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Design of next-generation cross-linking structure for elastomers toward green process and a real recycling loop

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ABSTRACT

Currently adopted cross-linking methods in rubber industry are suffering from variable persistent issues, including the utilization of toxic curing packages, release of volatile organic compounds (VOCs) and difficulties in the recycling of end-of-life materials. It is of great importance to explore a green cross-linking strategy in the area. Herein, we report a new “green” strategy based on hydrolyzable ester cross-links for cross-linking diene-typed elastomers. As a proof of concept, a commercial carboxylated nitrile rubber (XNBR) is efficiently cross-linked by a bio-based agent, epoxidized soybean oil (ESO), without any toxic additives. ESO exhibits an excellent plasticization effect and excellent scorch safety for XNBR. The cross-linking density and mechanical properties of the ESO-cured XNBR can be manipulated in a wide range by changing simply varying the content of ESO. In addition, zinc oxide (ZnO) performs as a catalyst to accelerate the epoxide opening reaction and improve the cross-linking efficiency, serving as reinforcement points to enhance the overall mechanical properties of the ESO-cured XNBR. Furthermore, the end-of-life elastomer materials demonstrate a closed-loop recovery by selectively cleaving the ester bonds, resulting in very high recovery of the mechanical performance of the recycled composites. This strategy provides an unprecedented green avenue to cross-link diene elastomers and a cost-effective approach to further recycle the obtained cross-linked elastomers at high efficiency.

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1. Introduction

The covalent cross-linking of elastomers is one of the most important steps for achieving high elasticity and proper mechanical properties of the product. This process occurs by forming cross-links among elastomer chains, resulting in the formation of a three-dimensional network. Since Charles Goodyear discovered sulfur cross-linking technique in 1839, sulfur cross-linking system has been the dominant way to cross-link polyolefin elastomers. To date, various cross-linking additives, such as activators and accelerators, have been developed to improve the cross-linking rate and efficiency of sulfur cross-linking system [1]. However, there is an increasing concern over the negative environmental problems caused by the sulfur cross-linking system [2]. For example, some commonly used accelerators have been classified as dangerous substances [3]. In addition, some cross-linking additives tend to

release some toxic volatile organic compounds (VOCs) during the cross-linking process, which simultaneously give off an unpleasant smell. As another commonly used cross-linking method, peroxide cross-linking system can also lead to the releases of volatile by-products during the cross-linking process [4]. Nowadays, these two cross-linking systems are mainly used for elastomers. The sulfur cross-linking system yields S–S and C–S covalent cross-links while the peroxide system yields C–C covalent cross-links in the elastomer networks. Hence, the covalently cross-linked elastomers are inherently difficult to be recycled and reprocessed, resulting in serious environmental problems and resource waste at their end of life. Some recycling methods, such as desulfurization, have been developed as promising strategies for elastomer recycling. However, the current recycling methods cannot selectively break the cross-linking bonds without destroying the main chains during the recycling process. Therefore, it is highly desirable but challenging to explore an effective cross-linking strategy for the elastomers toward green cross-linking process and high-efficiency recycling of end-of-life elastomers.

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To tackle the above-mentioned inherent issues, researchers have focused on the design of introducing new type of cross-linking structures into the cross-linked elastomer networks. In one demonstration, based on the reaction between epoxy groups and carboxyl groups, an epoxy-functionalized elastomer was efficiently cross-linked by dicarboxylic acids, producing exchangeable β -hydroxy ester cross-linkages among the elastomer chains [5–7]. The β -hydroxy ester cross-linking bonds endowed the elastomer with a recycling ability in the presence of a catalyst at high temperature [8–11]. Additionally, this cross-linking strategy avoided the use of toxic cross-linking agents and release of VOCs. However, the reactions between epoxy groups and carboxyl acids are rather complex because of several side reactions, which have a significant influence on transesterification reactions [12]. Although a stoichiometry of one acid to one epoxide ring can partly avoid the side reactions, it is detrimental to the regulation of the cross-linking density and mechanical properties of the elastomers [13]. Some other cross-linking strategies have also been developed based on exchange reactions, such as imine exchange [14–16], transamination [17–19], transcarbamoylation [20,21], and olefin metathesis [22]. However, these strategies are mainly applied toward tailor-made elastomers, inhibiting their application in industry at a large scale [23–25]. In addition, only a limited number of exchange reactions can be adopted to achieve the precise control of the exchange kinetics, so it is highly challenging to enable fast processing at high temperatures yet low creep at the service temperature [18,26–30]. Furthermore, the polyolefin elastomer chains containing a large number of double bonds would easily undergo irreversible cross-linking or oxidative degradation at high temperature, which is detrimental to the reprocessing ability of the cross-linked elastomers.

Carboxyl-functionalized elastomers are a common class of commercial elastomers, which are synthesized by a free-radical copolymerization using a relatively small amount of acrylic or methacrylic acid as the carboxyl-containing monomer [31]. It is reported that carboxyl-functionalized elastomers can be neutralized by metal oxides such as zinc oxide (ZnO) and magnesium oxide (MgO) to form an ionic cross-linked network [32–34]. The ionic cross-linked elastomers are considered as thermoplastic elastomers because of their thermo-reversible nature, endowing them with a recycling ability [35–39]. However, there are some performance shortages for the ionic cross-linked elastomers, such as poor flexible properties, thermal stability, and scorch safety [37,40]. Furthermore, the poor thermal stability of the ionic cross-linked network leads to a high compression set and poor mechanical properties at elevated temperatures, limiting the potential applications of the elastomers [37]. There is no doubt that these cross-linking methods have achieved a great process and exhibited potential as alternatives to the conventional cross-linking ones; however, further investigation is still required to achieve a feasible and green industrial technology.

Our goal is to develop a facile and green approach to prepare cross-linked elastomers and initiate a real recycling loop toward practical use. To achieve this goal, the rational design of cross-linking reactions and structure is a promising strategy. Recently, based on the reactions between the elastomer macromolecules with functional groups and the green organic molecules with di- or multi-functionality, we have proposed that an effective and green cross-linking strategy was put forward [41]. Moreover, our previous study [10] has demonstrated that the epoxy-acid reaction could be used to design a green cross-linking system. What's more, the preparation of carboxyl-functionalized elastomers and epoxy-functionalized elastomers is very easy to implement, which is conducive to large-scale practical use. As is well-known, carboxylated nitrile rubber (XNBR) and carboxylated butadiene styrene rubber (XSBR) are commercially available. Hence, the cross-linking strat-

egy based on the epoxy-acid reaction is an appropriate choice for designing next-generation cross-linking systems. Because of the existence of ester bonds, an efficient chemical recycling strategy could be developed by selective cleavage of the cross-linking bonds. Recently, it was found that the ester bonds of unsaturated polyester could be selectively cleaved into carboxyl groups and hydroxyl groups under mild conditions [42–45]. Inspired by these findings, we set out to explore a facile and green cross-linking strategy and a chemical recycling method by selective cleavage of the ester cross-linking bonds, aiming to develop green chemistry and achieve a real recycling loop of the elastomers.

Herein, we report a facile and green method for cross-linking commercial XNBR. The carboxyl groups on the elastomer chains serve as cross-linking sites, while the bio-based epoxidized soybean oil (ESO) serves as a plasticizer and cross-linking agent. We demonstrate that ESO has a good plasticization effect on XNBR/carbon black (CB) compounds before the cross-linking reaction occurs. Based on the epoxy-acid reaction, XNBR was successfully cross-linked by the ESO without additional additives, producing ester cross-links between the XNBR chains. The mechanical properties and cross-linking density of the XNBR/CB composites can be regulated by manipulating ESO content. Additionally, ZnO was selected as a catalyst to accelerate the cross-linking reaction. Meanwhile, due to the addition of ZnO, the formation of ion pairs and clusters serves as additional ion cross-links and reinforcing points to enhance the overall mechanical properties of the ESO-cured XNBR/CB composites. Hence, the cross-linking and mechanical properties of the XNBR/CB composites can also be regulated by manipulating the ZnO content. Furthermore, the ester-based cross-links of the XNBR could be selectively cleaved into carboxyl groups and hydroxyl groups under mild conditions, resulting in a recycling ability of the XNBR. Hence, this work provides a facile and green chemical method for high-efficiency recycling and reuse of end-of-life elastomers.

2. Experimental

2.1. Preparation of XNBR/CB composites

First, the chamber temperature and the rotor speed of a Haake mixer were set to 100 °C and 60 r/min, respectively. Then, XNBR, antioxidant 4020 and CB were successively mixed in the Haake mixer for about 10 min to obtain the XNBR/CB compounds. Finally, the compounds were taken out, cooled and kneaded with the ESO on a 6 in. two-roll mill for 6 min at room temperature. The compounds contain 2.0 phr (parts per hundreds of rubber) of antioxidant 4020, 40.0 phr of CB, x phr of ESO ($x = 4.0, 8.0, 12.0, 16.0, 20.0$), and y phr of ZnO ($y = 0, 0.5, 1.0, 2.0$). According to their optimum curing time (t_{90}) determined by a rotorless rheometer (GT-M2000-A, Gotech Testing Machines Inc.), the XNBR/CB compounds were subjected to a compression molding to prepare the XNBR/CB composites under a pressure of 15 MPa at 180 °C. To verify the occurrence of the cross-linking reaction, Fourier transform infrared spectroscopy (FTIR) was performed on a Bruker Tensor 27 spectrometer equipped with a heating cell. An average of about 32 scans with a resolution of 2 cm^{-1} was recorded for each measurement.

XNBR composites were also fabricated with the use of the sulfur curing systems and served as a control group. The preparation procedure was the same as that for the ESO-cured XNBR/CB composites, and the recipe was as follows: XNBR 100.0 phr, antioxidant 4020 2.0 phr, CB 40.0 phr, ZnO 3.0 phr, stearic acid 1.0 phr, accelerator CZ 1.0 phr and sulfur 1.0 phr. The sulfur-cured sample was cured at 150 °C.

2.2. The typical procedure for chemical recycling of ESO-cured XNBR

To perform the chemical recycling process, the ESO-cured XNBR sample was cut into small pieces. Typically, ESO-cured XNBR (5 g) was swollen in tetrahydrofuran (THF, 100 g) for 24 h. Afterwards, the H_2SO_4 (1.5 g) diluted in deionized water (5 g) was added to the solution and used as the catalyst for cleaving of the C–O bonds. The chemical recycling reaction was carried out in a round bottom flask with a reflux unit for 12 h at 70 °C. The obtained homogeneous mixture solution was coagulated in water, and then thoroughly washed with and then soaked in deionized water for 24 h. Finally, the obtained recycled XNBR was dried to constant weight under vacuum at 60 °C. Similarly, the ESO-cured XNBR/CB sample was recycled at 80 °C for 24 h. Then, the recycled XNBR/CB composite was cross-linked by ESO again. The detail information for materials and characterizations for rubber process analyzer (RPA) measurements, differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR), mechanical properties, dynamic thermomechanical analysis (DMA), and gel permeation chromatography (GPC) is shown in Supplementary materials (online).

3. Results and discussion

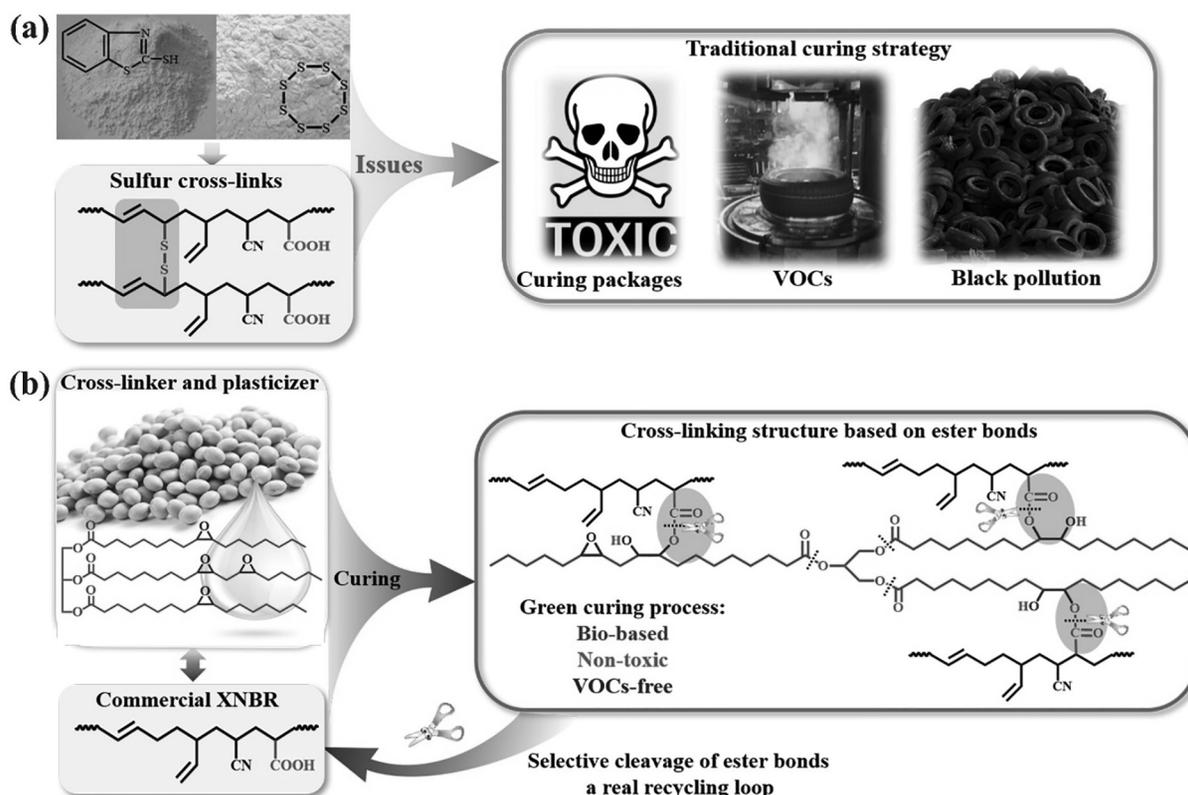
3.1. Design of novel cross-linking strategy based on epoxy-acid reaction

As mentioned in the introduction, the epoxy-acid reaction is an appropriate choice for designing next-generation cross-linking systems. Hence, a novel cross-linking strategy based on epoxy-acid reaction is put forward to cross-link carboxyl-functionalized elastomers. As is well-known, the carboxyl-functionalized elastomers,

such as XNBR, are a common class of commercial elastomers. The carboxyl groups on the elastomer chains could serve as cross-linking sites, while the bio-based ESO was selected as a green, non-toxic and cost-effective cross-linking agent in place of sulfur. As illustrated in Scheme 1, the cross-linked network structure containing β -hydroxyl ester bonds are formed based on the chemical reactions between the carboxyl groups in XNBR chains and the epoxy groups in ESO. Moreover, the bio-based ESO as a derivative of plant oils may have a good plasticization effect on XNBR before the cross-linking reaction occurs. Finally, the ester bonds in the cross-linked structure are expected to be selectively cleaved off, and the linear XNBR could be achieved again. In other words, the recycling method for a closed-loop recovery of the end-of-life elastomer materials could be provided.

3.2. Plasticizing effect of ESO on XNBR

As is well-known, the nonvolatile compounds with low molecular weight are widely used as plasticizers to reduce the viscosity of elastomers and improve the processability of elastomers in rubber industry. At present, the petroleum-based and coal-based compounds with low molecular weight, such as aromatic oils and aliphatic oils, predominate as the plasticizers in rubber industry. However, the aromatic oils generally contain polycyclic aromatic hydrocarbons (PAHs) which have carcinogenic effects on human health. Therefore, it is of great importance to explore environmentally friendly and renewable substitutes for replacing these petroleum-based and coal-based plasticizers. Due to their low cost, sustainability and non-toxicity, plant oils have been found to be very desirable substitutes for conventional plasticizers. As a derivative of the plant oils, ESO may have a plasticizing effect on XNBR. Thus, the plasticizing effect of ESO on XNBR/CB compounds was studied. As shown in Fig. 1a, the XNBR/CB compound without



Scheme 1. (Color online) (a) Schematic showing the current sulfur cross-linking strategy which are suffering from several persistent issues, and (b) the design of next generation cross-linking strategy based on ESO for XNBR via epoxy-acid reaction.

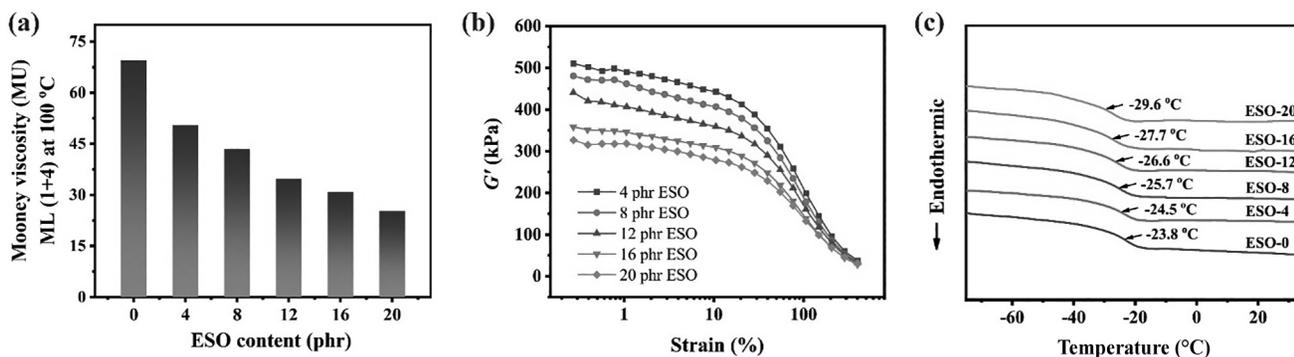


Fig. 1. (Color online) Mooney viscosities (a), G' -strain curves (b), and DSC curves (c) of XNBR compounds plasticized by various contents of ESO.

ESO exhibits the highest Mooney viscosity because of the strong molecular polarity of XNBR. It can be observed that the addition of ESO results in a significant reduction in Mooney viscosity, demonstrating that ESO exhibits an excellent plasticizing effect on the XNBR/CB compounds, and could improve the processability of XNBR. In order to further demonstrate the plasticizing effect of ESO, the rheological measurements of the XNBR/CB compounds by RPA are shown in Fig. 1b. At low strains (less than 10%), the storage modulus (G') of the XNBR/CB compounds decreases with the increase of the ESO content, which may be due to the reduction in the filler-filler and filler-elastomer interaction by the lubrication action of the plasticizer. In addition, because the presence of a plasticizer usually causes a decrease in glass transition temperature (T_g) of the elastomer compounds, the T_g of the ESO-plasticized XNBR/CB compounds were determined by DSC. As shown in Fig. 1c, the T_g of the XNBR/CB compounds decrease slightly with the increase of the ESO content, which could be attributed to that the addition of ESO causes the decrease of the interactions among the XNBR chains.

The excellent plasticizing effect of ESO on XNBR could be attributed to good compatibility between ESO and XNBR chains. On the one hand, the compatibility may be attributed to forming hydrogen bonds between the carboxyl groups in XNBR chains and the epoxy groups in ESO. To verify the formation of hydrogen bonds, *in situ* FTIR was carried out at various temperatures (Fig. S1 online). With the increase of temperature from 40 to 140 °C, the absorption related to the C=O groups in the bonded carboxyl groups shifts from 1699 to 1702 cm^{-1} , together with the decrease in the intensity. Simultaneously, the absorption related to the C=O groups in free carboxyl groups shifts from 1736 to 1739 cm^{-1} together with the decrease in the intensity as well. Besides, the FTIR spectra of the XNBR/ESO compound were collected during the cooling process, and the results are almost identical to those collected during the heating process. These results indicated the formation of hydrogen bonds between epoxy and carboxyl groups. Moreover, the solubility parameter, which is a powerful tool to predict the compatibility of materials, was calculated by Materials Studio (MS) simulations to gain a better insight into the compatibility of ESO with XNBR. The solubility parameter values for XNBR and ESO at 298 K are 19.48 and 18.24 (J/cm^3)^{0.5}, respectively. The results suggest that the mixtures of XNBR and ESO are thermodynamically compatible because of their similar solubility parameter values [46].

3.3. Covalent cross-linking of XNBR with bio-based ESO

To verify the occurrence of the epoxy-acid reaction, the FTIR spectra of XNBR, ESO, XNBR/ESO compound and ESO-cured XNBR composite were monitored (Fig. 2a). Moreover, the evolutions of the absorption peaks of ester and epoxy groups involved in the

reaction were also monitored by FTIR spectra at 180 °C (Fig. S2 online). The absorption peaks at 1700 cm^{-1} are due to the C=O stretching vibration of carboxyl groups in XNBR chains. In the FTIR spectra of the XNBR/ESO compound, due to the addition of ESO, the characteristic peak at 824 cm^{-1} appears, which is related to the asymmetric epoxide ring stretching deformation vibration of epoxy groups in ESO. Besides, the absorptions related to ester bonds appear at 1740 cm^{-1} . After the cross-linking reaction occurs, the peaks related to epoxy groups gradually disappear. Simultaneously, the intensity of characteristic peaks related to ester bonds increases, while that related to carboxyl groups decreases. These results demonstrate the chemical reactions between carboxyl groups and epoxy groups, resulting in β -hydroxyl esters.

In order to further investigate the cross-linking process, the cross-linking behavior of the XNBR/CB compounds was monitored by measuring the torque in a rheometer. Fig. 2b shows the curing curves of the XNBR/CB compound under different temperature. It can be obviously observed that the torque value increases first and then reaches equilibrium over time, which should be attributed to the formation of cross-linking structures based on the epoxy-acid reaction. With the increase of cross-linking temperature, the cross-linking rate increases consistently. In addition, the value of the maximum torque (M_H) almost keeps as the same at different temperature, indicating that the cross-linking reactions are all completed in this typical range of temperatures. The curing characteristics of various XNBR/CB compounds with different ESO content are analyzed on an oscillating disk rheometer at 180 °C and the characteristic parameters are summarized in Table 1. As shown in Fig. 2c, all curing curves exhibit a classic curing behavior, indicating the occurrence of cross-linking reactions. With the increase of the ESO content, the value of torque difference (ΔM) between the minimum torque M_L and the maximum torque M_H significantly increased. These results indicate that the cross-linking density increased, which is in accordance with the equilibrium swelling tests (Fig. 2d). Additionally, the low sol fraction for ESO-cured XNBR composites indicates their high cross-linking density. As the ESO content increases, more effective cross-linking points could be provided, resulting in the increase of the cross-linking density of the XNBR/CB composites. Besides, the increase of ESO content could also lead to a slight increase in t_{90} , indicating that longer period of time was required for achieving an equilibrium to the cross-linking reaction. Additionally, the epoxy-acid cross-linking system shows excellent scorch safety to the obtained composites, which another important characteristic related to the cross-linking process (Fig. S3 online).

3.4. Mechanical properties of ESO-cured XNBR/CB composites

The influence of ESO content on the tensile properties of XNBR/CB composites was investigated. Fig. 3a shows the typical stress-

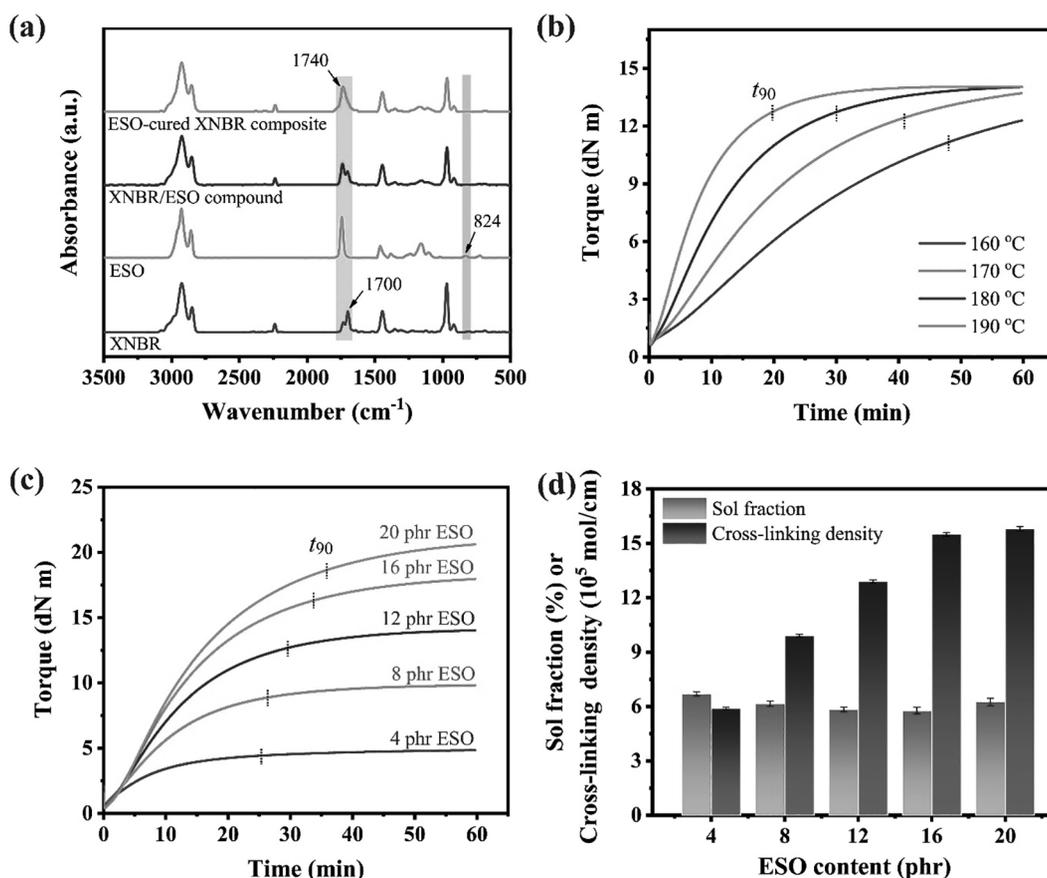


Fig. 2. (Color online) (a) FTIR spectra of XNBR, ESO, XNBR/ESO compound and ESO-cured XNBR composite. The spectra are normalized by using the absorption intensity of $-\text{CH}_3$ at 2924 cm^{-1} as an internal reference. (b) Curing curves of XNBR/CB compound with 12.0 phr of ESO at different curing temperature. (c) Curing curves of XNBR/CB compound with different contents of ESO. (d) Cross-linking density of XNBR/CB composites with different contents of ESO.

Table 1

The curing characteristic parameters of XNBR/CB compounds with different contents of ESO.

ESO content (phr)	M_H (dN m)	M_L (dN m)	$\Delta M = M_H - M_L$ (dN m)	t_{90} (min)
4.0	4.9	0.7	4.2	25.5
8.0	9.9	0.7	9.2	26.7
12.0	14.0	0.6	13.4	29.6
16.0	18.0	0.5	17.5	33.0
20.0	20.6	0.4	20.2	35.5

strain curves of XNBR/CB composites, and their mechanical properties are summarized in Table S1 (online). It can be found that the increase of ESO content leads to remarkable improvements on the modulus of the XNBR/CB composites while the elongation at break is compromised, which should be ascribed to the increased cross-linking density. Specifically, the modulus at 300% strain is regulated over a wide range from 2.4 to 14.1 MPa, which could meet the mechanical requirements for a range of applications. Besides, the tensile strength of the XNBR/CB composites increases firstly, then reaches to a maximum value with the incorporation of 12.0 phr ESO, and then decreases with the further increase of ESO content. The reason can be attributed to the fact that the increase in cross-linking density could restrain the orientation of the elastomer chains segment, and lead to reduction in the elongation at break.

The influence of the ESO content on the dynamic behavior of the XNBR/CB composites was further investigated by performing DMA. The temperature dependence of the loss factor ($\tan\delta$) of the XNBR/CB composites with different ESO content is displayed in Fig. 3b.

With the increase of the ESO, the value of $\tan\delta$ decreased consistently at relatively high temperatures, which can be attributed to the enhanced restriction of chain motion due to the increased cross-linking density. However, the peak value of $\tan\delta$ and T_g slightly decreases, which is contrary to the increased cross-linking density. To further explain this phenomenon, we performed RPA to investigate the strain amplitude dependence of the storage moduli (G') and $\tan\delta$ of the XNBR/CB composites with different contents of ESO. From Fig. S4 (online), the value of $\tan\delta$ gradually decreases at the same strain, which is in accordance with the results from DMA experiments. In addition, G' decreases continuously by increasing ESO content at low strains. In particular, when the ESO content reaches 20.0 phr, the G' is reduced to a greater extent. Obviously, the results of the dynamic modulus are inconsistent with that of the static modulus. We speculate that the results could be attributed to the cross-linking structure. The ESO can be considered as a three-armed molecule, which could result in the formation of different types of cross-linked structures (Fig. S5 online). Although almost all ESO participated in the cross-linking

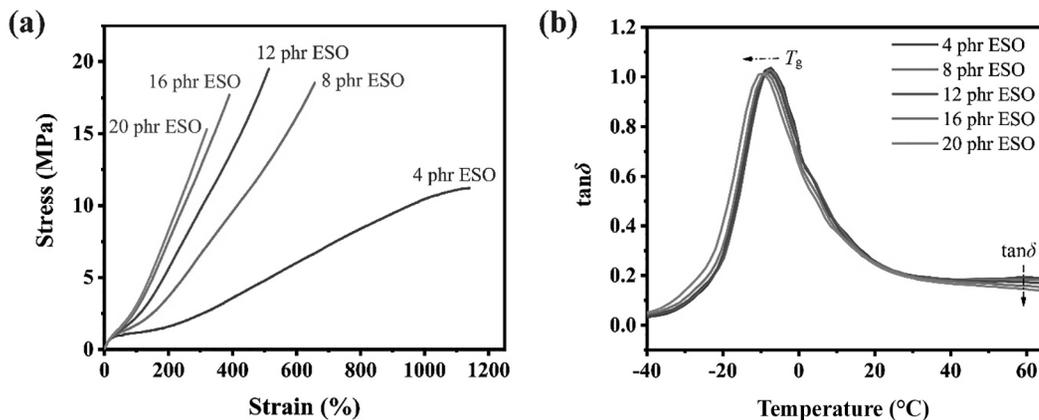


Fig. 3. (Color online) Typical stress-strain curves (a) and temperature dependence of $\tan\delta$ (b) of XNBR/CB composites.

reactions (Table S2 online), not each arm of the ESO could be involved in the reactions. Therefore, the arms that are not involved in the cross-linking reactions are present in the form of branched chains, and the number of branched chains increases with the increase of ESO content. The branched chains in the cross-linking structure exhibit a plasticizing effect, leading to a decrease in dynamic modulus and T_g .

3.5. The catalytic effect of Zn^{2+} ion on cross-linking reaction

As is well-known, Lewis acids (e.g., zinc salts) have the catalytic effect on the curing of epoxy resins and can accelerate the epoxide

ring-opening reaction [47–49]. In order to improve cross-linking efficiency, ZnO was selected to catalyze the cross-linking reaction. The carboxylic groups incorporated in the nonpolar elastomer main chains could be neutralized by ZnO to form ion pairs or clusters, which could act as cross-links and reinforcing points. Hence, the effect of ZnO content on the properties of the XNBR/ESO compounds was investigated. Fig. 4a shows the curing curves of XNBR/ESO compounds with different contents of ZnO, and the characteristic parameters are summarized in Table S3 (online). It is found that a relatively small amount of ZnO could lead to a significant reduction in t_{90} , and the cross-linking rate further increases consistently with the increase of ZnO content. Meanwhile, the ΔM value

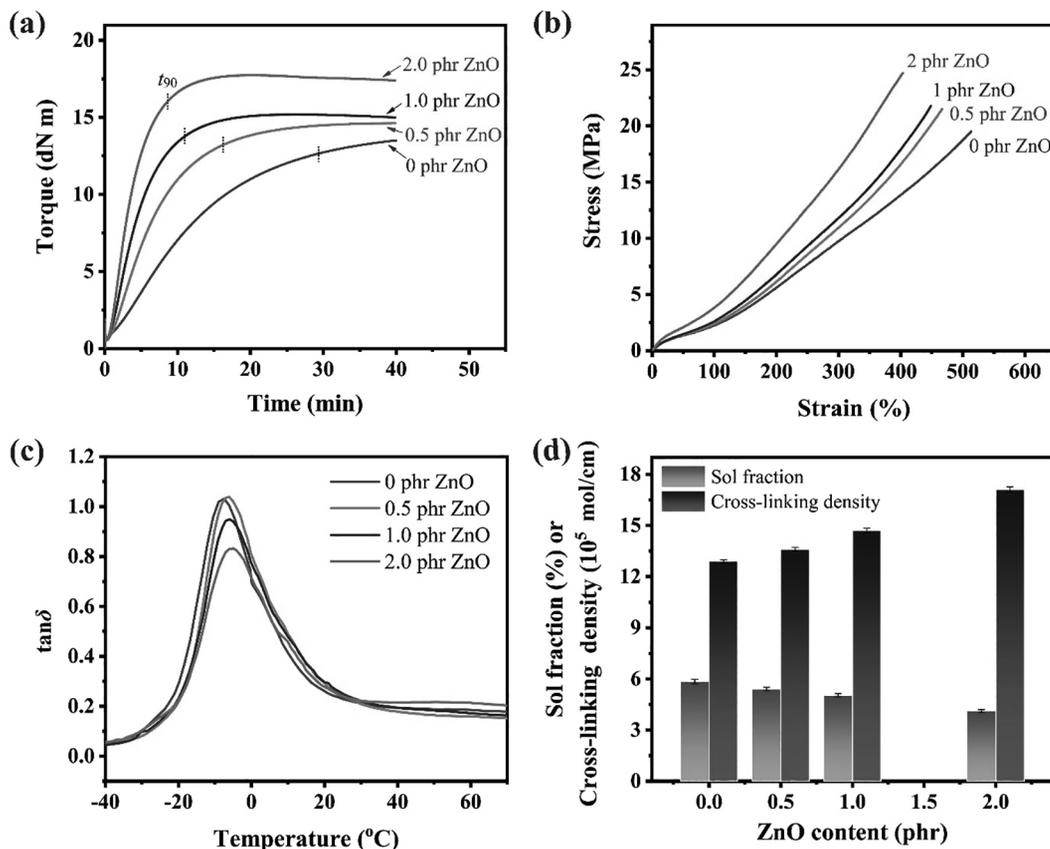


Fig. 4. (Color online) Curing curves (a), typical stress-strain curves (b), temperature dependence of $\tan\delta$ (c), and cross-linking density (d) of ESO-cured XNBR/CB composites with the use of different contents of ZnO while the content of ESO was set as 12.0 phr.

increased, which may be ascribed to the increase in the extent of cross-linking reaction and additional ionic cross-links. Moreover, the curing behaviors were also examined under different curing temperature (Fig. S6, Tables S4 and S5 online). It can be concluded that the addition of ZnO could lead to a decrease in the curing temperature. For example, in the presence of 1.0 phr ZnO, the curing temperature of the XNBR/ESO compounds was decreased by 20 °C. Besides, the XNBR could not be effectively cross-linked by ZnO in the absence of ESO (Fig. S7 online). This phenomenon could be attributed to the following two reasons. On the one hand, Zn^{2+} has a catalytic effect on the cross-linking reaction and accelerates the epoxide opening reaction (Fig. 5a). On the other hand, the existence of ion pairs or clusters results in the formation of domains with high carboxyl group concentration (inhomogeneity), so the collision between the carboxyl groups in XNBR chains and the epoxy groups in ESO molecules is more prone to form valid cross-links relative to the case in the absence of ZnO. Furthermore, although the addition of ZnO could lead to the reduction in scorch time, the scorch time of the epoxy-acid cross-linking system is still longer than that of the sulfur cross-linking system (Figs. S8 and S9 online).

The influence of ZnO content on the mechanical properties of ESO-cured XNBR/CB composites was investigated. As shown in Fig. 4b and Table S6 (online), the tensile strength and modulus of the ESO-cured XNBR/CB composites increase obviously with the increase of ZnO content. Besides, the mechanical properties of ZnO-cured XNBR/CB composites are poor in the absence of ESO (Fig. S10 online). These results may be ascribed to two reasons. First, the addition of ZnO could lead to an increased extent of cross-linking reactions. Second, the presence of ion pairs or clusters could provide additional ionic cross-links and act as reinforcing points (Fig. 5b). As shown in Fig. 4c, $\tan\delta$ of ESO-cured XNBR/CB composites with various ZnO content were measured from DMA under temperature sweep conditions. Compared with that of the sample in the absence of ZnO, the peak value of $\tan\delta$ is significantly suppressed and gradually shifts to a higher temperature with the increase of ZnO content. This phenomenon suggests that the segmental relaxation of XNBR is restricted by the remarkably

enhanced cross-linking density, which is accounted from the increase in the extent of cross-linking reaction and additional ionic cross-links. In addition, a broad peak of $\tan\delta$ at around 60 °C are observed in the dual-cross-linking XNBR/CB composites, especially for the sample in presence of 2.0 phr ZnO, indicating an additional relaxation process of the breaking of ionic bonds [35]. To verify the existence of the ionic bonds, cyclic uniaxial tension tests are performed. As shown in Figs. S11 and S12 (online), the ESO-cured XNBR/CB composites exhibit obvious hysteresis loop in the first cycle, arising from the Mullins effect and the rupture of the ionic bonds. With the increase of the ZnO content, the increased ionic cross-links mainly contribute to the irreversible stress softening upon the initial extension. Additionally, the addition of ZnO could also lead to an increase in the extent of chemical cross-links, which would also have an influence on the hysteresis. Hence, it can be concluded that hysteresis energy is increased with the increase of ZnO content, suggesting that the number of ionic bonds is increased. Based on the above discussion, the ionic bonds behave in a sacrificial manner to dissipate energy during stretching, which can remarkably contribute to the enhancement of the overall mechanical properties of the ESO-cured XNBR/CB composites [50,51]. Furthermore, the curing and mechanical properties of ESO-cured XNBR/CB composite are compared to that of sulfur-cured XNBR/CB composite. As shown in Fig. S13a and Table S7 (online), the cross-linking rate of ESO-cured XNBR/CB composite is slower than that of sulfur-cured XNBR/CB composite; but the value is still acceptable for practical application. Besides, the tensile strength of ESO-cured XNBR/CB composite is comparable to that of the sulfur-cured XNBR/CB composite (Fig. S13b and Table S8 online).

3.6. Chemical recycling by selective cleavage of ester bonds

Because of the formation of ester bonds in the cross-linked structure, we envision that the selective cleavage of the ester bonds could be one of the most promising and advantageous methods for recycling and reutilization of end-of-life elastomer materials. Scheme 2 illustrates the process of the chemical recycling of

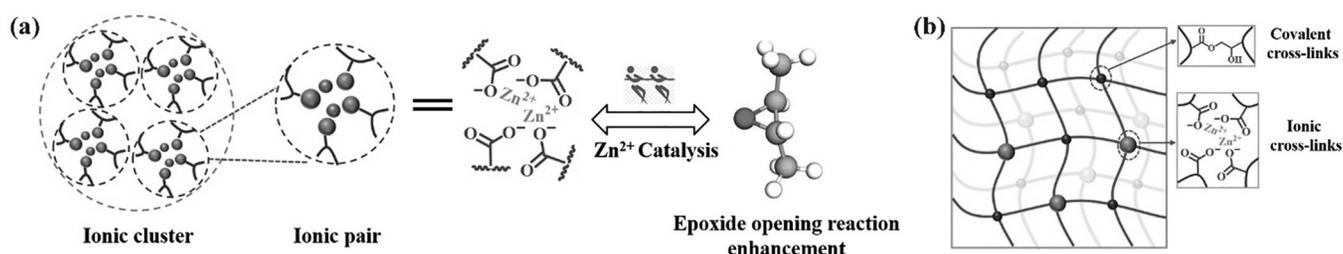
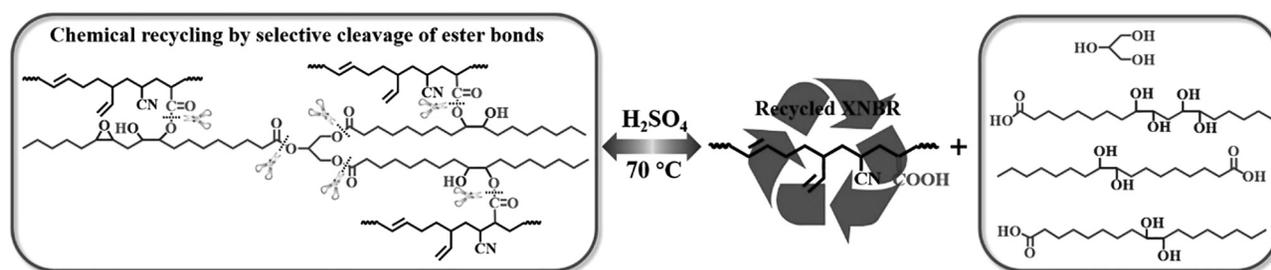


Fig. 5. (Color online) Schematic illustrating the catalytic effect of Zn^{2+} ion on the enhancement of the epoxide ring opening reaction (a), and proposed dual-cross-linking structure in ESO-cured XNBR/CB composites in the presence of ZnO (b).



Scheme 2. (Color online) Schematic illustration of the chemical recycling process of ESO-cured XNBR.

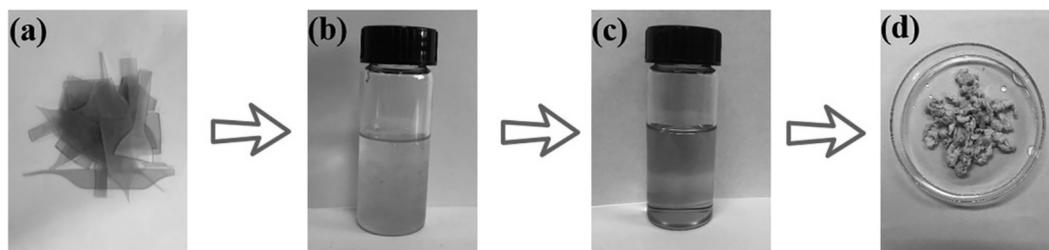


Fig. 6. (Color online) The chemical recycling process of ESO-cured XNBR. (a) The original, (b) post-swelling, (c) post-recycling reaction, and (d) post-coagulating of the ESO-cured XNBR sample.

the ESO-cured XNBR. As shown in Fig. 6, the swollen ESO-cured XNBR pieces disappeared after the chemical recycling reaction, and the homogeneous mixture solution was obtained. Therefore, we could speculate that the ester bonds of ESO-cured XNBR sample were successfully cleaved off. In addition, the molecular weights of the original XNBR and recycled XNBR were characterized by GPC (Table 2). It was found that the molecular weight of recycled XNBR is almost the same to that of the original XNBR. In addition, the recycled XNBR was characterized using FTIR spectroscopy (Fig. 7a). The results showed that the absorptions related to ester bonds at 1740 cm^{-1} disappeared, indicating that the ester bonds of the cross-linked XNBR were cleaved off. ^1H NMR spectra of the original XNBR and the recycled XNBR are shown in Fig. S14 (online), and the results are in accordance with that from FTIR experiments. Similarly, the CB filled ESO-cured XNBR was also recycled according to this method (Fig. S15 online). However, due to the adsorption of elastomer chains on CB, the chemical recycling reaction of CB filled ESO-cured XNBR requires a longer time and higher temperature than that of unfilled XNBR. For its reutilization, the recycled XNBR/CB composite was directly used to prepare an ESO-cured XNBR/CB composite again. As shown in Fig. 7b, the mechanical properties of the recycled samples are well-restored. The strength, modulus, and elongation at break of the recycled samples are able to recuperate most of their initial mechanical properties. As a result, this recycling strategy is a facile and cost-effective approach for high-efficiency recycling. What's more, this

work provides new insight to the closed-loop recycling of end-of-life elastomers.

4. Conclusions

In this study, we demonstrate a novel and green cross-linking strategy for carboxyl-functionalized elastomers using renewable bio-based ESO, a derivative of plant oils, as the cross-linking agent. It can avoid the use of toxic cross-linking agents and prevent the release of toxic VOCs. Due to the mixtures of XNBR and ESO with similar solubility parameter values and the hydrogen bonds between the carboxyl groups in XNBR chains and the epoxy groups in ESO, the ESO exhibits excellent plasticization effect on XNBR. The cross-linking mechanism is based on the reactions between the epoxy groups in ESO and the carboxyl groups in XNBR chains, producing β -hydroxyl esters. Specifically, this cross-linking strategy shows excellent scorch safety, which is suitable for practical elastomer processing. By increasing the content of ESO, the mechanical properties of the fabricated compounds can be improved, especially the striking improvement in modulus while the elongation at break is compromised. Specifically, the tensile strength of the XNBR/CB composites can reach up to 20 MPa, and the modulus at 300% strain is regulated over a wide range from 2.4 to 14.1 MPa. Moreover, due to the catalytic effect of Zn^{2+} ion on the epoxide opening reaction, ZnO can catalyze the cross-linking reaction to further improve the cross-linking efficiency. Meanwhile, due to the formation of ion pairs and clusters as additional ionic cross-links and reinforcing points, the addition of ZnO can enhance the overall mechanical properties of the ESO-cured XNBR/CB composites. Hence, the cross-linking and mechanical properties of the XNBR/CB composites can also be regulated by manipulating the content of ZnO. What's more, the chemical recycling upon the selective cleavage of ester bonds is put forward to achieve a closed-loop recovery of the end-of-life elastomer

Table 2
Molecular weights of the original XNBR and recycled XNBR.

Sample	$M_n/10^4$ (g/mol)	$M_w/10^4$ (g/mol)	Polydispersity index (PDI)
XNBR	9.8	26.8	2.72
Recycled XNBR	9.1	28.9	3.16

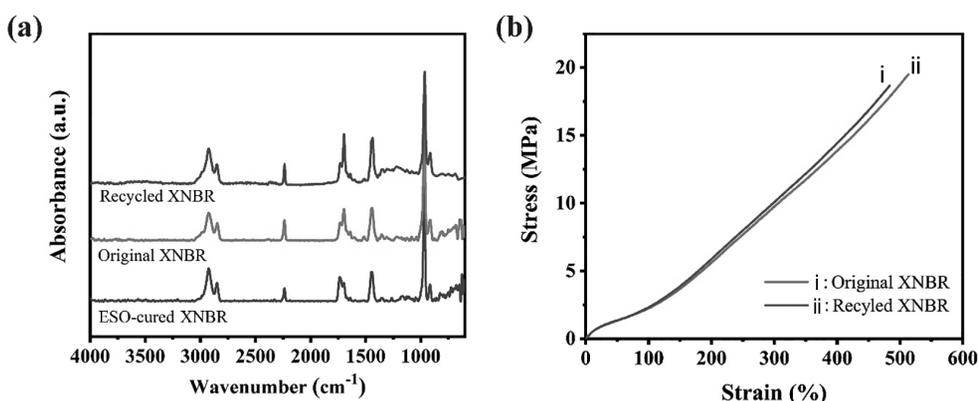


Fig. 7. (Color online) (a) FTIR spectra of original XNBR and recycled XNBR. (b) Typical stress-strain curves of original and recycled XNBR/CB composite with 12.0 phr of ESO.

materials. Meanwhile, this recycling strategy is a simple, mild, and cost-effective approach for achieving a high-efficiency recycling. We envision that this new green cross-linking strategy for carboxyl-functionalized elastomers exhibits promising applications in rubber industry.

Conflict of interest

The authors declare that they have no conflict of interest.

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Author contributions

Ganggang Zhang designed the experiments, analyzed the data and wrote the paper. Ganggang Zhang, Haoran Feng and Kuan Liang carried out experiments, and performed material characterization. Baochun Guo and Liqun Zhang conceived the idea of the study. Xinxin Zhou, Baochun Guo and Liqun Zhang revised the manuscript. All authors discussed the results and were involved in writing the manuscript.

Appendix A. Supplementary materials

Supplementary materials to this article can be found online at <https://doi.org/10.1016/j.scib.2020.03.008>.

References

- Ikeda Y, Higashitani N, Hijikata K, et al. Vulcanization: new focus on a traditional technology by small-angle neutron scattering. *Macromolecules* 2009;42:2741–8.
- Li H, Zhao T, Chen M. Green tire and new type rubber materials. *Chin Sci Bull* 2016;61:3297 (in Chinese).
- Zhang XH, Tang ZH, Guo BC. Regulation of mechanical properties of diene rubber cured by oxo-michael reaction via manipulating network structure. *Polymer* 2018;144:57–64.
- Aprem AS, Joseph K, Thomas S. Recent developments in crosslinking of elastomers. *Rubber Chem Technol* 2005;78:458–88.
- Pire M, Norvez S, Iliopoulos I, et al. Imidazole-promoted acceleration of crosslinking in epoxidized natural rubber/dicarboxylic acid blends. *Polymer* 2011;52:5243–9.
- Pire M, Lorthioir C, Oikonomou EK, et al. Imidazole-accelerated crosslinking of epoxidized natural rubber by dicarboxylic acids: a mechanistic investigation using NMR spectroscopy. *Polym Chem* 2012;3:946–53.
- Pire M, Norvez S, Iliopoulos I, et al. Epoxidized natural rubber/dicarboxylic acid self-vulcanized blends. *Polymer* 2010;51:5903–9.
- Montarnal D, Capelot M, Tournilhac F, et al. Silica-like malleable materials from permanent organic networks. *Science* 2011;334:965–8.
- Capelot M, Unterlass MM, Tournilhac F, et al. Catalytic control of the vitrimer glass transition. *ACS Macro Lett* 2012;1:789–92.
- Zhang G, Zhou X, Liang K, et al. Mechanically robust and recyclable EPDM rubber composites by a green cross-linking strategy. *ACS Sustainable Chem Eng* 2019;7:11712–20.
- Tang Z, Liu Y, Guo B, et al. Malleable, mechanically strong, and adaptive elastomers enabled by interfacial exchangeable bonds. *Macromolecules* 2017;50:7584–92.
- Imbernon L, Norvez S, Leibler L. Stress relaxation and self-adhesion of rubbers with exchangeable links. *Macromolecules* 2016;49:2172–8.
- Capelot M, Montarnal D, Tournilhac F, et al. Metal-catalyzed transesterification for healing and assembling of thermosets. *J Am Chem Soc* 2012;134:7664–7.
- Taynton P, Ni H, Zhu C, et al. Repairable woven carbon fiber composites with full recyclability enabled by malleable polyimine networks. *Adv Mater* 2016;28:2904–9.
- Taynton P, Yu K, Shoemaker RK, et al. Heat- or water-driven malleability in a highly recyclable covalent network polymer. *Adv Mater* 2014;26:3938–42.
- Geng H, Wang Y, Yu Q, et al. Vanillin-based polyschiff vitrimers: reprocessability and chemical recyclability. *ACS Sustainable Chem Eng* 2018;6:15463–70.
- Denissen W, Rivero G, Nicolay R, et al. Vinylogous urethane vitrimers. *Adv Funct Mater* 2015;25:2451–7.
- Stukenbroeker T, Wang WD, Winne JM, et al. Polydimethylsiloxane quenchable vitrimers. *Polym Chem* 2017;8:6590–3.
- Liu Z, Zhang C, Shi Z, et al. Tailoring vinylogous urethane chemistry for the cross-linked polybutadiene: wide freedom design, multiple recycling methods, good shape memory behavior. *Polymer* 2018;148:202–10.
- Zheng N, Fang Z, Zou W, et al. Thermoset shape-memory polyurethane with intrinsic plasticity enabled by transcarbamoylation. *Angew Chem Int Ed* 2016;55:11421–5.
- Chen X, Li L, Jin K, et al. Reprocessable polyhydroxyurethane networks exhibiting full property recovery and concurrent associative and dissociative dynamic chemistry via transcarbamoylation and reversible cyclic carbonate aminolysis. *Polym Chem* 2017;8:6349–55.
- Lu Y, Tournilhac F, Leibler L, et al. Making insoluble polymer networks malleable via olefin metathesis. *J Am Chem Soc* 2012;134:8424–7.
- Nishimura Y, Chung J, Muradyan H, et al. Silyl ether as a robust and thermally stable dynamic covalent motif for malleable polymer design. *J Am Chem Soc* 2017;139:14881–4.
- Feng Z, Yu B, Hu J, et al. Multifunctional vitrimer-like polydimethylsiloxane (PDMS): recyclable, self-healable, and water-driven malleable covalent networks based on dynamic imine bond. *Ind Eng Chem Res* 2019;58:1212–21.
- Ishibashi JSA, Kalow JA. Vitrimeric silicone elastomers enabled by dynamic Meldrum's acid-derived cross-links. *ACS Macro Lett* 2018;7:482–6.
- Chen Y, Tang Z, Zhang X, et al. Covalently cross-linked elastomers with self-healing and malleable abilities enabled by boronic ester bonds. *ACS Appl Mater Interfaces* 2018;10:24224–31.
- Rottger M, Domenech T, van der Weegen R, et al. High-performance vitrimers from commodity thermoplastics through dioxaborolane metathesis. *Science* 2017;356:62–5.
- Ruiz de Luzuriaga A, Martin R, Markaide N, et al. Epoxy resin with exchangeable disulfide crosslinks to obtain reprocessable, repairable and recyclable fiber-reinforced thermoset composites. *Mater Horiz* 2016;3:241–7.
- Azzune I, Odriozola I. Aromatic disulfide crosslinks in polymer systems: self-healing, reprocessability, recyclability and more. *Eur Polym J* 2016;84:147–60.
- Denissen W, Driesbeke M, Nicolay R, et al. Chemical control of the viscoelastic properties of vinylogous urethane vitrimers. *Nat Commun* 2017;8:14857.
- Basu D, Das A, Stöckelhuber KW, et al. Nanostructured ionomeric elastomers. Berlin: Springer; 2017. p. 235–66.
- Ibarra L, Alzoriz M. Vulcanization of carboxylated nitrile rubber (XNBR) by a mixed zinc peroxide-sulphur system. *Polym Int* 2000;49:115–21.
- Ibarra L, Alzoriz M. Ionic elastomers based on carboxylated nitrile rubber and magnesium oxide. *J Appl Polym Sci* 2007;103:1894–9.
- Ibarra L, Rodríguez A, Mora-Barrantes I. Crosslinking of unfilled carboxylated nitrile rubber with different systems: influence on properties. *J Appl Polym Sci* 2008;108:2197–205.
- Malmierca MA, González-Jiménez A, Mora-Barrantes I, et al. Characterization of network structure and chain dynamics of elastomeric ionomers by means of ¹H low-field NMR. *Macromolecules* 2014;47:5655–67.
- Basu D, Das A, Stöckelhuber KW, et al. Evidence for an *in situ* developed polymer phase in ionic elastomers. *Macromolecules* 2014;47:3436–50.
- Mora-Barrantes I, Malmierca MA, Valentin JL, et al. Effect of covalent crosslinks on the network structure of thermo-reversible ionic elastomers. *Soft Matter* 2012;8:5201.
- Xu C, Huang X, Li C, et al. Design of “Zn²⁺ salt-bondings” cross-linked carboxylated styrene butadiene rubber with reprocessing and recycling ability via rearrangements of ionic cross-linkings. *ACS Sustainable Chem Eng* 2016;4:6981–90.
- Yan M, Cao L, Xu C, et al. Fabrication of “Zn²⁺ salt-bondings” cross-linked SBS-g-COOH/ZnO composites: thiol-ene reaction modification of SBS, structure, high modulus, and shape memory properties. *Macromolecules* 2019;52:4329–40.
- Ibarra L, Marcos-Fernández A, Alzoriz M. Mechanistic approach to the curing of carboxylated nitrile rubber (XNBR) by zinc peroxide/zinc oxide. *Polymer* 2002;43:1649–55.
- Zhang G, Zhou X, Zhang L. Current issues for rubber crosslinking and its future trends of green chemistry strategy. *Express Polym Lett* 2019;13:406.
- Wang Y, Cui X, Yang Q, et al. Chemical recycling of unsaturated polyester resin and its composites via selective cleavage of the ester bond. *Green Chem* 2015;17:4527–32.
- Liu T, Guo X, Liu W, et al. Selective cleavage of ester linkages of anhydride-cured epoxy using a benign method and reuse of the decomposed polymer in new epoxy preparation. *Green Chem* 2017;19:4364–72.
- An W, Wang X, Yang Y, et al. Synergistic catalysis of binary alkalis for the recycling of unsaturated polyester under mild conditions. *Green Chem* 2019;21:3006–12.
- Zhao X, Wang X, Tian F, et al. A fast and mild closed-loop recycling of anhydride-cured epoxy through microwave-assisted catalytic degradation by trifunctional amine and subsequent reuse without separation. *Green Chem* 2019;21:2487–93.
- Gupta J, Nunes C, Vyas S, et al. Prediction of solubility parameters and miscibility of pharmaceutical compounds by molecular dynamics simulations. *J Phys Chem B* 2011;115:2014–23.

- [47] Jouyandeh M, Ali JA, Aghazadeh M, et al. Curing epoxy with electrochemically synthesized ZnFe_2O_4 magnetic nanoparticles. *Prog Org Coat* 2019;136:105246.
- [48] Sari MG, Saeb MR, Shabani M, et al. Epoxy/starch-modified nano-zinc oxide transparent nanocomposite coatings: a showcase of superior curing behavior. *Prog Org Coat* 2018;115:143–50.
- [49] Liu H, Chen F, Liu B, et al. Super toughened poly(lactic acid) ternary blends by simultaneous dynamic vulcanization and interfacial compatibilization. *Macromolecules* 2010;43:6058–66.
- [50] Liu Y, Tang Z, Wu S, et al. Integrating sacrificial bonds into dynamic covalent networks toward mechanically robust and malleable elastomers. *ACS Macro Lett* 2019;8:193–9.
- [51] Zhou X, Guo B, Zhang L, et al. Progress in bio-inspired sacrificial bonds in artificial polymeric materials. *Chem Soc Rev* 2017;46:6301–29.



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