

Preparation, Characterization, and Properties of Crosslinked Hydroxylated Poly(styrene-*b*-butadiene-*b*-styrene) Triblock Copolymer

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ABSTRACT: Hydroxylated poly(styrene-*b*-butadiene-*b*-styrene) triblock copolymer (HO-SBS), with crosslinked networks, was prepared using various amounts of toluene diisocyanate (TDI). The amount of TDI was 0, 0.5, 1, 2, and 5 wt %. The effects of different contents of TDI on the microstructure, thermal properties, and mechanical properties of the crosslinked networks were investigated in detail. Fourier transform infrared spectra indicates that the reaction between —OH and —N=C=O have take place, and the solid-state nuclear magnetic resonance spectra confirms that the crosslinked structure has been obtained. The results of scanning electron microscopy show that the mode of fracture surfaces transmits gradually from tough fracture to brittle fracture, but the structure of microphase separation is still observed at the same time. Mechanical

test indicates that crosslinking is a useful method to regulate mechanical properties of the HO-SBS. The results of dynamic mechanical thermal analysis display that there are two glass transition temperatures, which also means that the microphase separation is still in existence. Moreover, the glass transition temperature of the polybutadiene domains shifts to higher temperature. Accordingly, the microstructure, glass transition temperature, solvent resistance, and mechanical properties of the HO-SBS are influenced obviously by the crosslinking of TDI. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 1162–1169, 2011

Key words: hydroxylated poly(styrene-*b*-butadiene-*b*-styrene); crosslinking; mechanical properties; thermoplastic elastomer

INTRODUCTION

Thermoplastic elastomer (TPE), a polymer category of attractive elastic properties and convenience in processing and recycling, is widely used in industry.¹ The poly(styrene-*b*-butadiene-*b*-styrene) triblock copolymer (SBS), one of the most productive and important TPE, is widely used in various domains, such as footwear and impact modifiers in engineering plastics and adhesives, because of its good balance of mechanical properties along with favorable processability and recyclability.^{2–6} However, for the weak polarity and the presence of large amounts of unsaturated double bonds in polybutadiene segments, SBS block copolymers do not possess good thermal stability, resistance to organic solvents, weather, and UV stability. By reducing the level of unsaturation via polarity and crosslinking, the physi-

cal, mechanical and chemical properties of the copolymers can be improved and satisfy some specific demands.

Crosslinking is an effective way to form three-dimensional polymer networks to endow polymeric materials with enhanced properties.^{7–10} Some researches have shown that SBS could be crosslinked by chemical reagents.^{11–15} Crosslinked PB chains of SBS molecules with small amounts of dicumyl peroxide (DCPD) were prepared by Wang and Chang.¹¹ Furthermore, they used both a conventional tear test and a newly developed cutting test to determine the fracture energies of the crosslinked SBS specimens. Ahankaria and Kar¹² processed styrene butadiene rubber-carbon black nanocomposites with the sulfur and accelerator to introduce the gradation of the crosslinked density. Mohammady et al.¹³ prepared crosslinked SBS block and SBR random copolymers by using DCPD as crosslinking agent. Furthermore, the effect of crosslinking on the molecular dynamics of those two copolymers were investigated and compared. Sakurai et al.¹⁴ used 1,1-bis(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane as a crosslinking agent (peroxide) to crosslink the SBS sample. They found that the degree of the microphase separation was suppressed because of the crosslinking. In addition,

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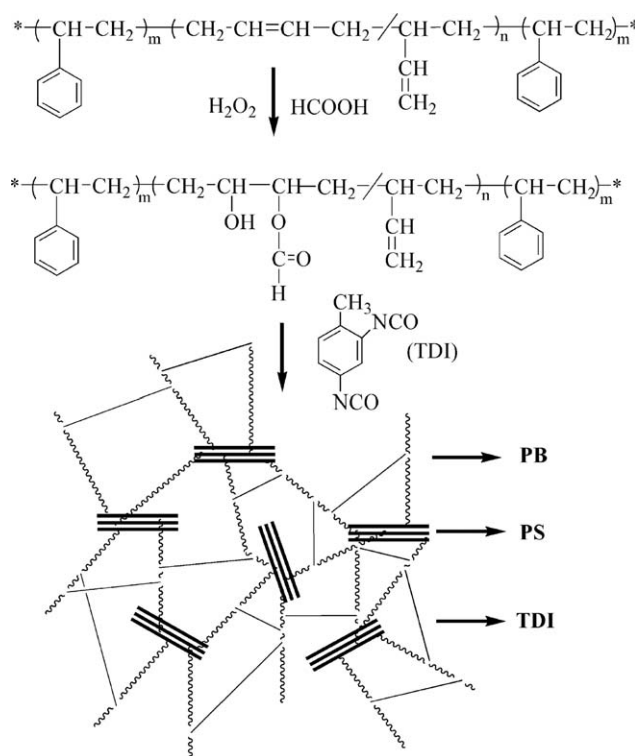
they also revealed that crosslinking in the disordered state was a useful method to improve mechanical properties of the SBS thermoplastic elastomers. Kaur et al.¹⁵ reported the crosslinking of sulfonated styrene-butadiene-styrene (SSBS) triblock copolymer through condensation of sulfonic acid groups with bis (4-aminophenyl) sulfone to form sulfonamide linkages using a coupling agent (carbonyldiimidazole). Besides crosslinking by the chemical agent, UV crosslinking was also a familiar methods to crosslink SBS. Decker et al.^{16–18} obtained UV-crosslinked SBS by using a crosslinking agent of trimethylolpropane mercaptopropionate (TRIS) together with a photoinitiator, and they found that the crosslinking reaction could be completed within 3 s. Lim et al.¹⁹ used thiolene reactions to prepare the UV-crosslinked styrene-isoprene-styrene triblock copolymer (SIS)/SBS blends, which were used for hot-melt pressure sensitive adhesive, and their thermal stability increased obviously. Mateo et al.²⁰ used two kinds of photoinitiator (benzophenone and 2,2-dimethoxy-2-phenylacetophenone) to prepare the photo-crosslinked SBS films, and the diffusion of organic solvents through them was studied. Kim et al.²¹ reported that the crosslinking of the polybutadiene (PB) block could be achieved after 3 min of irradiation of UV light under nitrogen environment. These examples indicated that the chemical and physical properties of SBS thermoplastic elastomer could be altered significantly through modification of the butadiene elastomeric segment via crosslinking.

Nevertheless, from what's mentioned above, no report can be found on the crosslinked HO-SBS. Therefore, in this article, HO-SBS, a polar copolymer, was synthesized, and crosslinked networks were prepared by using toluene diisocyanate (TDI) as a crosslinking agent. Furthermore, the microstructure, heat resistance, glass transition temperature, solvent resistance, and mechanical properties of the crosslinked samples were studied in detail.

EXPERIMENTAL

Materials

The triblock polymer SBS was provided by Baling Petrochemical Co., Ltd., China, and used without further purification. The SBS (YH-792) was sold with 0.14 wt % 2,6-di-*tert*-butyl-4-methylphenol (BHT) antioxidant. Gel permeation chromatography analysis of the SBS in tetrahydrofuran gave M_n fractions of 22,800 (polystyrene domains) and 68,400 (polybutadiene domains) with polydispersity of 1.15. TDI was purchased from Aldrich (Beijing, China) and used directly without further purification. Toluene, peroxide hydrogen, and formic acid, of analytical



Scheme 1 Scheme for the synthesis of the HO-SBS and its crosslinked polymer.

grade, were supplied by Shanghai Chemical Reagent Co., Ltd., China.

Preparation of HO-SBS triblock copolymer

HO-SBS was synthesized according to the method presented in the literature.²² In a typical hydroxylation run, 5 g of SBS was dissolved in 50 mL of chloroform in a 250-mL three-neck glass flask equipped with a condenser, a mechanical stirrer, and a thermometer. Then 50 mL of formic acid and 5 mL of peroxide hydrogen were added into the flask. The reactant solution was stirred for 1 day at 50°C. After the completion of the reaction, the polymer was coagulated in methanol and was purified by re-coagulating twice. The coagulated polymer was then dried at 40°C under a vacuum. The molecular structure of the resulting HO-SBS is shown in Scheme 1. Proton nuclear magnetic resonance (1H -NMR; $CDCl_3$): δ 1.22–2.15 (m, $-CH_2-$), 2.96 (m, $-C(Ar)H-$), 3.52–4.01 (m, CH), 4.95 ($-CH=CH_2$), 5.15 (m, $-OH$), 5.37–5.40 (m, $-CH=CH-$), 6.45–7.21 (b, 10H, Ar-H), 8.07 (s, $HCOO-$). FT-IR %T (cm^{-1}): 3533, 1720, 1170, 967.

Preparation of crosslinked SBS

The preparation of crosslinked SBS was carried out in solvent of toluene in a 100-mL four-neck glass flask equipped with stirrer, thermometer, condenser, and nitrogen inlet. A brief description of the proce-

ture is as follows: 3 g of HO-SBS was dissolved in 30 mL toluene, and then a certain amount of TDI was added by dropping. The reactant solution was stirred at room temperature for 6 h and then at 60°C for another 2 h. Subsequently, the resulting solution was poured into a petridish. After complete evaporation of the toluene, the homogeneous crosslinked SBS was obtained. Then, the crosslinked materials were immersed in toluene for 1 day to extract unreacted TDI and uncrosslinked polymers. The crosslinked samples were extracted at least five times by using toluene. Finally, the crosslinked SBS sample was obtained by evaporating toluene thoroughly from the swollen material, leading to 0.5, 1, 2 and 5 wt % of TDI crosslinked SBS samples. For comparison, uncrosslinked sample was cast by toluene solution with an initial polymer concentration of 10 wt %. The crosslinked process is shown in Scheme 1.

Gel fraction and degree of swelling was measured according to the method presented in the reference.²³ Gel fraction of the crosslinked polymer was determined by extracting the sample in Soxhlet extractor (Beijing China) with toluene for 48 h. The insoluble polymer was vacuum-dried at 100°C to constant weight. The gel fraction (w) was obtained by

$$W = \frac{M_2 - M_1}{M_0} \times 100\% \quad (1)$$

where M_0 is the weight of the sample before extraction, M_1 is the weight of the filter paper after extraction, and M_2 is the total weight of the sample and filter paper after extraction. Degree of swelling (volume ratio of absorbed solvent to dry gel sample) is calculated using the following eq. (2):

$$\text{Degree of swelling } (q) = \frac{W_s - W_g}{W_g} \times \frac{\rho_p}{\rho_{\text{toluene}}} \quad (2)$$

where W_g is the weight of dry gel component in the crosslinked SBS sample, W_s is the weight of gel component swollen at room temperature for 48 h in toluene ρ_p and ρ_{toluene} are densities of the crosslinked SBS and toluene, respectively.

Analytical instruments

¹H-NMR spectra were collected using an Inova 400 spectrometer (Palo Alto, CA) using CDCl₃ as solvent. The solid-state NMR measurements were made on a Bruker Avance III-400 spectrometer, operating at 100.2 MHz for ¹³C. All of the NMR experiments were obtained using cross-polarization and magic angle spinning. The optimum contact time used for all the ¹³C spectra is 3000 μ s, and all

the spectra were obtained at room temperature (about 20°C). Fourier transform infrared (FT-IR) analysis was performed on a WQF-410 FT-IR spectrometer (Beijing, China) between 4000 and 400 cm⁻¹ in the form of KBr pellets. The thermal stability of the samples (about 7 mg) was investigated with a thermal gravimetric analyzer (TGA, a Netzsch STA 449C) under nitrogen from room temperature (about 30°C) to 800°C at a heating rate of 10°C/min. The morphological modifications produced on the HO-SBS and the crosslinked HO-SBS fracture surfaces were analyzed using a scanning electron microscopy (SEM, JEOL-6700, Japan). The crosslinked samples were gold-coated before analysis and the energy of the electron beam was 20 kV. Dynamic mechanical thermal analysis (DMTA) was carried out on the TA Instruments DMTA-V with a tensional module at the frequency of 1 Hz and at the heating rate of 5°C/min from -130 to 110°C. The specimens (size 1.5 × 6.5 × 50 mm³) were cut from the center of the samples. The tensile properties of the samples were measured in accordance with ISO 527 at room temperature (about 20°C) using a tensile tester (Instron-4302). The stress-strain experiments have been done three times for each sample and the average values have been presented.

RESULTS AND DISCUSSION

Structure characteristics of HO-SBS and crosslinked HO-SBS

The chemical groups of the HO-SBS and its crosslinked polymer with different amounts of TDI are investigated by FT-IR spectra as shown in Figure 1. Compared with the spectra of the pure SBS [Fig. 1(a)], the band at 967 cm⁻¹, corresponding with the C-H out of plane bending in *trans*-1,4-C=C, obviously weakens, and the two bands are observed at about 3533 and 1720 cm⁻¹ [Fig. 1(b)], which are due to the stretching vibrations of -OH groups and carbonyl groups, respectively. These indicate that most double bonds of PB blocks are hydroxylated. A new absorbance band, obviously observed in the FT-IR spectra of the crosslinked SBS besides the typical bands in the pure SBS and HO-SBS is observed at 3370 and 1530 cm⁻¹, which is attributed to the N-H stretch. With the increase of TDI from 0 to 5 wt %, the intensity of N-H in-plane bending peaks increases obviously, which proves that the reaction between -OH and -N=C=O have taken place, but it can not confirm that the crosslinked structure is obtained. Furthermore, when the content of TDI is 5 wt %, it can be clearly seen that the -OH stretching peak at 3533 cm⁻¹ decreases and the -N=C=O symmetric stretching peak at 2270 cm⁻¹ increases. It can be explained that the bonds between TDI and

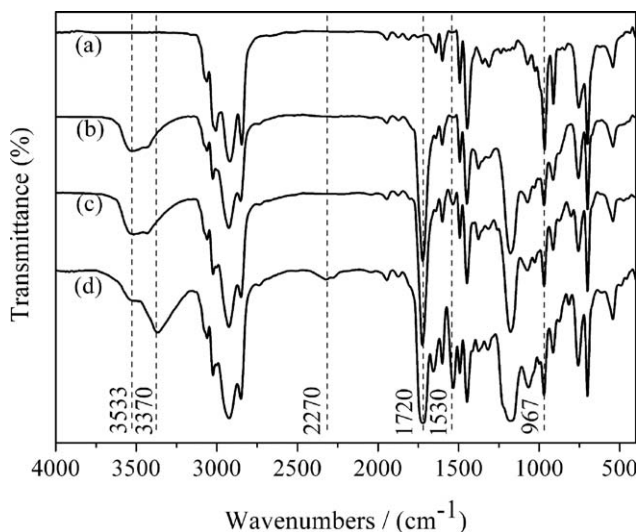


Figure 1 FTIR spectra obtained from: (a) SBS, (b) HO-SBS, (c) crosslinked sample with 0.5 wt % TDI, (d) crosslinked sample with 5 wt % TDI.

HO-SBS impeded the movement of $-OH$ and $-N=C=O$, and so they still have residual groups of $-OH$ and $-N=C=O$. The evidence above indicates that the reaction between $-OH$ and $-N=C=O$ have taken place, but it can not confirm that the crosslinked structure is obtained. Therefore, we

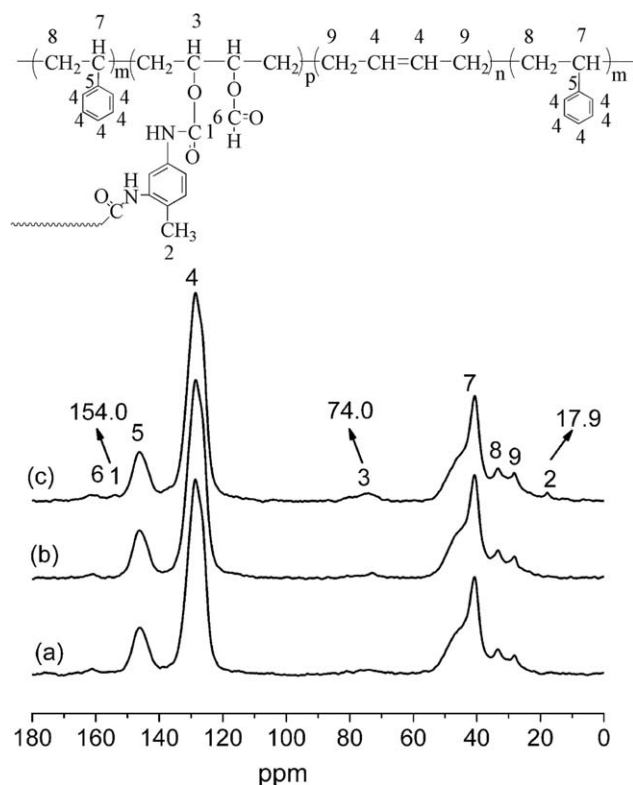


Figure 2 ^{13}C Solid-state NMR spectra of (a) HO-SBS, (b) crosslinked sample with 0.5 wt % TDI, (c) crosslinked sample with 5 wt % TDI.

need other methods to characterize the crosslinked structure.

The crosslinked structure was evident, confirmed by the solid state ^{13}C -NMR spectrum. Many researchers have used solid state ^{13}C -NMR spectra to study SBS material.²⁴⁻²⁷ It has been suggested that solid state ^{13}C -NMR spectra is a convenient method to study crosslinked sample. Figure 2 shows the solid state ^{13}C -NMR spectra of the pure SBS, SBS/TDI 0.5 wt %, and SBS/TDI 5 wt %. The assignments of peaks were based on typical chemical shift values of the chemical structures, shown as inset. Especially, three new peaks (C_1 , C_2 , and C_3) (Fig. 2) appear at 154.0, 17.9, and 74.0 ppm, and the assignments of these peaks are shown in Figure 2, respectively. So it can be confirmed that the crosslinked structure was successfully obtained.

Characterization of the crosslinked SBS

If the crosslinked network structure is required to be quantitatively characterized, the averages molecular weight between adjacent crosslinking points should be evaluated by means of, for example, the Flory-Rehner theory.²⁸ In this evaluation system, the interaction parameter between the polymer molecule and the swelling solvent is needed. As is known, it is difficult to choose the solvent in which interaction parameter for the SBS molecule is similar to YH-792. Hence, the qualitative characterization of the crosslinked specimens is done by evaluating the weight fraction of the macroscopically crosslinked HO-SBS molecules. The gel fraction is valuated by the eq. (1). The gel fraction of the crosslinked HO-SBS samples containing different amounts of TDI are shown in Figure 3. With the increase of TDI contents, the gel fraction of crosslinked HO-SBS increases. It shows clearly that the crosslinking of the HO-SBS starts at a very low concentration of TDI (below 0.5 wt %).

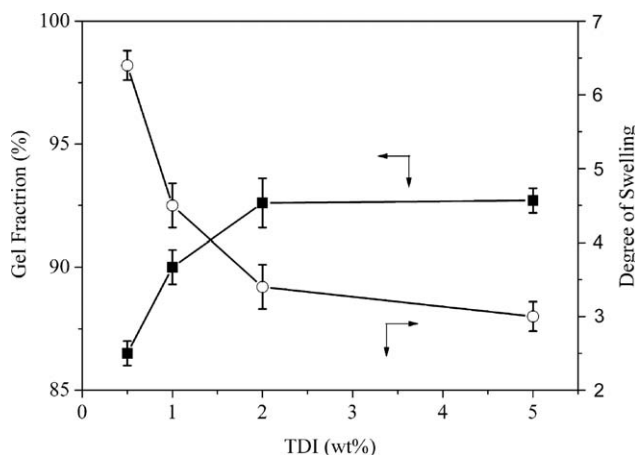


Figure 3 Gel fraction and degree of swelling of cross-linked HO-SBS as a function of TDI concentration.

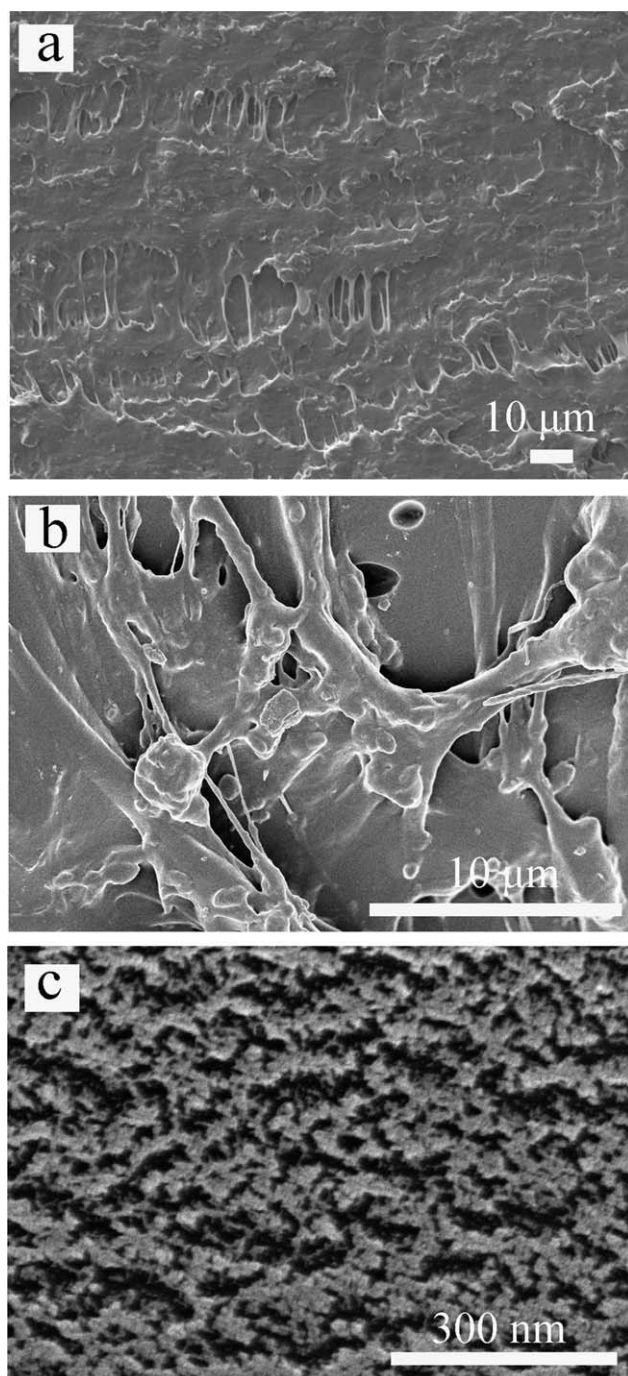


Figure 4 Scanning electron micrograph (SEM) photos of the fracture surfaces of the HO-SBS (a) and its crosslinked sample with 1.0 wt % TDI (b and c).

It is noted that the gel fraction reached 86.5 and 92.6%, when the concentration of the TDI are 0.5 and 2 wt %, respectively. But after that the gel fraction remains basically unchanged. Thus, the TDI is very convenient when it is used for crosslinking of HO-SBS, and the crosslinked SBS exhibits high solvent resistance.

The crosslinking density of HO-SBS samples is indicated by the degree of swelling (DS), and a low

degree of swelling implies a high crosslinked density. It can be observed in Figure 3 that the DS decreases with the increase of TDI contents, which is consistent with the increase of the gel fraction.

Morphologies of the crosslinked SBS

The SEM of the un-crosslinked and crosslinked HO-SBS sample with 1.0 wt % TDI are shown in Figure 4. Examination of the fracture surfaces of the samples by SEM gives information about how the TDI affects the morphology of the crosslinked samples. A distinction can be made between the HO-SBS whose fracture surface is very rough with many fibrous glitches [Fig. 4(a)], but the fracture surface of cross-linked HO-SBS is relatively smooth [Fig. 4(b)]. As depicted in Figure 4, when the photo is amplified to 300 nm [Fig. 4(c)], the structure of microphase separation is obviously observed. So, the mode of fracture surfaces transmits gradually from tough fracture to brittle fracture with the crosslinking. Because the HO-SBS is crosslinked by the TDI, the size of dispersive phase (polystyrene) diminishes, and there are fewer crazes and sheared zones under the function of force, which is the character of the tough fracture.^{29,30} In this situation, the properties of the crosslinked samples are mainly determined by the type of the polymer phase. The samples with this phase morphology should have higher tensile modulus, which is supported by the following testing of the mechanical property.

Mechanical properties of the crosslinked polymer

Figure 5 and Table I show the representative tensile properties of HO-SBS and crosslinked samples prepared by using different amounts of TDI. The

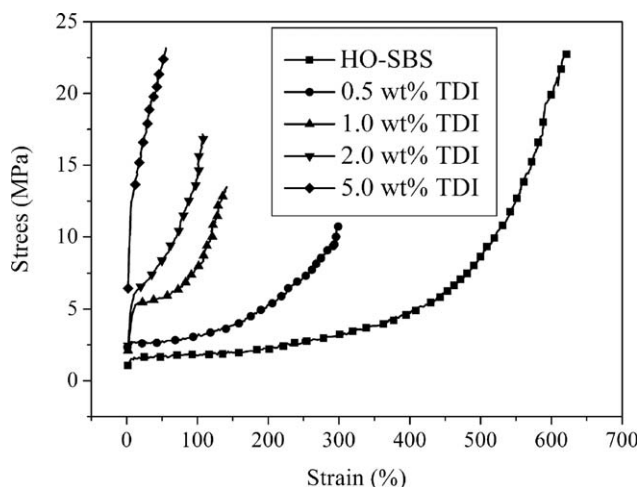


Figure 5 Strain–stress curves of the HO-SBS and its crosslinked polymer prepared by different amounts of TDI.

TABLE I
Mechanical Properties of the HO-SBS and Its Crosslinked Samples

Samples	Tensile strength (MPa ± 1)	Tensile modulus (MPa ± 1)	Elongation at break (% ± 10)
HO-SBS	22.94	25.9	623.67
0.5 wt % TDI	10.79	71.9	299.89
1 wt % TDI	13.48	83.3	141.31
2 wt % TDI	17.16	94.4	108.27
5 wt % TDI	23.15	218.6	55.43

crosslinked structure can be introduced into HO-SBS by TDI, which results in the increase of the tensile modulus and the decrease of elongation at break. It may be attributed to the crosslinking structure which stiffens the HO-SBS material. However, the increase of gel fraction and crosslink density makes the crosslinked HO-SBS more brittle and less stretchy, which is supported by the photos of scanning electron micrograph (Fig. 4). As seen in Figure 5, it is also noticed that the tensile strength of the crosslinked samples increases sharply with the gel fraction and crosslinked density increasing. The highest tensile strength of crosslinked HO-SBS, obtained from the sample of 5 wt % TDI with 92.7% gel fraction and 2.5 DS (Fig. 3), is 23.15 MPa.

Figure 6 shows the dependence of strain and stress at break on the concentration of the TDI. It is obvious that stress at break increases gradually with the concentration of the TDI, and it is almost a linear correction. However, the strain at break decreases sharply and then decreases gradually with the concentration of the TDI. Therefore, it can be stated that the crosslinking in the PB block chains affects elongation and strength of the material. From this result, it is concluded that crosslinking is a useful method to regulate mechanical properties of the SBS thermoplastic elastomer.

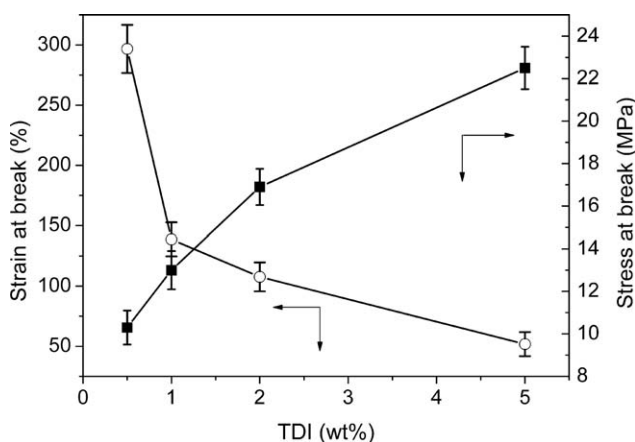


Figure 6 Dependence of strain and stress at break on the concentration of TDI.

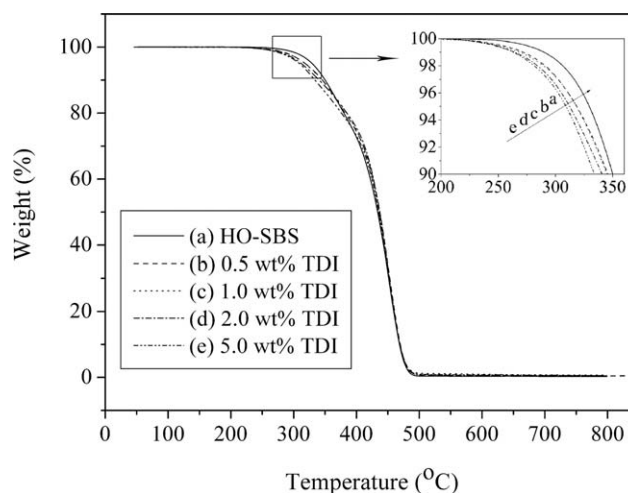


Figure 7 TGA traces obtained from the HO-SBS and its crosslinked samples.

Thermal properties of the HO-SBS and its crosslinked polymer

The thermal stability of the HO-SBS and its cross-linked samples is evaluated by TGA. The results are presented graphically in Figure 7 and Table II. It can be seen that onset degradation temperature of HO-SBS appears at 329°C. With the increase of TDI from 0 to 5 wt %, the onset degradation temperatures of the crosslinked samples gradually decreases. When TDI increases to 5 wt %, the temperature shifts to a low temperature, which is about 21°C lower than that of HO-SBS. There are two explanations for this phenomenon: the first reason is that the crosslinking agent, TDI, doesn't have good heat resistance and the HO-SBS crosslinked by 5 wt % TDI has relatively more C–N bonds than any others, and the bond energy of C–N is 305 kJ/mol, which is lower than that of the C–C (332 kJ/mol) and C=C (611 kJ/mol); and the other reason is that there is residue of the crosslinking agent, TDI. So onset degradation temperature of 5 wt % TDI crosslinked HO-SBS is lower than others.

TABLE II
Thermal Stability of the HO-SBS and Its Crosslinked Samples

Samples	Onset degradation temperature (°C)	Maximum degradation temperature (°C)	Elastic T_g (°C)	Plastic T_g (°C)
HO-SBS	329	452.1	-11.3	96.3
0.5 wt % TDI	318	451.8	-7.6	95.3
1 wt % TDI	316	451.5	-7.0	95.2
2 wt % TDI	311	451.4	-1.9	91.6
5 wt % TDI	308	451.0	-1.7	77.4

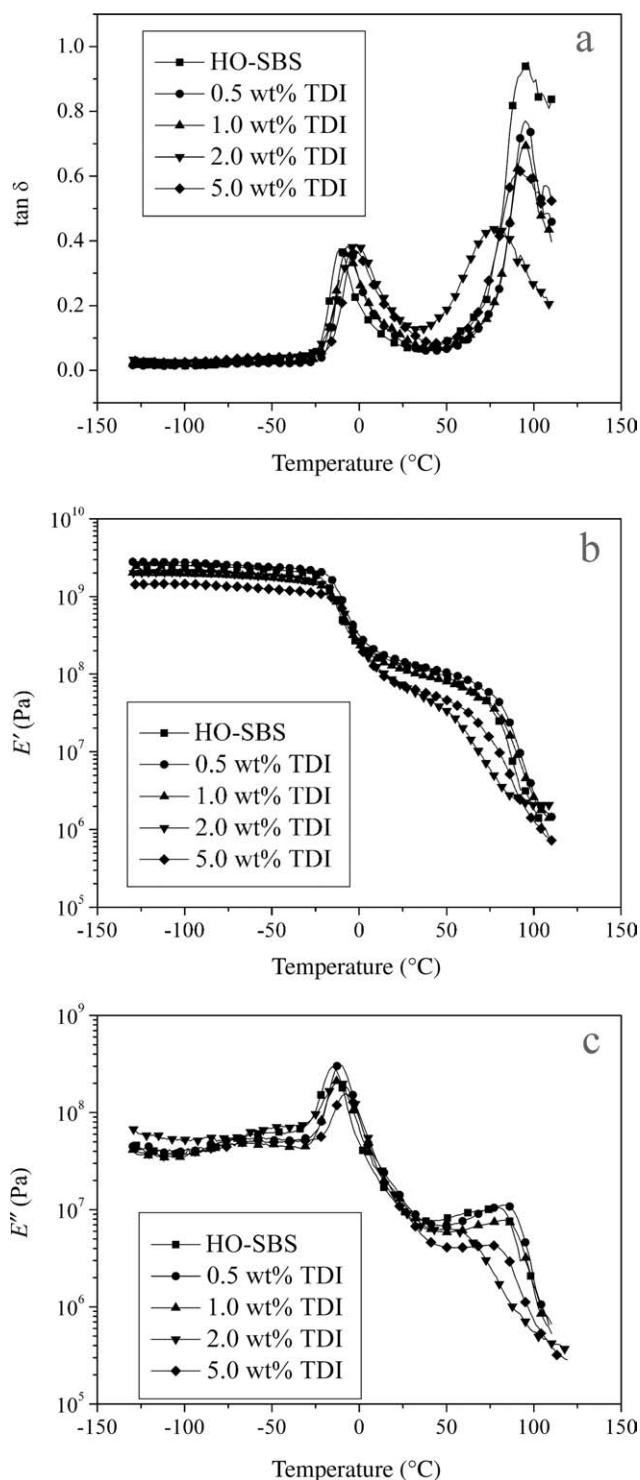


Figure 8 Dynamic mechanical thermal spectra of the HO-SBS and its crosslinked samples: (a) temperature dependence of $\tan \delta$, (b) temperature dependence of dynamic storage modulus (E'), (c) temperature dependence of dynamic loss modulus (E'').

Dynamic mechanical thermal properties of the HO-SBS and its crosslinked polymer

The loss factor ($\tan \delta$), dynamic storage modulus (E'), and dynamic loss modulus (E'') versus tempera-

ture for the HO-SBS and its crosslinked samples are plotted in Figure 8. As shown in Figure 8(a), in all cases, two glass transition temperatures are observed, which shows that the structure of microphase separation is still existent. The same results were also obtained when Sakurai et al.¹⁴ examined structure–property relationships of the chemical crosslinked SBS using dynamic viscoelastic measurements and tensile stress–strain tests. The lower temperature transition at -10°C is characteristic of the polybutadiene domains, whereas the higher temperature transition, at about 95°C , is characteristic of the polystyrene domains. As the gel fraction and crosslinked density increase, the value of $\tan \delta$, relevant to the polybutadiene domains, increases, whereas the value of $\tan \delta$, relevant to the polystyrene domains decreases, and the mechanical relaxation shrinks. All the corresponding data of $\tan \delta$ are summarized in the Table II. This may be attributed to the chemical bond of crosslinking structure blocking the movement of molecule and decreasing the free volume of polymer.

In the E' and E'' curves [Fig. 8(b,c)], the variations of dynamic storage modulus and dynamic loss modulus as a function of temperature for the HO-SBS and its crosslinked samples containing different TDI amounts can be clearly observed. The E' values of 0.5 wt % TDI, 1 wt % TDI, 2 wt % TDI, and 5 wt % TDI at -100°C are 2.75, 2.06, 2.01, and 1.45 GPa, respectively. Compared with HO-SBS (2.51 GPa), the crosslinked samples show lower storage modulus because of the crosslinking structure of the polybutadiene domains. This is consistent with increase of the mechanical properties of the cross-linked samples. The same results were also obtained when Mohammady et al.¹³ investigated and compared the effect of crosslinking on the molecular dynamics of two triblock copolymers and a random copolymer.

CONCLUSIONS

Crosslinking structures can be effectively introduced into HO-SBS in the presence of a small amount of crosslinking agent (TDI), which results in the thermal and mechanical properties of crosslinked samples that are mainly determined by the gel fraction and crosslinked density. With the introduction of crosslinking structure, the T_g of the polybutadiene domains shifts to higher temperature and the mechanical properties are affected, which is indicated by tensile test and DMTA results. However, the increase of brittleness with the introduction of a highly crosslinked structure is a problem that needs to be overcome and will be considered in our future work.

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