

Tailoring the Properties of Diels-Alder Reaction Crosslinked High-performance Thermosets by Different Bismaleimides

Kai-Ju Luo, Li-Bo Huang, Yan Wang*, Jun-Rong Yu, Jing Zhu, and Zu-Ming Hu*

State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Material Science and Engineering, Donghua University, Shanghai 201620, China

Abstract A series of Diels-Alder reaction cross-linked thermosets with recyclability and healability were prepared from furan-containing aromatic polyamide and bismaleimides with different chemical structures. The structures of synthesized bismaleimides were confirmed by ^1H nuclear magnetic resonance (^1H -NMR) spectroscopy; their reversible cross-linking with the furanic polyamide was further detected by ^1H -NMR technique and sol-gel transition behavior. The dynamic mechanical analysis and tensile test revealed the variable thermal and mechanical properties of thermosets cross-linked by different bismaleimides and with different molar ratios of maleimide group to furan group ($I_{\text{ma/fur}}$). The tensile test also demonstrated that the better recyclability and solvent-assisted healability of thermosets cross-linked could be achieved by more flexible bismaleimides. This work is expected to provide valuable information for design of recyclable and healable high-performance thermosets with desired properties.

Keywords Recyclability; Reparability; Thermosets; Diels-Alder reaction

Citation: Luo, K. J.; Huang, L. B.; Wang, Y.; Yu, J. R.; Zhu, J.; Hu, Z. M. Tailoring the properties of Diels-Alder reaction crosslinked high-performance thermosets by different bismaleimides. *Chinese J. Polym. Sci.* 2020, 38, 268–277.

INTRODUCTION

Thermosets are famous for their distinguished chemical and creep resistance, dimensional stability, and good thermomechanical properties due to the covalently crosslinked networks, and thus have been used widely in the last few decades.^[1–4] However, the insoluble and infusible characters have greatly restricted their reprocessability once they are subject to damage or failure, which raises serious environmental and economic problems.^[5,6] This situation stimulates the urgent demands for establishing new kinds of thermosets with prolonged service lifetime and facile healability or recyclability.^[7–13]

In the last years, great efforts have been devoted worldwide to addressing this issue, and the employment of reversible chemical reactions to construct dynamically cross-linked networks has attracted broad attention.^[14–19] Compared with traditional thermo-curing, the dynamic reactions, such as Diels-Alder (D-A) reaction,^[20–22] disulfide exchange reaction,^[23–25] transesterification,^[5,26] and so on, could generate dynamic bonds that behave as traditional covalent bonds at ambient condition but dissociate/re-associate under certain stimuli. Among them, the D-A reaction is particularly impressive for its unparalleled merits such as the highly purified products, the mild process without any catalysts or initiators,

and the good tolerance to other functional groups.^[27,28] Thus, considerable work has been done to design healable or recyclable thermosets from furan or maleimide containing polymers such as polyurethane,^[29–31] polyether,^[32,33] synthetic rubber,^[34,35] silicon elastomer,^[36] and so on. Nevertheless, the high-performance polymers, including aromatic polyamide, have been much less investigated in D-A reaction-based materials, which is in conflict with their crucial roles in the fields of aerospace, automotive, cable, electronics, and so on.^[37–39] This discrepancy might be attributed to the rigid backbone and multiple interchain interactions of aromatic polymers, which endow them with notorious insoluble and infusible features that hamper their facile post-functionalization with cross-linkable furan or maleimide groups. In previous work, we have designed and synthesized a new class of aromatic polyamide with pendent furan groups. This polyamide possessed good processability and could readily react with bismaleimide to afford crosslinked thermoset.^[40] The reversible D-A reaction between furan and maleimide groups also allowed this thermoset to be recycled and reprocessed in solution, which provided a new pathway to synthesize recyclable and high-performance thermosets.

On the other hand, it is well known that the macroscopic properties of thermosets are generally determined by the structure of molecular chains as well as the crosslinked polymer networks. Therefore, the structure of crosslinker could make a big difference in the final performance. While many researchers utilized commercialized bismaleimide (*N,N'*-4,4'-diphenylmethane-bismaleimide, BMI) as the crosslinker to

* Corresponding authors, E-mail: wy@dhu.edu.cn (Y.W.)

E-mail: hzm@dhu.edu.cn (Z.M.H.)

Received May 28, 2019; Accepted July 8, 2019; Published online September 19, 2019

crosslink furan containing polymers, few have focused on the structure of crosslinkers, let alone to make a comparison in detail.^[31,41–43] In fact, the length and flexibility of bismaleimides would directly affect the structure of network and mechanical performance of substrate. The motion ability of segments is also crucial to the healing and recycling of the network. In our previous study, we have also used BMI to crosslink our furanic polyamide and demonstrated the improved mechanical properties. However, the crosslinking of an aromatic matrix with short and benzene ring abundant BMI resulted in relatively brittle material because of the dense crosslinked network and rigid molecular backbone. Moreover, the crosslinked network can only be recycled and reprocessed in solution, but can hardly be healed in solid state. Therefore, it is important to tune the mechanical behavior and realize the facile healing of polyamide-based thermoset for wider applications.

Given the above consideration, herein, we reported a series of furanic polyamide-based thermosets by using different bismaleimides as crosslinkers via D-A reaction. The effects of the molecular structures of bismaleimides on thermal, mechanical, and recycling properties of the resulting thermosets were thoroughly investigated. The possibility to heal the damaged thermosets in solid state was also evaluated.

EXPERIMENTAL

Materials

Furfural, 5-aminoisophthalic acid, anhydrous sodium sulfate, glacial acetic acid, sodium borohydride, methanol, pyridine, and triphenyl phosphate (TPP) were commercially available and used directly as received. The aromatic diamine 4,4'-diaminodiphenyl ether (ODA) was purchased from J&K. Aliphatic diamine poly(propylene glycol) bis(2-aminopropyl ether) (D230) was purchased from Sigma-Aldrich. 1,6-Hexanediamine and ethylenediamine were obtained from Sinopharm Chemical Reagent Co.,

Ltd. All diamines were used without any treatment. The solvent *N*-methyl-2-pyrrolidinone (NMP) was stored over 4 Å activated molecular sieves for at least one week before use. Lithium chloride was dried overnight in muffle furnace under 400 °C for 6 h prior to use.

Synthesis of Different Bismaleimides

The general method for the preparation of bismaleimides is shown in Fig. 1. Three kinds of diamines with different structures were firstly reacted with maleic anhydride to acquire an intermediate and then dehydrated to obtain the final products.

Synthesis of 1,1-(ethane-1,2-diyl)bis(1*H*-pyrrole-2,5-dione) (EBM)

EBM was prepared as follows. Ethylene diamine (20 mmol) in chloroform (50 mL) was added drop-wise into the solution of maleic anhydride (50 mmol) in chloroform (100 mL) at 0 °C under the protection of nitrogen. The slurry was then stirred for 2 h at room temperature to obtain the corresponding intermediate bismaleamic acid; the intermediate was filtrated and dried for 4 h at 60 °C. Next, the bismaleamic acid (4.35 g) and sodium acetate trihydrate (1.07 g) were dissolved in acetone (100 mL), followed by the addition of triethylamine (1.52 mL) and acetic anhydride (10.21 mL). Then, the mixture was refluxed at 70 °C for 6 h and rotary evaporated to remove the solvent. The resulting crude product was washed with deionized water for three times to give the final product.

Synthesis of 1,1-(hexane-1,6-diyl)bis(1*H*-pyrrole-2,5-dione) (HBM)

HBM was prepared in a similar way as described above. In detail, 1,6-hexanediamine (20 mmol) was first dissolved in anhydrous ether (50 mL) and added dropwise into the solution of maleic anhydride (50 mmol) in anhydrous ether (100 mL) at 0 °C under the protection of nitrogen. The slurry was then stirred for 2 h at room temperature to give the corresponding intermediate bismaleamic acid; the intermediate was filtrated and dried for 4 h at 60 °C. Next, the intermediate bismaleamic acid (5.31 g) and

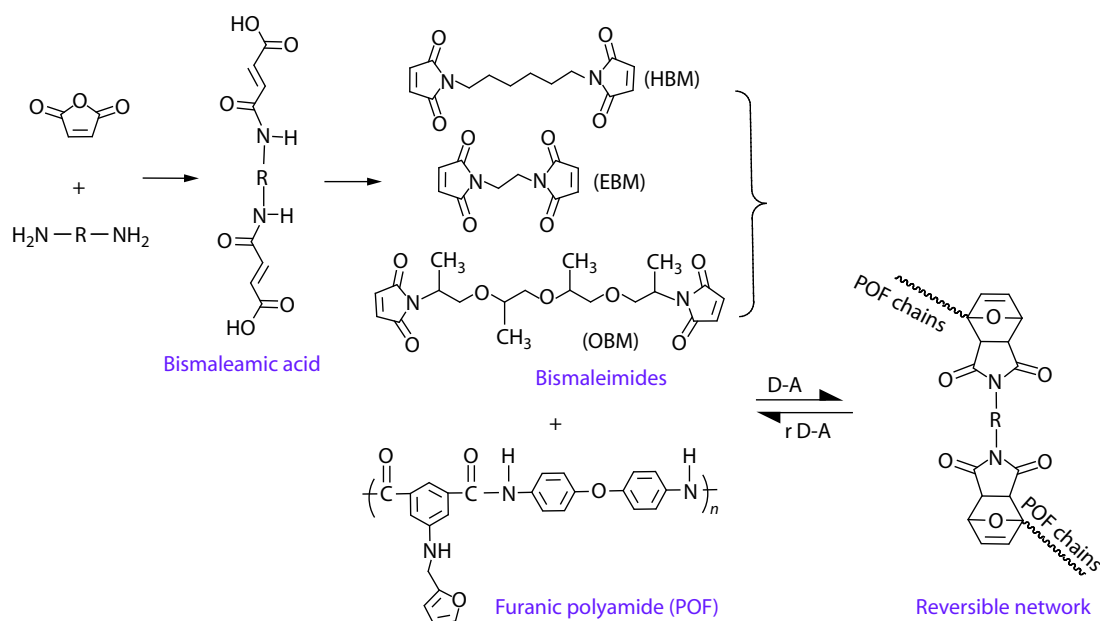


Fig. 1 Synthetic procedures of different bismaleimides and their reversible reactions with POF.

sodium acetate trihydrate (1.07 g) were dissolved in acetone (100 mL), followed by the addition of triethylamine (1.52 mL) and acetic anhydride (10.21 mL); the mixture was then refluxed at 70 °C for 6 h and rotary evaporated to remove solvent. The resulting crude product was washed with deionized water for three times to give the final product.

Synthesis of 1-((1-((1-(2-(2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)propoxy)propan-2-yl)oxy)propan-2-yl)oxy)propan-2-yl)-1H-pyrrole-2,5-dione (OBM)

OBM was prepared as follows. D230 (20 mmol) in anhydrous ether (50 mL) was added drop-wise to maleic anhydride (50 mmol) in anhydrous ether (100 mL) over 1 h under the protection of nitrogen at 0 °C. The mixture was stirred for 2 h at room temperature. The solvent was then replaced with fresh anhydrous ether (150 mL × 3) and subsequently, sodium acetate (1.26 g), triethylamine (1.79 mL), and acetic anhydride (12 mL) were added in turns. After 8 h reaction at 40 °C, the solvent was rotary evaporated to give crude product, which was washed with water for three times to obtain a yellow viscous product.

Polymerization Procedure of Furanic Pendant Polyamide (POF)

The synthetic route to aromatic furanic polyamide was developed by our group previously^[40] and could be described briefly as follows. Furfural and 5-aminoisophthalic acid were dissolved in methanol with anhydrous sodium sulfate as the water absorbent and glacial acetic acid as the catalyst to form unstable intermediate, and then quadruple amount of sodium borohydride was added in batches to reduce the double-bond. The obtained furan-containing diacid monomer was reacted with 4,4-diaminodiphenyl ether (ODA) at 130 °C in NMP solution with the aid of pyridine, TPP, and LiCl to give the final furanic polyamide, whose structure is shown in Fig. 1 and was named as POF.

Cross-linking of POF with Different Bismaleimides

POF was dissolved in NMP (solid content of 8 wt%) to form a polymer solution and mixed with different bismaleimides with variable molar ratio of maleimide/furan ($I_{\text{ma/fur}}$ = 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6). The mixtures were casted on glass plates and dried

at 60 °C for 3 days to obtain the corresponding crosslinked films (named as POF-X-Y, where X is the value of $I_{\text{ma/fur}}$ and Y is the kind of bismaleimides).

Characterizations

¹H-NMR spectra were obtained under 298 K in DMSO-d₆ or CDCl₃ with tetramethylsilane (TMS) as an internal reference by a Bruker 600-MHz NMR spectrometer. The dynamic thermal-mechanical properties were tested on a dynamic mechanical thermal analyzer (DMA Q800, TA instruments, Co., Ltd. USA) with rising temperature from 40 °C to 180 °C, during which the frequency was maintained at 1.0 Hz and the heating rate was set at 10 °C/min. The mechanical properties of samples (30 mm × 6 mm × 0.06–0.18 mm) were measured on MTS model C44-104 electronic universal testing machine. The crosshead speed was fixed at 5 mm/min with an initial length of 15 mm under room temperature and humidity of about 65%. To test the recyclability of crosslinked films, the samples were cut into pieces and re-dissolved in NMP at 130 °C to unlock the reversible linkage. Subsequently, the homogenous solution was casted on glass plate and dried at 60 °C for 3 days to obtain the reprocessed films, which were then characterized by tensile test. Polarized optical microscopy (LWT300LPT) and tensile test were also employed to observe the repairing efficiencies of the broken samples.

RESULTS AND DISCUSSION

Structural Characterizations of Different Bismaleimides

The structures of obtained bismaleimides were confirmed by ¹H-NMR spectroscopy and the results are shown in Fig. 2. The signals around 7.0 ppm appearing in all three kinds of bismaleimides were attributed to the protons in maleimide groups, indicating the successful conversion of amine groups into maleimide groups in all diamines. The signals of methylene under different chemical environments in EBM and HBM were marked as b, B, C, and D, while the protons ascribed to methyne, methylene, and methyl in OBM were labeled as 2, 3, 4, 5, 6, and 7, respectively. Combining the characteristic signals with their

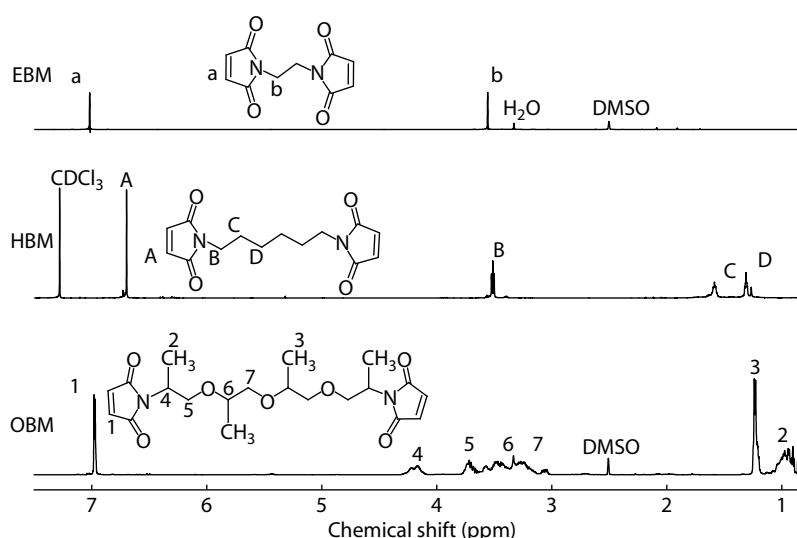


Fig. 2 ¹H-NMR spectra of different bismaleimides.

integral areas ($I_a/I_b = 1.00:1.03$; $I_A/I_B/I_C/I_D = 1.00:1.16:1.08:1.06$; $I_1/I_2/I_3/I_4/(I_5 + I_6 + I_7) = 1.00:1.62:1.74:0.45:2.89$), the chemical structures of these bismaleimides could be evidently confirmed.

Reversible D-A Reaction between POF and Bismaleimides

The presence of side furan group in POF not only improved its solubility in common solvents, but also offered abundant reactive sites for the subsequent crosslinking with bismaleimides to obtain enhanced polymer networks. Moreover, the thermal reversibility of D-A reaction proposed a potential way for our thermosets to be used as recyclable materials. The D-A reaction between POF and bismaleimides was detected by $^1\text{H-NMR}$ spectroscopy and the results are shown in Fig. 3(A). Due to the reversibility of D-A reaction, the content of maleimide groups in bismaleimides was six-fold to that of furan groups in POF, so as to prompt the forward reaction and the accumulation of D-A adduct as much as possible. As can be seen, the signals marked as j, h, and i attributed to the protons in furan ring were obviously decreased, and new signals ascribed to the D-A adduct (labeled as j', h', i', o, and p) appeared after reaction. Moreover, the newly emerging signals in green box were considered to be caused by the stereoisomerism of D-A adduct. Taking the above changes into consideration, a conclusion could be easily drawn

that our POF could readily react with all bismaleimides. The reversible processes of D-A and retro D-A reactions were evaluated by using POF/EBH mixture as a model due to the simple structure of EBH. In this set of experiment, the mixture was placed at 60 °C for 24 h to ensure the completion of D-A reaction and subsequently heated at 130 °C for half an hour to unlock the D-A linkage, and then the cycle was repeated once more. As could be seen in Fig. 3(B), compared with the de-crosslinked state (2 and 4), there was a significant decrease in the intensity of signals as h, i, and j in the cross-linked state (1 and 3), demonstrating the consumption of furan groups. Moreover, the new signals attributed to D-A adduct (signed as h', i', j', o, and p) appeared in crosslinked state and disappeared in de-crosslinked state regularly, making it clearly that the D-A and retro D-A reactions indeed proceeded and could be repeated.

At the same time, the reversible crosslinking between POF with bismaleimides was also investigated from a macroscopic view by the sol-gel transition using POF-0.4-EBM as an example, as shown in Fig. 4. The sample displayed excellent resistance to solvent and was only swollen in NMP after 24 h at room temperature, while virgin POF was completely dissolved in NMP, proving the crosslinking between POF and EBM. Under the assistance of external stimulus (130 °C for 0.5 h),

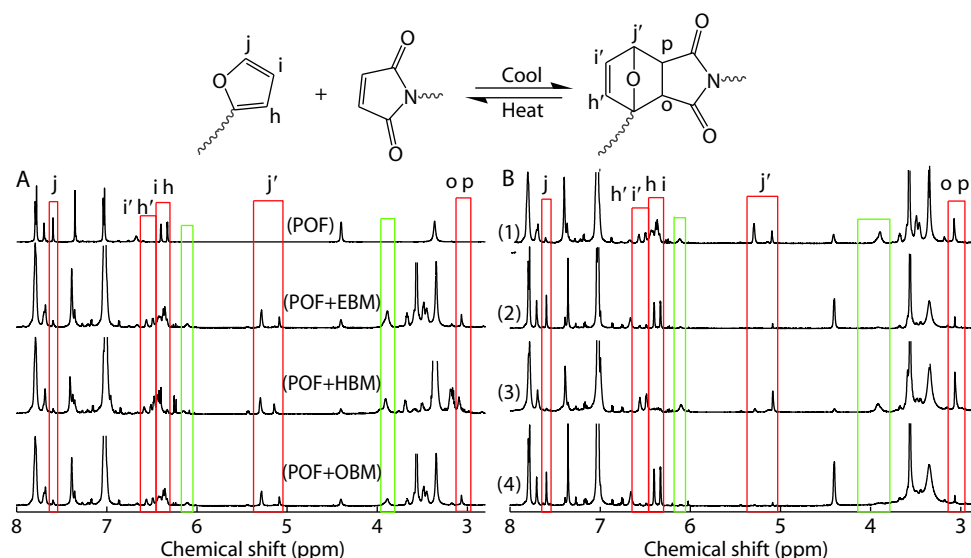


Fig. 3 $^1\text{H-NMR}$ spectra of (A) the D-A crosslinking reactions of POF with different bismaleimides and (B) the cyclic process of D-A and retro-D-A reaction performed on POF-EBH for its simple structure: (1) placed at 60 °C for 24 h; (2) exposed to 130 °C for 0.5 h; (3) re-placed at 60 °C for 24 h; (4) re-exposed to 130 °C for 0.5 h.

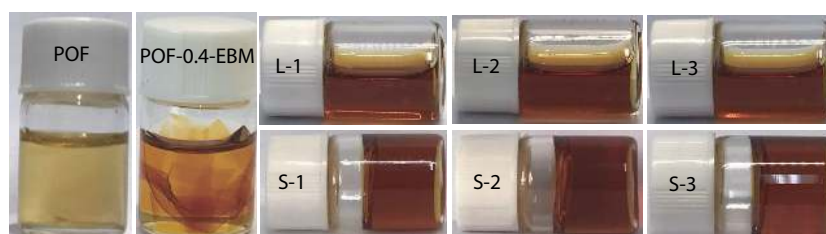


Fig. 4 Solvent resistance test of POF and the crosslinked film (POF-0.4-EBM), and the changes of phase behavior for POF-0.4-EBM in NMP: L-1 and S-1 correspond to POF-0.4-EBM film treated at 130 °C for half an hour and then cooled at 60 °C for 24 h; L-2 and S-2 stand for the second cycle while L-3 and S-3 for the third cycle.

the network in POF-0.4-EBM was de-crosslinked and homogenous solution with low-viscosity was formed (L-1). However, its viscosity increased gradually within 2 h and then it became a block of solid without fluidity after 24 h at 60 °C (S-1), which could be explained by the regeneration of the cross-linking. This cycle could be repeated for at least three times (L-2, S-2 and L-3, S-3). The sol-gel transition test between POF and other bismaleimides gave the same results. ¹H-NMR and sol-gel transition tests demonstrated the good reversibility of D-A reaction between POF and all bismaleimides.

Mechanical Properties of Crosslinked Films

The dynamic mechanical properties of POF crosslinked by different bismaleimides as a function of $I_{\text{ma/fur}}$ were investigated by DMA, as shown in Fig. 5. The storage modulus (G') at 50 °C and

glass transition temperature (T_g) of all samples are listed in Table 1. It was clearly seen that the storage modulus rose gradually with the increasing $I_{\text{ma/fur}}$ and reached a maximum value of 2286, 2280, and 1710 MPa, corresponding to 87.4%, 86.9%, and 40.2% increment as compared to that of virgin POF (1220 MPa). It indicates that the increased stiffness was largely attributed to the increase of cross-linking density. The values of storage modulus started to decrease with increasing $I_{\text{ma/fur}}$ when it surpassed the critical point, indicating a decrease of cross-linking density. Moreover, the variation of storage modulus depending on the molecular chains of cross-linkers demonstrated that chain mobility also made a big difference and that the ultimate values were determined by the synergistic effect of cross-linking density and chain mobility. The variation trend of T_g s reflected by the peaks of $\tan\delta$ was similar to that of storage modulus and

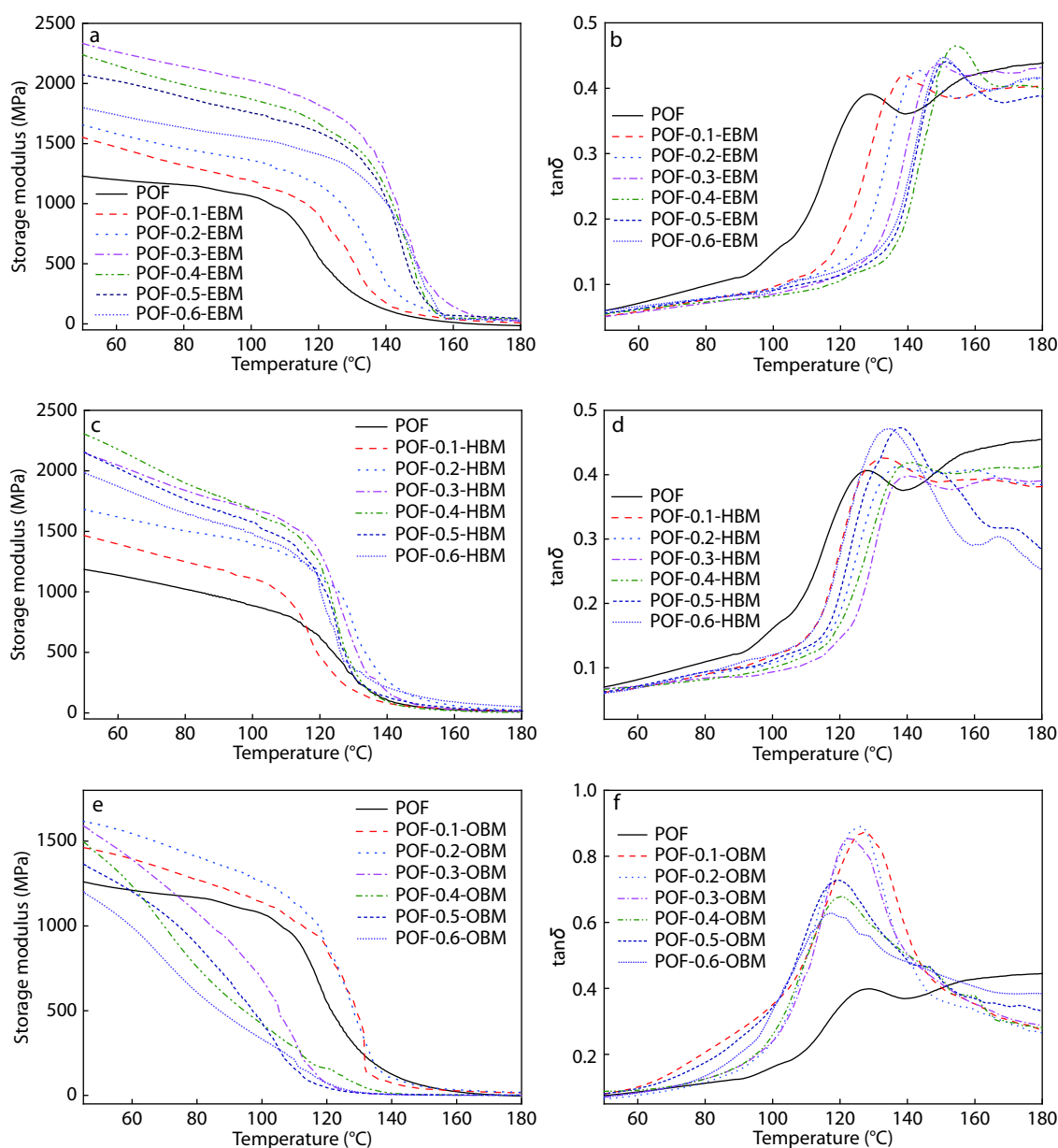


Fig. 5 (a, c, e) Storage modulus and (b, d, f) $\tan\delta$ of cross-linked films with crosslinkers of (a, b) EBM, (c, d) HBM, and (e, f) OBM as a function of $I_{\text{ma/fur}}$.

increased with the increase of $I_{\text{ma/fur}}$ to some extent and subsequently decreased from the maximum values, except for

Table 1 Effects of cross-linkers on DAM properties as a function of $I_{\text{ma/fur}}$

	0	0.10	0.20	0.30	0.40	0.50	0.60
G_E' (MPa)	1220	1548	1657	2286	2215	2060	1795
$T_{g,E}$ (°C)	128.6	137.3	143.1	148.6	154.5	151.0	149.3
G_H' (MPa)	1220	1465	1670	2130	2280	2115	1984
$T_{g,H}$ (°C)	128.6	132.8	137.6	140.2	141.6	138.1	134.3
G_O' (MPa)	1220	1325	1396	1518	1576	1710	1565
$T_{g,O}$ (°C)	128.6	127.5	125.6	123.2	120.7	118.6	116.8

Note: E, H, and O are shorts for the crosslinkers of EBM, HBM, and OBM, respectively.

POF- $I_{\text{ma/fur}}$ -OBM, whose T_g s continuously decreased along with the increase of $I_{\text{ma/fur}}$. The rising T_g s were attributed to the restriction of chain mobility resulting from the cross-linking and the linkage density decreased when $I_{\text{ma/fur}}$ reached its peak which resulted in negative effect on the increase of T_g s. However, because of the longer chain and higher flexibility of OBM, the positive effect of extensibility surpassed the restriction effect of cross-linking and led to a decrease of T_g s along with the increase of $I_{\text{ma/fur}}$ (from 128.8 °C of virgin POF to 116.8 °C of POF-0.60-OBM). In fact, the melting point of bismaleimide OBM was so low (below 50 °C) that the thick liquid decreased T_g s significantly, if they were not for the assistance of cross-linking network.

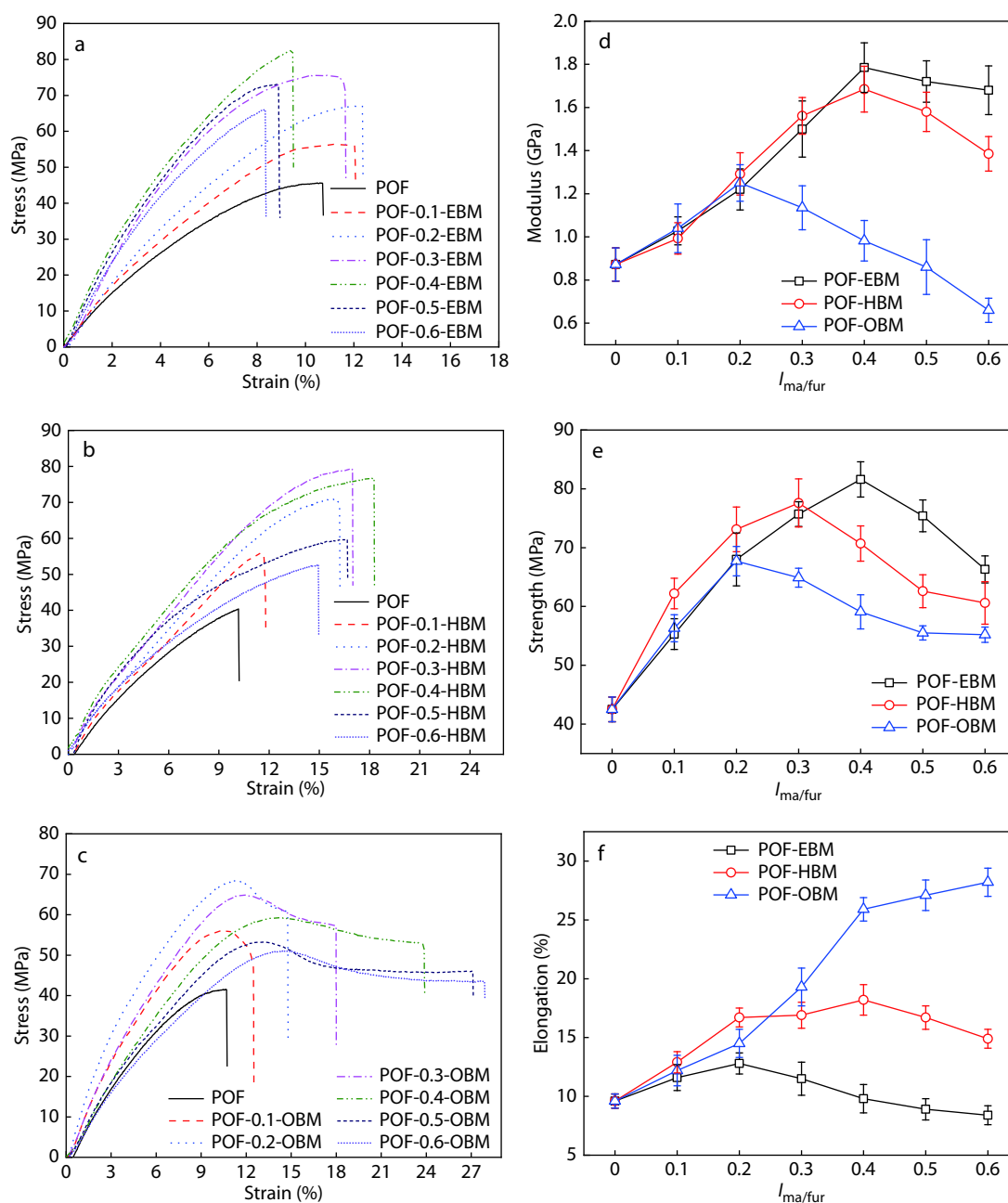


Fig. 6 (a–c) Typical stress-strain curves of POF- $I_{\text{ma/fur}}$ -Y and (d–f) the comparison of mechanical properties.

The influence of cross-linkers and their contents ($I_{\text{ma/fur}}$) on mechanical properties was investigated by tensile test, and the typical stress-strain curves and the corresponding line charts are shown in Fig. 6. The three key indexes for polymeric materials, including the Young's modulus (E), tensile strength (σ), and elongation at break (ϵ), are extracted in Table 2. As can be seen, the final mechanical properties were dependent on the kinds of bismaleimides and could be tailored through the variation of $I_{\text{ma/fur}}$. While the elongation at break of POF- $I_{\text{ma/fur}}$ -EBM increased at lower bismaleimide contents ($I_{\text{ma/fur}} < 0.20$) and then decreased as $I_{\text{ma/fur}}$ further increased, the ones of POF- $I_{\text{ma/fur}}$ -HBM and POF- $I_{\text{ma/fur}}$ -OBM still rose with the increase of $I_{\text{ma/fur}}$ to a higher value. The initial increasing stage was considered to be caused by the linking of polymeric chains to increase the molecular weight and to form loosely

cross-linked network. ϵ should be decreased for all cross-linkers along with the increase of $I_{\text{ma/fur}}$ as the restriction effect of chain mobility by dense cross-linking surpassed the positive effect on extensibility, while the results of POF- $I_{\text{ma/fur}}$ -HBM and POF- $I_{\text{ma/fur}}$ -OBM were on the contrary. It was not surprising at all because the un-reacted one side of bismaleimide would hang on the backbone to form branch that served as internal plasticizer, and the longer and softer the cross-linkers were, the looser the network formed would be. However, the variation of strengths was similar for all three types of polymers, with the tendency of first rising and then dropping. The strength increased sharply from 41.3 MPa for virgin POF to 81.6 MPa for POF-0.4-EBM, 77.6 MPa for POF-0.3-HBM, and 67.7 MPa for POF-0.2-OBM, corresponding to an increment of 97.5%, 87.9%, and 63.9%, respectively. While $I_{\text{ma/fur}}$

Table 2 Mechanical properties of polymer films as a function of $I_{\text{ma/fur}}$

	0	0.10	0.20	0.30	0.40	0.50	0.60
E_{f} (MPa)	872 ± 77	1028 ± 65	1220 ± 95	1500 ± 130	1785 ± 115	1720 ± 96	1680 ± 113
σ_{f} (MPa)	42.5 ± 2.1	55.3 ± 2.6	68.0 ± 4.5	75.7 ± 2.1	81.6 ± 3.0	75.4 ± 2.7	66.3 ± 2.3
ϵ_{f} (%)	9.6 ± 0.6	11.6 ± 1.1	12.8 ± 0.9	11.5 ± 1.4	9.8 ± 1.2	8.9 ± 0.9	8.4 ± 0.8
E_{H} (MPa)	872 ± 77	993 ± 73	1292 ± 98	1561 ± 85	1685 ± 106	1580 ± 91	1385 ± 80
σ_{H} (MPa)	42.5 ± 2.1	62.2 ± 2.6	73.1 ± 3.8	77.6 ± 4.1	70.7 ± 3.0	62.6 ± 2.8	60.6 ± 3.6
ϵ_{H} (%)	9.6 ± 0.6	12.9 ± 0.9	16.7 ± 0.8	16.9 ± 1.1	18.2 ± 1.3	16.7 ± 1.0	14.9 ± 0.8
E_{O} (MPa)	872 ± 77	1040 ± 113	1250 ± 85	1135 ± 102	982 ± 94	860 ± 127	660 ± 56
σ_{O} (MPa)	42.5 ± 2.1	56.3 ± 2.3	67.7 ± 2.5	64.9 ± 1.6	59.1 ± 2.9	55.5 ± 1.2	55.2 ± 1.3
ϵ_{O} (%)	9.6 ± 0.6	12.2 ± 1.3	14.5 ± 1.2	19.3 ± 1.6	25.9 ± 1.0	27.1 ± 1.3	28.2 ± 1.2

Note: E, H, and O are shorts for the corsslinkers of EBM, HBM, and OBM, respectively.

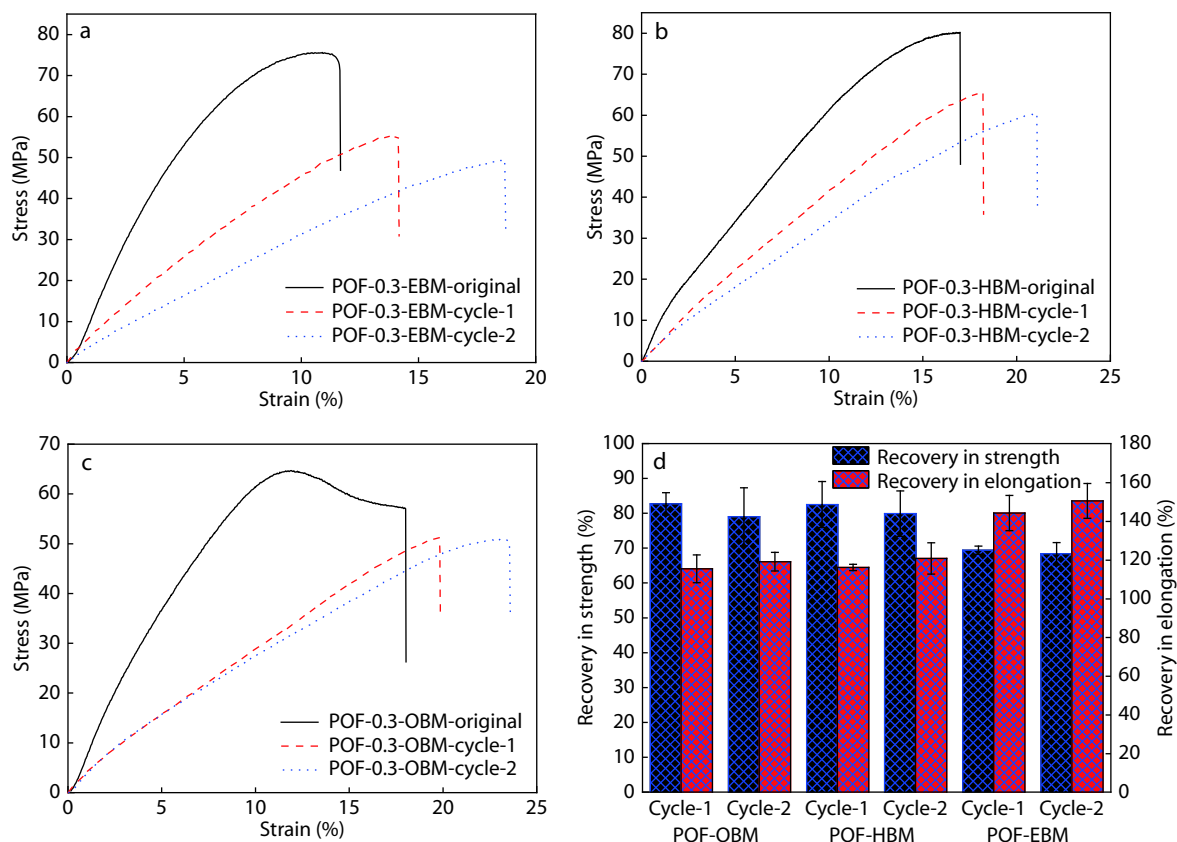


Fig. 7 (a–c) Typical stress-strain curves of recycled films cross-linked by different bismaleimides; (d) Recovery efficiencies of strength and elongation.

for the maximal strengths differed from each other, σ in the ranging of 0.2 to 0.4 was almost the same. As a consequence, the tensile results demonstrated that our furanic polyamide POF could be effectively cross-linked by bismaleimides and the overall mechanical properties varied easily with the change of $I_{\text{ma/fur}}$.

Recyclability of Crosslinked Films

Due to the thermally reversible character of D-A reaction, our crosslinked films could also be recycled after failure. To probe the effects of bismaleimides on the recyclability of crosslinked films, we carried out tensile test on the reprocessed samples crosslinked by different bismaleimides with $I_{\text{ma/fur}} = 0.3$, as shown in Fig. 7. It was found that after the first cycle of reprocessing, σ of POF-0.3-OBM and POF-0.3-HBM could return to about 82.5% with ϵ increased to around 120% due to the lower

crosslinking density in reprocessed samples. However, σ of POF-0.3-EBM decreased to 70% and ϵ increased to around 150%. The relatively low recovery in strength and increase in elongation at break of POF-0.3-EBM were thought to be originated from the shorter length of EBM as compared to HBM and OBM, which made the linking of two separated polymer chains more difficult and thus resulted in further decrease of crosslinking density. The recovery ratio of σ and ϵ of EBM, HBM, and OBM crosslinked POF samples after the second cycle of reprocessing were similar to those of the first reprocessed ones, suggesting the good recyclability.

Healability of Crosslinked Films

The healability is of crucial importance in polymer materials for the sake of safety, durability, and extended lifetime. However, most attention for the repairable materials was paid to soft

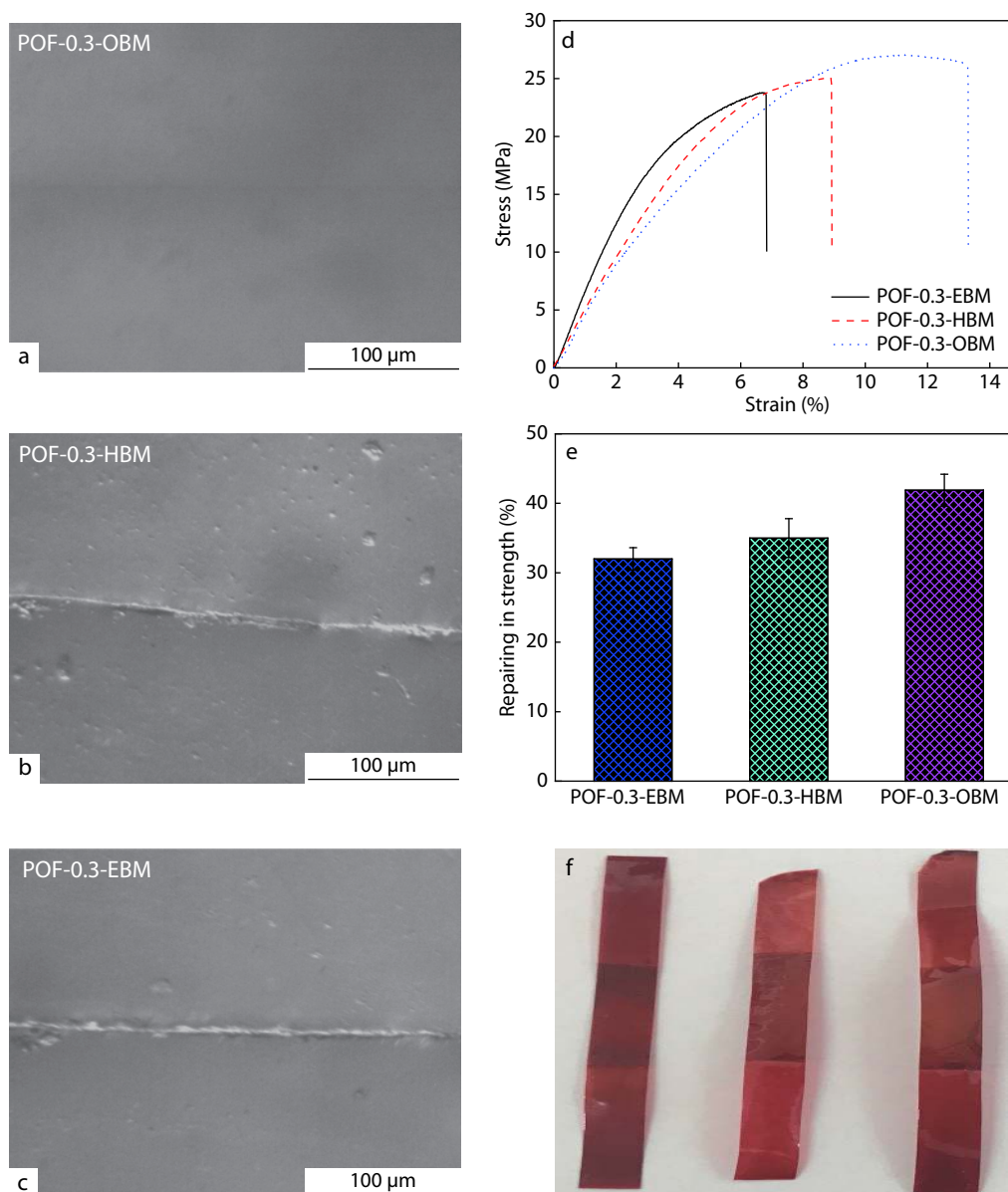


Fig. 8 The healing properties of cross-linked materials with different bismaleimides: (a–c) the polarized light micrographs of rejoined blocks after repairing; (d–f) the healing of overlapped cross-linking films.

elastomers and few literatures were focused on the healing of high-performance polymers because of their tough molecular structure. To investigate the healing performance of our cross-linked POF, three kinds of crosslinked blocks ($I_{\text{ma/fur}} = 0.3$) were cut into two pieces and the two counterparts were subsequently rejoined by certain pressure. The blocks were then heated at 130 °C for 1 h to de-crosslink the D-A linkage and stored at 60 °C for 3 days to allow the re-crosslinking. However, it was found that there was nearly no healing effect in this set of experiments, which was attributed to the limited chain mobility of POF. In addition, the large fraction of POF chains could also prevent the free motion of bismaleimide molecules despite their flexible feature. Therefore, we employed solvent (NMP) to assist the healing of crosslinked POF. In the healing process, a drop of solvent was used to wet the fracture surfaces, and then the fracture surfaces were pressed together and heated at 60 °C for 3 days. As can be seen from Fig. 8, all the broken blocks were clearly healed after these treatments, indicating that the healing process was activated by the swelling and motion of polymer chains around the cracks to offer more opportunity for the rejoining of furan and maleimide groups. In addition, POF-0.3-OBM exhibited the best healing performance because only slight trace was left on surface after healing process, while POF-0.3-HBM and POF-0.3-EBM exhibited inferior healing efficiency with more obvious scar left on the surface. Moreover, the repairing efficiencies were also investigated by tensile test. The overlapped films were heated at 130 °C for 1 h and then healed for 3 days at 60 °C under the assistance of solvent and pressed to avoid wrinkle in the process. The resultant films and the typical stress-strain curves are shown in Figs. 8(f) and 8(d) with efficiencies in strength Fig. 8(e) of 32%, 35%, and 42%, respectively.

CONCLUSIONS

Three bismaleimides were synthesized and applied as reversible cross-linkers to build thermosets with comb-shaped aromatic polyamide by Diels-Alder reaction. ¹H-NMR spectroscopy confirmed the structures and their reaction with furanic polyamide. The reversibility of our cross-linked network was demonstrated by both ¹H-NMR technique from molecular level and gelation testing from macroscopic view. Although the variation of storage modulus, T_g , tensile strength, and elongation at break of all three kinds of cross-linked POF showed similar tendency, the impacts of cross-linking on the thermal and mechanical properties of thermosets were dependent on the chemical structures of bismaleimides as demonstrated by DMA and tensile tests. Our cross-linked networks exhibited good recyclability by triggering the retro D-A reaction in NMP at high temperature to re-form integrated films for at least three times with recovery efficiency around 80%. Moreover, the thermosets also showed solvent-assisted healability with healing efficiency varied from 32% to 42% depending on the chemical structure of bismaleimides. This work is expected to provide new opportunity for recyclable and repairable high-performance thermosets.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (No. 51473031), the Natural

Science Foundation of Shanghai (No. 17ZR1401100), and the doctoral innovation foundation (No. CUSF-DH-D-2017037).

REFERENCES

- Lu, Q.; He, Y. B.; Yu, Q.; Li, B.; Kaneti, Y. V.; Yao, Y.; Kang, F.; Yang, Q. H. Dendrite-free, high-rate, long-life lithium metal batteries with a 3D cross-linked network polymer electrolyte. *Adv. Mater.* **2017**, 29, 1604460.
- Chang, G.; Wang, C.; Du, M.; Liu, S.; Yang, L. Metal-coordination crosslinked *N*-polyindoles as recyclable high-performance thermosets and nondestructive detection for their tensile strength and glass transition temperature. *Chem. Commun.* **2018**, 54, 2906–2909.
- Zhao, S.; Abu-Omar, M. M. Recyclable and malleable epoxy thermoset bearing aromatic imine bonds. *Macromolecules* **2018**, 51, 9816–9824.
- Lin, C. H.; Chang, S. L.; Shen, T. Y.; Shih, Y. S.; Lin, H. T.; Wang, C. F. Flexible polybenzoxazine thermosets with high glass transition temperatures and low surface free energies. *Polym. Chem.* **2012**, 3, 935–945.
- Montarnal, D.; Capelot, M.; Tournilhac, C.; Leibler, L. Silica-like malleable materials from permanent organic networks. *Science* **2011**, 334, 965–968.
- Colquhoun, H. M. Self-repairing polymers: materials that heal themselves. *Nat. Chem.* **2012**, 4, 435–436.
- Zhang, Y.; Ying, H.; Hart, K. R.; Wu, Y.; Hsu, A. J.; Coppola, A. M.; Kim, T. A.; Yang, K.; Sottos, N. R.; White, S. R.; Cheng, J. Malleable and recyclable poly(urea-urethane) thermosets bearing hindered urea bonds. *Adv. Mater.* **2016**, 28, 7646–7651.
- Ogden, W. A.; Guan, Z. Recyclable, strong, and highly malleable thermosets based on boroxine networks. *J. Am. Chem. Soc.* **2018**, 140, 6217–6220.
- Neal, J. A.; Mozdehi, D.; Guan, Z. Enhancing mechanical performance of a covalent self-healing material by sacrificial noncovalent bonds. *J. Am. Chem. Soc.* **2015**, 137, 4846–4850.
- Ma, S.; Webster, D. C. Degradable thermosets based on labile bonds or linkages: a review. *Prog. Polym. Sci.* **2018**, 76, 65–110.
- García, J. M.; Jones, J. O.; Virwani, K.; McCloskey, B. D.; Boday, D. J.; Huurne, G. M.; Horn, H. W.; Coady, D. J.; Bintaleb, A. M.; Alabdulrahman, A. M. S.; Alsewaleem, F.; Hedrick, J. L. Recyclable, strong thermosets and organogels via paraformaldehyde condensation with diamines. *Science* **2014**, 344, 732–735.
- Arsilan, M.; Kiskan, B.; Yagci, Y. Benzoxazine-based thermosets with autonomous self-healing ability. *Macromolecules* **2015**, 48, 1329–1334.
- Zhang, B.; Kowsari, K.; Serjouei, A.; Dunn, M. L.; Ge, Q. Reprocessable thermosets for sustainable three-dimensional printing. *Nat. Commun.* **2018**, 9, 1831.
- Mueller, E.; Alsop, R. J.; Scotti, A.; Bleuel, M.; Rheinstädter, M. C.; Richter, W.; Hoare, T. Dynamically cross-linked self-assembled thermoresponsive microgels with homogeneous internal structures. *Langmuir* **2018**, 34, 1601–1612.
- Schmolke, W.; Perner, N.; Seiffert, S. Dynamically cross-linked polydimethylsiloxane networks with ambient-temperature self-healing. *Macromolecules* **2015**, 48, 8781–8788.
- Zhang, C.; Liu, Z.; Shi, Z.; Yin, J.; Tian, M. Versatile approach to building dynamic covalent polymer networks by stimulating the dormant groups. *ACS Macro Lett.* **2018**, 7, 1371–1375.
- Wang, Z.; Pan, Q. An omni-healable supercapacitor integrated in dynamically cross-linked polymer networks. *Adv. Funct. Mater.* **2017**, 27, 1700690.
- Roy, N.; Bruchmann, B.; Lehn, J. M. Dynamers: dynamic polymers as self-healing materials. *Chem. Soc. Rev.* **2015**, 44, 3786–3807.
- Zou, W.; Dong, J.; Luo, Y.; Zhao, Q.; Xie, T. Dynamic covalent

- polymer networks: from old chemistry to modern day innovations. *Adv. Mater.* **2017**, 29, 1606100.
- 20 Chen, X.; Dam, M. A.; Ono, K.; Mal, J.; Shen, H.; Nutt, S. R.; Sheran, K.; Wudl, F. A thermally re-mendable cross-linked polymeric material. *Science* **2002**, 295, 1698–1702.
 - 21 Heo, Y.; Malakooti, M. H.; Sodano, H. A. Self-healing polymers and composites for extreme environments. *J. Mater. Chem. A* **2016**, 4, 17403–17411.
 - 22 Fu, G.; Li, Y.; Liang, G.; Gu, A. Heat-resistant polyurethane films with great electrostatic dissipation capacity and very high thermally reversible self-healing efficiency based on multi-furan and liquid multi-maleimide polymers. *J. Mater. Chem. A* **2016**, 4, 4232–4241.
 - 23 Yoon, J. A.; Kamada, J.; Koynov, K.; Mohin, J.; Nicolay, R.; Zhang, Y.; Balazs, A. C.; Kowalewski, T.; Matyjaszewski, K. Self-healing polymer films based on thiol-disulfide exchange reactions and self-healing kinetics measured using atomic force microscopy. *Macromolecules* **2012**, 45, 142–149.
 - 24 Du, X.; Li, J.; Welle, A.; Li, L.; Feng, W.; Levkin, P. A. Reversible and rewritable surface functionalization and patterning via photodynamic disulfide exchange. *Adv. Mater.* **2015**, 27, 4997–5001.
 - 25 Black, S. P.; Sanders, J. K.; Stefankiewicz, A. R. Disulfide exchange: Exposing supramolecular reactivity through dynamic covalent chemistry. *Chem. Soc. Rev.* **2014**, 43, 1861–1872.
 - 26 Zhang, H.; Cai, C.; Liu, W.; Li, D.; Zhang, J.; Zhao, N.; Xu, J. Recyclable polydimethylsiloxane network crosslinked by dynamic transesterification reaction. *Sci. Rep.* **2017**, 7, 11833.
 - 27 Gandini, A. The furan/maleimide Diels-Alder reaction: a versatile click-unclick tool in macromolecular synthesis. *Prog. Polym. Sci.* **2013**, 38, 1–29.
 - 28 Dewar, M. J. S.; Pierini, A. B. Mechanism of the Diels-Alder reaction. Studies of the addition of maleic anhydride to furan and methylfurans. *J. Am. Chem. Soc.* **1984**, 106, 203–208.
 - 29 Yu, S.; Zhang, R.; Wu, Q.; Chen, T.; Sun, P. Bio-inspired high-performance and recyclable cross-linked polymers. *Adv. Mater.* **2013**, 25, 4912–4917.
 - 30 Yang, Y.; Urban, M. W. Self-repairable polyurethane networks by atmospheric carbon dioxide and water. *Angew. Chem. Int. Ed.* **2014**, 53, 12142–12147.
 - 31 Li, J.; Zhang, G.; Deng, L.; Zhao, S.; Gao, Y.; Jiang, K.; Sun, R.; Wong, C. *In situ* polymerization of mechanically reinforced, thermally healable graphene oxide/polyurethane composites based on Diels-Alder chemistry. *J. Mater. Chem. A* **2014**, 2, 20642–20649.
 - 32 Zeng, C.; Seino, H.; Ren, J.; Hatanaka, K.; Yoshie, N. Bio-based furan polymers with self-healing ability. *Macromolecules* **2013**, 46, 1794–1802.
 - 33 Zeng, C.; Seino, H.; Ren, J.; Hatanaka, K.; Yoshie, N. Self-healing bio-based furan polymers cross-linked with various bis-maleimides. *Polymer* **2013**, 54, 5351–5357.
 - 34 Trovatti, E.; Lacerda, T. M.; Carvalho, A. J.; Gandini, A. Recycling tires? Reversible crosslinking of poly(butadiene). *Adv. Mater.* **2015**, 27, 2242–2245.
 - 35 Polgar, L. M.; van Duin, M.; Broekhuis, A. A.; Picchioni, F. Use of Diels-Alder chemistry for thermoreversible cross-linking of rubbers: the next step toward recycling of rubber products? *Macromolecules* **2015**, 48, 7095–7105.
 - 36 Zhao, J.; Xu, R.; Luo, G.; Wu, J.; Xia, H. A self-healing, re-moldable and biocompatible crosslinked polysiloxane elastomer. *J. Mater. Chem. B* **2016**, 4, 982–989.
 - 37 Bera, R.; Mondal, S.; Das, N. Nanoporous triptycene based network polyamides (TBPs) for selective CO₂ uptake. *Polymer* **2017**, 111, 275–284.
 - 38 Duan, J.; Pan, Y.; Pacheco, F.; Litwiller, E.; Lai, Z.; Pinnau, I. High-performance polyamide thin-film-nanocomposite reverse osmosis membranes containing hydrophobic zeolitic imidazolate framework-8. *J. Memb. Sci.* **2015**, 476, 303–310.
 - 39 García, J. M.; García, F. C.; Serna, F.; de la Peña, J. High-performance aromatic polyamides. *Prog. Polym. Sci.* **2010**, 35, 623–686.
 - 40 Luo, K.; Li, J.; Duan, G.; Wang, Y.; Yu, J.; Zhu, J.; Hu, Z. Comb-shaped aromatic polyamide cross-linked by Diels-Alder chemistry: towards recyclable and high-performance thermosets. *Polymer* **2018**, 142, 33–42.
 - 41 Li, J.; Zhang, G.; Deng, L.; Jiang, K.; Zhao, S.; Gao, Y.; Sun, R.; Wong, C. Thermally reversible and self-healing novolac epoxy resins based on Diels-Alder chemistry. *J. Appl. Polym. Sci.* **2015**, 132, 42167.
 - 42 Wang, A.; Niu, H.; He, Z.; Li, Y. Thermoreversible cross-linking of ethylene/propylene copolymer rubbers. *Polym. Chem.* **2017**, 8, 4494–4502.
 - 43 Toncelli, C.; De Reus, D. C.; Picchioni, F.; Broekhuis, A. A. Properties of reversible Diels-Alder furan/maleimide polymer networks as function of crosslink density. *Macromol. Chem. Phys.* **2012**, 213, 157–165.