

Synthesis of a self-healing polymer blend containing dynamic diels-alder and h-bond crosslinks

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ABSTRACT

Introduction: It is unquestioned that self-healing polymers are being applied in numerous applications due to their indiscernible advantages, such as the extension of materials' life span. Not surprisingly, researchers throughout the world concentrate on boosting the progression of the polymer. However, it takes 24 h or 48 h for the self-healing process of polymer-based materials in manifold studies to be efficacious. This can be thought of as a problematic hurdle slowing its advancement and application. Therefore, our research was conducted in an attempt to create a blended structure through hydrogen interplay between (thio)urethane bonds and H-acceptor heterocyclic moieties. **Method:** The integration of 5 wt%, 10 wt% and 20 wt% blended copolymer capable of forming H-bonds into the network structure was performed to gain a network blend. Furthermore, ATR-FTIR spectroscopy, shape-memory and self-healing tests were employed for the determination of hydrogen bond formation coupled with various properties. **Result:** From the ATR-FTIR results, the occurrence of H-bonds was proven. In addition, the blends' rates of shape recovery and shape fixity rates were more than 99%. It contributes to the mechanical recovery at 82.75% with the addition of 10 wt% of the blended copolymer after 10 h at 70 °C, surpassing those of the 5 wt% and 20 wt% blends. **Conclusion:** This study will pave the way for self-healing polymers to be utilized in different fields in the future.

Key words: Self-healing time, Polymer blend, Diels-Alder, Hydrogen bonds

INTRODUCTION

The healable polymer is likely to recover after suffering from mechanical damage. It is a reality that the degradation of material is unavoidable. For instance, the aging process in the long run gives rise to cracks, compromising the material's utility. From the sound of it, there is a need for repairing materials to extend their lifespan; not surprisingly, the exclusive property is of great importance in doing so^{1,2}. It is no wonder that this area is attracting a large number of research groups around the globe. However, in a number of studies³⁻⁶, it took a plethora of time to efficaciously undertake the self-healing process. It is imperative that the enhancement of the self-healing speed of the material be made as soon as possible.

Of the self-healing mechanisms, the Diels-Alder (DA) reaction is referred to as one of the most extensively utilized reversible-thermal equilibrium reactions to form inherently reversible covalent polymer-based healable networks. In particular, DA cycloadducts are generated from the cycloaddition of furan, which is seen as a conjugated electron-rich diene, and maleimide, which is viewed as an electron-poor dienophile⁷. Since the DA reaction is ascribed to the transformation of two π bonds to σ bonds, the

DA retro reaction is endothermic, requiring heat for the occurrence of the DA reaction. The principal gain of the reversible DA reaction is that it is capable of re-curing with a lack of additional catalysts for serving the self-healing process⁸. Additionally, Diels-Alder chemistry is considered a click response because of its remarkably high efficacy.

Furthermore, reforming bonds can solely occur with a proper closure of two crack surfaces even without being restrained by chain mobility⁹. In an attempt to tackle the complicated hindrance, numerous approaches, such as the manual injection of a solvent or introduction of the shape-memory effect, have been implemented. The system of urethane-thiourethane with shape-memory and healable properties was formed with the use of DA chemistry. Bis-/trismaleimide, bismaleimide, bisfuranic, or trisfuranic monomers were employed in semicrystalline polycaprolactone (PCL) circuits; herein, PCL can be deemed the switching segment. For such a network, 70-80% recoveries of the mechanical strengths as well as nearly complete evaporation of scratches were recorded after the healing process at approximately 60 °C for 1 to 3 days.¹⁰

Thermoplastic polyurethanes (TPUs) carrying urethane repeating units are primarily obtained from

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the addition polymerization of polyisocyanates and macropolyols with chain extenders¹¹. Polyurethane materials generally have some outstanding virtues, such as high tensile strength and low-temperature wear resistance. TPUs have been utilized in numerous fields in a widespread way. The addition of self-healing capability has considerably enhanced the service life coupled with the possibility of recycling TPUs¹². The diisocyanate, dihydroxy telechelic prepolymer and chain extender in polyurethane synthesis determine the final characteristics of polyurethanes, especially their self-healing ability. Other elements, such as side reactions during the production of PU accompanied by the appearance of catalysts, could also have an influence¹³. The fast-paced development of designing multifunctional TPUs has paved the way for combining outstanding mechanical strength along with superior self-healing efficiency. In addition, reversible covalent bonds together with noncovalent links play a crucial role in enabling self-healing polyurethanes to achieve many healing cycles.

Poly(4-vinylpyridine) (P4VP) possesses saturated carbon chains in its structure in view of the polymerization of vinyl groups, with its pyridine rings acting as a good hydrogen-bonding acceptor, bringing about the formation of reversible hydrogen bonds. Thus, polymers with pyridine groups are apt to be harnessed in the domain of self-healing materials. Furthermore, poly(stearyl methacrylate) possesses a glass transition temperature below $-60\text{ }^{\circ}\text{C}$ ¹⁴; in addition, the stearyl side chains can crystallize with a melting point in the range of $35\text{--}45\text{ }^{\circ}\text{C}$ ¹⁵. The stearyl side chains' entropy gain above this melting point could induce an increase in mobility for the copolymer chain bearing a resemblance to the mechanism of the shape recovery effect in polymers. There have also been published scientific studies concerning the utilization of shape-memory polymers by the group^{16,17}. In addition, the hydrophobic interaction of the stearyl group together with the interlocking capability can also be beneficial for the healing process of the material.

In this research, with the objective of synthesizing a new self-healing polymer blend, the poly(caprolactone-thiourethane) lattice (network) from the reaction of furfuryl thiourethane-telechelic polycaprolactone (PCLfuran), 1,1'-(methylenedi-4,1-phenylene)bismaleimide (BMI) and the tris-furan crosslinker carried out in our previous study¹⁸ was blended with 5 wt%, 10 wt% and 20 wt% of the copolymer poly(4-vinylpyridine-*random*-stearyl methacrylate) (P(4VP-SMA)) obtained from our previous research¹⁹. It could diffuse through the

thiourethane network and simultaneously form hydrogen bonds with the network. Thus, the healing process in the resultant blends would occur not only via the reversibility of DA and hydrogen bonds and the PCL-based shape-memory effect but also with the assistance of the diffusion of P(4VP-SMA) chains. Therefore, it could expedite the self-healing process. Consequently, the blend with 10 wt% P(4VP-SMA) (Network-blend10) exhibits a high self-healing efficiency of 82.75% after 10 h, surpassing those of other blends with 5 wt% and 20 wt% P(4VP-SMA) (Network-blend5 and Network-blend20, respectively). The material has enormous potential to be applied in practice.

EXPERIMENTATION

Materials

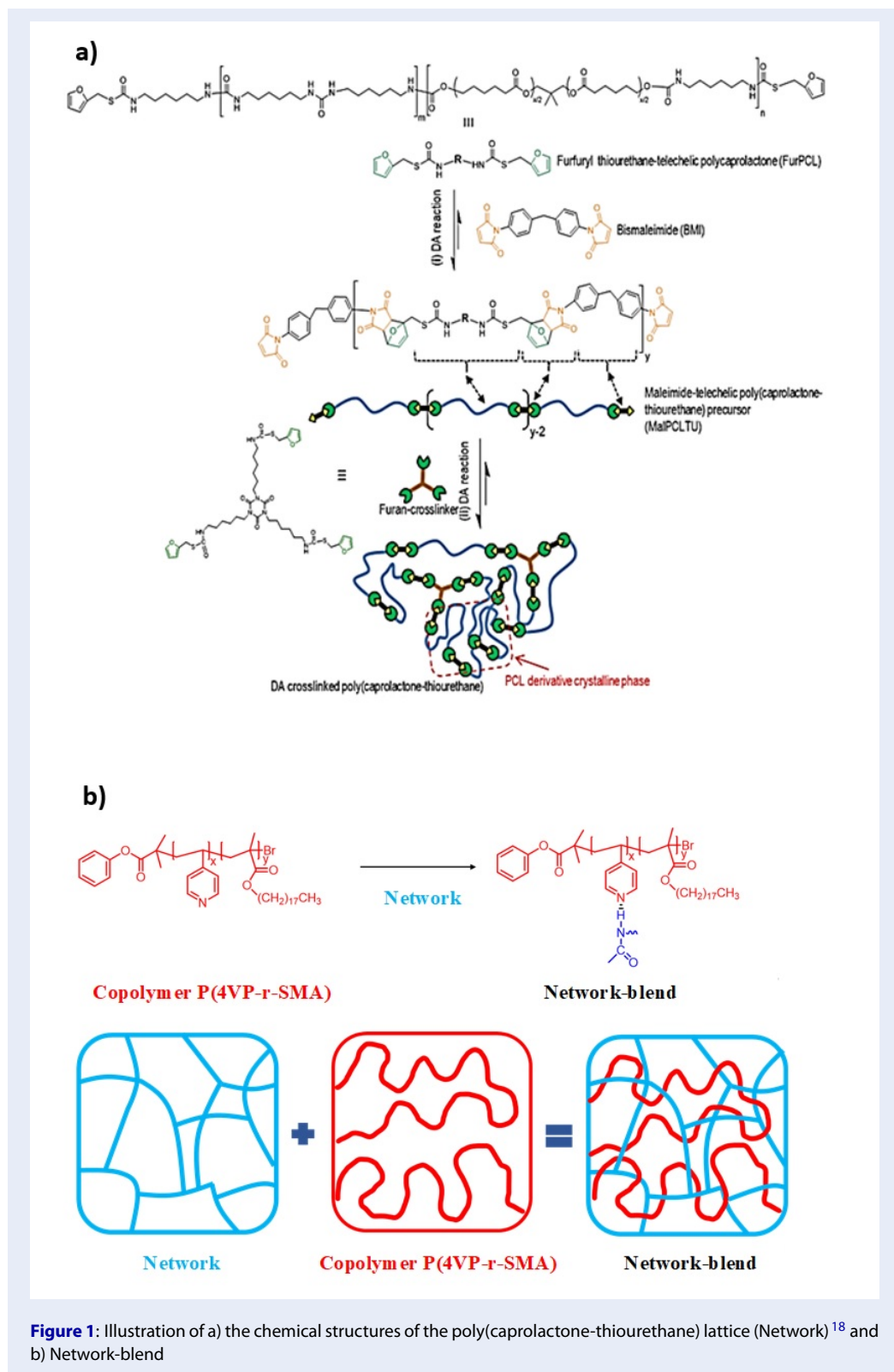
1,1'-(Methylenedi-4,1-phenylene) Bismaleimide (95%, Sigma-Aldrich), Furfuryl thiourethane-telechelic polycaprolactone (PCLfuran) illustrated in the preceding study¹⁸, the tris-furan crosslinker synthesized according to the previously reported procedure²⁰, and the copolymer poly(4-vinylpyridine-*random*-stearyl methacrylate) P(4VP-*r*-SMA) prepared according to the reference¹⁹.

The synthesis of the network blend

PCLfuran was initially linked with excess BMI in a one-pot process using the DA reaction between furan and maleimide groups at $50\text{ }^{\circ}\text{C}$ during the 12-hour period (step 1), followed by the addition of the tris-furan crosslinker (step 2). After that, the mixture was not immediately injected into the mold as opposed to adding P(4VP-*r*-SMA) to it. After being mixed for one hour at $50\text{ }^{\circ}\text{C}$, the mixture was injected into a mold, and the curing process was witnessed for 24 hours at $50\text{ }^{\circ}\text{C}$. In the final stage, the blend was attained.

Characterization

On an FT-IR Tensor 27 spectrometer supplied with a Pike MIRacle ATR attachment with a diamond/ZnSe element, attenuated total reflectance (ATR) FT-IR spectra were acquired as the average of 128 scans with a resolution of 4 cm^{-1} . Using a 1000 N load cell and a Tensilon RTC-1210A tensile testing machine, mechanical properties were quantified. The dog bone-shaped samples met the specifications of ASTM D638-type IV but had scaled-down proportions, with an effective gauge length of 11 mm, a width of 2 mm, and a thickness of 1.5 mm. For each component, at least four samples were examined. An Olympus GX51F microscope was used to capture optical



microscopy images.

To assess the shape-memory property of the samples, they were stretched to 40% with the assistance of a Tensilon RTC-1210A tensile testing machine. First, their original lengths (L_0) were recorded; then, they were exposed to the environment at 70 °C prior to being deformed. In this stage, these lengths from the process of deformation (L_1) were also documented. Next, they were cooled to room temperature without being under stress, thanks to which, their temporary shapes were obtained. Their sizes in this step (L_2) were measured. In the final phase, the samples were placed in the aforementioned heated environment to return to their original length. These lengths (L_3) were noted. Equations (1) and (2) were used to compute the shape recovery and fixity ratios, R_r and R_f , respectively.²¹

$$R_r (\%) = \frac{L_2 - L_3}{L_2 - L_0} \times 100\% \quad (1)$$

$$R_f (\%) = \frac{L_2 - L_0}{L_1 - L_0} \times 100\% \quad (2)$$

Surface cuts and surface denting recovery experiments using optical microscopy (OM) were first performed to explore the healing characteristics of the materials. Macroscratches were created with a scalpel blade, and dent damages were created with a hardness test pencil (318S, Erichsen) as well as 10 N of normal load on the surface of the samples. On an Olympus GX51F microscope, microscopic photos of the scraping and dent damage were taken before and after healing.

To investigate the effectiveness of self-healing, the samples underwent significant tensile deformations at 50% of the respective break strain. The extended sample was in a 70 °C environment over a 24-hour timescale to enable complete shape recovery and repair of the broken DA along with hydrogen bonds after the removal of the load. The self-healing efficiency was determined via the following formulation²².

$$\begin{aligned} & \text{Healing efficiency (\%)} \\ &= \frac{\text{Tensile strength}}{\text{Starting Tensile Strength}} \times 100\% \end{aligned} \quad (3)$$

RESULTS

The FTIR spectrum of P(4VP-*r*-SMA) exhibited bands at 2952 and 2854 cm^{-1} (corresponding to the SMA block C-H stretching vibrations) and pyridine vibrational bands at 1594 cm^{-1} (pyridine C=C stretching mode) and 992 and 813 cm^{-1} (pyridine C-H bending). A comparison of the ATR FTIR spectra

of Network and Network-blend10 exhibited the retention of the bands at 1594 cm^{-1} and 818 cm^{-1} ascribed to poly(4-vinyl pyridine).¹⁹

It is apparent that the shape recovery accompanied by fixity ratios of the blends were exceptional owing to the appearance of PCL bringing about the shape-memory effect. In detail, Network-blend5, Network-blend10 and Network-blend20 proclaimed R_r and R_f values of 98.5%, 99.1% and 96.4% together with 98.06%, 99.35% and 97.1%, respectively.

As demonstrated in Figure 3, Network-blend10 has a reasonably good self-healing capacity, mending the scratches entirely after 10 hours at 70 °C. The results showed that the incision was completely healed. In contrast, scratches on the surfaces of Network-blend5 and Network-blend20 exhibited no signs of disappearance in tandem.

The highest tensile stress and strain values of the original blend are 22.9 ± 8.2 MPa and $60.8 \pm 8.2\%$, respectively. With respect to the self-healing efficacy, over the period of 10 hours, the figure for Network-blend10 is 82.75% after 24 h.

DISCUSSION

The synthesis of the novel self-healing polymer blend from the poly(caprolactone-thiourethane) lattice (Network) and the copolymer poly(4-vinylpyridine-random-stearyl methacrylate) P(4VP-SMA) was conducted using 5 wt%, 10 wt% and 20 wt% P(4VP-*r*-SMA). In the following stage, the research centered on comparing the properties of the blends, especially the healable capacity after 10 h.

It goes without saying that infrared spectroscopy is a mighty instrument in attempts to study hydrogen interactions. In addition, the frequency shift is widely recognized as a measure of hydrogen bonding strength. The peak shift of the pyridine functional group on the IR spectra when engaging in hydrogen bonding was used to evaluate hydrogen bond formation. The distinctive signal of the pyridine ring moves from 813 cm^{-1} to 818 cm^{-1} . The creation of hydrogen bonds in the blend polymer caused these changes; nevertheless, the interactions were weak, and hence, the displacement was relatively minor. Additionally, the shift of the NH vibration from 3338 cm^{-1} to 3342 cm^{-1} confirmed the formation of hydrogen bonds between urethane groups' C=O and N-H along with the pyridine ring and N-H urethane groups^{23,24}. This means that synthesizing the polymer blend was successful.

It is critical to make tight and intimate contact between the fracture surfaces to assist the self-healing process. This may be accomplished by utilizing the

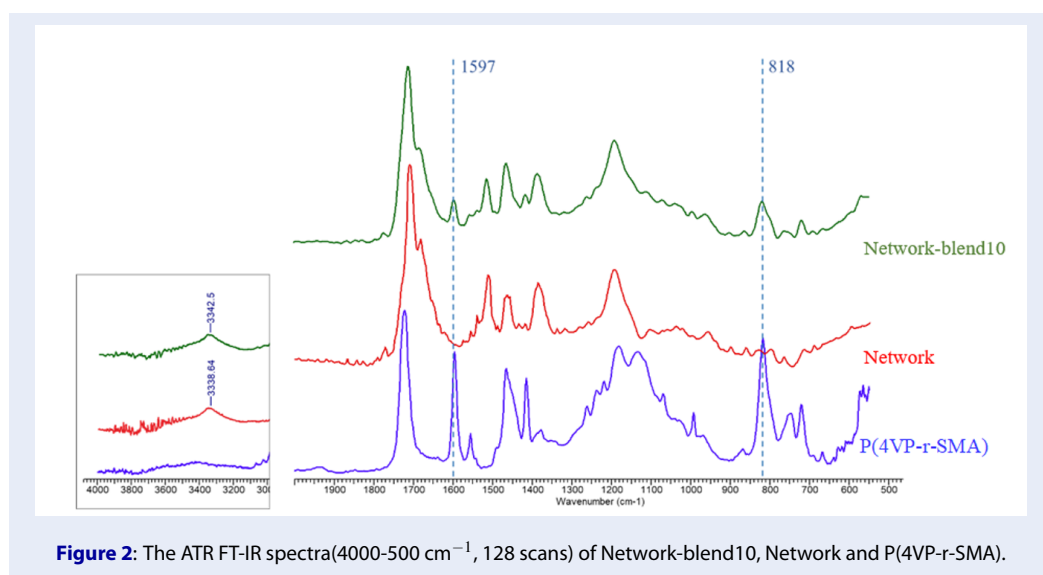


Figure 2: The ATR FT-IR spectra(4000-500 cm^{-1} , 128 scans) of Network-blend10, Network and P(4VP-r-SMA).

Table 1: Summary of the shape recovery and shape fixity ratios of Network-blend5, Network-blend10 and Network-blend20.

Product	R_r (%)	R_f (%)
Network-blend5	98.5	98.06
Network-blend10	99.1	99.35
Network-blend20	96.4	97.1

Table 2: Summary of the mechanical characteristics and self-healing efficiency of Network-blend10 measured by the tensile test.

Product	Ultimate Tensile stress (MPa)	Ultimate Strain (%)	Self-healing efficiency (%)
Network-blend10	22.9 ± 8.2	60.8 ± 8.2	
Network-blend10 (Healing for 10 h)	18.95 ± 5.6	44.3 ± 8.4	82.75

shape recovery feature. Specifically, in the temperature range where the material poly(ϵ -caprolactone) (PCL) melting transformation occurs, polymer chains with cracked diels-alder (DA) moieties preserve a reasonable amount of mobility. Furthermore, the existence of multiple intermolecular entanglements between permanent crosslinks provides a strong driving force for network segment repair, supporting the healing process^{25,26}. This phenomenon brings about more entropic elasticity recovery within the network, supporting optimum shape restoration. Consequently, the chosen healing temperature grounded on the aforementioned thermal analysis data is specifically near or in the melting transition zone of PCL segments, which coincides with a favorable manifestation of the Diels-Alder reaction. Following initial

visual monitoring of the healing operation, a temperature of 70 °C was identified as the healing temperature for the blends. Erstwhile research has additionally demonstrated that the DA response is best generated at temperatures ranging from 50 to 70 °C^{27,28}. Regarding the shape-memory ability, in comparison with those of Network-blend5 and Network-blend20, the R_r and R_f of Network-blend20 are better. It stems from incorporating P(4VP-r-SMA) into the blend, leading to the entanglement of polymer chains. Consequently, it could restrict the displacement of molecular chains on a large scale, giving rise to storing entropic energy²⁹ indeed, it is referred to as the driving force for the shape-memory effect³⁰. Network-blend20, because of the low PCL content, led to a downward trend in these values.

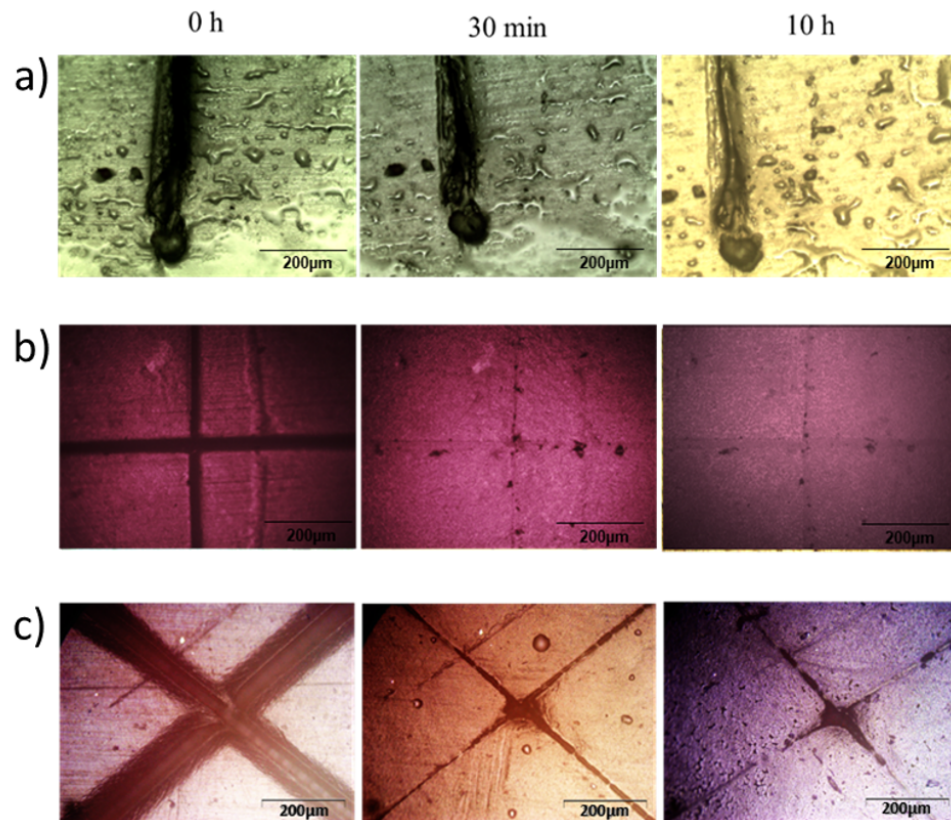


Figure 3: Optical microscopy (OM) images of a) Network-blend5, b) Network-blend10 and c) Network-blend20 samples before and after the healing process at 70 °C

Notably, the self-healing process of Network-blend10 is fast to some extent. It comes from the reality that during the timescale of 10 hours, the tensile strength blend recovered to over 80%. Furthermore, with the images from the microscope, it appears that the presence of a small quantity of P(4VP-*r*-SMA) in the blend resulted in a reduced healing time. In this case, the diffusion of P(4VP-*r*-SMA) chains across the crack and the reformation of hydrogen bonds along with the PCL-derived shape memory effect effectively assisted the process of closing cracks. Nevertheless, at a higher content of the copolymer, at 20 wt%, it is possible that the decreased contents of PCL segments as well as DA groups are insufficient for efficient shape recovery and healing reactions to occur. Apparently, a proper balance between the content of the DA linkages, PCL segments and P(4VP-*r*-SMA) chains as a diffusion agent is necessary.

CONCLUSIONS

The healable polymer blends were successfully synthesized by means of mixing the network with the

P(4VP-*r*-SMA) linear copolymer as a forming-H-bond and diffusion agent. Moreover, blending the network with 10 wt% P(4VP-*r*-SMA) not only made the healing process quick with a healing efficacy of 82.75% after 10 h but also maintained a high self-healing efficiency with the support of the shape-memory ability ($R_r, R_f > 99\%$). This shows enormous potential for technological as well as industrial applications.

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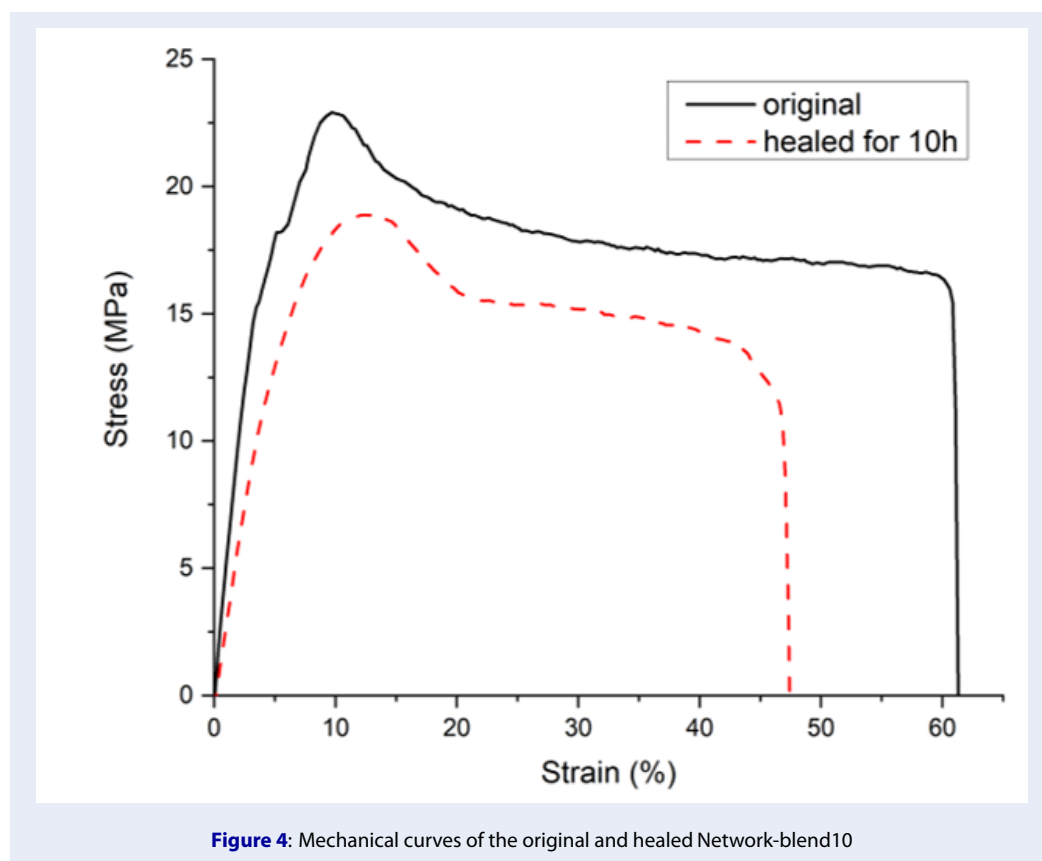
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LIST OF ABBREVIATIONS

ATR-FTIR: Attenuated total reflectance Fourier transform infrared spectroscopy

DA: Diels-Alder

rDA: Retro-Diels-Alder



R_r : The shape recovery ratio

R_f : The shape fixity ratio

AUTHOR CONTRIBUTION

Mai Ly Nguyen Thi, Viet Quoc Nguyen: methodology, investigation, Mai Ly Nguyen Thi, Duc Anh Nguyen Song: investigation, formal analysis, Thuy Thu Truong: supervision. All authors read and approved the final manuscript.

CONFLICT OF INTEREST

The authors declare that they have no competing interests.

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