Healing Process Affected by Morphology of PCL/Epoxy Blends

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ABSTRACT

In this study, a blend of epoxy and polycaprolactone (PCL) was prepared to investigate its properties. Different weight percentages of thermoplastic PCL (0.25, 0.5, 1, 2 wt%) were combined with epoxy coatings. The final morphology revealed PCL scattered as spherical particles within the epoxy phase, which was functioning as a continuous matrix. The coating showed toughness and rigidity when it had fully cured. The PCL phase had a special behavior when heated, called "bleeding," in which it filled any open surfaces of its own volition. By using molten PCL to fill in cracks, this property can be used for self-healing applications. The self-healing efficacy of blends with different PCL contents was assessed. The self-healing efficacy of the various mixes was determined by dividing the width of the self-healed crack by the width of the original crack. The results showed that the highest thermal-mending efficiencies, reaching 100%, were achieved with a PCL/epoxy blend containing co-continuous phases, specifically at a 1 wt.% PCL content. Fourier-transform infrared (FTIR) analysis indicated that there was physical interaction between the epoxy and PCL phases, but no chemical bonding occurred between them.

Keywords: *Self-healing; Epoxy; Blend; polycaprolactone PCL; Morphology.*

1. INTRODUCTION

The degradation, damage, and failure of materials are inevitable in their application. The development of stronger materials or nondestructive assessment methods for material inspection has been the main goal of prior engineering research. All developed materials do, however, eventually deteriorate [1-2]. The ability of a material to self-heal and recover from different types of damage is referred to as self-healing. Materials with the ability to cure themselves can be either naturally occurring or man-made, and they can be categorized as autonomous or non-autonomous based on whether outside assistance is needed [3-5]. There is a rising emphasis in the construction sector on reducing corrective maintenance expenses. As a result, substantial research is being performed to improve the self-healing properties of thermosetting polymers, notably in terms of damage and fracture repair [6]. To achieve self-healing capability, many approaches such as encapsulation, reversible chemistry, microvascular networks, nanoparticle phase separation, polyionomers, hollow fibers, and monomer phase separation have been investigated [7].

One method for repairing damaged regions in polymer composites is to fuse fresh materials into the damaged region or to reconnect the broken surfaces. By stimulating chain entanglements between the interacting polymer surfaces, this technique tries to restore the original physical attributes of the injured region. Surface

rearrangement, surface approach, wetting, and diffusion all contribute to the fusing of the two surfaces and the completion of the repair [8]. Microcapsules are another prominent way for generating self-healing coatings. When fractures appear, microcapsule-based coatings begin the healing process by releasing a liquid healing ingredient into the crack. Through different chemistries and methods, the agent fills the fracture and solidifies, providing a protective coating [9-10]. Vascular Materials that repair themselves retain the healing ingredient in a capillary or hollow channel network until injury occurs. These networks can be linked in a one-dimensional (1D), two-dimensional (2D), or three-dimensional (3D) fashion. Following the first delivery of the healing agent and damage to the network, the network can be replenished from an outside resource or an undamaged section of the network, permitting several local healing procedures [1,11 Another way to get self-healing capabilities is to combine epoxy polymers with thermoplastic additives. When compared to the inclusion of functional composite materials, this technique provides the advantage of recurrent healing. Furthermore, because the healing process is reversible and ongoing, encapsulation is unnecessary. Zako et al. [46], for example, introduced tiny thermoplastic particles to epoxy/glass fiber composites, which melted when heated and mended fractures [10]. Because of the reversibility of their chemical bonds, epoxy polymers may self-heal. Through reversible processes, the link between the glass transition temperature (Tg) and the curing temperature (Tc) of epoxy polymers has a

substantial impact on the self-healing mechanism. The thermosetting resin is typically cured to a glassy state below both Tc and Tg. Heating the healing region above Tc elevates the temperature of the epoxy network structure over Tg, causing it to become rubbery and change its mechanical characteristics. At high temperatures, the healing process of epoxy polymers based on reversible bonds can have a deleterious impact on their mechanical characteristics [10].

Polycaprolactone (PCL) is a crucial component as an agent that heals itself when combined with epoxy resins due to its low melting point and varying patterns of extensive bleeding, and lack of reactivity with epoxy. This study looks at how varied weight percentages of PCL, a thermoplastic polymer, affect the morphology of epoxy/PCL blends and the self-healing behavior of the epoxy coating matrix. Depending on the PCL % and mixing procedures, the blend morphology might have continuous or discontinuous separated phases. The study's goal is to assess the influence of varied geometries and enhanced thermoplastic phase distribution on the healing percentage.

2. MATERIAL AND METHODS

2.1 Material

An epoxy resin that contains from two parts, DGEBA as the resin and 4,4′-diaminodiphenyl sulfones (DDS) as the hardener, has been purchased from Sika AG chemicals. Polycaprolactone (PCL) with a melting point of 60 °C and molecular weight Mw~ 65000 (g/mol) were purchased from Aldrich. The structures of epoxy and PCL are shown in Figure 1.

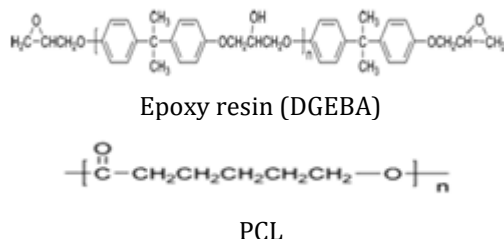Epoxy resin (DGEBA)

PCL

Figure 1 The structure of DGEBA and PCL

2.2 Preparation of Epoxy/PCL composites

At 80 °C, PCL was dissolved in DGEBA resin. The homogeneous mixture underwent a degassing process under vacuum settings for a duration of 10 minutes in order to remove any potential air bubbles that may be present in the resulting cured blend. Then, a stoichiometric amount of hardener was added.

2.3 Materials characterization

2.3.1 FTIR test

FTIR (type IR Affinity-1) analysis instrument used to identify changes in the structure for samples with different additives through the change in band values.

2.3.2 Mechanical Tests (Pull-off, Hardness test)

The ASTM D4541 standard for Pull-Off Strength of Coatings Using Portable Adhesion Testers was formulated with the purpose of evaluating the adhesive strength between a coating and metal substrates. The sample's hardness was measured using Shore D Hardness ASTM D2240. The average of three readings at a different location was taken for each sample.

2.3.3 Morphology by SEM

SEM analysis. A scanning electron microscope (TM = 1000 Hitachi tabletop Japan) was used to investigate the morphologies of epoxy and epoxy blended with PCl.

3. THE RESULTS AND DISCUSSION

3.1 Structural test

3.1.1 FTIR Test Analysis

Figure (2) and Table (1) show the FTIR spectrum of Epoxy, PCL and their blends. For pure Epoxy the obtained bands are as follow: 3417 cm^{-1} for OH, 2924.09 cm^{-1} for CH$_2$ asymmetric stretch, and 2854.65 cm^{-1} for CH$_2$ sym.stretch. The bands at 1720.05 cm^{-1}, 1705.07 cm^{-1} for Carbonyl stretching C=O and the bands at 1273.02 cm^{-1}, 1149.57 cm^{-1}, and 1111 cm^{-1} are for C-O stretch in the crystalline phase. While the bands at 1234 cm^{-1}, 1188.15 cm^{-1} for CH wagging. The bands at 1651 cm-1, 1612 cm-1 and 1373 cm-1 are for C=C stretch and CH$_2$ rocking respectively, as shown in Figure (2). However, for pure PCL the obtained bands are as follows: 3417.96 cm^{-1} for OH stretch, 2924.09 cm^{-1} for CH$_2$ asy.stretch, and 2854.65 cm^{-1} for CH$_2$ sym. Stretch. 1720.5 cm^{-1}, and 1705.07 cm^{-1} for Carbonyl stretching C=O, 1651.07 cm^{-1}, 1612.49 cm^{-1} for C=C stretch. The band at 1465.9 cm^{-1} for CH stretching, and the band at 1180.44 cm^{-1} for CH wagging, 1111 cm^{-1} C-O stretch. The bands at 933.55 cm^{-1}, and 894.97 cm^{-1},833.25 cm^{-1} for OH bend as shown in Figure (2). For the Epoxy/PCL blend the same bands appeared with some shifting in C=O stretch, and in CH$_2$ symmetric and asymmetric stretching bands as shown in table (1). From the above analysis it is found that there is no chemical interaction occur between the blend (Epoxy/PCL) only physical interaction.
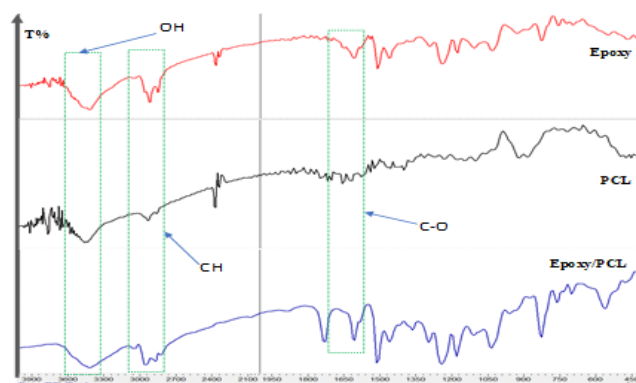

Figure 2 FTIR analysis of Epoxy, PCL, and Epoxy/PCL blend.

Table 1 FTIR band values for Epoxy, PCL, Epoxy/PCL blend

Bands	PCL	Epoxy	PCL/Epoxy blend
OH stretch	3417	3417	3417
CH_2 asymmetric stretch	2924	2924	2954
CH_2 symmetric stretch	2854	2854	2870
C=O stretch	1720 1705	1720 1705	1728
`	1273,1149,1111	1273, 1149, 1111	1273, 1149, 1111
C=C	1651, 1612	1651, 1612	1651, 1612
CH wagging	1180	1234, 1188	1365, 1296, 1242, 1180
OH bending	933, 894, 833	933, 894, 833	956, 825, 763, 702
CH_2 stretch	1465	1465	1458
CH rocking	1373	1373	1365

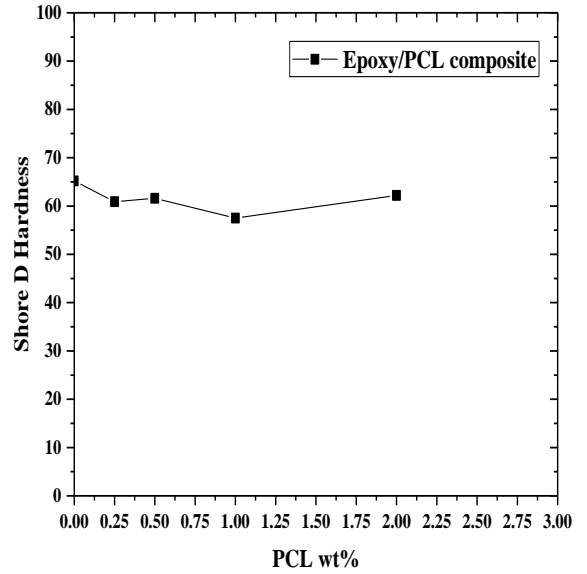## 3.2 Mechanical tests Results

3.2.1 Pull-off test

The adhesion behavior of epoxy /PCL blend coating on the stainless-steel substrate were carried using pull-off apparatus ASTMD 4541-02, the results showed that the adhesion force was decreased after incorporate PCL Figure 3, were the adhesion force for pure coating (net Epoxy) is 117 N, after adding PCL the adhesion force decreased to 84 N with 1wt% of PCL, and this behavior may be due to the formation of two heterogeneous phases**.**
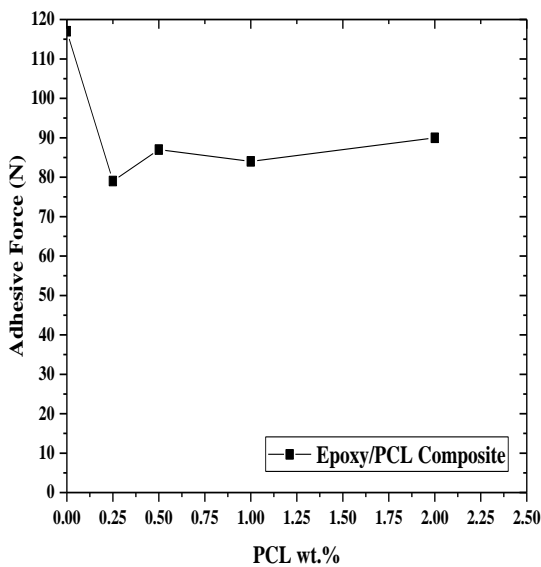

Figure 3 The Pull - Off test.

Figure 4 The Shore D hardness.

3.2.2 Hardness test

In general, it is noted that hardness behavior may be similar to all samples, and this may be due to the low percentage of PCL that added to the epoxy matrix, which caused a slight decrease in the hardness of the resulting blend Figure 4. The morphological analysis of broken surfaces provides valuable insight into the mechanical behavior of thermoplastic/thermosetting mixtures. Figure 4 depicts the fracture surfaces of epoxy composites doped with percentages PCL.

3.2.3 Self-Healing Properties

While PCL has a relatively low melting point (69 °C), the self-healing mechanism of PCL/epoxy blends is dependent upon the thermoplastic's ability to melt and flow, hence facilitating the filling of fractures Even though co-continuous phase morphology blends tend to have greater morphological variation, their thermomechanical properties are often weaker (Figure 5).
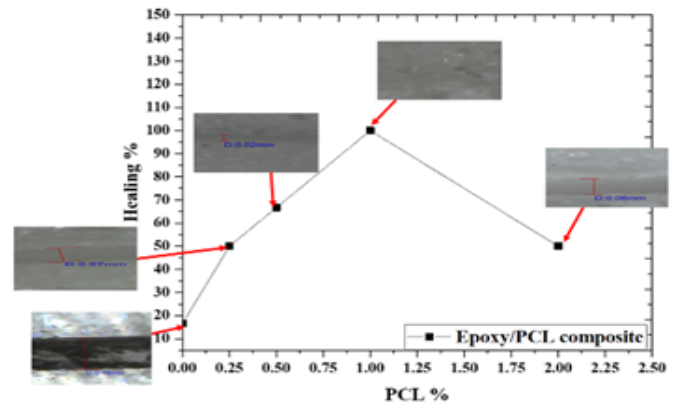

Figure 5. Healing percentage behavior.

Due to this, the effectiveness of self-healing for blends with various PCL contents was examined in this study. In Figure

5, we see the ratio of self-healed crack width to neat crack width, which is a measure of the self-healing efficiency of the mixes under study. According to expectations, the PCL/Epoxy blend with co-continuous phases (1wt% PCL) showed the best self-healing properties. Yet, PCL's low melting point of 69 °C facilitates the anomalous flow to fill the crack.
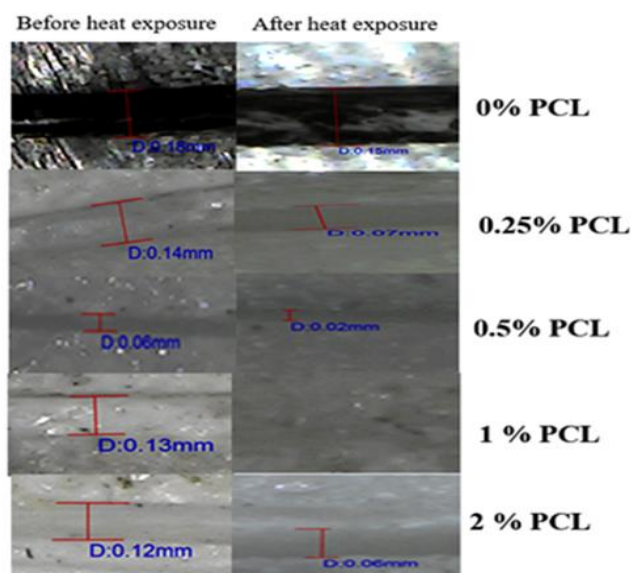

Figure 6. Healing percentage behavior.

The most effective self-healing technology is typically a thermoplastic and thermosetting material that is linked and permeable. However, these loans with co-continuous phase morphology typically have worse thermomechanical characteristics and more morphological variation (Figure 6). Due to this, the self-healing effectiveness of tissues with various PCL contents was examined in this study. Demonstrates the studied lends' ability to heal themselves by comparing the diameters of the self-healed and tidy cracks. For two minutes, the self-healing process was initiated at 90 °C. 68 °C is the minimum temperature required to effectively induce self-healing materials, despite polycaprolactone's lower melting point.

3.3 Blend Morphology

SEM images of the resulting structure's morphology are depicted in Figure 7. The scattered PCL phase served as a reservoir for the self-healing agent to fill the cracks when the PCL level was low. It is important to highlight that once thermal healing was applied, this self-healing thermoplastic solidified into granules after cooling. This cooling would be managed to prevent it because of this. Future works will study this phenomenon. PCL/epoxy mixes' SEM pictures are summarized in Figure 7. Examples are limited to a few studied blend formulations.
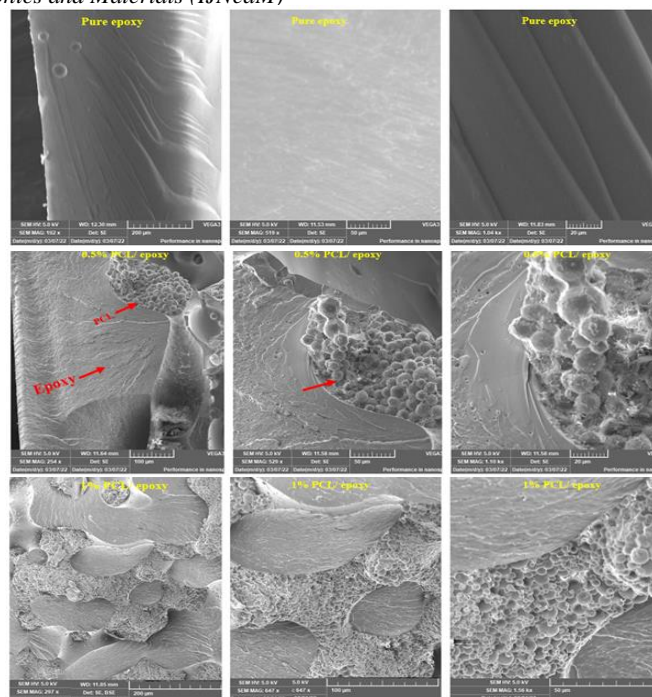

Figure 7. SEM images for pure epoxy and PCL/ Epoxy blends

It can be shown that the rich-PCL phase exists apart from the epoxy matrix. In low thermoplastic PCL/epoxy mixes, the PCL is dispersed throughout the epoxy matrix as spherical particles. Since the entropic contribution to the free energy of mixing decreases as the molecular weight of the epoxy resin increases during curing, phase separation of blends typically occurs during this reaction. When a thermoplastic or rubber phase is incorporated into an epoxy thermosetting matrix, the brittle resin usually becomes more flexible.

4. CONCLUSION

PCL/epoxy mixtures have been investigated as self-healing coating materials. The epoxy coating was mixed with different weight percentages of the thermoplastic polycaprolactone, and the results showed that the co-continuous blends had the highest self-healing efficiency. Their thermal, mechanical, and self-healing capabilities were all highly dependent on the blend morphology. The best self-healing material was a PCL/Epoxy blend with co-continuous phases (1wt% PCL).

REFERENCES

[1] B. J. Blaiszik, S. L. B. Kramer, S. C. Olugebefola, J. S. Moore, N. R. Sottos, and S. R. White, "Self-Healing Polymers and Composites," *Annu. Rev. Mater. Res. 2010.*, vol. 40, pp. 179–216, 2010.

[2] Y. C. Yuan, T. Yin, M. Z. Rong, and M. Q. Zhang, "Self healing in polymers and polymer composites. Concepts, realization and outlook: A review," *Express Polym. Lett.*, vol. 2, no. 4, pp. 238–250, 2008.

[3] A. Nellesen, A. M. Schmidt, I. P. Bond, R. Martin, and A. Rekondo, "Review of research and developments in self healing composite materials," *IOP Conf. Ser. Mater. Sci. Eng.*, no. 346, 2018.

[4] S. Zechel *et al.*, "Intrinsic self-healing polymers with a high E-modulus based on dynamic reversible urea bonds," *NPG Asia Mater.*, vol. 9, no. 8, p. e420, 2017.

[5] A. Lutz, O. van den Berg, J. Wielant, I. De Graeve, and H. Terryn, "A Multiple-Action Self-Healing Coating," *Front. Mater.*, vol. 2, no. January, pp. 1–12, 2016.

[6] A. Jim, G. Del Rosario, X. Xos, and S. Gonz, "Influence of Morphology on the Healing Mechanism of PCL / Epoxy Blends," 2020.

[7] B. Soo, H. Cho, S. R. White, and P. V Braun, "Self-Healing Polymer Coatings.

[8] D. Y. W. Ã, S. Meure, and D. Solomon, "Self-healing polymeric materials : A review of recent developments," *prograss Polym. Sci.*, vol. 33, pp. 479–522, 2008.

[9] A. A.-K. Alaa MOHAMMED, Ahmed HAMZA, "AUTONOMOUS SELF-HEALING COATING OF PMMA MICROCAPSULES FILLED WITH EPOXY," *DIAGNOSTYKA*, vol. 23, no. 1, pp. 1–7, 2022.

[10] F. Zhang and L. Zhang, "A review on the self-healing ability of epoxy polymers," no. June, pp. 1–14, 2020.

[11] J. A. L. J. Hansen, Willie Wu, Kathleen S. Toohey, Nancy R. Sottos, Scott R. White, "Self-Healing Materials with Interpenetrating Microvascular Networks," *Adv. Mater.*, vol. 21, pp. 1–5, 2009.

[12] B. J. Blaiszik, S. L. B. Kramer, S. C. Olugebefola, J. S. Moore, N. R. Sottos, and S. R. White, "MR40CH08-White Self-Healing Polymers and Composites," *Annu. Rev. Mater. Res*, vol. 40, pp. 179–211, 2010.