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Self-healing Behavior of Ethylene Propylene Diene Rubbers Based on Ionic Association

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Electronic Supplementary Information

Abstract To meet the increasing demand for safe, environmentally friendly and high-performance smart materials, self-healing rubbers are highly desired. Here, the self-healing performance of ethylene propylene diene monomer rubber (EPDM) is reported, which was designed by graft-polymerization of zinc dimethacrylate (ZDMA) onto rubber chains to form a reversible ionic cross-linked network. Single ionic cross-linked network and dual network, combining covalent and ionic cross-links, could be tuned by controlling vulcanization process to achieve tailorable mechanical and self-healing properties. It was found that ionic cross-linked EPDM showed a recovery of more than 95% of the original mechanical strength through a healing process of 1 h at 100 °C. The covalent cross-links could improve mechanical properties but block self-healing. Adding 50 wt% liquid rubber to “dry” EPDM could effectively enhance self-healing capability of the dual cross-linked network and the healed tensile strength could reach 0.9 MPa. A compromise between mechanical performance and healing capability could be potentially tailored by controlling vulcanization process and liquid rubber content.

Keywords Ionic bond; Self-healing; Ethylene propylene diene rubber; Dual-network

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INTRODUCTION

Rubbers exhibit unique dynamic features such as high resilience, low-elastic modulus, and viscoelasticity, which are known as strategically important materials and indispensable in tires, seals, belts, shock absorbers, and other industrial products. However, the cross-linking of rubbers is a prerequisite for acquiring the high strength and stretchability. At present, sulfur vulcanization and peroxide curing are the main cross-linking techniques, which yield covalent cross-linked networks.^[1,2] Due to the irreversibility of the covalent cross-links, damages caused by force and deformation in the use process, once formed, will not disappear at later stages. End-of-life rubber products are causing a serious environmental concern as well as a significant waste of resources. In the earlier reported works, intensive efforts have been made to solve this issue.^[3–5] In recent years, the concept of self-healing offers a solution from another angle, which may have a significant improvement of functionalization, safety, service life, and recycling of the products and

devices.^[6–9] Conventional vulcanized rubbers do not have self-healing ability because of the establishment of a stable covalent cross-linked network to achieve excellent and stable mechanical properties. Recently, dynamic cross-linked networks based on reversible bonds have been designed for self-healing polymer with low glass transition temperature (T_g), such as hydrogen bonds,^[10–12] metal-ligand coordination,^[13,14] and ionic bonds.^[15–17] The weak dynamic bonds acting as cross-links are key elements for self-healing which are preferentially broken under force and reform once reconnecting.^[18]

Ethylene propylene diene monomer rubber (EPDM) with saturated carbon backbones is one of the most frequently used synthetic rubbers. Due to high loading of fillers and its remarkable resistance to oxygen, ozone, UV, heat, and stress cracking, EPDM can be found in many outdoor applications, automotive, roofing applications, and sporting goods. However, EPDM shows poor resistance to mechanical damages. Designing EPDM with potential self-repair capability may improve the service life of EPDM. Many studies of self-healing polymers were focused on rubbers with low T_g and good diffusion property, such as PDMS^[14] and ENR.^[15] Unfortunately, the study on modification of commercial EPDM rubber with proper self-healable ability has rarely been concerned. It is still a huge challenge to en-

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dow EPDM with self-healing capability because of the following shortcomings. Firstly, EPDM has saturated chain and less reactive sites, so it is difficult to be modified for constructing reversible network. Secondly, diffusion capacity of EPDM molecular chain is poor, which reduces the possibility of reconstructing networks through reforming reversible bonds.^[19]

Rubber materials containing ionic groups have already been found to exhibit self-healing performance.^[16,20–24] For example, Das *et al.*^[17] converted bromobutyl rubber into self-healing material by incorporating reversible ionic associates as physical cross-linking unit. Miwa *et al.*^[24] reported an ionically cross-linked polyisoprene elastomer with dynamic network owing to continual hop of ionic moieties between ionic aggregates. This elastomer could self-heal at room temperature spontaneously without external energy or other healing agents. Zinc dimethacrylate (ZDMA) can be easily graft-polymerized onto rubber chains during a peroxide-induced curing and form ionic association.^[25,26] This method involves no complicated chemical modification to change rubber molecular structures. The strong electrostatic interaction between PZDMA and EPDM rubber chains can restrict the mobility of rubber chains, further form reversible physical cross-linked networks, and thereby endows rubber with self-healing property.^[22,26–29]

Here, we introduced self-healing property into EPDM through reversible ionic network cross-linked by PZDMA. Single ionic network can be prepared by controlling vulcanization process. However, solely physical cross-linked networks are usually weaker than covalent cross-linking and hence, combining covalent and dynamic cross-links in rubber materials can lead to good mechanical properties together with self-healing capability.^[30–32] In the present work, the self-healing ability of EPDM rubber with dual network combining dynamic ionic bonds and covalent cross-links has also been researched. Given the poor diffusion capability of EPDM chains, liquid EPDM with low molecular weight was used to achieve good self-healing ability. By varying the covalent cross-linking density and rubber molecular chain structure, the mechanical properties and the self-healing capability can be systematically tuned.

EXPERIMENTAL

Sample Preparation

The ethylene propylene diene monomer rubber (Lanxess 4450, German) used in this study, with a Mooney viscosity (ML (1 + 4) 125 °C) of 46, was commercially available. Liquid EPDM used was TRILENE® 67 (Lion Elastomers LLC, American). Zinc dimethacrylate (ZDMA) 634, was purchased from HaoShen Chem. (Shanghai, China). Dicumyl peroxide (DCP) was purchased from Aladdin Chemical Co. Ltd. (China).

The rubber compound comprised 100 g of EPDM, 30 g of ZDMA, and 3 g of DCP. The curing rubbers were prepared as follows. First, EPDM was mixed in an internal mixer (HAAKE torque rheometer, Rheomix3000OS, Germany) for 2 min with a rotor speed of 60 r/min at 80 °C and then ZDMA was added into the mixer in two batches, allowing to

mix for 2 min after each addition and the temperature was kept lower than 120 °C. After that, the rubber compound was cooled to around 80 °C before adding DCP and continued to mix for 2 min. Before initiating the curing procedure, the rubber compound was masticated in a two-roller mill at 40 °C. Curing curves of the EPDM/ZDMA compound were monitored using a MDR 2000 (Alpha, American) vulcameter at different temperatures. The curing experiment was carried out on a XLB-D500*500 flat-panel curing machine (Huzhou Eastern Machinery Co., Ltd. China)

Characterizations

Differential scanning calorimetry (DSC) measurements were performed on a TA Instruments Q1000 device to determine graft-polymerization temperature of ZDMA and curing temperature of EPDM induced by DCP. The samples were heated from −50 °C to 220 °C at a rate of 10 °C/min. FTIR spectra were recorded on a Bruker VERTEX70 spectrometer (Germany) under attenuated total reflectance (ATR) with a resolution of 4 cm^{−1} and an accumulation of 32 scans.

Equilibrium swelling experiments were conducted to determine the cross-linking density of the resultant rubber materials. The pre-weighed samples were immersed in toluene at room temperature for 3 days to achieve their swollen equilibrium. Then, the excess toluene was gently wiped off with filter paper and the samples were immediately re-weighed. Finally, the swollen samples were dried in a vacuum oven at 60 °C until constant weight was achieved. The cross-linking density of the polymer was calculated with Flory-Rehner equation:^[33]

$$-\left[\ln(1 - \Phi_r) + \Phi_r + \chi\Phi_r^2\right] = V_0 n \left[\Phi_r^{1/3} - \frac{\Phi_r}{2}\right] \quad (1)$$

where Φ_r is the volume fraction of polymer in the swollen sample, V_0 is the molar volume of the solvent (106.2 cm³ for toluene), n is the number of active network chain segments per unit of volume (cross-linking density), and χ is the Flory-Huggins polymer-solvent interaction term. The value of χ for toluene is 0.49. The value of Φ_r was attained according to the method used by Bala *et al.*^[34]

$$\Phi_r = \frac{m_2/\rho_2}{m_2/\rho_2 + (m_1 - m_2)/\rho_1} \quad (2)$$

where m_1 and m_2 are the masses of swollen sample before and after dried, respectively. ρ_1 and ρ_2 are the densities of toluene ($\rho_1 = 0.865$ g/cm³) and rubber, respectively.

The whole cross-linking density was determined by the covalent cross-linking and ionic cross-linking. To exclude the contribution from ionic cross-linking, samples were immersed in a mixture of toluene/hydrochloric acid/ethanol (90/10/0.3 by volume) for 4 days and subsequently immersed in toluene for 3 days to calculate the residual cross-linking density.^[26] Obviously, the residual network should be constructed by covalent cross-links completely, so the residual cross-linking density is covalent cross-linking density. The ionic cross-link could be calculated by subtracting the covalent cross-linking density from the total cross-linking density.^[25,27]

Tensile tests were carried out on a Zwick/Roell Z2005

universal electronic tension testing machine (Germany) with dumbbell-shaped specimens (total length: 75 mm, thickness: 2 mm, width of the parallel part: 4 mm). The specimens were stretched until failure at a cross-head speed of 500 mm/min at 23 °C and each sample was tested at least three times.

The morphology of samples with partially fractured surfaces was observed by a stereoscopic microscope (Nikon SMZ 1500, Nikon, Japan). For further self-healing tests, samples were cut into two separate parts with a clean scalpel. The fracture surfaces were placed back together with a slight pressure immediately. Then, the cut samples were healed at set temperature for a certain period of time and then subjected to stress-strain tests at room temperature. The healed samples were stretched to fracture again. Healing efficiency was evaluated from the comparison of tensile strength of the healed samples and the virgin ones.

RESULTS AND DISCUSSION

Investigation of the Reversible Ionic Cross-linked EPDM

Here, we introduced ZDMA onto EPDM *via* graft-polymerization induced by DCP to construct a reversible supramolecular network. It is well known that DCP as a radical initiator can induce grafting reaction of ZDMA as well as curing reaction of rubber. Firstly, the reaction temperature of graft-polymerization of ZDMA and curing temperature of EPDM induced by DCP were investigated using DSC, as shown in Fig. 1(a). The DSC trace of EPDM/DCP only exhibits a thermal transition at 185.3 °C with a good symmetrical peak shape, which is attributed to the cross-linking of EPDM molecules induced by DCP.^[27] But, the DSC trace of EPDM/ZDMA displays an asymmetric peak and a new significant coupling peak is detected at lower temperature, which is caused by the polymerization of ZDMA. Besides, the increase of heat liberated from EPDM/ZDMA at lower temperature should be attributed to homo-polymerization and graft-polymerization of ZDMA.^[26] So, it can be inferred that the graft-polymerization of ZDMA happened at lower temperature than the cross-linking process of EPDM rubber molecules did.

The reaction product of ZDMA grafting onto EPDM was confirmed by FTIR spectroscopy. The sample was first treated with toluene/hydrochloric acid/ethanol mixed solvent to destroy the electrostatic interaction between ion pairs^[26] and to transform the carboxylic acid salt into $-\text{COOH}$ groups. Then the treated sample was dried and examined, with the FTIR spectra shown in Fig. 1(b). Compared with that of gum EPDM, a new absorption peak at 1700 cm^{-1} is observed, which represents the characteristic absorption peak of $-\text{COOH}$.^[22] This result supported that ZDMA has graft-polymerized onto EPDM, which gave the possibility to construct a reversible ionic cross-linked EPDM network by multiple ionic interaction in PZDMA.

From Fig. 1, we can see that the graft-polymerization of ZDMA occurred at a lower temperature. Based on this, we tried to build reversible cross-linking network by controlling the curing time and curing temperature to prepare the self-healing material. First, the effect of curing condition on EPDM cross-link was studied using torque curves, as shown in

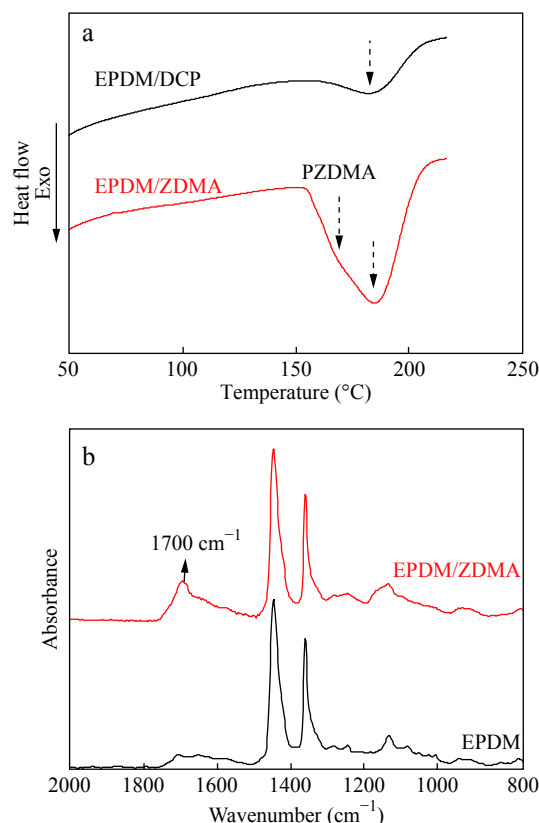


Fig. 1 (a) DSC curves of EPDM/DCP and EPDM/ZDMA compounds; (b) FTIR spectra of EPDM and EPDM/ZDMA compounds treated by mixture of toluene/hydrochloric acid/ethanol

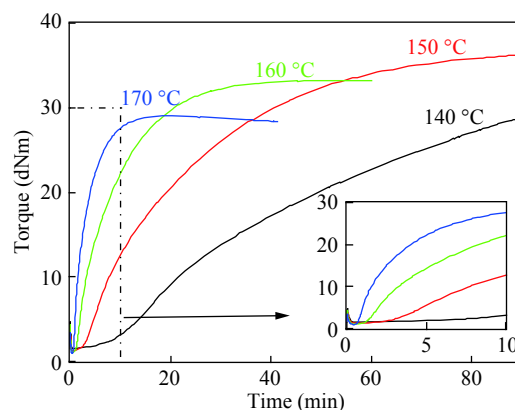


Fig. 2 Torque curves of the EPDM/ZDMA compound at 140, 150, 160, and 170 °C

Fig. 2. At a commonly employed temperature of 170 °C, the cross-linking of EPDM/ZDMA compound was almost completed after 10 min of thermal treatment. When the curing temperature was reduced from 170 °C to 160 °C, t_{90} (the time for torque to increase by 90%) increased from 7.93 min to 20.68 min. At the temperatures of 150 and 140 °C, the torque increased constantly, which suggests that cross-linking process was not completed even after 90 min. It also supports that cross-linking rate of EPDM could be reduced effectively by lowering the curing temperature. Besides, at lower temperature, the torque increased slightly at the initial period of several minutes. There was even no distinct torque

increasing phenomenon for the first 5 min at 140 °C indicating low covalent cross-linking degree. Therefore, a possible supramolecular network could be formed at a low curing temperature in short curing time by electrostatic interaction in PZDMA. The schematic illustration for graft-polymerization and the formation of cross-linked network is shown in Fig. 3(a).

To intuitively confirm the formation of ionic cross-linked network, dissolution/swell experiments were performed for the sample cured at 150 °C for 150 s in toluene. It is clearly seen that the resultant sample was only swollen in toluene, which brought about a piece of translucent gel, thereby suggesting the existence of cross-linked network. However, after further immersing in the mixture of toluene/hydrochloric acid/ethanol for a period, the sample dissolved fully and a muddle solution could be observed instead of gel. This phenomenon demonstrates that the cross-linked network in EPDM/ZDMA cured at 150 °C for 150 s was mainly dominated by a relatively developed ionic cross-links without significant covalent cross-linked network. Although the covalent cross-linked network of EPDM was not formed, EPDM/ZDMA compound with ionic cross-link network showed a certain mechanical strength (Fig. S1 in electronic supple-

mentary information, ESI).

Self-healing Properties of Ionic Cross-linked EPDM

The reversibility of ionic association may endow the ionic cross-linked EPMD/ZDMA with healing performance by temperature or stress-induced rearrangements. Therefore, the self-healing behavior of EPDM/ZDMA composite cured at 150 °C for 150 s was observed under a stereoscopic microscope. Magnified images of the broken samples and thermally treated ones are shown in Fig. 4(a). The samples were partially fractured in two ways to avoid the separation into two pieces—a scratch by scalpel or small holes by needle, and then underwent a heating process at 100 °C for 1 h. After thermal treatment, complete healing of scratches as well as holes could be clearly observed on the EPDM/ZDMA sample surfaces without any visible fracture, confirming the effective crack self-healing behaviors. But, the control of EPDM cured by DCP could not repair itself under the same conditions as shown in Fig. 4(b) due to irreversible covalent cross-links. It manifests that weak dynamic ionic bonds are responsible for the self-healing properties.

In order to further evaluate the self-healing performance, the tensile tests of fully cut samples after healing were fulfilled. The corresponding healing ability of the 150 s-cured

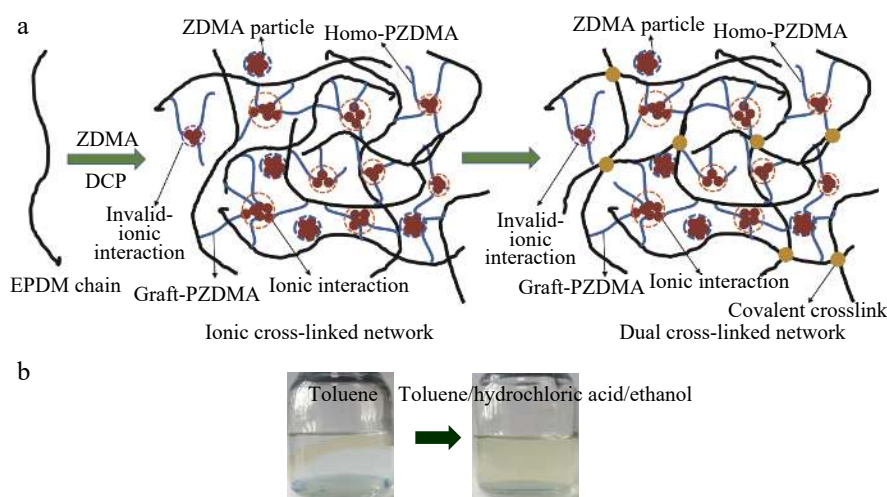


Fig. 3 (a) Schematic illustration for graft-polymerization and the formation of cross-linked network; (b) Photographs of dissolution/swell experiment

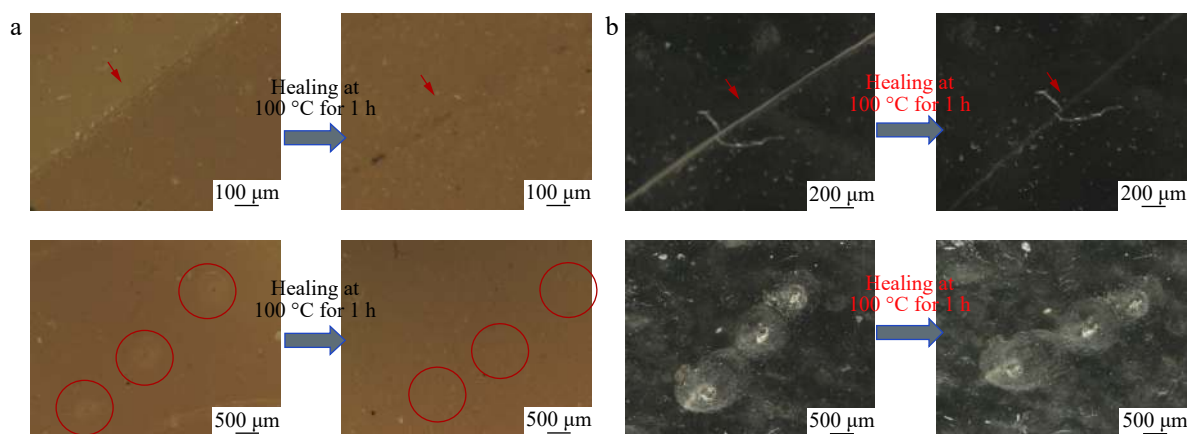


Fig. 4 Stereomicroscope images of self-healing behavior of (a) EPDM/ZDMA and (b) EPDM/DCP compounds

EPDM/ZDMA compound through a different healing progress is shown in Fig. 5. The first set of experiments consisted of varying the healing temperature for 1 h after cutting. In the second set, damaged samples were healed at 100 °C for different periods of time. Fig. 5(a) shows the stress-strain curves of pristine and healed EPDM/ZDMA compounds at different healing temperatures for 60 min. Results indicate that a recovery of more than 95% of the initial mechanical strength could be obtained within the tested temperature range. Besides, increasing healing temperature could improve the healing of elongation at break. After a healing process at 100 °C for 1 h, the fracture strain of healed sample reached 270%. Obviously, although the electrostatic interaction of ion pairs could be destroyed at high temperatures,^[17,22] a higher temperature (100 °C) was still beneficial for the healing of EPDM/ZDMA compound. This can be explained by the increased chain mobility and interdiffusion at higher temperature, which promote the chain rearrangement and allow the dynamic ionic groups to meet together.^[35] However, when the curing temperature was further raised to 120 °C, the healed samples showed a higher mechanical strength and modulus (Fig. S2 in ESI) than those of the sample, which is caused by further cross-link reaction occurring. At the same time, the formation of covalent reduced healing ability, meaning that the material would lose its stable self-healing ability. Hence, a very high healing temperature is not conducive to the consistency of properties.

Fig. 5(b) shows the stress-strain curves of cut samples after healing at 100 °C for different periods of time. More than 95% of the initial mechanical strength was recovered just 10 min later. Prolonging healing time resulted in gradually healed fracture strain from 72% to 270% for 10 min to 60 min healing time. It can be seen that both prolonging healing time and raising healing temperature facilitated self-healing of EPDM/ZDMA compound. Similarly, the healing behaviors of 210 s-cured EPDM/ZDMA compound were measured (Fig. S3 in ESI) under the same illumination conditions as those of 150 s-cured EPDM/ZDMA. Comparatively, the control of EPDM sample cured by DCP at 150 °C for 150 s exhibited low healed mechanical strength and fracture strain, because only physical interaction was available at the interfaces (Fig. 5c). It further confirms that dynamic ionic hydrogen bonds are responsible for the self-healing properties.

Self-healing Properties of Single Network and Dual-network

Self-healing polymers cross-linked by solely reversible non-covalent bonds are constitutionally weaker than covalently cross-linked system. Introducing covalent cross-links into a reversible network would improve mechanical strength. Here, the self-healing performance of EPDM/ZDMA compound combining covalent and ionic cross-linked network is presented. The EPDM/ZDMA compound was cured at 150 °C for different periods of time to obtain samples with

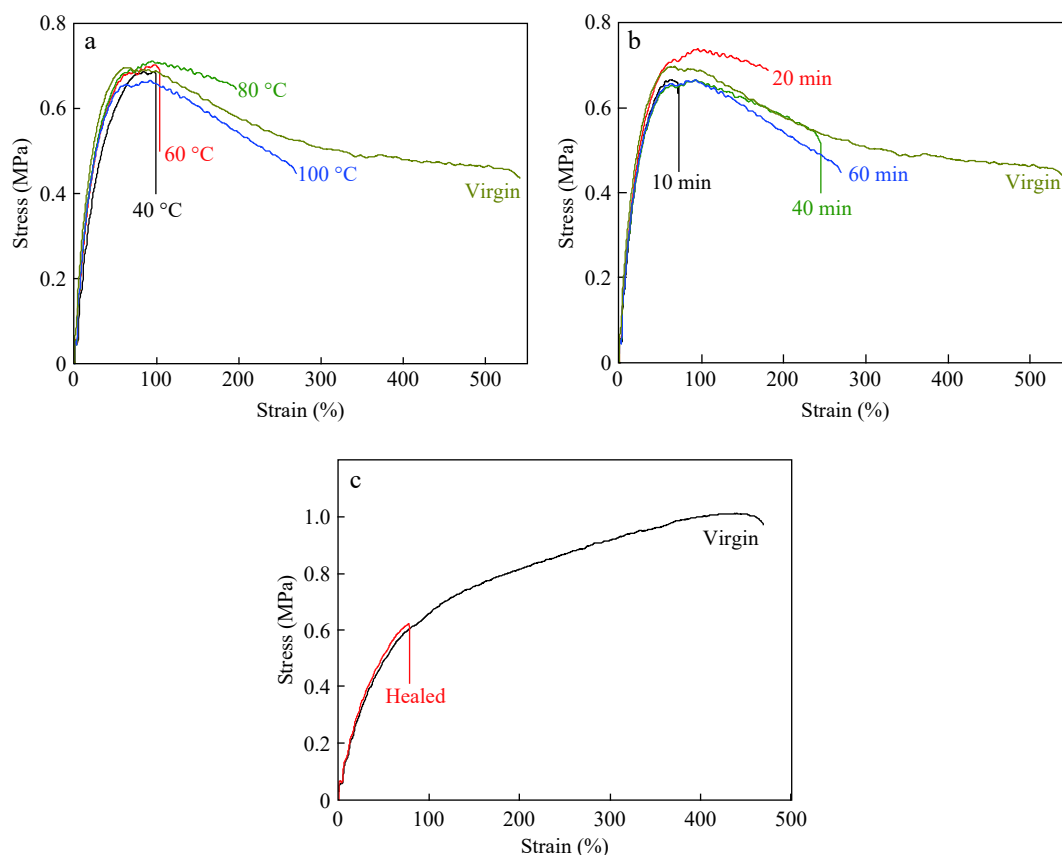


Fig. 5 The stress-strain curves of healed samples: (a) EPDM/ZDMA healed at different temperatures for 60 min; (b) EPDM/ZDMA healed at 100 °C for different periods of time; (c) EPDM cured by DCP healed at 100 °C for 60 min

different covalent and ionic cross-linking densities.

The composition of cross-linked network was investigated by an equilibrium swelling experiment and the cross-linking density was analyzed as presented in Fig. 6(a). As expected, both the total cross-linking density and ionic cross-linking density increased with an increase in curing time. The result shows that when the curing time increased from 150 s to 210 s, the total cross-linking density increased from $2.5 \times 10^{-7} \text{ mol/cm}^3$ to $2.4 \times 10^{-6} \text{ mol/cm}^3$ without residual gel in toluene/hydrochloric acid/ethanol mixed solution. These results suggest that only ionic cross-linked network developed at this curing time range and there was no significantly covalent cross-linking network. However, by prolonging the curing time to 240 s, the total cross-linking density increased further and a residual gel could be clearly observed. This suggests that the cross-linked EPDM network has been changed from single-network to dual-network containing ionic cross-link and covalent cross-link. With the increase in curing time, the covalent cross-linking density increased and mechanical performance of compounds was enhanced (Fig. S4 in ESI).

Fig. 6(b) shows the stress-strain curves of healed EPDM/ZDMA samples with varying curing times. Before testing, the 150, 180, 210, 240, 300, 600 s-cured cut samples were treated at 100 °C for 1 h. However, the healing phenomenon, which is testified by disappearance of the cut surface and recovery of the mechanical properties, was only

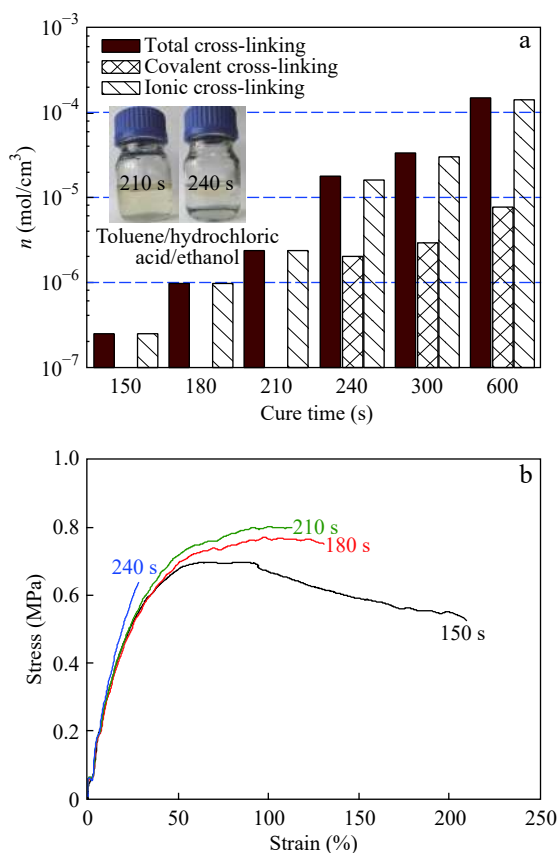


Fig. 6 (a) Cross-linking density of EPDM/ZDMA samples cured for different periods of time; (b) Stress-strain curves of the self-healed EPDM/ZDMA

observed for 150, 180, 210, 240 s-cured samples. Notably, with the increase of curing time, the breaking elongation after healing decreased from 209% to 28% and the healed mechanical strength increased at first but decreased subsequently. The improvement of healed strength is ascribed to the increase of ionic cross-links in EPDM/ZDMA compound with increasing curing time. Even more remarkably, the lowest failure strain and lowest strength were both observed for 240 s-cured sample caused by the appearance of covalent cross-links. This can be attributed to the fact that irreversible covalent cross-links block the mobility and diffusion of polymer chains,^[36] resulting in the decrease in healing efficiency. Although dissociation ionic cross-linking bonds on sample surface can be reformed, the diffusion ability of polymer chains is still the key factor for self-healing^[19,37] which provides the possibility of ionic groups to meet together and network to be rearranged.

To improve the diffusion of EPDM macromolecular chains and achieve better healing capability, liquid rubber which has lower molecular weight, better mobility, and the same chemical structure with “dry” rubber, was added into the “dry” EPDM composites with the same indicated formulation. The mass ratio of liquid EPDM to “dry” EPDM is 2:8 and 5:5 in this study and the compounds are denoted as EPDM/L/ZDMA-20 and EPDM/L/ZDMA-50, respectively. Torque curves and stress-strain curves of the EPDM/L/ZDMA-20 and EPDM/L/ZDMA-50 compounds are presented in Figs. S5 and S6 in ESI and the cured samples were acquired at 150 and 145 °C, respectively. The cross-linking density of EPDM/L/ZDMA-20 and EPDM/L/ZDMA-50 cured for different periods of time and the corresponding stress-strain curves of healed samples are shown in Fig. 7. All samples were healed at 100 °C for 1 h. Fairly similar to EPDM/ZDMA, the total cross-linking density and ionic cross-linking density of cured EPDM/L/ZDMA both increased with increasing curing time (Figs. 7a and 7c). For EPDM/L/ZDMA-20, the dual cross-linked network began to develop when the curing time prolonged to 300 s. Compared to the healed EPDM/ZDMA, a higher fracture strain of 450% (Fig. 7b, black line) was observed for the healed ionic cross-linked EPDM/L/ZDMA-20, which is ascribed to the good mobility of the liquid rubber. However, the healed 300s-cured sample, including dual network, still showed the lowest mechanical strength and failure strain caused by the formation of covalent cross-linked network (Fig. 7b), and the 600 s-cured EPDM/L/ZDMA-20 sample could not be repaired macroscopically. Fig. 7(d) shows the stress-strain curves of healed cut EPDM/L/ZDMA-50 samples cured for different periods of time. Even though covalent cross-linked network was formed in 14 min-cured and 20 min-cured EPDM/L/ZDMA-50 samples (Fig. 7c), an obvious self-healing phenomenon was still observed and the healed tensile strength could reach 0.9 MPa. This means EPDM/L/ZDMA-50 with more liquid rubber content showed better healing ability than EPDM/L/ZDMA-20 and EPDM/ZDMA did. All results support that EPDM/ZDMA with a single reversible cross-linking network possess good self-healing capability, whereas the dual cross-linking network improved mechani-

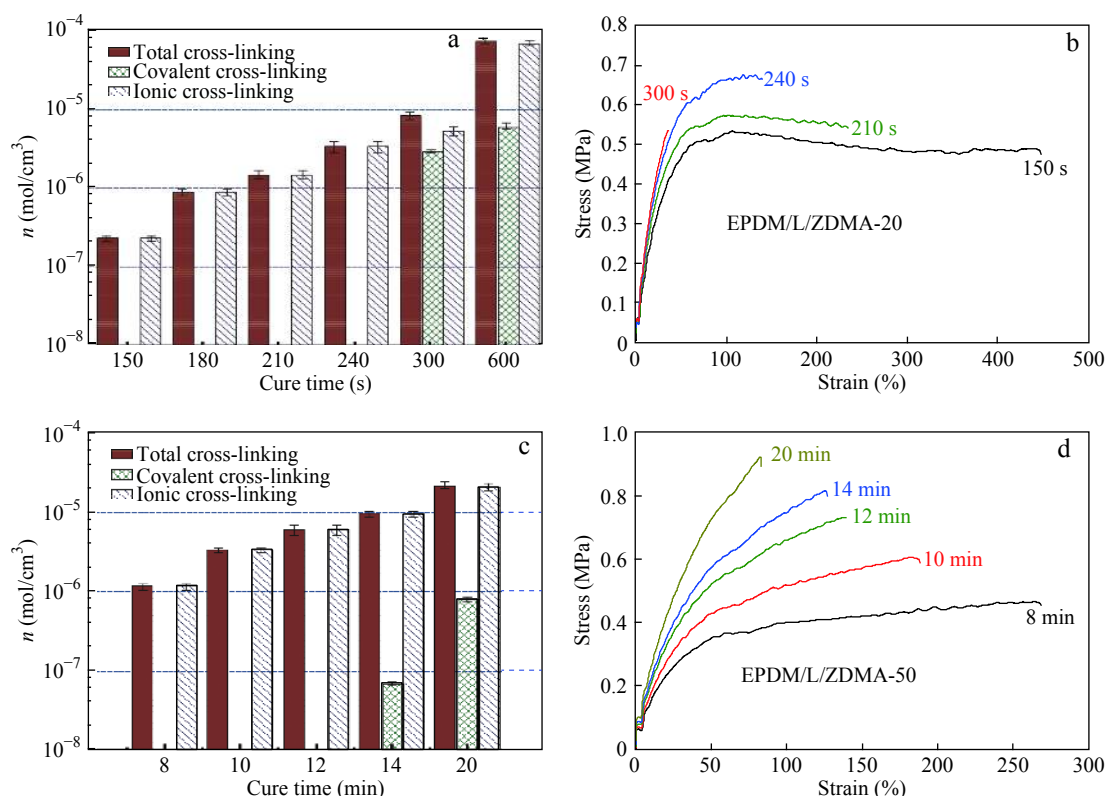


Fig. 7 Cross-linking density and stress-strain curves of self-healed EPDM/L/ZDMA with different contents of liquid rubber cured for different periods of time: (a, c) Cross-linking density of EPDM/L/ZDMA-20 (a) and EPDM/L/ZDMA-50 (c) cured for different periods of time; (b, d) Stress-strain curves of EPDM/L/ZDMA-20 (b) and EPDM/L/ZDMA-50 (d) healed at 100 °C for 60 min

cal properties but reduced repair capability of EPDM. Meanwhile, liquid rubber is beneficial for healing process, and maintains certain self-healing capability of dual cross-linking network.

CONCLUSIONS

In this work, we reported the self-healing EPDM constructed by introducing ionic cross-links *via* graft-polymerization of ZDMA onto EPDM. The reversible ionic cross-linked network, a dual network combining covalent and ionic cross-links, can be generated by controlling the vulcanization process. The study reveals that raising healing temperature and extending healing time can both provide better self-healing performance which is attributed to the boost of rubber chain diffusion ability. The sample with ionic cross-linked network, healed for 1 h at 100 °C, showed a recovery of more than 95% of the original mechanical strength. However, the covalent cross-links lowered the healing efficiency. Adding liquid rubber is an effective way for enhancing self-healing capability of EPDM with dual-network because of the improved mobility and diffusion ability of EPDM. When the mass ratio of liquid EPDM to “dry” EPDM was 5:5, the dual cross-linked network still reserved a certain self-healing property. A compromise between mechanical performance and healing capability can be potentially tailored depending on the cross-link degree, types of cross-linked network, and liquid rubber content.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-019-2241-0>.

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