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Dynamic crosslinked poly(styrene-*block*-butadiene-*block*-styrene) *via* Diels–Alder chemistry: an ideal method to improve solvent resistance and mechanical properties without losing its thermal plastic behavior†

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Poly(styrene-*block*-butadiene-*block*-styrene) (SBS) is a typical example of thermal plastic elastomers (TPE). People usually encounter a well-known paradox for SBS, where improving its poor solvent resistance and low mechanical properties usually means it suffers from losing its thermal plastic remolding ability, one of most important characters for TPE. In this paper, we propose a novel solution for this problem. SBS was first modified with furan *via* a thiol–ene reaction and then reacted with bismaleimide to form thermally dynamic reversible crosslinking linkages for SBS *via* a Diels–Alder reaction. As a result, the dynamic crosslinked SBS could only swell in the toluene with improved solvent resistance at ambient temperature. The mechanical properties showed great improvement. As an example, the maximum tensile strength was obtained at 14.96 MPa, increased by almost 8 times in comparison with the pure SBS and the tensile strain was still kept above 800%. More importantly, the crosslinked SBS could still be thermal plastic remolded due to the de-crosslinking reaction *via* a retro-DA reaction at higher temperature and the mechanical properties still remained almost the same even after 3 generations of remolding. The merits of this modified SBS originate from its dynamic crosslinking network to improve its mechanical properties and solvent resistance without sacrificing its thermal plastic remolding ability.

Introduction

Poly(styrene-*block*-butadiene-*block*-styrene) (SBS) is a commonly-used thermoplastic elastomer (TPE) which offers interesting morphologies and properties due to its soft and hard segments.[1] Because of the physical cross-links induced by the vitrification of PS domains (hard segments), the material can be thermoplastic molded at high temperature while it can used as a rubber at room temperature. Therefore, TPE can be remolded to produce new products in an eco-friendly way which is quite different from conventional vulcanized rubbers without the remolding ability. Nowadays, these kinds of materials are widely used in various areas, such as adhesives, impact modifiers and toughening agents in engineering plastics due to this favorable processing behavior.[2–5] However, several drawbacks associated with physical cross-links, especially poor solvent resistance and low mechanical properties, limit its application area. To address these two shortcomings for the thermoplastic elastomer, there are two common-used methods. One is that SBS is usually incorporated with the thermosetting resins such as epoxy[6–9] and poly-benzoxazine resin.[10] The other is to form chemical crosslinking structure.[11,12] For example, C. Decker made the crosslinked elastomer *via* photo-initiated polymerization of the vinyl on the chains of SBS.[11] Our group[10,13] has done some work to improve the solvent resistance and mechanical properties of the thermoplastic elastomer by crosslinking reaction based on thiol–ene reaction. As a result, the solvent resistance and mechanical properties are improved greatly. However, thermal plastic remolding ability, the most important property for SBS, was lost due to the formation of permanent crosslinked structure where the chains of SBS could not be liberated from the network to remold at high temperature. Therefore, we had to face a challenging problem that the improvement on the solvent resistance and mechanical properties would sacrifice its remolding ability. By now, there has been still no satisfactory reported method to keep the balance between improved solvent resistance and mechanical properties and thermal plastic remolding ability. Inspired by recent work on the malleable crosslinked epoxy[14,15] and polyurethane resins,[16,17] we want to use dynamic crosslinked network based on Diels–Alder

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(DA) reaction toward SBS to improve the solvent resistance and mechanical properties without losing its thermal plastic remolding ability.

DA and its retro DA (rDA) reaction is one of typical examples to build reversible dynamic bonds,[14,15,17–25] where the linkage based on DA reaction can be formed between a conjugated diene and a dienophile at ambient temperature and the linkage can be broken *via* a rDA reaction at high temperatures above 120 °C.[26] Moreover, this reversible process can be repeated under proper thermal treatment without any noticeable side reactions,[27] which is one of important reasons for its application on recycling and self-healing of the materials.[25,28–38]

Here, we use DA reaction to build the crosslinked network for the SBS and rDA reaction to liberate the polymer chains from the network at high temperature.

In order to achieve this goal, the furan group (a conjugated diene) was firstly attached to the chains of SBS *via* UV-induced thiol–ene click reaction[39] between the double bonds from SBS and furfuryl mercaptan. The furan groups attached SBS could further react with bismaleimide (a dienophile) to form the thermally reversible dynamic network based on DA reaction. In this way, the crosslinked SBS could show great improvement in the solvent resistance and mechanical properties. In the meantime, the remolding ability could still be maintained due to its dynamic crosslinking network which could be broken to unlock the polymer chain at higher temperature.

Experimental section

Materials

Toluene, chloroform, were purchased from Sinopharm Chemical Reagent Co., Ltd., 4,4′-bismaleimido-diphenylmethane (>96%) was purchased from TCI Chemical Co., Ltd. Furfuryl mercaptan was purchased from J&K Chemical Co., Ltd. SBS ($M_w \sim 153\,000$–$185\,000$) was purchased from Sigma-Aldrich. All the reagents were used as received.

The chemical modification of SBS with furfuryl mercaptan (SBS–*x*Fu) *via* thiol–ene reaction

SBS (70% PB block contained, $M_w \sim 153\,000$–$185\,000$, linear polymer), furfuryl mercaptan (FM) and the photoinitiator I907 were dissolved in toluene. The content of FM was changed according to the double bond content of PB block in SBS. Take the sample SBS–2Fu for example; the addition of furfuryl mercaptan was 2% of the molar of the double bond on PB block of SBS and the samples were named according to the content of the furan groups for addition. Its recipe was as follows: 2 g SBS, 0.0595 g furfuryl mercaptan and trace amount of photoinitiator I907 were dissolved in 20 ml toluene. Then the solution was irradiated with UV light (365 nm) for 12 h. Modified SBS with different molar ratio of furan to double bonds were obtained including 2%, 5%, 10%, 15% and 20%. The recipes and nomination for different samples were showed in Table S1.† The results from elemental analysis (Table S2†) verified that the final grafting content of the furan groups was almost the same as the addition content of furfuryl mercaptan due to the high efficiency of thiol–ene click reaction (Scheme 1).

The preparation of the films for modified SBS

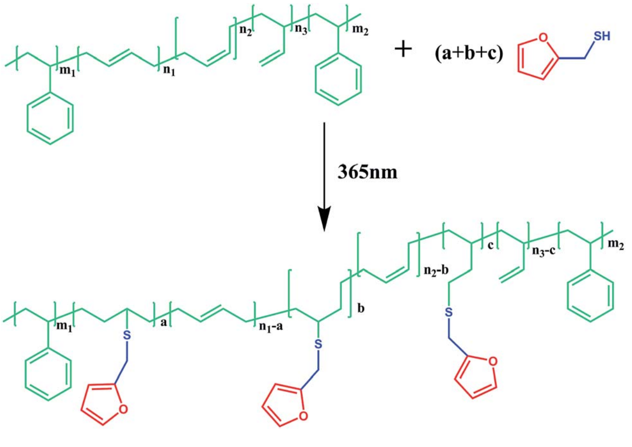
Bismaleimide was added into the SBS–*x*Fu solution. After homogeneous mixing, the solution was cast onto a glass plate and dried in an air oven at 80 °C for 12 h with different molar ratio of bismaleimide and furan groups attached on the chain of SBS. Two important properties of crosslinked SBS, including the crosslinking degree and mechanical properties could be tuned by adjusting two parameters: the addition ratio of furan group to the double bonds on PB block (RF) and the ratio of furan to maleimide (RFM). Two independent crosslinked systems were designed. One was SBS–*x*Fu–M system in which RF (*x*) was changed and RFM was fixed at 1 : 1; the other was SBS–15Fu–*y*M system where RFM (*y*) was varied and RF was fixed at 15%. Meanwhile, films of modified SBS without crosslinking were made in the same way and named as SBS–*x*Fu series. And the recipes for different samples of the crosslinked series were showed in Tables S2 and S3.†

Measurements

^{1}H NMR spectra were carried out on a Varian Mercury Plus 400 MHz instrument with $CDCl_3$ as the solvent and tetramethylsilane (TMS) as an internal standard at room temperature.

Fourier transform infrared (FT-IR) spectra measurements were measured on a Spectrum 100 Fourier transformation infrared absorption spectrometer (PerkinElmer, Inc., Waltham, MA) from 3200 to 800 cm^{-1} at a resolution of 4 cm^{-1}. In all cases, 64 scans at a resolution of 2 cm^{-1} were used to record the spectra. The samples were prepared by dropping the solution onto silicon wafers which permit the infrared light to go through.

The morphology of the samples was recorded with atomic force microscopy (TM-AFM) in tapping-mode. TM-AFM measurements were carried out in a SII Nanonavi E-sweep under ambient conditions. The measurements were performed with commercial Si cantilevers at a nominal spring



Scheme 1 The chemical modification of SBS with furfuryl mercaptan.

constant and resonance frequency at about 40 N m^{-1} and 300 kHz, respectively (AFM Probes, NSC11).

The tensile property of films was measured on an Instron 4465 instrument at room temperature with a humidity of about 30% and at a crosshead speed of 100 mm min^{-1}. Dumbbell specimens were cut from the cast films with width of 4 mm and length of 30 mm. The thickness of films was about 0.2–0.4 mm. Data analyses were based on five specimens performed at the same conditions.

Elemental analysis was carried on Vario-EL Cube (Elementar).

The gel fraction and swelling ratio of samples were determined by soaking the sample in toluene for 48 h at room temperature. After that, the insoluble polymer was dried at 80 °C to the constant weight (W_3). The original weight of the sample was expressed as W_1. The weight of the swollen sample immediately taken out of toluene was signed as W_2. Therefore, the gel fraction (GF) and the swelling ratio (SR) were calculated according to the follow formulas.

$$\mathrm{GF} = W_3/W_1 \times 100\%;\ \mathrm{SR} = W_2/W_1$$

Result and discussion

The analysis of structure by NMR and FT-IR for furan modified SBS

The structure of the furan modified SBS (SBS–Fu) was firstly characterized by ^{1}H NMR and FT-IR. SBS–Fu was prepared by the grafting the furan groups to the chains of SBS *via* thiol–ene click reaction between the thiol groups on furfuryl mercaptan and double bonds on the polybutadiene block of SBS. Fig. 1A showed the ^{1}H NMR result of SBS–Fu and the pure SBS. Compared with the pure SBS, the peaks at $\delta = 6.34$, 6.28 and 7.35 ppm were assigned to the protons a, b, c of the furan ring respectively. The peak at $\delta = 3.68$ was the signal of the proton connecting to the carbon atom between furan ring and the sulphur atom. The appearance of these signals verified that the furan groups have successfully grafted to SBS. The FTIR spectra of the modified SBS and the pure SBS were shown in Fig. 1B. Compared with SBS, SBS–Fu exhibited characteristic absorption peaks of furan rings at 1240 and 1148 cm^{-1}. The results of the spectral analyses both proved the successful grafting of furan groups to the chains of SBS.

The fabrication of modified SBS films

To study the effect of grafting ratio and crosslinking reaction on the properties and inner structure of the elastomer, the samples were classified into three systems. SBS–*x*Fu represented the film for SBS after modified with furan and *x* stood for the amount of grafted furan (RF). SBS–*x*Fu–M represented the film where RF was changed and the ratio of furan groups to bismaleimide (RFM) was set at 1 : 1. SBS–15Fu–*y*M represented the film where RFM (*y*%) was changed from 20 to 100% and RF was set as 15%. All the films prepared by a solution-casting method. After homogeneous mixing, the solution was cast onto glass plates and dried in an air oven at 80 °C for 12 h. For the samples with the presence of bismaleimide, DA reaction happened between bismaleimide and furan groups grafting on the polybutadiene block of SBS. The mechanism for the preparation of film was illustrated in Scheme 2.

Solubility behavior verified by the gel fraction and swelling ratio

Fig. 2 showed some typical plots of the insoluble fraction for the SBS–*x*Fu–M and SBS–15Fu–*y*M blends. It was found that the dynamic crosslinked SBS could only swell in toluene which was good solvent for the pure SBS. This difference in solubility behavior verified that the SBS had actually been crosslinked by the incorporation of the bismaleimide *via* DA reaction between bismaleimide and furan groups attached on the chains of SBS with improved solvent resistance. For SBS–*x*Fu–M series, at low furan content, the SBS polymer could only be swollen with low gel fraction and the gel fraction was increased by increasing furan content. For example, the gel fraction was increased from 65.3 to 81.9% and the swelling ratio was decreased from 21.9 to 13.4 when the RF increased from 2 to 20%. For SBS–15Fu–*y*M, as RFM increased from 20 to 100% with RF at 15%, the gel fraction increased from 55.3 to 78.5%. In the meantime, the swelling ratio decreased from 22.5 to 13.6. Therefore, increasing RF and RFM could increase the crosslinking density. As a result,

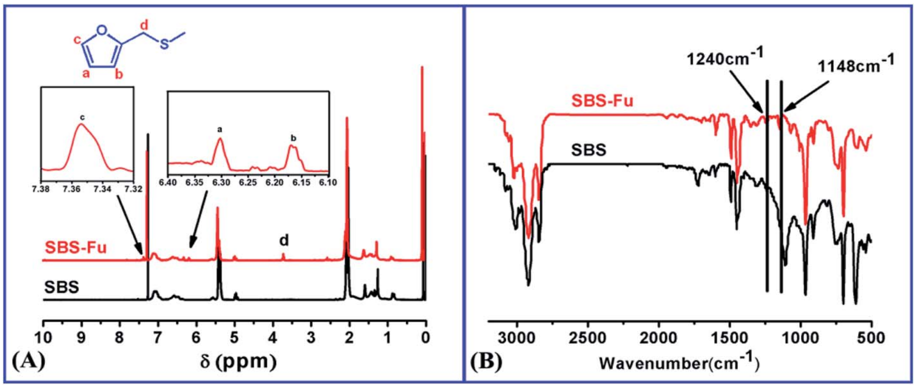
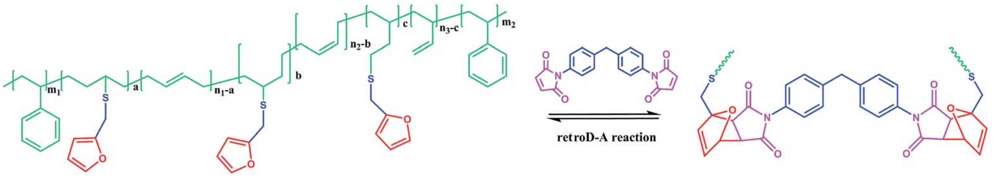


Fig. 1 (A) ^{1}H NMR spectrum. (B) FTIR of SBS and SBS–Fu.



Scheme 2 The crosslinking and decrosslinking reaction scheme of the films *via* DA and rDA reaction.

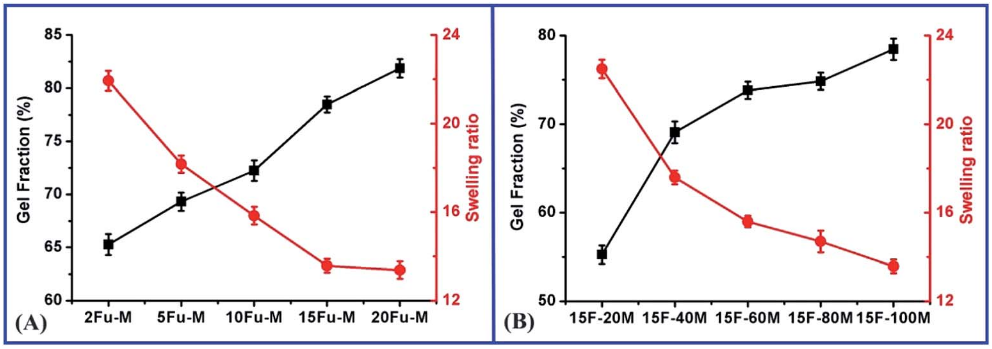


Fig. 2 Gel fraction and the swelling ratio of the SBS–*x*Fu–M (A) and SBS–15Fu–*y*M (B) series.

there was up for gel fraction and down for swelling ratio and the solvent resistance was greatly improved.

Morphologies for SBS in two steps of modification

SBS was known to self-assemble into a variety of morphologies by micro-phase separation between the soft and hard domains and these morphologies could affect the final mechanical properties. Based on their different hardness, AFM could easily detect the PB's and PS's phase. Commonly, cantilever oscillation acting on surface with different hardness lost different energy and generates different phase contrast, where the bright region represented the hard phase (PS phase) and the dark region stood for the soft phase (PB phase) in the phase image. AFM measurements were applied here to investigate its variation on morphologies before and after two steps of modification (furan grafting and crosslinking reactions). Fig. 3 illustrated the change of morphology for the SBS with furan attached. As the grafted sites were only located in the PB phase in the first step of reaction with furan, the ability of movement for PB chains was reduced due to the increased chains' interaction by the incorporation of polar furan group, which finally resulted in great transformation in the morphology. For example, as RF was about 2%, the hard phase (PS) had changed from disk like particle to dotted sphere particles dispersed in PB phase. With further increasing RF to about 5%, the dotted sphere particle gradually disappeared with emergence of lamellar structure. As RF was above 10%, bi-continuous phases morphology was obtained which indicated that the presence of attached furan in PB phase had affected the interaction of PS chain so that the physical cross-links introduced by the vitrification of PS domains were partly destroyed and the PS domains had transferred from dispersed to continuous phase.

After the second stage of crosslinking reaction, two effects on phase separation were considered. In the first effect, more crosslinking degree led to more content of hard phase since the crosslinking structure attributed to the hard phase. In the second effect, interaction between the soft and hard domains was further strengthened due to the crosslinking reaction happened in the PB domains. These two effects were combined together to finally affect its interaction between soft and hard phase, as reflected in the final morphologies. For example, SBS–2Fu–M (Fig. 3) showed the lamellar structure with bright and dark phases interwinding together. As RF was increased to 5% (SBS–5Fu–M), homogeneous structure was observed, where soft and hard phase were difficult to detect clearly. With further increasing RF up to 10% (SBS–10Fu–M), microphase separated structure appeared again and the PB domains had changed from the continuous phase to dispersed phase. Similar phenomena were also observed for the blends of SBS–15Fu–*y*M as shown on Fig. 3.

Mechanical properties for SBS in two steps of modification

On the basis of the investigation of morphologies for the modified SBS materials, it was found that morphologies underwent great transformation as the result of the improved interaction between soft (PB) and hard phase (PS block of SBS and bismaleimide) *via* two steps modification. It was known that the mechanical properties had close relationship with the morphologies. Therefore, it was very interesting to study the mechanical properties under different morphologies.

Part (A) of Fig. 4 were typical stress–strain curves for SBS attached by the furan *via* the thiol–ene click reaction and tensile stresses at 300%, 500% and 700% were summarized on Table S5.† All the samples for SBS–*x*Fu possessed higher modulus,

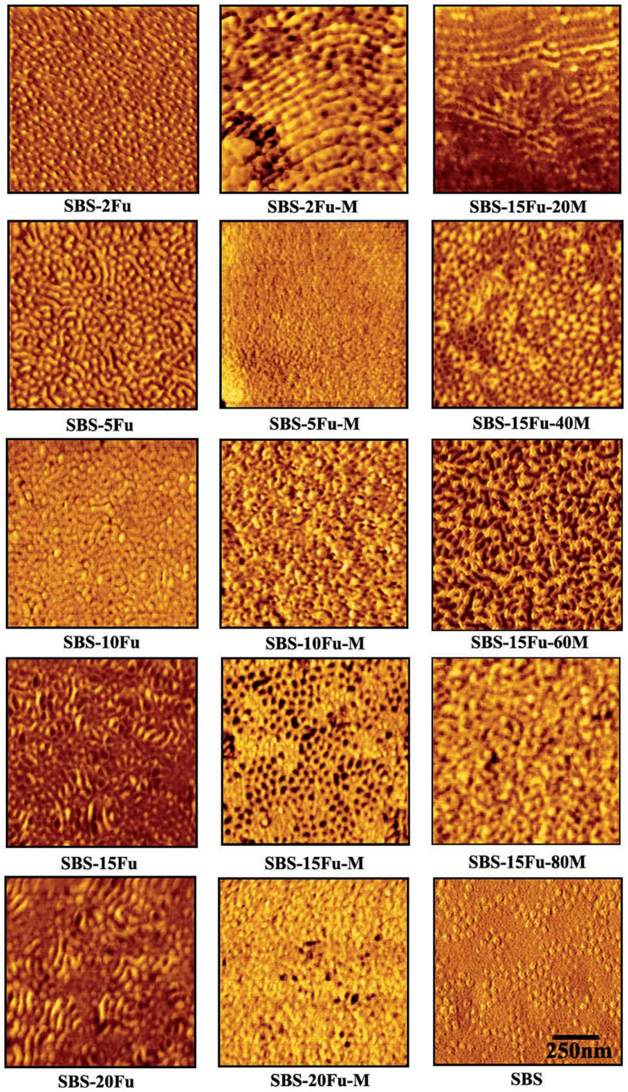


Fig. 3 AFM phase images of different samples including SBS–*x*Fu and SBS–*x*Fu–M series.

increased tensile strength and ultimate strain compared with the pure SBS. As the furan groups were less than 10%, the interaction in the PB domains was increased due to polar interaction from the attached furan. Therefore, the mechanical properties of SBS were increased with maximum data for tensile strength and ultimate strain at break obtained at 16.62 MPa and 1095.18% respectively for SBS–5Fu. With further increasing RF, the vitrification of PS domains was gradually destroyed with bi-continuous phase morphologies obtained for samples (SB–15Fu and SBS–20Fu) (Fig. 3) which finally softened the modified SBS and the tensile strength of sample was reduced to 3.26 MPa for SBS–20Fu.

The tensile-stress curves of the SBS–*x*Fu–M series were shown in Fig. 4B. As compared with SBS–*x*Fu series, these samples showed higher strength and modulus but lower ultimate strain *via* the crosslinking reaction based on DA reaction between furan groups on PB block of SBS and bismaleimide. As an example, for SBS–5Fu–M the tensile strength and tensile strain at break were 14.47 MPa, 706.35% respectively, the tensile strength almost increased by 8 times as compared with the pure SBS. It was interesting to find that the crosslinked SBS had yield region as RF was increased above 10%, which could be explained with the change of the inner structure as reflected in AFM. As shown in Fig. 3, the hard phase was gradually changed from dispersed phase to continuous phase with increasing RF. Therefore, the samples became from "soft" to "hard" with the yield region finally appeared on tensile curves. These similar phenomena were also observed for SBS–15Fu–*y*M as shown in Fig. 3 and Table S7.†

As a result, the mechanical properties of the modified SBS were increased greatly by the incorporation of dynamic cross-linking network.

Remolding ability of the modified SBS

To prove the remolding ability of the modified SBS materials, two methods were used. One was sol–gel method and the other was to remold material under thermal treatment.

On the sol–gel method, the solid sample was put into 1,2-dichlorobenzene solution. At room temperature, the sample could only swell in 1,2-dichlorobenzene indicating the existence of DA cross-linked networks. As the sample was heated to the temperature around 120 °C, the swollen sample started to dissolve. At above 160 °C, a clear and transparent solution was formed, indicating the disconnection of DA linkage due to the rDA reaction at high temperature. When cooled down to room temperature, a homogenous and transparent gel was formed from solution and the gel could be dissolved again at high temperature. We have done three circles and found that even after three circles the phenomenon was almost the same as the first circle. This repeated process could prove that the current system was completely thermal reversible for at least three times.

The other way to prove the remolded ability was to thermally remold the broken material. The film was firstly cut into small pieces and then remolded under a pressure of 10 kPa for 5 min at 160 °C. Finally, a solid polymer film was formed. This process was repeated for 3 times. The tensile test of the remolded sample was taken 2 days after cooling to temperature from 160 °C. After 3 generations of recycling as shown on Fig. 4D, it was found that there was a slight decrease in modulus and tensile strength through remolded generations and ultimate strain increased slightly from the original to the 3rd recycling generation. The result proved that the dynamic crosslinked SBS showed the improvement in the solvent resistance and mechanical properties. In the meantime, it did not lose the function of the thermal plastic remolding behavior with the presence of the thermally reversible chemical linkage. At high temperature, the rDA reaction destroyed the crosslinked structure which made the remolding process realizable. However, when the temperature went down, the chemical crosslinking linkage was formed again to insure the solvent resistance and improved mechanical properties. Such process had been also characterized by FT-IR spectroscopy for the crosslinked SBS (SBS–15Fu–80M) in the solid state under the selected two

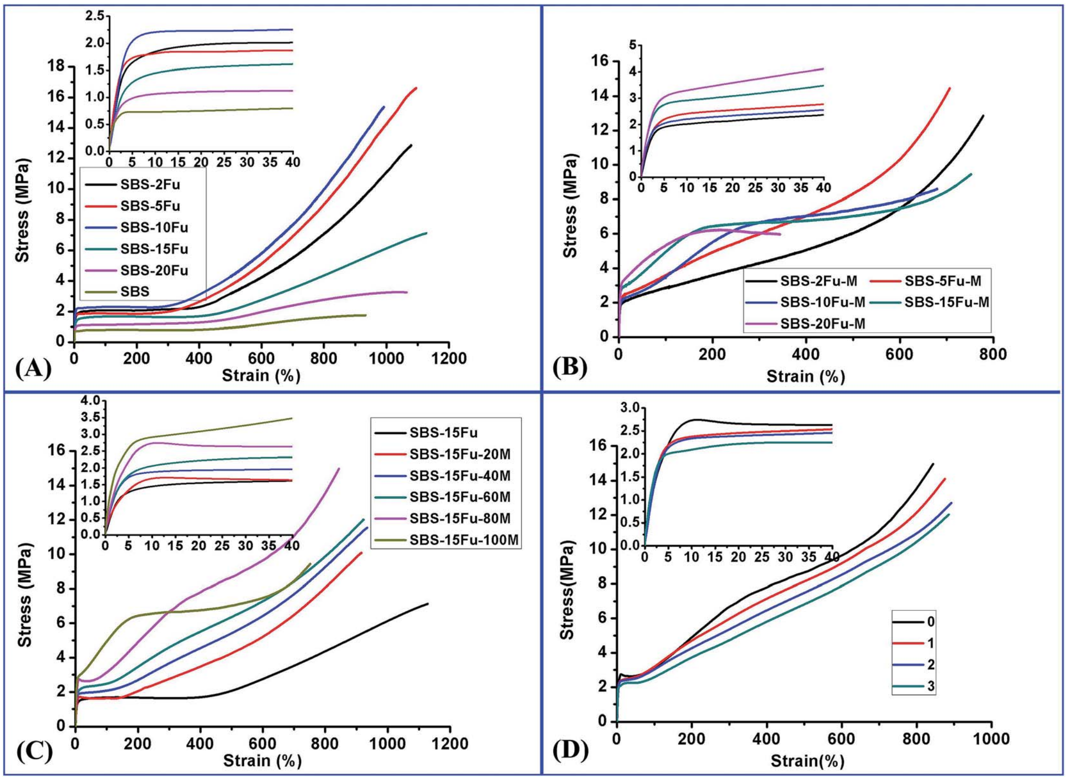


Fig. 4 (A) Stress–strain curves of the series of SBS–*x*Fu. (B) Stress–strain curves of series of SBS–*x*Fu–M. (C) Stress–strain curves of the series of SBS–15Fu–*y*M materials. (D) Stress–strain curves for the sample SBS–15Fu–80M through 3 generations of recycling from pieces to films.

different temperature for DA–rDA–DA reaction (Fig. 5B). The obvious change in the process is the increase and decrease of the intensity of the absorption peak at 1184 cm^{-1}. Once heated to 160 °C and kept for 3 min, it was observed that intensity of the absorption peak at 1184 cm^{-1} ((II) of Fig. 5B) went down. The peak at 1184 cm^{-1} could be ascribed to the debonding of the DA adduct (C–O–C) *via* the retro-reaction.[23] After slow cooling from 160 °C to 20 °C at 5 °C min^{-1}, (III) in Fig. 5B showed that the intensity at 1184 cm^{-1} recovered to the original state as (I) of Fig. 5B. This phenomenon can be explained with the regeneration of the DA adduct (C–O–C) during the cooling process. Three cycles of rDA and DA reactions were observed, and similar results were obtained. Therefore, it could be concluded that the furan modified SBS could be decrosslinked and re-crosslinked with bismaleimide repeatedly even in the solid state. All the above methods proved that the modified SBS materials did not lose the thermal plastic remolding ability while both the solvent resistance and the mechanical properties were simultaneously enhanced.

Besides remolding behavior, it was also found that the crosslinked SBS showed good self-healing property (Fig. 6). The film was firstly cut with a surgical blade and formed a crack on it. The film with crack was put onto the heating stage at a rate of 10 °C min^{-1} and photographs were taken at different temperature during the heating process to observe the change of the crack. When heated to about 90 °C, the crack began to decrease but still could be observed. The driving force for the decrease of crack in this stage was the compression formed at the back of interface. When the temperature continued to increase to about 160 °C, the crack disappeared completely. The driving force was

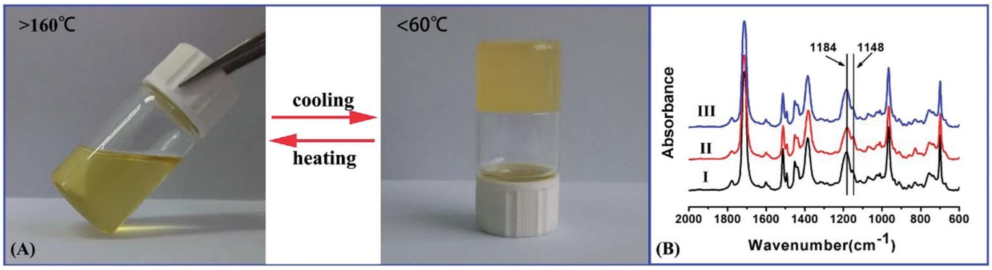


Fig. 5 (A) The sol–gel process of the sample (SBS–15Fu–80M) in dichlorobenzene when the temperature changed. (B) FTIR spectra of the cross-linked sample (SBS–15Fu–80M) (I) before heat treatment at 20 °C, (II) upon heating to 160 °C for 3 min, and (III) after cooling to 20 °C.

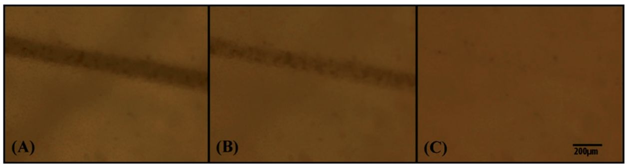


Fig. 6 Digital images for healing process of sample (SBS–15Fu–80M). The photo of the film with a crack at room temperature (A), at 90 °C (B) and at 160 °C (C).

from the rDA reaction happened 160 °C and the liberated polymer chain could move together to totally heal the crack. Therefore, the modified SBS also had good self-healing property.

Conclusions

In this article, the common-used thermoplastic elastomer SBS was modified with furan groups *via* UV-induced thiol–ene click reaction which was an easy and convenient method. Then the modified SBS formed the dynamic crosslinking 3D network with bismaleimide based on DA reaction *via* a thermally reversible mode. Therefore, the solvent resistance and mechanical properties were greatly enhanced. Moreover, it could still be thermally remolded. Based on the adjustment of ratio of the RF and RFM, the properties of the material could be tailored in great freedom to meet different application. Therefore, we have provided the ideal solution to keep the balance of thermal plastic remolding ability and enhancement of solvent resistance and mechanical properties.

Acknowledgements

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