



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 37 vol% 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 25 vol% 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 min. These composites can thus provide efficient crack healing, but remain more sensitive to initial crack propagation due to confinement of the thermoplastic phase.

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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

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(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 15 vol% 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 min, 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 25 vol% 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 min to investigate their self-healing capacity.

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 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 2 × 2 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 68 × 5 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.

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 $m_{\text{epoxy}}:m_{\text{PCL}}$	PCL volume fraction in matrix [%] ϕ_{PCL}	Fibre volume fraction in sample [%] 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

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 [%]	σ_{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)

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