



Temperature-dependent synergistic self-healing in thermoplastic-thermoset blends: Unraveling the role of thermoplastics and dynamic covalent networks

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ABSTRACT

Two different self-healing approaches are studied in this work to analyze the possible contribution of each of the self-healing mechanisms at different temperatures and the possible synergetic effects between them. Thermal and mechanical properties were differently affected by the addition of each of the thermoplastic polymers. This was caused by different phase separations induced during the curing reaction in terms of size and number of the thermoplastic phase domains dispersed within the epoxy matrix and due to the different amounts of thermoplastic polymer that remain solved in the matrix. When using the vitrimeric matrix, phase separation only occurred at the nanometer scale when utilizing poly(bisphenol-A-co-epichlorohydrin) (PBAE) as a thermoplastic agent or higher contents of polycaprolactone (PCL).

Self-healing capabilities showed a strong dependence on the temperature used and the type of crack. Low temperatures allowed the thermoplastic phase to flow and fill partially the cracks with moderate levels of self-healing which were only available when phases were separated. Higher temperatures allowed dynamic bonds to induce material healing reaching very high efficiencies but, more importantly, a synergic effect was observed when material was removed from the cracks. In these cases, the flow of the thermoplastic phase filled better the crack and there was an enhanced cooperation between the two healing mechanisms. At higher self-healing temperatures, materials with nanometric size phase separation enabled greater self-healing efficiencies (above 90 %) due to the vitrimeric self-healing capability while the thermoplastic phase helped fill the gaps due to material removal.

1. Introduction

Epoxy resins are commonly used as adhesives, coatings, and matrix of composites due to their good wettability, ease of processing, and high thermal, chemical, and mechanical properties. They can be subjected to different stresses and environment conditions during their service life as well as differences depending on the manufacturing process and composition, which strongly affects their performance [1,2]. For example, epoxy composites usually show high mechanical strength and stiffness but low resistance to fatigue and impact. The most common initial failures are associated with matrix-micro-cracking and interfacial matrix-fiber debonding [3,4]. Due to this aspect, the self-healing of epoxy thermosets is being widely studied for expanding their life expectancy. Several reviews [5–8] have been published about the

self-healing ability and mechanisms of epoxy resins to summarize all the research approaches. Self-healable resins are usually classified into two categories [5,6]: i) intrinsic self-healing ones, which can heal cracks by the polymers themselves, only requiring an energy supplement to act; and (ii) extrinsic self-healing ones, which require a healing agent to be pre-embedded, requiring a functional material supplement. As a function of the self-healing supplement required, epoxy polymers are divided into two categories: material supplement and energy supplement.

Among the intrinsic self-healing polymers, several chemical structures have been proposed like the inclusion of Diels-Alder adducts, disulfide bonds, or imines, which have shown good self-healing capabilities for thermoset and elastomer [9] polymers. Moreover, the exploration of synergic or complementary behaviour of different approaches has also attracted the interest of the scientific community. For

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example, Guo et al. [10] produced an ultra-stretchable elastomer with good self-healing capabilities due to the synergetic behaviour when including disulfide bonds at the same time that strong cooperative hydrogen bonds and weak anti-cooperative hydrogen bonds.

The extrinsic self-healable resins require the addition of hollow fibers or microcapsules that initially contain the healing agents that, in the event of a crack, will flow and repair it. Another type of extrinsic self-healable resin that does not require a container is based on a thermoplastic/thermosetting (TP/TS) blend. Compared with other approaches of self-healing mechanism, with a material supplement, the self-healable blend is repetitive, reversible, and infinite, and it does not need encapsulation. The TP additive must be separated in a second phase and homogeneously dispersed into the epoxy matrix. Moreover, the high-volume fraction of thermoplastic needed to heal large cracks has favored the use of TP/TS blends at the critical TP composition, showing a co-continuous phase morphology. The TP phase can flow by short-distance diffusion of the molecular chain which melts upon heating and repairs the damaged cracks. For that reason, a main critical requirement is that the melting point of the TP polymer must be lower than the glass transition temperature (T_g) of the TS network. Furthermore, a low viscosity of the molten polymer and a high thermal expansion during the phase change, which means a high increase of volume from solid to liquid state. These are desired conditions for the selection of a self-healing TP agent. In addition to self-healing properties, another main advantage of the TP addition is the toughening of the epoxy resin due to the crack deflection and cavitation mechanisms.

The most common approach for manufacturing TP/TS blends is by a reaction-induced phase separation (RIPS) [11,12], which has been known since the early 1980s. The final blend morphology depends on the miscibility of the polymers and the thermodynamic and kinetic aspects of the phase separation mechanism. Initially, the TP must be soluble in the TS monomers, but when the curing reaction begins, there is a point where the thermoplastic becomes insoluble in the growing cross-linking network, causing the phase separation. To get the separated TP phase embedded into the continuous epoxy matrix, the TP content must be lower than the critical composition. At higher TP content, phase inversion occurs, being the epoxy resin the separated phase while the TP becomes the matrix. At the critical TP composition, co-continuous phases and double-phase separation can be developed.

One of the most common TP polymers used as a healing agent for epoxy resin is polycaprolactone (PCL) [13–16], whose melting point is in the range of 55–75 °C. In addition, PCL increases up to 14 % in volume from room temperature (RT) to 150 °C. Other TP polymers used as self-healing agents of epoxy blends are poly(bisphenol-A-co-epichlorohydrin) (PBAE) [17] and poly[ethylene-co-(methacrylic acid)] (EMMA) [18,19]. The melting point of PBAE is close to 120 °C, increasing the thermal stability of the blend but hindering the healing since it requires a higher temperature for the healing to occur.

On the other hand, intrinsic self-healable resins must contain reversible or dynamic functional bonds in their three-dimensional (3D) network structure. The dynamic reaction can be photo- and thermo-reversible, based on the formation of Diels-Alder adducts, photocycloaddition, transesterification, disulfide bond exchange, or imine reactions, among others. Particularly, reversible disulfide bonds have received significant scientific attention to achieve the self-healing of epoxy resins [20,21]. Vitrimers obtained by the crosslinking reaction between epoxy and diamine monomers, in which one or both contain disulfide bonds, display excellent mechanical and thermodynamic properties, together with new properties such as reprocessability, weldability, and self-healing. Moreover, they show short relaxation time and low activation energy, maintaining high thermal stability, and showing relatively high T_g [7,22,23].

In this work, the self-healing efficiency of intrinsic and extrinsic self-healing mechanisms and their combination are analyzed. For this purpose, a conventional epoxy monomer, bisphenol A diglycidyl ether

Table 1

Nomenclature of the different materials tested.

Components			Thermoplastic content	Designation	
Epoxy monomer	Amine hardener	Thermoplastic	in per hundred resin (phr) units		
DGEBA	DDS	PCL	15	15%PCL/DGEBA/DDS	
			20	20%PCL/DGEBA/DDS	
		PBAE	15	15%PBAE/DGEBA/DDS	
			20	20%PBAE/DGEBA/DDS	
		AFD	PCL	15	15%PCL/DGEBA/AFD
				20	20%PCL/DGEBA/AFD
	PBAE		15	15%PBAE/DGEBA/AFD	
			20	20%PBAE/DGEBA/AFD	
	–		–	–	DGEBA/AFD
				–	DGEBA/AFD

(DGEBA), is cured with a conventional aromatic diamine, diaminodiphenylsulfone (DDS), or a disulfide bond-containing diamine, 4-aminophenyl disulfide (AFD), and different weight loads of two different thermoplastic polymers, PBAE and PCL, which have a melting point lower than the T_g . Their thermomechanical and mechanical behavior is analyzed together with their self-healing ability. The main goal is to determine if there is a synergic effect between both self-healing mechanisms. At this point, it is worth noting that the intrinsic, unlike extrinsic, self-healing mechanism requires direct contact, which is achieved by the application of pressure. Therefore, the repair of surface cracks will be different if the crack generation implies the dragging of materials. Due to the good behaviour of epoxy resins when used as protective coatings, the repair of surface cracks is of great importance for the improvement of their life in service when used as coatings.

2. Experimental part

2.1. Materials

The epoxy resins were composed of DGEBA (molecular weight of 340.41 g/mol and density of 1.16 g/mL) cured with DDS (molecular weight of 210.36 g/mol and 97 % of purity) and with AFD (molecular weight of 248.37 g/mol and 98 % of purity) in the stoichiometric ratio. The TP additive, PBAE (molecular weight of 40,000 g/mol and melting point of 120 °C) and PCL (molecular weight of 14,000 g/mol and melting point of 60 °C), were added in a weight proportion of 15 and 20 wt % (different compositions manufactured and tested are shown in Table 1). Chemicals were supplied by Sigma-Aldrich and were used as received. Both thermoplastics are initially soluble in DGEBA. The phase separation occurs during the crosslinking process. Previous studies [24, 25] confirmed that the critical composition of both TP/TS systems is higher than 30 wt %, ensuring the phase inversion, whose blend morphology is a TP matrix with dispersed epoxy phase, is avoided in this work.

2.2. Manufacturing

The samples were prepared as follows: (i) The thermoplastic, PCL or PBAE, was dissolved into DGEBA monomer through mechanical stirring (160 rpm) under vacuum conditions to remove the air bubbles. This process was carried out at 120 °C for 15 min and 150 °C for 4h for the PCL/DGEBA and PBAE/DGEBA mixtures, respectively. Despite the high temperature applied, it was confirmed by differential scanning

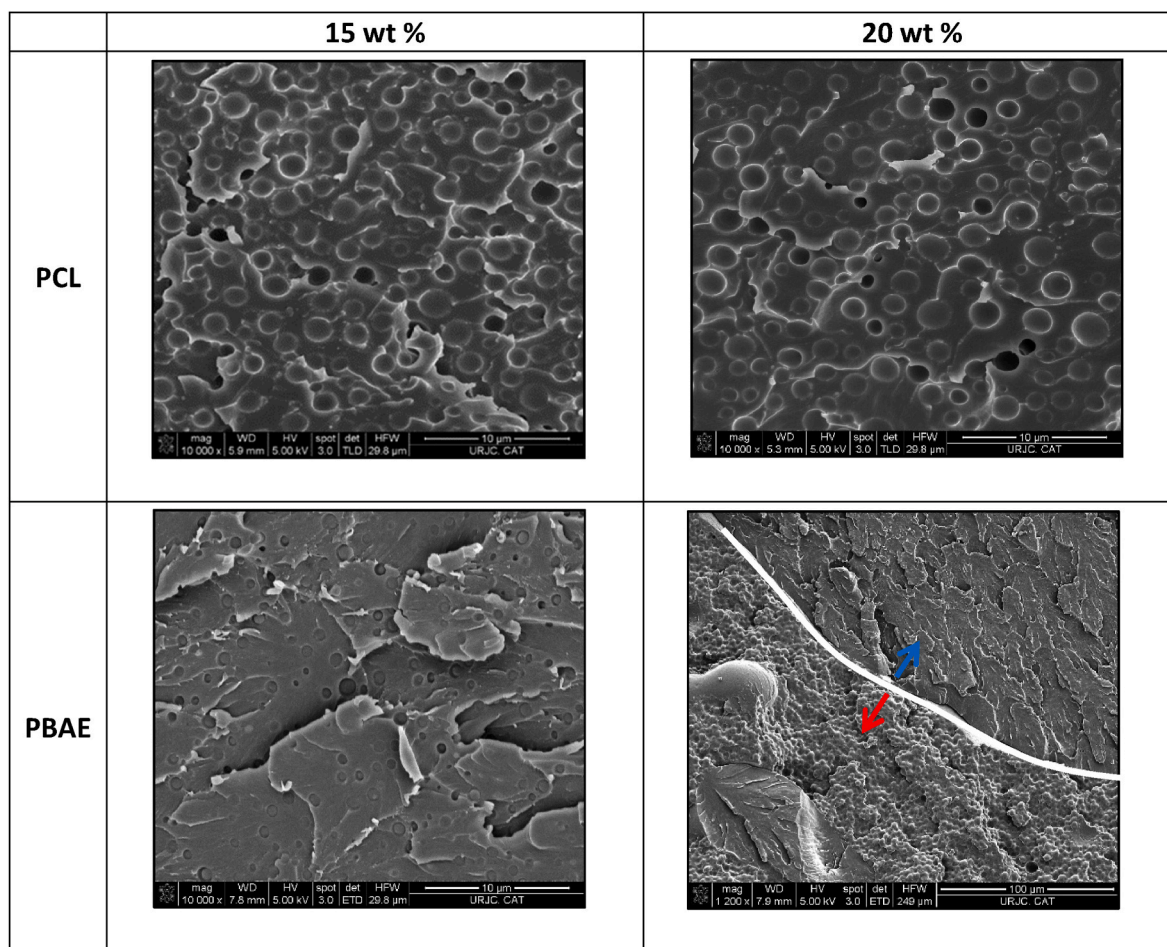


Fig. 1. FEG-SEM micrographs of DGEBA/DDS resins modified with 15 and 20 wt % PCL and PBAE.

calorimetry (DSC) that the epoxy homopolymerization reaction was negligible. (ii) Once a homogeneous mixture is obtained, the amine hardener, DDS or AFD, is added in a stoichiometric ratio. (iii) The curing process utilized consists of heating the mixture at 160 °C for 6h in an open mold, whose steel walls were previously treated with an anti-adherent coating. The curing treatment applied ensured a high cross-linking degree for all the studied samples, which was confirmed by DSC.

2.3. Characterization

Microstructural characterization of the TP phase distribution in the epoxy resins was determined by field emission gun scanning electron microscopy (FEG-SEM), using a Nova NanoSEM 230 device. To obtain a flat fragile cross-section surface, rough fracture mechanisms were avoided. First, a pre-crack was done in the samples and then, the fracture was forced under cryogenic conditions by immersion in liquid nitrogen for 5 min. Then, the samples were coated with a thin layer of Au and Pd. The images were analyzed the Image J analysis software. At least 35 measurements of different particles were taken and analyzed by digital image analysis in materials made with DDS as a crosslinking agent, although the ones using AFD have too small of a size to perform an accurate analysis.

Thermo-mechanical properties were evaluated by dynamic mechanical thermal analysis (DMTA) using a DMA Q800 V7.1 module from TA Instruments at temperatures ranging from 25 to 225 °C. Two samples with dimensions of $37.5 \times 12 \times 1.7 \text{ mm}^3$ were tested in single cantilever mode at 1 Hz frequency and an amplitude of 1 % of the thickness of the specimen. The temperature ramp was set at 2 °C/min. Glass transition temperature was set as the maximum of $\tan \delta$ curve.

Mechanical characterization of the manufactured samples was carried out at RT by a three-point bending test, in a Zwick universal tensile machine with a load cell of 5 kN. Five specimens of each condition were tested according to ASTM D790 [26].

Finally, the self-healing capabilities were evaluated by doing a controlled crack with a metal blade in a homemade crack bench device, which allows for controlling the width and depth of the crack. Two different self-healing heating treatments were performed at 120 and 200 °C for 30 min. According to previous studies, the self-healing capabilities of 2-AFD-based vitrimers could be activated above the T_g , with self-healing being activated between 140 and 220 °C [27]. Since the degradation temperature of the system is higher than 200 °C, this temperature was used to ensure complete activation of the disulfide bond repairing mechanism. A temperature of 120 °C was chosen to avoid the effect of the disulfide bond mechanism while allowing easier flow of the PCL, from previous studies of the research group that recommend not going below the interval 110–130 °C [28]. Optical profilometry of the crack before and after the healing process was carried out by using an optical profilometer ZETA Z-20, obtaining the surface profiles, where the geometry and depth of the cracks can be determined.

3. Results and discussion

3.1. Morphology

The morphology of the different TP/TS blends studied as a function of the thermoplastic added, PCL and PBAE, is shown in Figs. 1 and 2, depending on the hardener used, DDS or AFD, respectively.

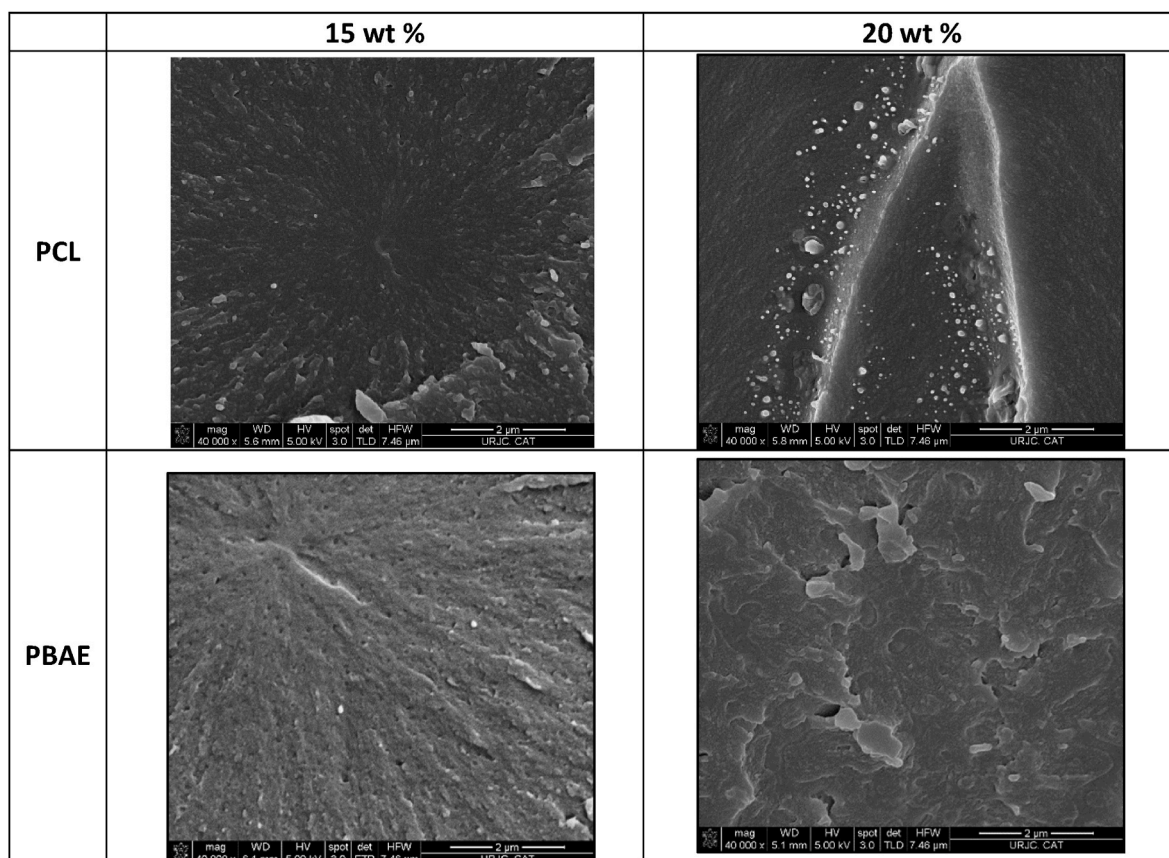


Fig. 2. FEG-SEM micrographs of DGEBA/AFD resins modified with 15 and 20 wt % PCL and PBAE.

The PCL/DDS/DGEBA blend shows the traditional TS/TP blend morphology with a TP content lower than the critical composition, where the separated spherical PCL phase is well distributed into the epoxy matrix. This means that the critical composition of the PCL/DGEBA/DDS is higher than 20 wt %. Moreover, the PCL/epoxy interphase is relatively strong, due to the TP phase not being separated during the sample preparation. In contrast, the observed morphology of the PBAE/DGEBA/DDS blends (Fig. 1) confirms that the critical composition must be in the range between 15 and 20 wt% PBAE, as at a content of 20 wt% PBAE a double-phase separation is observed, while at 15 wt% PBAE, a phase separation of individual separated PBAE particles in the epoxy matrix was obtained. This means that there are epoxy-rich

regions with separated PBAE phase (blue arrow) and PBAE-rich phase regions (red arrow). Furthermore, at a TP content lower than critical composition, 15 wt %, the size of the separated PBAE phase is lower than PCL. The PCL phase diameter and the particle density of PCL/DGEBA/DDS blends are 1.6 ± 0.5 and 1.8 ± 0.5 μm , modified with 15 and 20 wt % PCL, respectively, while the average size was 0.8 ± 0.2 μm for the material reinforced with PBAE15 %/DGEBA/DDS. As expected, the increase in TP content induces an increase in the TP particle size and a reduction in the number of TP particles per unit area.

The blend morphology significantly changes with the change of amine hardener due to its influence on the kinetic and thermodynamic aspects of the curing reaction. The blends with DGEBA/AFD resin do not

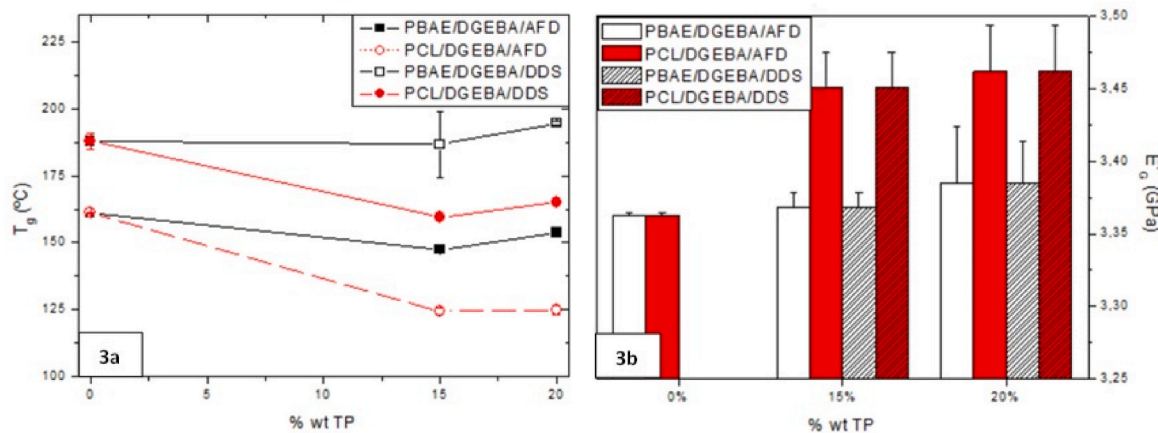


Fig. 3. DMTA Results. Glass transition temperature, measured by the maximum of tan δ peak, (3a) and glassy storage modulus at RT (3b) for epoxy blends as a function of the PCL and PBAE content added.

Table 2
Results of the three-point bending tests.

Sample	σ_B (MPa)	ϵ_B (%)	Sample	σ_B (MPa)	ϵ_B (%)
DGEBA/DDS	164.8 ± 2.3	6.6 ± 0.7	DGEBA/AFD	167.2 ± 0.5	5.5 ± 0.1
15%PCL/ DGEBA/DDS	85.0 ± 9.9	3.4 ± 0.8	15%PCL/ DGEBA/AFD	117.2 ± 26.5	5.0 ± 1.3
20%PCL/ DGEBA/DDS	60.3 ± 0.3	2.7 ± 0.4	20%PCL/ DGEBA/AFD	120.0 ± 5.3	6.0 ± 0.7
15%PBAE/ DGEBA/DDS	165.6 ± 3.3	5.9 ± 0.2	15%PBAE/ DGEBA/AFD	168.9 ± 0.9	5.3 ± 0.1
20%PBAE/ DGEBA/DDS	63.3 ± 12.2	2.7 ± 0.8	20%PBAE/ DGEBA/AFD	157.0 ± 3.8	7.5 ± 0.1

show a separated TP phase with micrometric size. The 15%PCL/DGEBA/AFD blend is homogenous, without phase separation, while the rest of the blends with DGEBA/AFD resin present a nanometric TP phase with a non-well-defined interphase. At 40,000× of magnification, they can be observed mainly in the PBAE case with a size in the nanometer scale. These clear differences in the morphology of the manufactured

blends allow for the evaluation of the effect of the TP phase size on the self-healing efficiency due to the thermoplastic being the material source for repairing at lower healing temperatures. Taking this into account, materials based on AFD as a crosslinker agent and 15 % PCL will not lead to high levels of recovery during self-healing at low temperatures, as there is not enough PCL separated from the matrix. Nevertheless, the nanometric scale of the PBAE and good distribution could lead to improved self-healing contribution of the PBAE (for example, filling cracks with material loss). The self-healing capabilities of the vitrimeric matrix should remain almost unaffected, thus, obtaining a complementary self-healing capability of both mechanisms. Additionally, the effect on the T_g and the mechanical properties will also be very differently affected, as the presence of nanometer size well distributed in the thermoset matrix will not negatively affect the mechanical strength. In contrast, partial or total dissolution will affect the T_g , as it will be shown later.

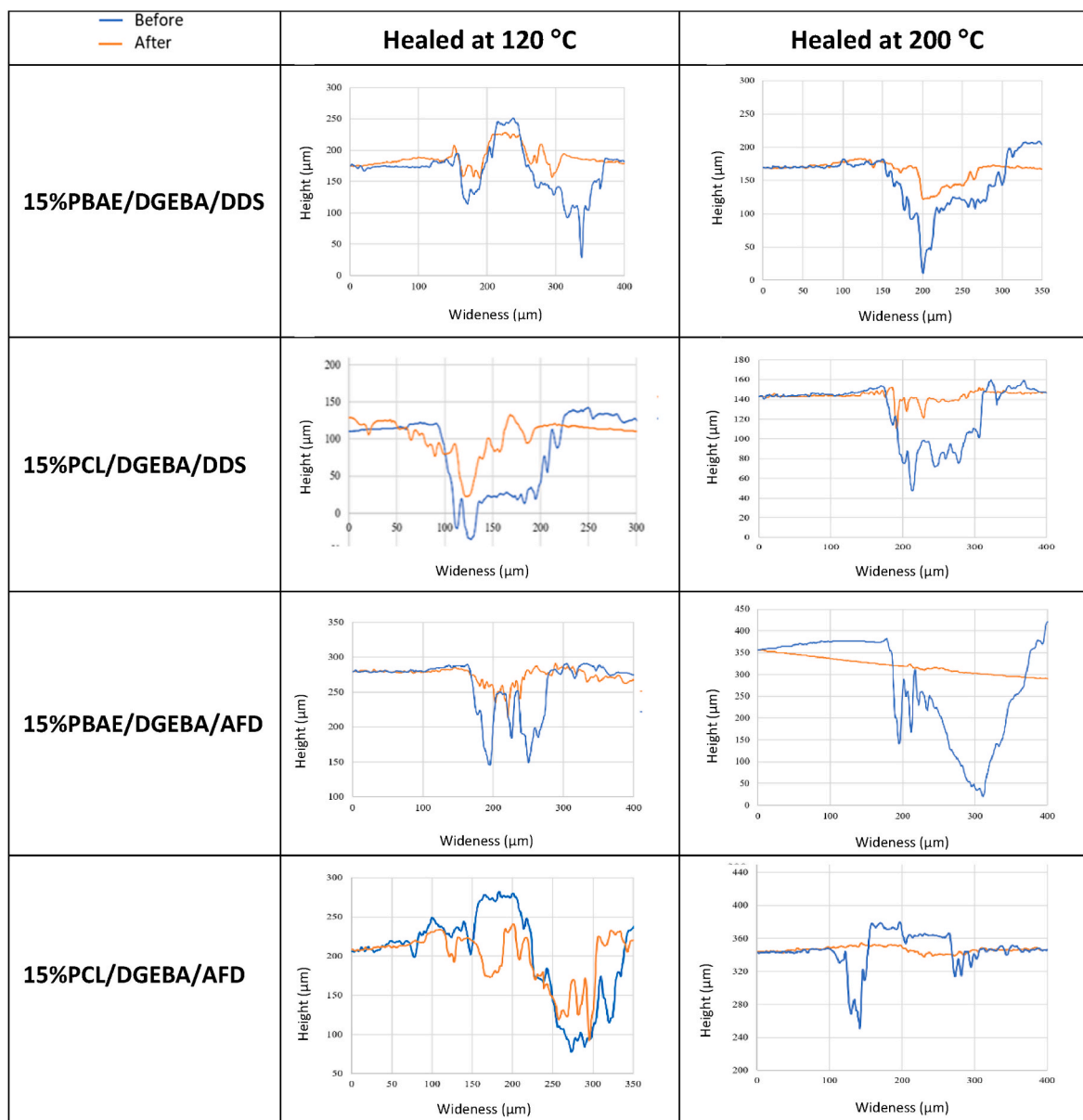


Fig. 4. Profiles of the cracks before and after the self-healing treatment at 120 and 200 °C or the resins doped with 15 wt % PBAE or PCL.

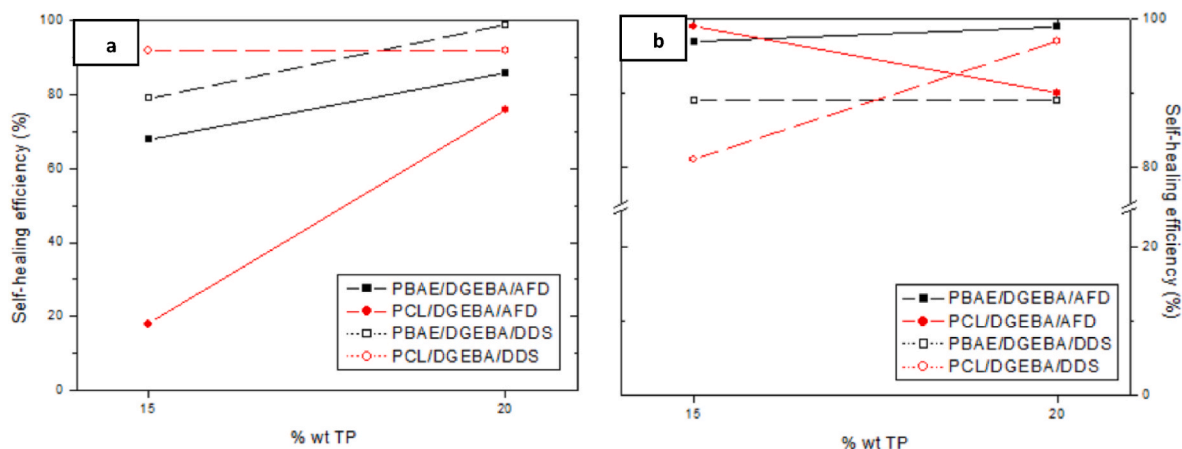


Fig. 5. Self-healing efficiency of epoxy blends as a function of the PCL and PBAE content added at 120 °C (5a) and 200 °C (5b).

3.2. Thermo-mechanical and mechanical properties

DMTA results (Fig. 3) show the α -relaxation temperature, measured by the maximum of the $\tan \delta$ peak, which means the T_g , and the storage modulus in the glassy state (E'_G) at RT, which is related to the stiffness of the material.

Fig. 3a shows the variation of T_g as a function of the TP content for the different blends studied. Both systems follow the same behavior. The addition of a thermoplastic additive, PCL or PBAE, induces a reduction of the T_g of the epoxy matrix, which is initially lower for the neat epoxy resin cured with AFD at 161 °C. Regarding the one cured with DDS at 188 °C, it is associated with the fact that dynamic exchange disulfide bonds (S–S) are weaker covalent bonds than sulfone group (SO₂). The T_g reduction by TP addition is due to the partial solubility of the thermoplastic into the epoxy network, following the mixture rule. The T_g of the TP modifiers is close to –60 and 100 °C for PCL and PBAE, respectively. This justifies the highest T_g drop measured by epoxy blends doped with PCL in comparison with the T_g of the modified ones with PBAE. In all cases, the T_g measured for the blends cured with DDS is lower than the one calculated by the mixing rule, confirming the phase separation. DMTA curves of the PBAE/DGEBA/DDS system show a secondary $\tan \delta$ peak with much lower intensity at 110 °C, which is associated with the separated PBAE phase (Fig. S1). The PCL peak could not be observed because the DMTA test started at room temperature. However, when the epoxy resin is cured with AFD, one single peak is observed, confirming the complete miscibility of PBAE into the thermosetting network.

It is worth noting that the $\tan \delta$ peaks in all studied samples are narrow, and that the error bar obtained by the standard deviation of two measurements is low. This fact confirms the high homogeneity of the manufactured blends.

Fig. 3b shows the storage modulus of the blends in the glassy state at RT. E'_G is 3.43 and 3.36 GPa for the neat epoxy resins cured with DDS and AFD, respectively. Despite the low miscibility of PCL compared to PBAE, the PCL addition induces an increase in the stiffness of the epoxy resins, while PBAE scarcely modifies it. This is associated with the much higher stiffness of PCL, which is a semicrystalline thermoplastic while PBAE is a more flexible amorphous polymer.

The mechanical behavior of the studied blends was analyzed by a three-point bending test, where the flexural strength (σ_B) and strain at failure (ϵ_B) were measured. The obtained results are collected in Table 2. Both neat epoxy resins show similar good mechanical behavior with a flexural strength of 165–167 MPa and a deformation at break of 5.5–6.6 %. The thermoplastic addition reduces these properties particularly for the epoxy resins cured with DDS. The addition of PCL causes a decrease of flexural strength and strain at failure of almost 50 % and around 60 % when adding 15 wt% and 20 wt%, respectively. The reason is the morphology of the DGEBA/DDS blend, which consists of a separated

micro-sized thermoplastic phase (Fig. 1). DGEBA/AFD blends do not present phase separation, or the separated TP phase is very small, with nanometric size. Moreover, the blends cured with AFD maintain their deformation ability while the strain of the ones cured with DDS also is significantly reduced. The reduction of the mechanical properties is a marker for blends doped with PCL due to the high stiffness of this thermoplastic additive.

The addition of PBAE has a slight effect at low contents due to the low separation phase observed, the small size, and good distribution, when compared with PCL. Nevertheless, higher contents led to a doubled phase separation previously mentioned, which led to a sharp decrease in the mechanical properties of the material DGEBA/DDS with 20 wt% PBAE. In the case of using DGEBA/AFD as the thermoset phase, the 20 wt% content of PBAE did not lead to such a decrease as the phase separation in this material is quite lower, remaining well-dispersed and of small size.

3.3. Self-healing ability

Once the blends were characterized, the self-healing ability was studied through surface cracks which were measured by optical profilometer. The self-healing mechanism was triggered by heating in an oven, without pressure application, at two different activation temperatures, 120 and 200 °C for 30 min. The selected temperatures are higher than the melting point of PCL and PBAE, close to 60 and 120 °C, respectively, and the topology freezing transition temperature (T_v) of the epoxy vitrimer cured with AFD is 86 °C [29]. Fig. 4 shows, as examples, some profiles of cracks before and after the self-healing treatment for blends modified with 15 wt % thermoplastic polymer, PCL, or PBAE. This table shows, for each material, the height profile (Y-axis) across a line (X-axis) that goes through the crack generated, before and after applying temperature. Self-healing efficiency for each blend studied is calculated as the variation in percentage of the crack area before and after the heating and the obtained results are shown in Fig. 5.

It is worth noting that at the lowest studied activation temperature of 120 °C, the lower self-healing efficiencies are measured for blends with the DGEBA/AFD matrix even though this system could have presented two possible self-healing mechanisms, thermoplastic melting, and reversible bonds. This is due to the experimental conditions applied for the self-healing activation, temperature, and time which are not enough. Their self-healing efficiency significantly increases at 200 °C, getting the total crack repair. This is justified by its relaxation time. Zhou et al. [29] confirmed that a similar vitrimer, constituted by a difunctional epoxy monomer cured with AFD, had a short relaxation time, 9s, at 200 °C while it reached 3 h at 130 °C. The reshaping, recycling, and self-healing processes of these systems, based on epoxy resins with reversible disulfide bonds, usually are carried out at temperatures equal to or higher

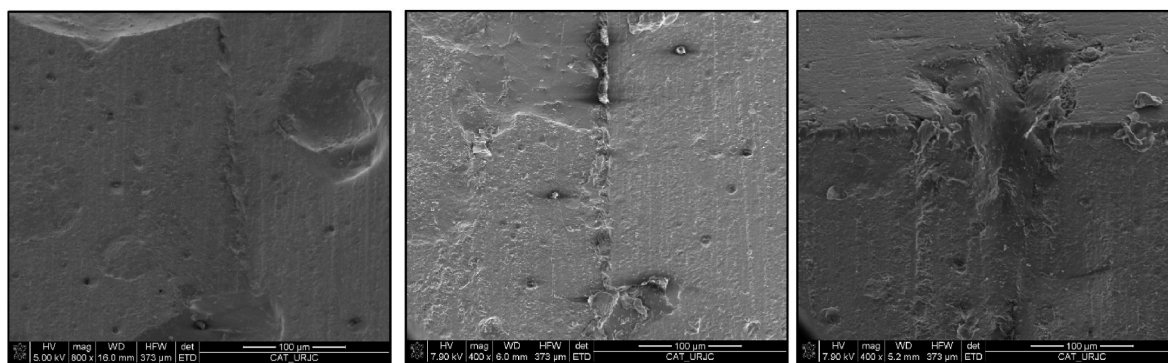


Fig. 6. Self-repaired crack of 15%PCL/DGEBA/DDS at 120 °C.

than 120 °C, under pressure, for 20–60 min [5,29]. The self-healing process by exchange dynamic reaction is enhanced if the cracked samples are heated above T_g [30], being in the range of 125–150 °C for the DGEBA/AFD system (Fig. 3) due to the higher polymer chain segmental motion. At a high triggering temperature, 200 °C, the highest self-healing efficiencies are obtained for the DGEBA/AFD blends with both self-healing mechanisms, TP melting, and exchange bonds, confirming the synergic effect.

On the other hand, it is possible to conclude that at temperatures lower than the T_g of the thermosetting network, the most efficient self-healing mechanism is thermoplastic melting. Analyzing the effect of different morphology of blends at low triggering temperatures where the self-healing mechanism by exchange bonds reaction is not effective, the micron size of the separated TP phase, obtained for the blends with DGEBA/DDS resin (Fig. 1), is more effective than the nano-sized phase, shown for the DGEBA/AFD blends (Fig. 2). In fact, the worst self-healing efficiency was measured by 15%PCL/DGEBA/AFD due to this TS/TP blend being homogeneous, without phase separation. The increment of PCL content, from 15 to 20 wt %, induces an important increase in self-healing efficiency due to the appearance of phase separation induced by the curing reaction. Finally, despite the different melting temperatures of the two studied thermoplastic polymers, PCL and PBAE, both have similar behavior as self-healing agents.

Without applying pressure, for relatively wide cracks where the edges are separated, the only effective self-healing mechanism is the one that has material support, in this case, the blends that are doped with a secondary thermoplastic phase. Fig. 6 shows micrographs confirming the filling of cracks with melted polymer.

It is easy to recognize the self-healing mechanism based on the thermoplastic melting and its flow to fill the crack. Those materials that allow to have this mechanism would have a complementary effect in self-healing efficiency as they would be able to fill cracks while the vitrimeric matrix, if used, would create a stronger crack healing due to new crosslinks created.

4. Summary and conclusions

In this work, two different self-healing mechanisms are studied, analyzing their possible combination or synergic effect. For this purpose, reversible exchange bonds, such as disulfide bonds, are incorporated into the epoxy crosslinked network, and, on the other hand, two different thermoplastic polymers (TP), with a low melting point, were added in relatively low content to obtain self-healable blends with thermoset polymers (TS). The combination and comparison allowed to extract the following main conclusions:

- The final TP/epoxy morphology strongly depends on the nature of the thermoplastic added and the amine hardener, due to the RIPS being influenced by the thermodynamic and kinetic aspects of the curing reaction.

- Glass transition temperature (T_g) of bisphenol A diglycidyl ether (DGEBA)/diaminodiphenylsulfone (DDS) blends are higher than the measured for DGEBA/4-aminophenyl disulfide (AFD) blends due to the weakness of the exchange disulfide bonds.
- T_g of epoxy matrix is reduced by the thermoplastic addition due to its partial solution.
- Polycaprolactone (PCL) addition induces an important increase in the blend stiffness. However, the bending strain is reduced in the thermoset polymer (TS)/TP blends due to the TP phase separation.
- PCL and poly(bisphenol-A-co-epichlorohydrin) (PBAE) behave as excellent self-healing agents. While phase separation occurs, the size of the separated phase, micro- or nano-sized, does not have a great influence on the self-healing efficiency.
- A complementary effect is confirmed in epoxy/TP blends with exchange bonds which can be used as a strategy to promote higher healing efficiencies and the use of different temperatures.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jmrt.2024.01.089>.

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