to the mixture. When the mixture became transparent, it was degassed at 120 °C for 20 min. The degassed blend was then cast immediately into hot silicone molds (Elastosil M4670) and cured at 180 °C for 3h, which was sufficient to ensure complete reaction at all the compositions investigated.

2.3. Morphological characterization

In situ observations of the morphology during cure were made on drops of the as-prepared blends inserted between two glass cover-slides immediately after degassing, using a transmission optical microscope (Olympus BX-60) equipped with a hot-stage held at 180 °C (Linkam THMS600/Linkam TMS92). The specimen was placed directly onto the hot-stage and images were taken every 20 seconds in order to determine the time for the onset of phase separation. The composition of the phases in selected blends was also assessed using Fourier transform infrared (FTIR) microscopy of polished sections (Perkin Elmer Spotlight 200 FTIR Imaging System)

Transmission optical microscopy (Olympus BH-2) of roughly 10 µm thick microtomed sections (Reichert-Jung Ultracut E/Diatome diamond knife) was used order to the estimate the mean diameters of the particulate inclusions (50 measurements per image). The same specimens were also observed by scanning electron microscopy (SEM, Philips XLF-30 FEG), for which they were first fractured in liquid nitrogen, treated with chloroform (Sigma Aldrich) where required in order to etch away the PCL, and then gold-coated.

2.4. Thermomechanical characterization and healing tests

2.4.1. Differential scanning calorimetry (DSC)

5-10 mg samples from the cured specimens were subjected to DSC (TA Q100, TA Instruments) heating scans from -90 to 300 °C at 10 K/min followed by cooling to 0 °C at the same rate. For *in situ* investigations of the cure rates, 10-15 mg samples taken from the blends immediately after degassing were maintained at 180 °C for 3 hours.

2.4.2. Dynamic mechanical analysis (DMA)

For the DMA measurements (TA Q800, TA Instruments) 35×12.5×2 mm³ strips were cut from the cast specimens (the dimensions were reproduced by grinding to a precision of ±0.05 mm). Tests were performed at 1 Hz in single-cantilever mode, with a displacement amplitude of 15 µm and assuming a Poisson's ratio, ν , of 0.4 in calculating E' from the bending stiffness. The temperature was ramped from -150 to 300 °C at 6 °C/min. Transition temperatures were defined as the temperatures corresponding to the peaks in $\tan \delta$ and each material was tested in triplicate.

2.4.3. Tensile testing

Tensile tests were carried out following the ASTM standard D638, type V samples [36] using a Universal Testing Machine (UTM, Walter & Bai AG, Switzerland) equipped with a 20 kN load cell. The extensometer gage length was set to 10 mm and the crosshead speed was 1 mm/min. The ends of the specimens were polished in order to avoid slippage in the grips and at least five specimens were tested for each composition.

2.4.4. Tapered double cantilever beam (TDCB) testing

The fracture toughness of the cured blends was evaluated from long-groove TDCB specimens using the UTM, equipped with a 1 kN load cell. The TDCB test geometry is convenient because precise measurements of the crack length are not needed for the characterization of the fracture toughness of linear elastic specimens [37,38] and it is currently widely used to quantify the healing efficiency of a variety of materials [39]. However, while TDCB testing is popular for the investigation of self-healing in microcapsule-based systems, its application to thermal mending systems is less frequently reported [9,10].

The TDCB specimens were prepared using the geometry and three-step procedure described in [40]. (1) EponTM 828EL mixed with diethylenetriamine (DETA, Sigma Aldrich) in the stoichiometric mass ratio 100:12 was cast into silicone molds corresponding to the external dimensions of the TDCB specimens, with a silicone spacer placed along the center of the mold in line with the molded-in starter notch. The Epon/DETA mixture was left for 1 h at room temperature and then cured at 140 °C for 1 h. (2) The molds were opened to remove the inner spacers, closed again and held at 160 °C for 20 min. (3) The degassed epoxy-PCL blend of interest was then immediately cast into the space left by the spacer, the temperature raised to 180 °C, and the blend allowed to cure for 3 h, providing excellent adhesion with the surrounding cured epoxy. After cure, a sharp pre-crack was created by tapping a fresh razor blade into the starter notch. This procedure allowed us to make optimum use of relatively small amounts of the epoxy-PCL blends.

For the TDCB geometry specified, the plane strain critical stress intensity factor for crack advance is given by:

$$K_{Ic} = \alpha \sqrt{\frac{E_{blend}}{E_{Epon}}} P_c \quad (1)$$

where P_c is the maximum load, $\alpha = 11.2 \cdot 10^{-3} \text{ m}^{-3/2}$ [41] and the factor $\sqrt{E_{blend}/E_{Epon}}$, where E_{blend} is the Young's modulus of the blend insert and E_{Epon} is that of the remainder of the specimen, takes into account the locally modified stiffness in the vicinity of the crack tip [42]. The specimens were deformed in tension with a loading point displacement rate of 5 $\mu\text{m/s}$. Once the crack had propagated over 2/3 of the initial ligament length of the virgin specimens (virgin cycle), the load was released by reducing the displacement at a speed of 20 $\mu\text{m/s}$. The samples were then healed by holding them at 150 °C for 30 min with a constant applied compressive load perpendicular to the crack faces of 0.39 kg (corresponding to about 50 kPa when normalized with respect to the crack area), then retested using the same procedure as for the virgin cycle (healed cycle). The healing efficiency was defined as the ratio of P_c measured during the healed and virgin cycles, respectively:

$$\eta = \frac{P_{c,healing}}{P_{c, virgin}} \quad (2)$$

3. Results and Discussion

3.1. Microstructural development in the blends

3.1.1. Determination of the cloud-point

The time to reach the cloud-point during cure was estimated by hot-stage microscopy for each specimen in Table 1. Figure 1 shows typical images from Epoxy-PCL(21.3) at a nominal temperature of 180 °C, for which the time to reach the cloud-point was estimated to be 26.3 min. Isothermal DSC heat flow curves normalized with respect to the total mass of the epoxy-hardener in the specimen (cf. Figure 2), were used to obtain the degree of conversion as a function of time at the same temperature, by comparing the instantaneous heat of reaction with the total heat of reaction determined from heating scans. A sharp increase in the slope of the heat flow rate curve was typically observed at intermediate times (cf. Figure 2). This was assumed to correspond to phase separation and the consequent increase in the local concentration of the reagents. As seen from Figure 3, the times to phase separate estimated in this way by DSC were comparable with the cloud-point times determined by hot-stage microscopy, although these latter tended to be systematically shorter. This discrepancy was attributed to inaccurate temperature control of the hot stage (recalibration using reference materials indicated that the effective temperature of the hot stage was up to 7 °C less than the nominal temperature in this range). For consistency, therefore, the degrees of conversion corresponding to the cloud-point curves referred to in the following section were determined directly from the DSC curves.

Figure 1: Evolution of the microstructure of Epoxy-PCL(21.3) as a function of cure time at a nominal temperature of 180 °C.

Figure 2: Isothermal DSC heat flow curves at 180 °C for the different blends. The dashed circles indicate the times corresponding to the onset of phase separation.

Figure 3: Time for phase separation determined from DSC heat flow curves (cf. Figure 2) and times to reach the cloud-point determined by optical microscopy as a function of the PCL volume fraction at a nominal temperature of 180 °C.

3.1.2. Phase behavior

PIPS may be described semi-quantitatively using the Flory-Huggins model and a single concentration-independent interaction parameter, χ , to account for the effect of the increase in molar mass on miscibility [43]. In the present case of a ternary blend of a polymeric modifier with an epoxy resin and a diamine hardener, the epoxy-hardener system was treated as a single monodisperse pseudo-component [43] with an initial number average molar mass, $M_n = 315$ g/mol, and no attempt was made to take into account local deviations from stoichiometry during phase separation. The molar volume of this pseudo-component may be estimated from the number average degree of polymerization for a given degree of conversion of the epoxy groups, p , which, for a stoichiometric mixture with a four-functional hardener [43], is assumed to be given by:

$$X_n(p) = \frac{1}{1 - 2p^2} \quad (3)$$

The values of p corresponding to the binodal and spinodal curves were then calculated as a function of PCL content for a given value of χ as described by Williams *et al.* [43], taking the molar volume of the PCL monomer be the reference volume. The results shown in Figure 4 were obtained by adjusting χ to provide an approximate fit to the experimental cloud-point conversion derived from the ratio of the enthalpy at the start of phase separation (as shown in Figure 2) and the total enthalpy of reaction. The PCL volume fraction corresponding to the critical point, where the binodal and spinodal are cotangent, is given by:

$$\begin{aligned} \phi_{crit} &= \frac{1}{1 + (Z_{PCL}/Z_{crit})^{1/2}} \\ Z_{crit} &= \left(\frac{1}{(2\chi)^{1/2} - (1/Z_{PCL})^{1/2}} \right)^2 \end{aligned} \quad (4)$$

where Z_{PCL} is the ratio of the molar volume of the PCL to that of the PCL monomer, which is approximately equal to 394 in the present case ($M_n = 45,000$ g/mol), and Z_{crit} is the reduced molar volume of the reacted pseudo-component corresponding to the critical point. Taking $\chi = 0.12$, the value used for the fit to the data in Figure 4, ϕ_{crit} was estimated to be about 10.3 vol% PCL (i.e. about 9.0 wt%). This should be considered a very rough estimate given the scatter and the lack of any clear trend in the experimental data points in Figure 4, and the various assumptions inherent in the Flory-Huggins approach, e.g. those of a monodisperse system at equilibrium in which stoichiometry is respected throughout and for which χ is independent of composition. However, it provides a convenient basis for the discussion of morphological development in this system.

Figure 4: Estimates of conversions corresponding to spinodal and binodal curves as a function of the PCL volume fraction for $\chi = 0.12$ according to the Flory-Huggins equation, along with experimental data points for the conversion at onset of phase separation.

3.1.3. Blend morphology

As shown in Figure 5(a), three types of morphology were observed by optical microscopy, depending on the PCL content: (i) at concentrations above 23.2 vol% PCL, the morphology consisted of an interconnected particulate epoxy phase and a co-continuous PCL phase, the epoxy particles decreasing in diameter as the PCL concentration increased, as shown in Figure 6; (ii) at concentrations up to 13.1 vol% PCL, the morphology consisted of a continuous epoxy phase with PCL inclusions; (iii) at concentrations between 13.1 and 23.2 vol% PCL, a complex morphology was observed with relatively large co-continuous PCL and/or epoxy domains containing much smaller epoxy and PCL inclusions respectively. This type of morphology is typified by the SEM image in Figure 7 of an etched freeze-fracture surface from Epoxy-PCL(19.5). On the left-hand side of the image, the epoxy forms a discrete particulate phase in a PCL-rich matrix, while on the right hand-side of the image the epoxy is the continuous phase and contains small cavities corresponding to PCL-rich particles removed during etching. Similar morphologies have been reported previously for this composition range [5,13,14,44], and, as shown in Figure 5(b), comparable results were also obtained here when Epon™ 828EL was substituted by the DGEBA used by Luo *et al.* [5], indicating phase separation to be insensitive to the molar mass per epoxide group within this range.

Figure 5: Morphology at different compositions for: (a) Epon™ 828 EL (Momentive) resin; (b) DGEBA (Sigma) resin.

Figure 6: Average epoxy particle diameter in microtomed sections as a function of the PCL volume fraction.

Figure 7: SEM image of Epoxy-PCL(19.5) at the interface between the coarse co-continuous domains visible in the optical micrograph in Figure 5(a) corresponding to the same composition.

The model phase diagram in Figure 4 suggested the critical point to be at about 10 vol% PCL for a reaction temperature of 180 °C, and in the vicinity of the critical point, the spinodal and binodal curves were predicted to be relatively close to each other. The dominant phase separation mechanism in this regime was therefore inferred to be spinodal decomposition rather than nucleation and growth [13]. Also, the shape of the binodal implied phase separation initially into roughly equal volumes of epoxy- and PCL-rich phases for PCL contents around and immediately above that corresponding to the critical point. It follows that co-continuous morphologies should be favored under these conditions. Moreover, the rapid increase in viscosity of the epoxy-rich phase as the conversion increases towards the gel point at $p \approx 0.7$, is expected to stabilize the coarse morphologies resulting from the early stages of phase separation. The decrease in miscibility with further increases in conversion then results in the formation of fine precipitates within the co-continuous domains as seen in Figure 7, and as discussed in detail e.g. by Williams *et al.* [34]. In the present case, co-continuous morphologies were observed in the range 17 to 22 vol% PCL, whereas discrete domains of PCL-rich particles in a continuous epoxy-rich matrix dominated at 13.1 vol% PCL, indicating the PCL content at the critical point to be somewhat higher than predicted from equation 4. This is consistent with previous investigations into similar systems, for which the experimental critical point was reported to be 13.8 vol% PCL [20,44].

3.1.4. Phase composition

Although the model phase diagram in Figure 4 implied high phase purity at equilibrium for high degrees of conversion, the observed microstructures were clearly influenced by kinetic factors. FTIR microscopy was therefore used to investigate the composition of the coarse structure in polished cross-sections from specimens containing 17.7 and 25 vol% PCL (the minimum sample size was 12×12 μm). The absorption spectra in the wavenumber range 1680 to 1780 cm⁻¹ (the carbonyl stretch band characteristic of the PCL) for samples containing 17.7 and 25.0 vol% PCL are shown in Figure 8 along with spectra for the pure epoxy and PCL. The discrete particles present at 25 vol% PCL and also those present in the nominally PCL-rich domains at 17.7 vol% PCL were confirmed to show no absorption in this range, while strong carbonyl peaks were obtained from the surrounding matrix. Even so, the carbonyl peaks tended to be weaker than those obtained from the pure PCL reference specimens, presumably because of the limited lateral and vertical resolution of the FTIR microscope.

Figure 8: FTIR spectra in the carbonyl stretch band (wavenumbers 1680-1780 cm^{-1}) from selected regions of (a) Epoxy-PCL(25.0) and (b) Epoxy-PCL(17.7) blends. Spectra for the pure epoxy and pure PCL are also shown for comparison.

3.2. Thermal transitions in the cured blends

Figure 9(a) and Figure 9(b) show DSC heating and cooling scans for the different blends after cure. Two characteristic transitions were observed for all the compositions. The endothermic peak at about 54 $^{\circ}\text{C}$ corresponded to melting of the PCL, whereas the small enthalpic peak and step-like increase in heat capacity at about 197 $^{\circ}\text{C}$ were associated with the glass transition of the epoxy. These transition temperatures were generally similar to those of the pure PCL and pure epoxy, indicating a high degree of phase purity, consistent with the FTIR results. The somewhat reduced melting temperature and lack of a clear exotherm in the cooling curves for Epoxy-PCL(13.1) was attributed to the high degree of dispersion of the PCL in the epoxy matrix in this case, which may retard crystallization.

Figure 9: DSC heating (a) and cooling (b) scans for the different blends after cure.

3.3. Mechanical properties

3.3.1. Dynamic mechanical analysis

Three distinct mechanical transitions were identified from the DMA scans, and their corresponding transition temperatures are summarized in Figure 10(a) as a function of PCL content. Those at about -25 $^{\circ}\text{C}$ and 200 $^{\circ}\text{C}$, denoted $T_{\alpha,\text{PCL}}$ and $T_{\alpha,\text{Epoxy}}$ respectively, were associated with the glass transitions of the PCL and the epoxy, while a third at around 75 $^{\circ}\text{C}$ was attributed to melting of the PCL and is denoted $T_{\beta,\text{PCL}}$. The storage modulus,

E' , is shown as a function of PCL content in Figure 10(b) for two different temperatures, 25 °C (room temperature) and 150 °C (the target healing temperature). At room temperature, a decrease in E' from 2.6 to close to 1.6 GPa was observed as the PCL content increased from 0 to 17.7 vol%, corresponding to the establishment of the co-continuous morphology visible in Figure 4. At 150 °C, E' decreased from about 1.75 to about 0.25 GPa in the same composition range, reflecting the molten state of the PCL. However, even at 150 °C, the blend behaved globally as a stiff elastic solid up to the highest PCL contents investigated, and no significant dimensional instabilities were observed, indicating the contacts between the epoxy particles to be sufficient to maintain structural integrity at the healing temperature, as found previously by Luo *et al.* [5]. In the present case, the interconnectivity of the epoxy particles at high PCL contents was also confirmed by direct observation of the thin sections used to determine the particle diameters (cf. Figure 6).

Upper (constant strain) and lower (constant stress) bound predictions of E' at 25 °C based on the moduli of the pure epoxy and the PCL have also been included in Figure 10(b). Comparison with the data suggested there to be a transition from a regime in which the epoxy is the continuous phase to a regime where the epoxy and PCL were effectively in a series arrangement, consistent with the observed morphologies. Hence, at the highest PCL contents, the PCL acted as a continuous layer and the bulk of the epoxy particles deformed relatively little. The relatively low E' observed at 150 °C at high PCL contents, where the contribution of the PCL was presumably negligible, also indicated the particulate epoxy phase to contribute relatively little to the overall stiffness at 25 °C, in spite of its interconnectivity.

Figure 10: DMA results: (a) transition temperatures as a function of the PCL volume fraction. (b) E' as a function of the PCL volume fraction at room temperature and the healing temperature (150 °C), along with upper and lower bound predictions for E' as indicated.

3.3.2. Tensile properties

The maximum stress observed during the tensile tests decreased approximately fourfold as the PCL content was increased from 0 to 26.9 vol% (Figure 11(a)), flattening off at about 20 MPa above 23.2 vol% PCL, which was close to the yield stress, σ_y , of pure PCL. The corresponding Young's moduli, E (Figure 11(c)), were consistent with the values of E' obtained by DMA (Figure 10(b)). As seen from Figure 12 (c), at high PCL contents, three modes of fracture co-existed: (i) failure of the epoxy-PCL interface, (ii) cohesive failure of the PCL and (iii) brittle failure of the interface between the interconnected epoxy particles. In the limit of low PCL contents (Figure 12 (a)), brittle failure of the epoxy dominated, implying the PCL particles not to promote matrix ductility, while at intermediate PCL contents (Figure 12 (b)), all the fractures modes were present. The decrease

in the strain-to-failure from about 4.5 %, where the epoxy was the continuous phase, to only about 2 % for Epoxy-PCL(25.0) and Epoxy-PCL(26.9), where the continuous phase was essentially PCL, was attributed to severe confinement of the relatively ductile PCL by the relatively stiff, high yield-strength epoxy particles (σ_y at least 4 times that of the PCL) and brittle behavior of the interfaces between the epoxy particles, rather than premature failure at the PCL-epoxy interface. Indeed, the strain-to-failure has been reported to increase with PCL content in similar systems, albeit for different cure conditions and stoichiometry, suggesting strong interfacial adhesion [20].

Figure 11: (a) Maximum stress, (b) strain-to-failure and (c) Young's Modulus as a function of the PCL volume fraction.

Figure 12: SEM image of the tensile fracture surfaces for (a) Epoxy-PCL(13.1); (b) Epoxy-PCL(17.7) and (c) Epoxy-PCL(25.0).

3.3.3. Fracture properties

Figure 13 shows K_{Ic} from the TDCB tests as a function of PCL content. For the pure epoxy, a mean value of 1.45 MPa m^{1/2} was obtained, i.e. 50 % higher than reported by Lee et al. for the same epoxy subjected to a post-cure heat treatment at 250 °C [45], but comparable with values for commercial systems [46]. Consistent with the trends in the maximum stress and the strain-to-failure in the tensile tests, K_{Ic} was generally observed to decrease on addition of PCL to the epoxy: (i) at 13.1 vol% PCL, where the PCL formed discrete inclusions in a continuous epoxy matrix, K_{Ic} fell to 1.04 MPa m^{1/2}; (ii) K_{Ic} rose slightly to 1.07 MPa m^{1/2} for the coarse bi-continuous microstructures observed at intermediate compositions; (iii) K_{Ic} fell to around 0.65 MPa m^{1/2} for the particulate epoxy morphology. Although addition of ductile thermoplastics, including PCL, to an epoxy matrix has frequently been reported to result in improved fracture resistance, in the present case, K_{Ic} for the unmodified epoxy was already comparable with values obtained in many optimized rubber-modified systems, accounting for the apparent absence of any toughening effect on PCL addition [20,47].

As with the strain-to-failure in the tensile tests, the reduced K_{Ic} at high PCL contents was interpreted as a confinement effect. If the epoxy particles are considered not to yield, and assuming brittle fracture of the contacts between the epoxy particles contributes little to energy dissipation, the continuous PCL phase may be modeled as a layer of mean initial thickness d_o , assumed to be of the order of 10 µm based on the observed morphology (epoxy particle diameters of about 20 µm), confined between parallel rigid plates whose plane is perpendicular to tensile axis. Given that d_o is very much less than the expected plastic zone size for unmodified PCL (literature values for the essential work of fracture of PCL (64 kJ/m²) imply plastic zone sizes that would exceed the specimen dimensions in the present case [48]), it may be assumed that cracks propagating through the

confined PCL layer are associated with yielding through the whole layer thickness, followed by either cohesive failure of the PCL or failure of the epoxy-PCL interface. The crack opening displacement, δ , and hence K_{Ic} , may then be determined from

$$\delta = (\lambda - 1)d_0 \quad \text{and} \quad K_{Ic} = \sqrt{\frac{E\sigma_y(\lambda - 1)d_0}{1 - \nu^2}} \quad (5)$$

where ν is the Poisson's ratio and λ is the characteristic deformation ratio of PCL, estimated to be 4 from the strain-to-failure for pure PCL in Figure 11(b). Taking $\sigma_y = 20$ MPa for pure PCL, $\nu = 0.4$ and $E = 1.5$ GPa for the blends with the particulate epoxy morphology, K_{Ic} is estimated to be around 1 MPa m^{1/2}, suggesting this scenario may account for the results in Figure 13. The relatively large scatter in K_{Ic} among the individual specimens, as reflected by the error bars in Figure 13 was attributed to variations in the geometry of the specimen side-grooves [49], and is commonly reported for TDCB tests, as for example in [50,51]. The use of an insert in combination with the TDCB geometry to measure the fracture properties of the blends (section 2.4.4) is also expected to lead to systematic errors in K_{Ic} of up to 20 % at high PCL contents owing to the reduced compliance of regions remote from the crack tip.

Figure 13: K_{Ic} as a function of PCL volume fraction.

After testing, the TDCB specimens were subjected to a healing treatment at 150 °C for 30 min as described in section 2.4.4. As indicated in section 3.2, all the blends behaved as stiff elastic solids at this temperature, but because of the large difference in the effective thermal expansion coefficient between the epoxy and the PCL, the unloaded crack faces tended to separate during healing. Hence, while fracture toughness recovery of up to 80 % was observed for the Epoxy-PCL(25.0) tested after unconstrained healing, the results showed significant scatter. Compressive stresses of between 0 and 250 kPa as defined in section 2.4.4 were therefore applied to the specimens during healing and it was found that a minimum of 50 kPa was necessary to maintain closure of the crack faces at for all the compositions considered. As shown in Figure 15, under these conditions, although the scatter was still rather high, in particular for high PCL content due to potential loss or inhomogeneity of the PCL during healing for these geometries, the healing efficiency increased as the PCL content increased, reaching a mean value of 78.5% at the highest PCL contents, although certain specimens showed healing efficiencies in excess of 100 %. After healing, the fracture surfaces were covered by a continuous layer of PCL, confirming the role of PCL bleeding in the healing process. Moreover, optical observation of the crack before and after healing

(Figure 14) indicated full recovery of the initial microstructure. The effect of multiple fracture and healing cycles was also investigated for Epoxy-PCL(25.0) and Epoxy-PCL(26.9). Figure 16 shows the evolution of the healing efficiency over three successive cycles. Although there was significant scatter, it was found that the healing efficiency decreased by less than 5% after each cycle, suggesting the present approach to be effective in the case of multiple damage events.

Figure 14: Reflected light optical microscopy of (a) a crack after testing and (b) the same crack after healing at 150 °C for 30 minutes.

Figure 15: Healing efficiency as a function of PCL volume fraction for an applied stress of 50 kPa during healing.

Figure 16: Multiple healing assessment for Epoxy-PCL(25.0) and Epoxy-PCL(26.9).

4. Conclusion

Blends of a commercial epoxy/DDS hardener with the thermoplastic PCL led to three types of morphologies after polymerization-induced phase separation: (i) an interconnected particulate epoxy phase and a co-continuous PCL phase at PCL concentrations greater than 23.2 vol%; (ii) a continuous epoxy phase containing PCL inclusions at concentrations of up to 13.1 vol% PCL; (iii) a complex morphology with relatively coarse co-continuous PCL and/or epoxy domains between 13.1 and 23.2 vol% PCL. These morphologies were consistent with simple model predictions, which suggested spinodal decomposition to be the dominant mode of phase separation over most of this composition range.

Increasing the PCL content reduced the dynamic and static tensile stiffness of the blends, which tended to a lower limit imposed by the presence of a continuous PCL phase at the highest PCL contents investigated. The stiffness nevertheless remained above 1 GPa, and the blends continued to behave as rigid elastic solids at the healing temperature of 150 °C, in spite of a sharp decrease in the Young's modulus at this temperature, owing to the interconnectivity of the epoxy-rich particulate phase.

A four-fold decrease in strength and a two-fold decrease in toughness were also observed for the blends containing a continuous PCL phase. These were attributed to both the high initial toughness of the baseline epoxy (1.45 MPa m^{1/2}), and severe spatial confinement of the nominally ductile PCL. After a moderate healing treatment at 150 °C for 30 min, toughness recovery increased strongly with PCL content, reaching 70 to 80 % efficiency for blends containing 25 and 26 vol% PCL. Because self-healing depends on the capacity of the PCL, which shows relatively high thermal expansion on melting, to expand, flow into newly formed cracks and bridge the crack faces, efficient healing is clearly contingent on the presence of a continuous PCL phase.

It follows that blends with morphologies comprising interconnected epoxy particles embedded in a continuous PCL matrix are most suited to provide a part with self-healing properties, while maintaining adequate mechanical properties both in service and at the healing temperature of 150 °C, i.e. above the melting point of the PCL. Moreover, because the blend is homogenous prior to cure, it is expected to be compatible with processing requirements for the matrix phase of a fiber reinforced composite, provided that its viscosity is not greatly increased. The analysis developed in this work also provides guidelines for the optimization of the blend

composition and the molar mass of the thermoplastic component so as to ensure healing at moderate temperatures while maintaining appropriate toughness in service.

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