

Effects of Binding Energy of Bioinspired Sacrificial Bond on Mechanical Performance of *cis*-1,4-Polyisoprene with Dual-crosslink

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Electronic Supplementary Information

Abstract Although bioinspired sacrificial bonds have been demonstrated to be efficient in improving the mechanical properties of polymer materials, the effect of binding energy of a specific dynamic bond on the ultimate mechanical performance of a polymer network with dual-crosslink remains unclear. In this contribution, diamine and sulfur curing package are introduced simultaneously into a sulfonated *cis*-1,4-polyisoprene to create dually-crosslinked *cis*-1,4-polyisoprene network with sulfonate-aminium ionic bonds as the sacrificial bonds. Three diamines (primary, secondary and tertiary) with the same spacer between the two nitrogen atoms are used to create the ionic bonds with different binding energies. Although the binding energy of ionic bond does not affect the glass transition temperature of *cis*-1,4-polyisoprene (IR), it exerts definite influences on strain-induced crystallization and mechanical performance. The capabilities of diamine in dissipating energy, promoting strain-induced crystallization and enhancing the mechanical performance are in the same order of secondary diamine > primary diamine > tertiary diamine. The variations in mechanical performances are correlated to the binding energy of the ionic bond, which is determined by pK_a values.

Keywords *cis*-1,4-Polyisoprene; Ionic bond; Sacrificial bond; Binding energy; Strain-induced crystallization

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INTRODUCTION

Natural rubber (NR) has found a great variety of important applications for its excellent comprehensive mechanical properties, such as high tensile and tear strength and excellent crack growth resistance^[1–3]. The outstanding mechanical performance of NR has been disclosed to be closely related to its unique capability of strain-induced crystallization (SIC)^[4–8]. Although the man-made *cis*-1,4-polyisoprene (IR) has almost the same molecular structure and high degree of *cis*-unit as NR, IR possesses much lower SIC capability and hence lower mechanical properties comparing to its natural counterpart^[9, 10]. It has been widely acknowledged that the high capability of SIC possessed by NR is attributed to the presence of non-rubber components, which play an important role in the formation of pseudo networking of NR chain^[11–15]. Consequently, the modification of synthetic IR to gain promoted SIC capability and hence superior mechanical properties are of great importance, in view of solving the shortage issue of NR.

Some researches have focused on the introduction of heterogeneous network into NR or IR to promote SIC by incorporating various kinds of nanofillers, such as organo-

clay and graphene oxide^[16–19]. Although in most cases, the incorporation of various nanofillers is necessary to obtain sufficient mechanical properties^[20, 21], there are still some important limitations or difficulties for nanofilling, such as deteriorated stretchability, dispersion/interface regulation and processing difficulty. In this regard, the modification of rubber network may offer an alternative solution in enhancing SIC capability of IR^[22, 23]. Sacrificial bonds have been disclosed to be one of the most important structural origins for exceptional combination of high strength and fracture toughness in many natural materials such as spider silks and mussel byssus^[24, 25]. When these materials are deformed, the sacrificial bonds rupture preferentially before the rupture of covalent bonds, while the structural integrity is preserved, which dissipates much mechanical energy and hence brings about significantly improved strength and fracture toughness^[26, 27]. The sacrificial bonding strategy has been successfully applied in the fabrication of highly tough hydrogels^[28–30]. Various non-covalent bonds such as hydrogen bonds and metal-ligand bonds can be utilized as sacrificial bonds. Sacrificial hydrogen bonds based on urazole^[31] or 2-ureido-4 [1H]-pyrimidinone (UPy)^[32] have been reported. For instance, Gold *et al.* prepared a dual-network of polybutadiene elastomer consisting of covalent-crosslinked network by hydrosilylation and the sacrificial hydrogen bond network by the association of urazole groups.

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The modified polybutadiene elastomer exhibits much enhanced mechanical properties, comparing to the network with only covalent crosslinks^[31]. Metal-ligand bonds, have also been widely found in many natural materials and already been used as sacrificial bonds in artificial polymer materials due to the versatility in structural design. Our group has engineered metal-ligand bonds into commercially available diene-based rubber networks, aiming at significantly improved strength, toughness and fatigue resistance. For example, Tang *et al.* introduced metal-ligand bond into a chemically cross-linked rubber network and 6.9 and 5.1 times increments in tensile strength and toughness have been observed^[33]. To maximize the efficiency of energy dissipation, Liu *et al.* incorporated multiple sacrificial bonds (weaker sacrificial hydrogen bonds and stronger Zn-based units) into a chemically cross-linked *cis*-1,4-polyisoprene network. Due to the successive rupture of hydrogen bonds and metal-ligand bonds, the tensile modulus and fracture toughness as well as flex-cracking resistance are concurrently improved^[34]. Comparing to other non-covalent interactions, such as hydrogen bonds and metal-ligand bonds, ionic bonds are normally stronger and less-directional^[35]. Excessive ionic bonds may aggregate into clusters as nanodomains, which complicates the mechanisms of reinforcement^[36, 37]. Sun *et al.* synthesized hydrogels with ionically and covalently crosslinked networks, where the ionic bonds were utilized as sacrificial bonds. The results showed that the fracture strength was increased up to 20 times comparing to that with covalent network only. Furthermore, the internal damages caused by the rupture of ionic crosslinks during stretching can recover after removing the loading^[38].

It has been revealed that the capacity of energy dissipation of sacrificial bonds may have significant influences on the mechanical properties of the network with dual-crosslink. However, most of the previous investigations focused on the effects from different types of dynamic bonds on the mechanical properties. The effects of binding strength of a specific dynamic bond on the mechanical properties of the elastomer with dual-crosslink remain unsolved. In this contribution, aiming to reveal effects of the subtle structural changes of ionic bonds on the mechanical properties of IR with dual-crosslink, diamine and sulfur curing package were simultaneously introduced into a sulfonated IR (IR-SO₃H) to create IR network with dual-crosslink. The ionic bonds formed between sulfonic acid and diamine act as sacrificial bonds. The binding energies of the sacrificial bonds were adjusted by the substituent groups on the nitrogen atom. The energy dissipation, mechanical properties and strain-induced crystallization were fully investigated to gain insights into the relationship between the structure of sacrificial bonds and mechanical performance.

EXPERIMENTAL

Raw Materials

IR (IR 2200, 98% *cis*-unit) was purchased from Zeonex (Japan). Concentrated sulfuric acid (98%) and acetic

anhydride were purchased from Guangzhou Chemical Reagent Factory. 1,6-Hexanediamine (HD) was obtained from Tianjin Kermel Chemicals Co. Ltd. *N,N*-dimethyl-1,6-hexanediamine (DHD) and *N,N,N',N'*-tetramethyl-1,6-hexanediamine (THD) were provided by Innocem Chemicals. Other rubber ingredients were industrially available products and used as received.

Preparation of Sulfonated IR (IR-SO₃H)

IR-SO₃H was prepared according to the literature method^[39]. Typically, the sulfonating agent (acetyl sulfate) was prepared by dropwise adding sulfuric acid into acetic anhydride at about 5 °C. Acetic anhydride/sulfuric acid molar ratio was set as 1.6. Sulfuric acid/isoprene molar ratio was in the range of 0.15–0.5. Acetyl sulfate was diluted by trichloromethane at room temperature.

IR (10 g) was dissolved in trichloromethane (500 mL) to obtain the IR solution. A certain amount of diluted acetyl sulfate was dropwise added into the IR solution at about 5 °C under vigorous stirring. After that, the temperature was raised to 20 °C and the reaction was lasted for 4 h. The solution was then precipitated in ethanol. The precipitated polymer was washed thoroughly with ethanol and dried in vacuum at 30 °C. The modified IR was coded as IR-SO₃H (*x*), in which *x* is the grafting percent (molar percent relative to isoprene units) of sulfonic acid.

Preparation of IR Network with Dual-crosslink

The diamine/toluene solution was added into IR-SO₃H solution (50 g/L). Amino/sulfonic acid molar ratio was adjusted in the range from 0.5:1 to 2:1. The reaction was conducted at room temperature for 6 h. After that, the solvent was evaporated. The rubber incorporating diamine was compounded with ingredients in an open two-roll mill, and compression moulded into specimens at optimized curing time, which is determined by a vulcameter. The basic formulation includes gum rubber (100 g), zinc oxide (5 g), stearic acid (1 g), *N*-cyclohexyl-2-benzothiazole (1.5 g), 2,2'-dibenzothiazole disulfide (0.5 g), and sulfur (1.5 g). The samples involving HD, DHD and THD were coded as IR-SO₃H-HD (*y*), IR-SO₃H-DHD (*y*) and IR-SO₃H-THD (*y*), respectively, in which *y* is amino/sulfonic acid molar ratio.

Characterizations

The grafting content of sulfonic acid is determined by titration^[40]. Specifically, IR-SO₃H (0.5 g) was dissolved in a toluene/methanol mixture (9/1, *V/V*, 100 mL). NaOH/methanol solution (0.01 mol/L) was added into the rubber solution dropwise under nitrogen. Phenolphthalein was used to monitor the neutralization point. The content of sulfonic acid was calculated according to following equation:

$$\text{Content of sulfonic acid (\%)} = \frac{68 \times cV}{m} \times 100 \quad (1)$$

where *c* and *V* are the concentration and volume of NaOH solution, respectively. *m* is the mass of IR-SO₃H.

Fourier transform infrared (FTIR) spectra were obtained by a Bruker Vertex 70 FTIR spectrometer. ¹H-NMR spectra were collected on a Varian NMR spectrometer (CDCl₃ as the solvent). Tensile tests and the hysteresis measurements were

performed with a U-CAN UT-2060 instrument (Taiwan). Tensile tests were performed according to ISO standard 37-2005. The cyclic loading-unloading tests were carried out with extension rate of 100 mm/min at a predefined strain of 400%, and the hysteresis energy was calculated from the area between the loading and unloading curves. Dynamic mechanical analysis (DMA) was performed in tensile mode with a TA DMA Q800 machine. The preload force and the dynamic strain were set as 0.01 N and 0.3%, respectively. The temperature sweeping was performed from $-80\text{ }^{\circ}\text{C}$ to $30\text{ }^{\circ}\text{C}$. The heating rate and frequency were set as $3\text{ }^{\circ}\text{C}/\text{min}$ and 1 Hz . The stress-relaxation experiments were also conducted with the TA DMA Q800 machine at $25\text{ }^{\circ}\text{C}$. The samples were stretched to 100% strain at the strain rate of $500\text{ }^{\circ}/\text{min}$. The constant strain was maintained to measure the relaxed stress. X-ray diffraction patterns of the stretched samples were collected in the 2θ range from 5° to 30° ^[34] by using a Bruker D8 Advance X-ray diffractometer with Cu K α radiation ($\lambda = 0.1542\text{ nm}$).

RESULTS AND DISCUSSION

Sulfonation of IR and Formation of Dual-crosslink

As shown in Fig. 1, IR is modified to introduce pendent sulfonic acid groups on the chain backbone (Fig. 1a). The sulfonation degree is well controlled by varying the reaction time and the amount of sulfuric acid in the preparation of acetyl sulfate (Table S1, in electronic supplementary information, ESI). Grafting contents of sulfonic acid ranging from 0.61% to 6.5% are accordingly achieved. Diamine is used to crosslink IR-SO₃H to form ionic crosslinking structure. Concurrently, the modified IR is crosslinked by sulfur, resulting in a network with dual-crosslink (Fig. 1b). It has been established that the glass transition temperature (T_g) of an ionomer usually increases with increasing concentration of ionic bonds^[40]. The evolution of tangent delta curves along the change in sulfonation degree for the diamine-cured IR-SO₃H is recorded (Fig. S1, in ESI). Explicitly, the T_g of the network increases rapidly along with

the increase in sulfonation degree.

The grafting of IR is verified by spectral results. Fig. S2 (in ESI) depicts the FTIR spectra of the samples. As shown in Fig. S2 (in ESI), compared with IR, IR-SO₃H samples exhibit additional peaks around 1020 and 1205 cm^{-1} , which are attributed to symmetrical and asymmetric stretch peaks of O=S=O, respectively^[40]. In addition, the intensities of the two characteristic peaks definitely increase along with sulfonation degree increasing. To maintain the chain flexibility of the network, IR-SO₃H with low sulfonation degree of 0.61% was used to react with different amounts of HD to prepare IR-SO₃H-HD. The amino/sulfonic acid molar ratio is varied from 0 to 2. Fig. 2(A) depicts the evolution of FTIR spectra of IR-SO₃H-HD with increasing diamine content. The stretching vibration of N—H is characterized by the adsorption around 3350 cm^{-1} . When the amino/sulfonic acid molar ratio is lower than 1, the characteristic peak at 3350 cm^{-1} cannot be observed, which illustrates that HD reacts with sulfonic acid sufficiently forming ionic bonds. With the amount of HD further increasing, the characteristic peak emerges, indicating that redundant HD remains. This result suggests that the equivalent amounts of amino groups are experimentally sufficient to fulfil the ionic crosslinking. The ionic bonding between IR-SO₃H and diamine is further identified by ¹H-NMR. Fig. 2(B) is the ¹H-NMR spectrum of HD, in which the assignments are made (1.09 ppm, d; 1.26 ppm, c; 1.38 ppm, a; and 2.62 ppm, b). Fig. 2(C) is the spectrum of IR-SO₃H-HD (1.0), in which the characteristic signals of *cis*-1,4-isoprene units are found (1.68 ppm, g; 2.04 ppm, f; and 5.12 ppm, e)^[10]. Due to the low grafting percent, the proton of sulfonic acid cannot be probed, which is consistent with the previous report^[41]. Fig. 2(D) is the magnified spectrum of Fig. 2(C). The proton signals of the methylene hydrogens adjacent to N atom shift from 2.6 ppm to 2.35 ppm, indicating protonation of amino by sulfonic acid^[41].

The vulcanization curves and modulus at 400% strain of IR-SO₃H-HD incorporating varying amount of diamine are presented in Fig. 3. It can be seen that the vulcanization time decreases with the increase of diamine content, which is

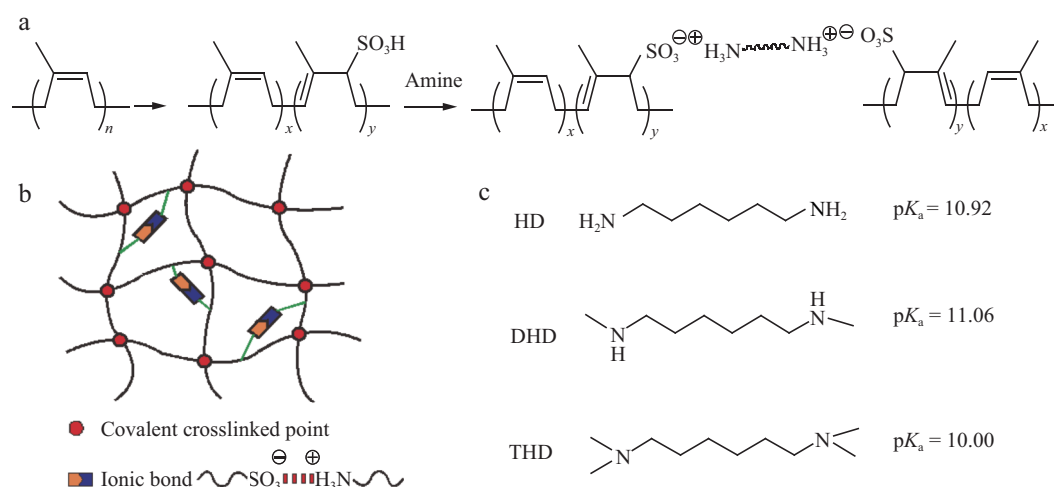


Fig. 1 (a) Scheme for crosslinking between IR-SO₃H and diamine; (b) IR network with dual-crosslink; (c) Structures of the diamines

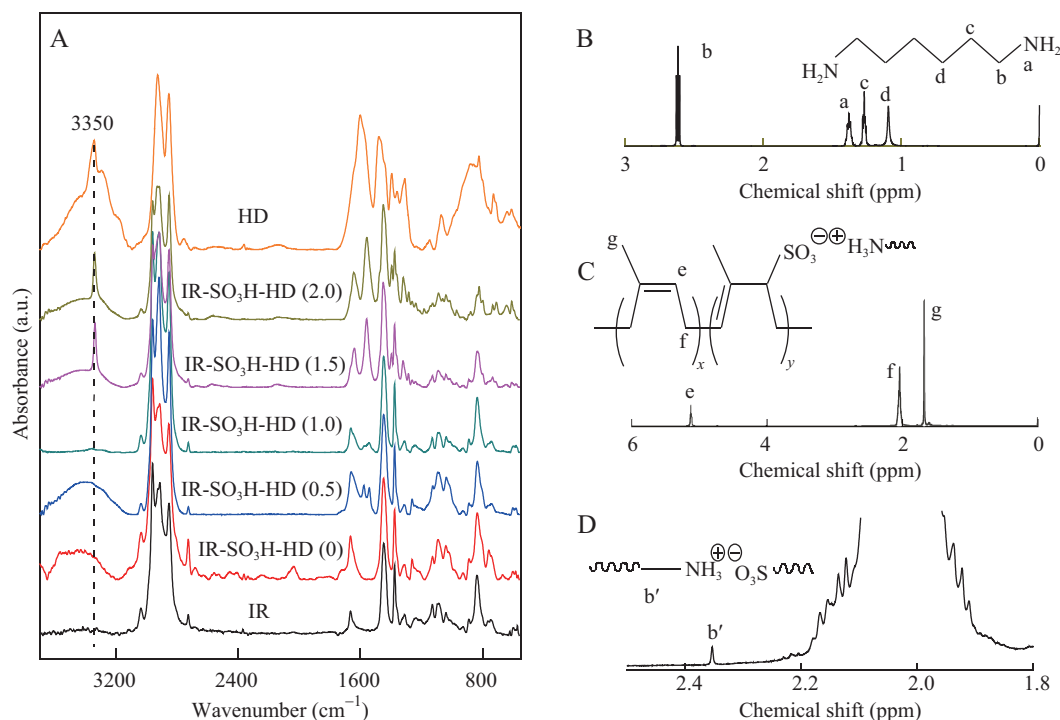


Fig. 2 (A) Evolution of FTIR spectrum of IR-SO₃H-HD with increasing diamine content; ¹H-NMR spectra of (B) HD, (C, D) IR-SO₃H-HD (1.0)

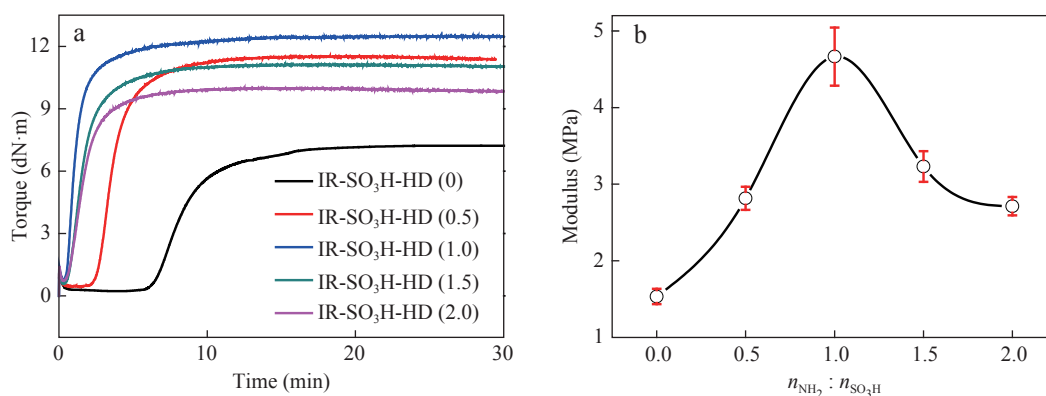


Fig. 3 (a) Vulcanization curves of IR-SO₃H-HD (γ); (b) Modulus (at 400% strain) of IR-SO₃H-HD (γ)

attributed to the increasing basicity caused by the diamine. When amino/sulfonic acid molar ratio is below 1, the equilibrium torque increases with the increase of diamine content, suggesting increasing crosslink density, which is attributed to the contribution of the increasing amounts of ionic bonding crosslinks. When the molar ratio increases further, however, the equilibrium torque starts to decline, which may be due to the plasticization effect of the excessive diamine.

The effect of amino/sulfonic acid molar ratio on the modulus of IR-SO₃H-HD is shown in Fig. 3(b). When the molar ratio is below 1, the modulus increases rapidly with increasing amino content, suggesting significant contribution to crosslinking density from ionic bonds. When the molar ratio is higher than 1, however, the modulus decreases due to the plasticization effect of the excessive diamine. The depen-

dences of modulus on amino/sulfonic acid molar ratio in IR-SO₃H-DHD and IR-SO₃H-THD systems are similar (Fig. S3, in ESI). The variation in tensile modulus along with the increase in the amino/sulfonic acid molar ratio is consistent with that for the equilibrium torque as described above. The variation of storage modulus determined by DMA method is similar to that observed in tensile tests. In addition, T_g is essentially not changed by increasing the amino content. Overall, the samples possess low T_g value which is favorable for the cold-resistant applications (Fig. S4, in ESI).

Effects of Binding Energy of Ionic Bond on Strain-induced Crystallization and Mechanical Properties

To probe the effect of binding energy of the ionic bond on mechanical properties, equivalent primary (HD), secondary (DHD) and tertiary (THD) diamines were used to crosslink the sulfonated IR. The ionic interaction between diamine and

sulfonic acid group is due to the proton exchange process. The proton of sulfonic acid group is easy to be absorbed by nucleophilic reagent such as amine, which provides the electron, leading to the formation of ionic bonds. The strength of interaction (binding energy) depends on the capacity of proton exchange, which is related to the electron cloud density and the steric hindrance of three kinds of amines. Generally speaking, the ability of proton exchange can be attributed to the alkalinity of amine^[42]. Their structures are depicted in Fig. 1(c). Theoretically, HD, DHD and THD have pK_a values of 10.92, 11.06 and 10.00, respectively. The higher the pK_a is, the stronger the alkalinity of amine is. DHD has the strongest capacity of proton exchange. Therefore, the interaction between DHD and sulfonic acid group should be stronger than the others. Consequently, the binding energy of the formed ionic bond follows the order of DHD > HD > THD. In addition, the three amines have the same spacer (sextuple methylene). Therefore, this experiment design enables the incorporation of sacrificial ionic bonds with varying binding energy into IR network.

Fig. 4 is the stress relaxation curve which can provide implications for the binding energies of the ionic bonds. As shown in Fig. 4, compared with the neat IR, the IR with dual crosslink can release the applied force faster, which is due to the presence of weaker interaction of ionic bonds. Among the IR samples with dual-crosslink, the rate of relaxation is also different. To further make a quantitative comparison of the stress relaxation, the characteristic relaxation time is determined according to following equation^[34]:

$$\sigma(t) = \sigma(0)e^{-t/\tau} \quad (2)$$

where $\sigma(t)$ is the stress at the time of t , $\sigma(0)$ is the initial stress, t is the relaxation time and τ is the characteristic relaxation time. $\sigma(t)/\sigma(0)$ of 0.98 is taken as the reference for all samples. Accordingly, the relaxation times for IR-SO₃H-THD (1.0), IR-SO₃H-HD (1.0), IR-SO₃H-DHD (1.0) are calculated as 274, 312 and 386 s, respectively. It can be seen that the rate of relaxation of IR-SO₃H-DHD (1.0) is slower than those of the others, indicating the stronger binding

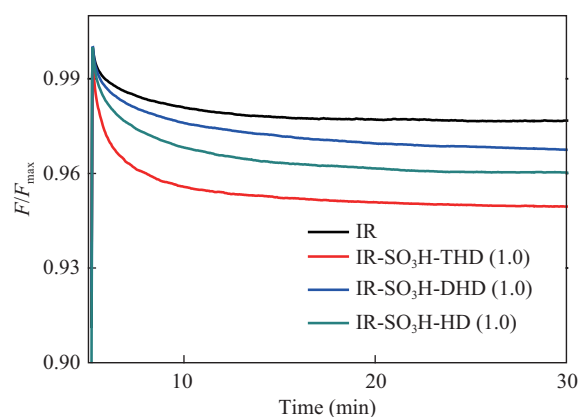


Fig. 4 Stress relaxation curves of IR, IR-SO₃H-THD (1.0), IR-SO₃H-DHD (1.0) and IR-SO₃H-HD (1.0)

energy of the ionic bonds in IR-SO₃H-DHD (1.0)^[43, 44]. IR-SO₃H-THD (1.0) possesses the fastest rate of relaxation, corresponding to the weakest binding energy of ionic bond. This result indicates that the binding energy with sulfonic acid group follows the order of DHD > HD > THD.

To substantiate the ability of the formed ionic bonds in dissipating energy during stretching, the hysteresis during loading-unloading cycling with the predefined strain (400%) is determined (Fig. 5). There is little hysteresis for sulfur-cured IR due to its high entropic elasticity ensured by covalent crosslinks. By contrast, the IR samples with dual-crosslink exhibit much increased hysteresis (Fig. 5a). Fig. 5(b) exhibits the hysteresis energy ΔW of different samples, which is calculated from the area of hysteresis loop^[45]. It can be seen that IR-SO₃H-DHD (1.0) possesses the highest ΔW values, followed by IR-SO₃H-HD (1.0) and IR-SO₃H-THD (1.0), suggesting that the capability in dissipating energy follows the order of IR-SO₃H-DHD (1.0) > IR-SO₃H-HD (1.0) > IR-SO₃H-THD (1.0).

It is well known that IR can show strain-induced crystallization (SIC)^[46]. Our previous works showed that the SIC of IR can be promoted *via* constructing sacrificial bonds in IR^[10, 47]. Herein, to investigate the effects of binding

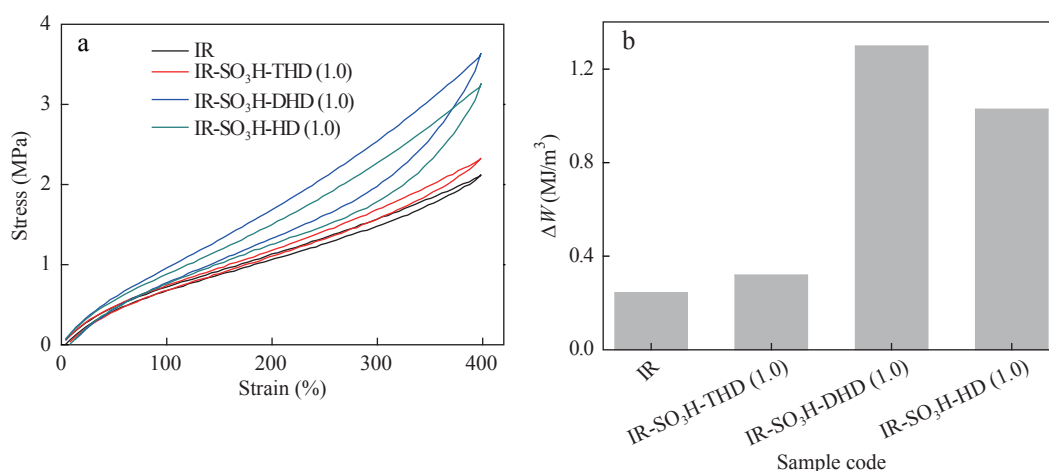


Fig. 5 (a) Loading-unloading curves of modified IR systems; (b) ΔW values for IR, IR-SO₃H-THD (1.0), IR-SO₃H-DHD (1.0) and IR-SO₃H-HD (1.0)

energy of sacrificial ionic bonds on SIC of IR, XRD profiles evolving along with the increase of strain for IR and three IR networks with dual-crosslink are obtained (Fig. S5, in ESI). The initial crystallization is evidenced by the emerging of characteristic diffraction at 14° ((200) plane) and 21° ((120) plane)^[48, 49]. The neat IR starts to crystallize when the strain is up to 600%. In contrast, the samples with dual-crosslink exhibit the two characteristic diffraction peaks at substantially lower strains. In addition, as the strain increases, the intensity of these two crystallization peaks increases rapidly, indicating the growth of crystals in the samples. Specifically, the XRD profiles at the strain of 550% for the IR samples with dual-crosslink are compared in Fig. 6. Clearly, the order of diffraction intensity for these samples is IR-SO₃H-DHD (1.0) > IR-SO₃H-HD (1.0) > IR-SO₃H-THD (1.0), suggesting the same order for crystallinity.

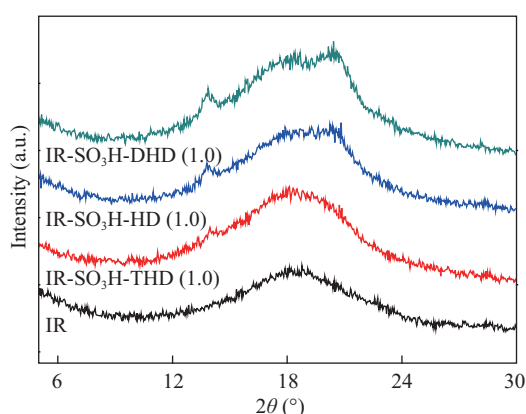


Fig. 6 XRD profiles for the IR samples with dual-crosslink at strain of 550%

The XRD profiles are deconvoluted to quantify the effect of ionic bonds on crystallinity. The mass fraction crystallinity is calculated using the following equation:

$$X_c(\%) = \frac{A_c}{A_c + A_a} \times 100 \quad (3)$$

where X_c is the mass fraction crystallinity. A_c is the area below (120) and (200) plane crystalline peaks and A_a is the area below the amorphous halo^[49, 50]. The calculated crystallinities are summarized in Table 1. Clearly, IR-SO₃H-DHD (1.0) possesses the highest SIC capacity, as evidenced by the lowest initial crystallization strain and the highest crystallinity, followed by IR-SO₃H-HD (1.0) and IR-SO₃H-THD (1.0).

According to the view point of Toki and Tosaka *etc.*^[4, 11], the short chains of NR are preferentially stretched to initiate the crystallization during deformation process. Then crystal growth maintains its character of chain-folding by

consuming those less stretched segments and further stretching extends those folded-chains, which will promote the formation and growth of crystal further. In the present study, we propose that the introduction of ionic bonds gives rise to an ionic bonding network that interlinks multiple chains with nonuniform lengths. When the sample is stretched, the ionic bonds with higher binding energy may favor the orientation of short chains and therefore the initial crystallization takes place at lower strain. Therefore, the onset strain for SIC follows the order of IR-SO₃H-DHD (1.0) < IR-SO₃H-HD (1.0) < IR-SO₃H-THD (1.0).

Stress-strain curves are presented in Fig. 7. The moduli of the IR with dual-crosslink are definitely higher than that of the neat IR, which can be explained by the fact that the ionic bonds in IR with dual-crosslink increase the whole crosslinking densities and can sustain certain loading at small deformation. Furthermore, IR-SO₃H-DHD (1.0) possesses the highest modulus, followed by IR-SO₃H-HD (1.0) and IR-SO₃H-THD (1.0). This can be attributed to the variation of binding energy of the sacrificial ionic bond and the capacity of SIC. It is believed that before the onset strain of SIC, the stronger the ionic bond is, the more energy is dissipated during deformation. Consequently, the system with DHD should consume more energy during stretching than others, hence leading to the highest modulus achieved. Further, with the increase of strain, the crystallization plays a leading role in mechanical property, which is suggested by the sharply upturn of the curves. The order of the strain at upturn of the samples is consistent with the results observed in XRD. Thus, IR-SO₃H-DHD has the highest modulus during the whole deformation, followed by IR-SO₃H-HD and IR-SO₃H-THD. In a word, the stronger the binding energy of the sacrificial ionic bond is, the more energy is dissipated during stretching, the smaller strain is needed to initiate crystallization and the higher modulus is obtained. In addition, what is noteworthy is that the binding energy of

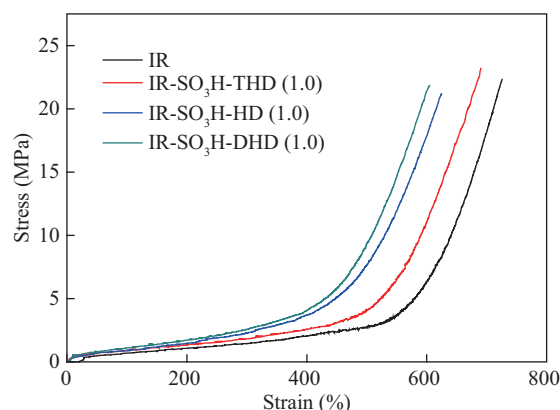


Fig. 7 Stress-strain curves for the IR systems with various diamine

Table 1 Crystallinities (%) at different strains for the neat IR and the IR networks with dual-crosslink

Strain	3.5	4.0	4.5	5.0	5.5	6.0
IR	/	/	/	/	3.76	18.53
IR-SO ₃ H-THD (1.0)	/	/	/	3.12	7.85	14.66
IR-SO ₃ H-HD (1.0)	/	1.06	4.31	9.84	13.77	23.84
IR-SO ₃ H-DHD (1.0)	/	2.10	8.95	12.18	18.93	30.40

sacrificial ionic bonds does not exert virtual effect on T_g of the samples (Fig. S6, in ESI).

CONCLUSIONS

In the present work, pendent sulfonic acid groups are grafted onto IR with the controlled sulfonation degree. Three kinds of diamine with different pK_a values and the same spacer are utilized to crosslink the modified IR to introduce ionic bonds into IR network. The introduction of ionic bonds improves the mechanical properties significantly. Although the structure of ionic bond does not affect the glass transition temperature of IR, it exerts definite influences on mechanical performance and strain-induced crystallization. The capabilities of diamine in dissipating energy, promoting strain-induced crystallization and enhancing mechanical performance are in the same order of secondary diamine > primary diamine > tertiary diamine. The variations in mechanical performance are correlated to the binding energy of the ionic bond, which is determined by pK_a values.

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/s10118-018-2131-x>.

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