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The Influence of *Trans*-1,4-poly(butadiene-*co*-isoprene) Copolymer Rubbers (TBIR) with Different Molecular Weights on the NR/TBIR Blends

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Abstract The molecular weight of a polymer is of prime importance and greatly influences the processing and mechanical properties of the polymer. *Trans*-1,4-poly(butadiene-*co*-isoprene) multi-block copolymer rubbers (TBIR) exhibit outstanding fatigue resistance, low heat build-up and good abrasion resistance, and are expected to be desirable candidate for high performance tire. Study on the influence of TBIR with different molecular weights on the structure and properties of TBIR and natural rubber (NR)/TBIR blends is essential to understand its contribution to the greatly improved dynamic properties of the rubber vulcanizates. TBIR with different molecular weights characterized by ^{1}H-NMR, ^{13}C-NMR, GPC, and DSC were highly *trans*-1,4-copolymers with similar chain sequence distribution and crystalline *trans*-1,4-polyisoprene (TPI) blocks. The green strength and modulus of TBIR increased with the increasing molecular weight. The NR/TBIR compounds filled with 40 phr carbon black were chemically cured by sulfur for the preparation of NR/TBIR vulcanizates. The compatibility between NR and TBIR, filler distribution, crosslinking bond and density, and properties of NR/TBIR vulcanizates were studied. The NR/TBIR vulcanizates showed increasing tensile strength, hardness, modulus, rebound, abrasion resistance, and flexural fatigue properties with increasing molecular weight of TBIR. Furthermore, they presented significant improvement in flexural fatigue resistance when compared with that of NR vulcanizate. The contribution mechanism of TBIR on the NR/TBIR blends was discussed. The TBIR with a wide range of molecular weight are ideal rubbers for high performance tires.

Keywords *Trans*-1,4-poly(butadiene-*co*-isoprene) copolymer rubber; Nature rubber; Blends; Molecular weight; Fatigue resistance

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INTRODUCTION

In view of the rapid development of automobile industry and the increasing security consciousness, high performance tire stocks with lower rolling resistance (oil saving), better fatigue and wear resistance (longer serving life), and higher wet skid resistance (safer) have attracted growing attention.[1−3] One of the most popular ways to manufacturing high performance tire stocks is the stock formula optimization, including rubber stock modification by changing or functionalizating the rubber materials based on commercialized rubbers like NR, *cis*-1,4-polybutadiene rubber (BR), and styrene-butadiene rubber (SBR),[4−7] or adjusting the kinds or ratios of fillers and/or the other additives.[8−11]

Trans-1,4-poly(butadiene-*co*-isoprene) copolymer rubbers (TBIR) as a novel kind of elastomers provide an opportunity for rubber stock modification. Our previous work[12−17] showed that TBIR were copolymers with multi-TPI blocks and presented melting temperature in the range of 25−40 °C, glass transition temperature in the range from −65 °C to −75 °C, and relatively high green strength and modulus. When the commercialized rubber stocks like NR, NR/BR, and SSBR/BR were blended with 10−30 phr TBIR, the modified blends presented superior flexural fatigue resistance, better abrasion resistance, improved wet skid resistance, and lower rolling resistance.[18−25] Therefore, TBIR show great potentials in the application of high performance tire. However, the influence of TBIR with different molecular weights was not considered which might influence the flexural fatigue properties and abrasion resistance of the modified blends. The higher the molecular weight of TBIR, the more superior the fatigue properties and abrasion resistance. Thus, evaluating the influence of TBIR with different molecular weights on the structure and properties of rubber blends is necessary for the formula optimization of high performance tire stocks. In this study, TBIR with different molecular weights were synthesized in our lab. The influences of TBIR with varied molecular weight on the physical and dynamic properties of TBIR and NR/TBIR blends were fur-

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ther studied.

EXPERIMENTAL

Materials

Nature rubber (NR), SMR 20, Mooney viscosity $ML_{1+4}^{100°C}$ = 80.0, M_w = 133 × 10^4, M_w/M_n = 7.9, was produced from Malaysia. *Trans*-1,4-poly(butadiene-*co*-isoprene) copolymer rubbers (TBIR) with different molecular weights were prepared by Shandong Huaju Polymer Materials Co., Ltd. The rubber additives, including carbon black (CB), treated distillate aromatic extract (TDAE) oil, zinc oxide (ZnO), stearic acid, antioxidant, accelerator, and sulfur, were used as received.

Formulation and Specimen Preparation

Recipes (weight fraction, parts per hundreds of rubber (phr))

Rubber 100, ZnO-80 5.0, stearic acid 2.0, antioxidant 2.5, CB N 330 40.0, TDAE oil 1.6, accelerator *N*-*tert*-butylbenzothiazole-2-sulphenamide (NS) 0.25, accelerator *N*,*N*-2-dicyclohexyl-2,2-two benzothiazole sulfonamide (DZ) 0.45, insoluble sulfur (IS, 7020) 2.5.

Preparation of the rubber compounds

The raw rubbers were mixed by a RM-200C Hapro torque rheometer (Harbin Hapro Electric technology Co., Ltd., Harbin, China) at 70 °C and 70 rad/min for 2 min. ZnO-80, stearic acid, antioxidant, and half amount of carbon black was added into the torque and mixed with the rubbers for 3 min; the other half amount of carbon black was then put into the torque rheometer and mixed for another 7 min. The master batch was taken out of the rheometer below 145 °C and stored at room temperature for 30 min, followed by putting into the torque rheometer again and mixing for another 8 min. Next, accelerator and sulfur were added into the rubber compounds by an open two-roll miller (Shanghai Kechuang Rubber Machinery Equipment Co., Ltd., Shanghai, China) at 60 °C, and the rubber compounds were sheeted for future use.

Preparation of the vulcanizates

The above mentioned rubber compounds were stored at room temperature for 48 h and then compression molded at 150 °C for optimum cure time (t_{c90}) under 10 MPa with a HS-100T-RTMO type automatic operation vulcanizing press (Jiaxin Electronic Equipment Technology Co., Ltd., Shenzhen, China).

Characterization

NMR, GPC, and DSC

^{1}H-NMR (500 MHz) and ^{13}C-NMR (100 MHz) spectra were recorded with a Bruker 500 MHz spectrometer at 25 °C in $CDCl_3$ containing tetramethylsilane as standard. The microstructures of TBIRs were calculated by the equations according to reference.[17] The weight-average molecular weight (M_w) and molecular weight distribution (M_w/M_n) of the TBIRs were determined by HLC-8320 GPC gel permeation chromatography (Tosohcorporation, Japan) in tetrahydrofuran at 40 °C and calibrated by polystyrene standards. Differential scanning calorimetry (DSC) characterization of TBIRs was conducted on a PerkinElmer DSC-8500 differential scanning dalorimeter under N_2 atmosphere. The sample was heated from 0 °C to 150 °C at a rate of 10 °C/min and maintained at 150 °C for 3 min to eliminate the thermal history, and then cooled to −90 °C at a rate of 10 °C/min. Then the samples were heated to 150 °C from −90 °C at a rate of 10 °C/min to record the heat flow versus time and determine the melting temperature (T_m).

Curing characteristics

The curing characteristics of the compounds were determined by a MDR 2000 DISC vulkameter (Alpha Technologies Co. US.) according to GB/T 16584-1996.

Mooney viscosity

The Mooney viscosities $ML_{1+4}^{100°C}$ and $ML_{3+4}^{100°C}$ were measured with an MV 2000 Mooney viscometer (Alpha Technologies Co. US.) at 100 °C according to GB/T1232.1-2000.

Crosslinking density (CLD)

The total crosslinking density of NR and NR/TBIR vulcanizates before probe chemical treatment, and the residual crosslink density including mono-sulfidic and di-sulfidic bonds after probe chemical treatment were determined using a XLDS-15 crosslink density analyzer and NMR spectrometer (IIC Innovative Imaging Corporation, Blieskastel, Ger many). After probe chemical treatment, the polysulfidic crosslinks of NR and NR/TBIR vulcanizates were cleaved.[26]

Mechanical properties

The green strength, tensile strength, and tear strength were measured with a Zwick/Roell Z005 electrical tensile tester produced by Zwick (Germany) according to ISO 9026-2007, GB/T 528-2009, and GB/T 529-2008, respectively. Flexural fatigue properties of NR and NR/TBIR vulcanizates were measured with Demattia rubber fatigue testing machine (Gaotie Chemical Machinery, China) according to GB/T 13934-2006. All the testing temperature was (23 ± 2) °C.

DMA

Dynamic mechanical thermal analysis (DMA, temperature sweep) was conducted on a Q 800 (TA Instruments, US) apparatus operated in a rectangular tension mode with temperature ranging from −80 °C to 100 °C with 3 °C/min heating rate, 10 Hz frequency, and 0.1% strain amplitude.

Carbon black distribution

The carbon black (CB) aggregation throughout rubber vulcanizates was observed by disper GRADERTM view (Alpha Technologies Co. US).

Swelling experiments

Equilibrium swelling experiments were carried out in toluene at (30 ± 1) °C according to the standard HG/T 3870-2008. About 50 mg of specimen with 2 mm thickness (weighed as m_1) in the fatigue section or un-fatigue section after the flexural fatigue test was cut off and immersed in 100 mL of toluene at (30 ± 1) °C for 12 h, and then taken out (weighed as m_2) after absorbing solvent onto the surface. The swelling coefficient φ was obtained according to the following equation $\varphi = m_1/m_2$.

Stress relaxations

Stress relaxations of NR and NR/TBIR vulcanizates were determined by a RPA 2000 Rubber Process Analyzer (Alpha Technologies Co. US). NR and NR/TBIR compounds were cured in RPA at 150 °C for optimum cure time, and then the

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stress relaxation test of the vulcanizate was carried out at 60 °C with 70% strain for 10 min.

RESULTS AND DISCUSSION

Characterizations of TBIR

The NMR spectra and GPC curves of *trans*-1,4-poly(butadiene-*co*-isoprene) copolymers are shown in Fig. 1. The assignments of chemical shifts for the obtained NMR spectra are analyzed based on our previous works.[17,27,28] The corresponding molecular structural parameters are also summarized in Table 1. As shown in Table 1, the molecular weight and Mooney viscosity of TBIR increased gradually from TBIR-1 ($M_{\rm w} = 46.5 \times 10^4$, ${\rm ML}_{3+4}^{100\,^{\circ}{\rm C}} = 30.0$) to TBIR-4 ($M_{\rm w} = 144.4 \times 10^4$, ${\rm ML}_{3+4}^{100\,^{\circ}{\rm C}} = 85.5$). All the copolymers had about 15 mol% butadiene (B) incorporation and high *trans*-1,4-*trans*-1,4 (T-T) linkages. The chain structure in formation including 22 mol%−25 mol% butadiene-isoprene (BI) and isoprene-butadiene (IB) dyad sequence concentration and 71 mol%−75 mol% isoprene-isoprene (II) dyad sequence concentration, 7.0−8.0 number-average sequence length for isoprene units ($n_{\rm I}$) and 1.3 number-average sequence length for butadiene units ($n_{\rm B}$) indicated that the TBIR were copolymers with multi *trans*-1,4-polyisoprene (TPI) blocks.

Physical and Mechanical Properties of TBIR

Molecular weight as one of the important factors influences the crystallization behavior and mechanical properties of polymer materials.[29−35] The DSC curves of TBIR with different molecular weights are shown in Fig. 2. TBIR are semi-crystalline copolymers with the melting temperature ($T_{\rm m}$) around 27−36 °C, which is much lower than that of TPI, indicating the imperfect crystal. With increasing molecular weight of TBIR, the crystallization temperature ($T_{\rm c}$), melting temperature ($T_{\rm m}$), and crystallization melting enthalpy (ΔH) of TBIR decreased slightly due to the increased chain entanglements which might lead to the crystal defects of the TPI blocks.

The stress-strain curves of TBIR with different molecular weights and NR raw rubber are shown in Fig. 3. The tensile strength of TBIR was in the range of 10−15 MPa and increased with increasing molecular weight, which was possibly caused by the enhanced chain entanglements.[28] Compared with the amorphous NR with about 0.4 MPa green strength, TBIR showed much higher green strength and Young’s modulus (the initial slope of the stress-strain curves in Fig. 3).

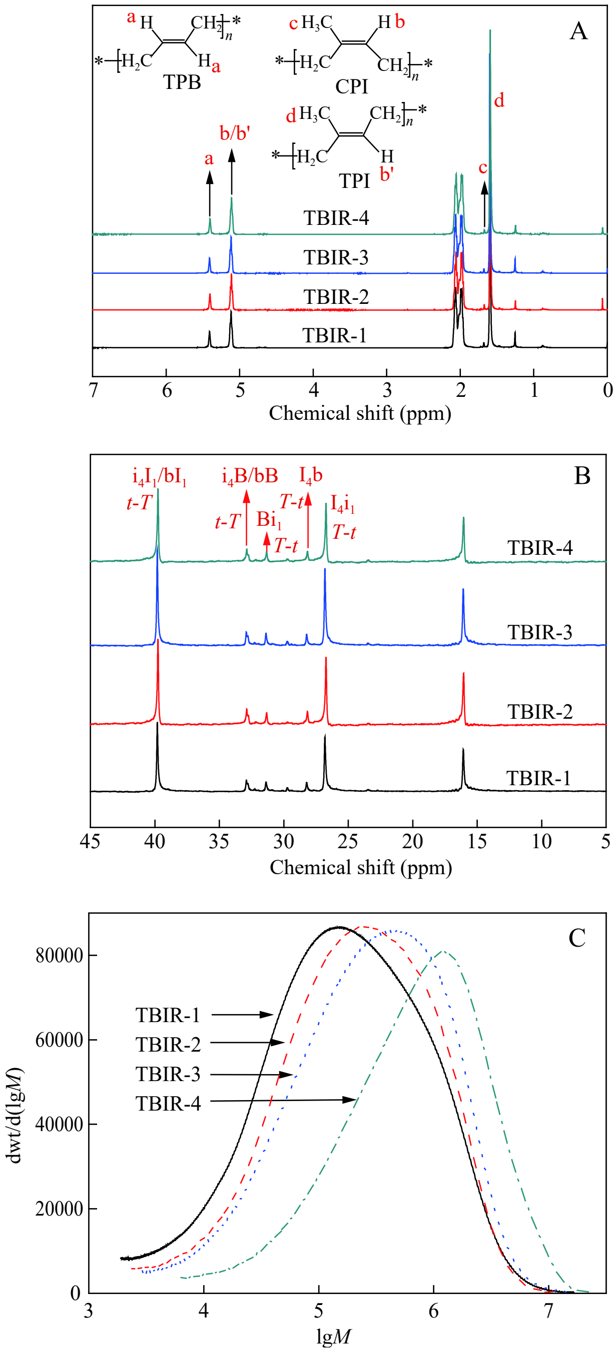

Fig. 1 (A) ^{1}H-NMR and (B) ^{13}C-NMR spectra and (C) GPC curves of TBIRs with different molecular weights

Curing Characteristics of NR and NR/TBIR Compounds

The curing characteristics of NR and NR/TBIR (80/20) compounds proceeding on vulka-meter at 150 °C are displayed in Table 2. The minimum torque ($M_{\rm L}$) of the NR/TBIR compounds reflecting the melt viscosity at 150 °C increased with the increasing TBIR molecular weight. The torque difference between the maximum and the minimum torque ($M_{\rm H} - M_{\rm L}$) of the compounds representing the crosslinking density after curing reaction[36] increased as the molecular weight of TBIR increased, which was further proved by the increased crosslinking density measured by the crosslinking density analyzer and NMR spectrometer. Beside the increased crosslinking density, the polysulfide-bond percentage in NR/TBIR (80/20) vulcanizates increased with the increasing molecular weight of TBIR. The similar scorch time ($t_{\rm c10}$) and optimum cure time ($t_{\rm c90}$) of NR/TBIR blends indicated that the curing characteristic was hardly affected by the molecular weight of TBIR. However, due to the relatively high Mooney viscosity and molecular weight of NR, the incorporation of 20 phr TBIR with relatively low molecular weight led to slight decrease in the crosslinking density of the NR/TBIR blends. Therefore, the NR/TBIR-4 vulcanizate with relatively high molecular weight TBIR-4 incorporation had the similar

Table 1 Micro-structures of TBIRs with different molecular weights

Rubber	$ML_{3+4}^{100°C}$	M_w [a] $\times 10^{-4}$	M_w/M_n [a]	B [b] (mol%)	Isoprene (I) unit [b]			Butadiene (B) unit [b]			Dyad sequence distribution [c]			n_B [c]	n_I [c]
					trans-1,4	*cis*-1,4	3,4-	*trans*-1,4	*cis*-1,4	1,2-	II	IB+BI	BB		
TBIR-1	30.0	46.5	10.9	15.2	96.4	2.6	1.0	96.7	0.7	2.6	71.1	25.4	3.5	1.3	6.6
TBIR-2	43.8	51.8	8.4	15.6	97.6	1.9	0.6	99.0	0.8	0.2	72.7	23.1	4.3	1.4	7.3
TBIR-3	63.4	65.2	8.5	14.9	97.5	2.4	0.1	97.5	2.2	0.3	75.1	21.7	3.3	1.3	7.9
TBIR-4	85.5	144.4	7.6	15.6	96.5	2.5	1.0	96.5	3.0	0.5	73.3	22.9	3.8	1.3	7.4

[a] Measured by GPC; [b] Measured by ^{1}H-NMR; [c] Measured by ^{13}C-NMR

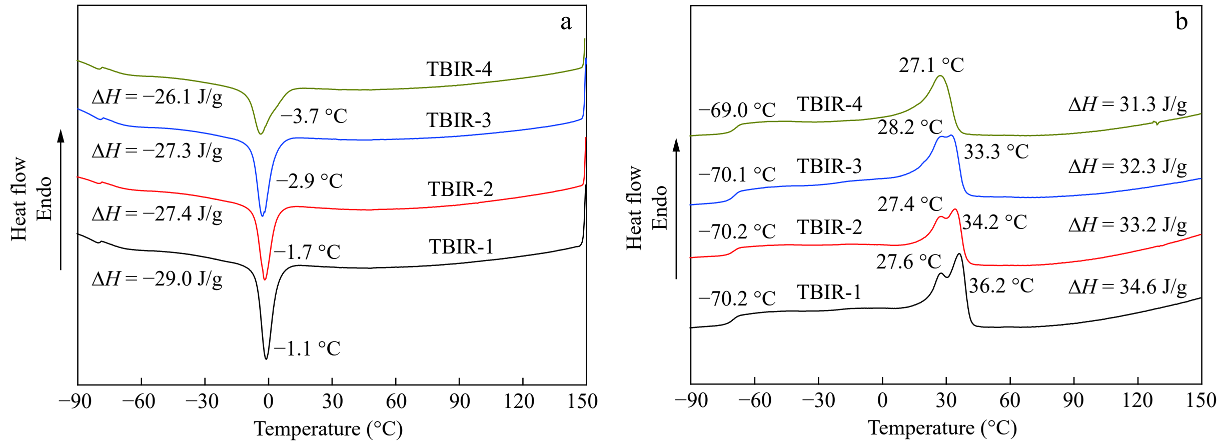

Fig. 2 DSC curves of TBIRs with different molecular weights: (a) cooling; (b) the second heating

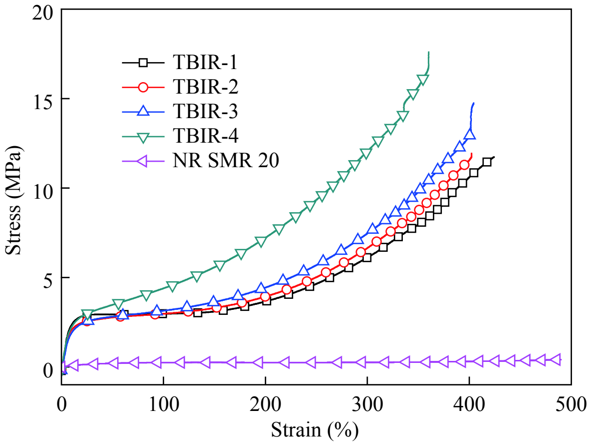

Fig. 3 Stress-strain curves of TBIRs with different molecular weights and NR

crosslinking density but an interestingly high polysulfide-bond percentage (88.4%) when compared with NR vulcanizate.

Characterization and Mechanical Properties of NR/TBIR Vulcanizates

NR or NR/TBIR compounds were compression molded at 150 °C for optimum cure time under 10 MPa, and the vulcanizates were finally obtained. The mechanical properties of NR and NR/TBIR (80/20) vulcanizates are displayed in Table 2. The results showed that, with the increase in molecular weight of TBIR, the tensile strength, modulus, hardness, rebound, and the abrasion resistance of the NR/TBIR vulcanizates increased, while the tear strength and elongation at break decreased. These can be explained by the increased crosslinking density of the NR/TBIR vulcanizates with higher molecular weight TBIR incorporation. Still, the tear strength of NR/TBIR-1 and NR/TBIR-2 vulcanizates was much higher than that of NR, which can be attributed to the improved adhesion from low molecular weight TBIR incorporation, but the lower crosslinking densities lead to the lower abrasion resistance and hardness of NR/TBIR-1 and NR/TBIR-2 vulcanizates than that of NR vulcanizate.

The tan*δ* versus temperature curves of NR and NR/TBIR vulcanizates are shown in Fig. 4. The tan*δ* peaks for both NR and NR/TBIR vulcanizates changed little for the position and the height, which indicated that TBIR had good compatibility with NR.

The flexural fatigue properties of NR and NR/TBIR (80/20) vulcanizates are displayed in Fig. 5. As can be seen, NR/TBIR with higher molecular weight TBIR showed a more significant increase in the fatigue resistance. The flexural fatigue time for both the 1st-class crack and the 6th-class crack of the NR/TBIR vulcanizates were distinctly increased when compared with that of NR vulcanizate. Even NR/TBIR-1 vulcanizate with the lowest molecular weight TBIR-1 incorporation showed almost 2 times higher flexural fatigue resistance than NR vulcanizate. Therefore, we can deduce that whether for NR/TBIR-1 with slightly decreased crosslinking density and polysulfide-bond percentage or for NR/TBIR-4 with similar crosslinking density and slightly increased polysulfide-bond percentage, the NR/TBIR vulcanizates presented much higher fatigue resistance than that of NR vulcanizate. Therefore, in this case, both the crosslinking density and polysulfide-bond percentage had no critical influence on the outstanding fatigue properties of the NR/TBIR vulcanizates.

Table 2 Micro-structures of TBIRs with different molecular weights

Rubber blends (weight ratio)	NR	NR/TBIR-1	NR/TBIR-2	NR/TBIR-3	NR/TBIR-4
	100	80/20			
Curing characteristics of the compounds					
M_L (dN·m)	1.15	1.20	1.25	1.29	1.50
M_H (dN·m)	12.78	12.15	12.32	12.56	13.19
$M_H - M_L$ (dN·m)	11.63	10.95	11.07	11.27	11.69
t_{c10} (min)	7.42	7.77	8.06	7.86	7.72
t_{c90} (min)	16.80	18.93	19.18	19.00	19.04
Crosslinking density of the vulcanizates					
Total CLD ($\times10^{-5}$ mol/cm^3)	11.2	9.71	9.85	10.57	10.97
Poly CLD ($\times10^{-5}$ mol/cm^3)	9.51	7.93	8.21	9.07	9.70
Poly CLD/Total CLD (%)	84.9	81.7	83.3	85.8	88.4
Properties of the vulcanizates					
Tensile strength (MPa)	27.8	25.8	25.7	26.4	28.0
Modulus at 100% (MPa)	1.7	1.4	1.5	1.6	1.6
Modulus at 300% (MPa)	8.5	6.1	6.4	6.9	7.7
Elongation at break (%)	644	750	722	728	702
Tear strength (kN/m)	56.0	75.4	62.7	59.9	40.4
Hardness (Shore A)	59	57	58	58	59
Rebound (%)	53	53	53	54	55
DIN abrasion (cm^3/40m)	0.157	0.162	0.161	0.151	0.148

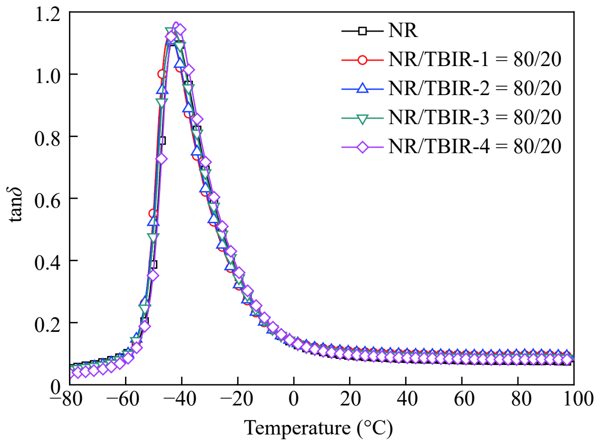

Fig. 4 tanδ versus temperature curves of NR and NR/TBIR vulcanizates

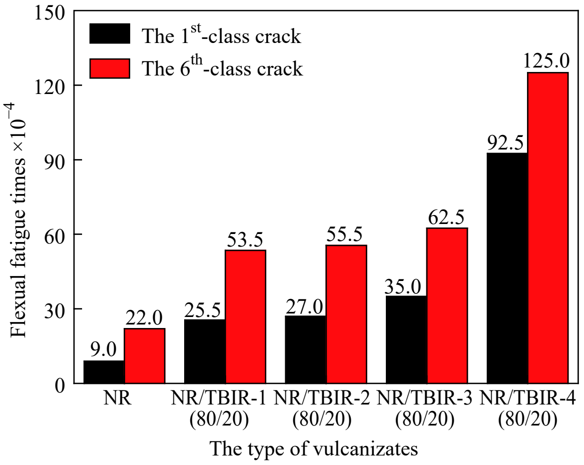

Fig. 5 Flexural fatigue properties of NR and NR/TBIR vulcanizates

The statistic distribution of CB agglomerates in the NR and NR/TBIR vulcanizates are shown in Fig. 6. A large number of agglomerates in the range of 20−40 μm were observed in the NR vulcanizate. Interestingly, the amount of larger CB agglomerates (20−40 μm) reduced obviously in the NR/TBIR vulcanizates, and the filler dispersion became much better with the higher molecular weight TBIR incorporation. Normally, the larger filler aggregates as structure flaws will yield cracks and accelerate failure of the rubber. The better filler dispersion will contribute to an improved flex fatigue resistance of NR/TBIR vulcanizates.

Table 3 shows the swelling coefficients (φ) of the specimens after flexural fatigue tests. It is interesting to see that φ of the NR vulcanizate in the fatigue section decreased when compared with specimen in the un-fatigue section, which indicated the decreased crosslinking density of the specimen undergoing fatigue test. We attribute this phenomenon to the degradation of NR vulcanizate during the long time flexural fatigue test. The φ values of NR/TBIR-1 and NR/TBIR-2 vulcanizates in the fatigue section changed little when compared with specimen in the un-fatigue section, while those of NR/TBIR-3 and NR/TBIR-4 vulcanizates increased after the fatigue test compared with those without suffering fatigue history. These results indicate that the incorporation of TBIR into NR helps to maintain the stability of the polymer network structure. The much faster stress relaxation of the NR/TBIR vulcanizates at 0.1 s than the NR vulcanizate as shown in Table 3 and Fig. 7 would weaken the stress concentration during fatigue and help NR/TBIR vulcanizates to present better fatigue resistance.

Therefore, the flexural fatigue properties of NR/TBIR (80/20) vulcanizates could be greatly improved by TBIR with different molecular weights (1.8 to 9.3 times higher

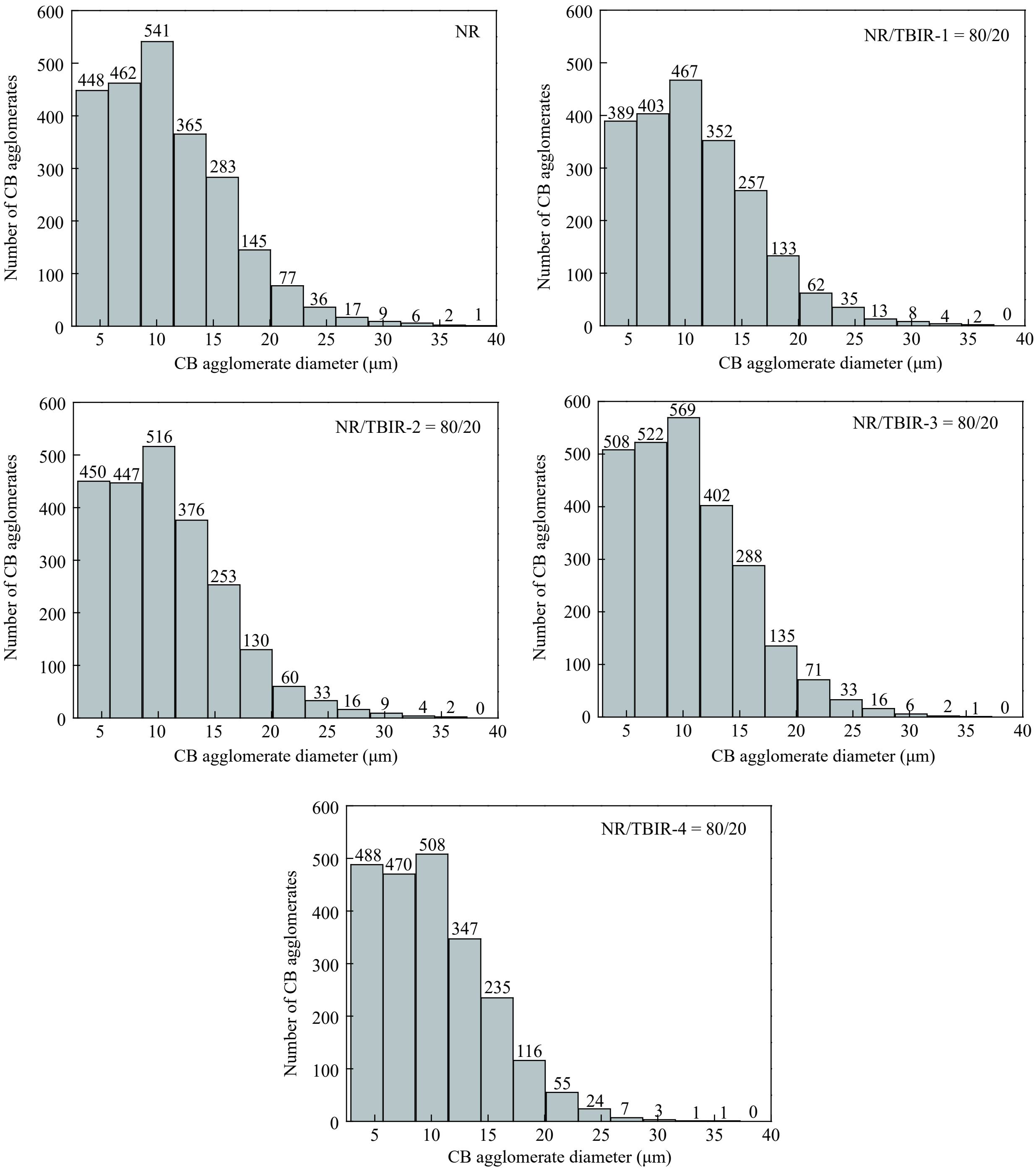

Fig. 6 Particle distribution of CB agglomerates in the NR and NR/TBIR vulcanizates

Table 3 Swelling coefficient and stress decline percentage of the NR and NR/TBIR vulcanizates

Rubber blends (weight ratio)		NR	NR/TBIR-1	NR/TBIR-2	NR/TBIR-3	NR/TBIR-4
		100	80/20			
φ	Un-fatigue section	0.325	0.309	0.308	0.291	0.303
	Fatigue section	0.311	0.308	0.309	0.317	0.318
Stress decline percentage at 0.1 s (%)		9.88	11.87	11.49	11.04	10.31

than that of NR vulcanizate) thanks to the unique features of TBIR like moderate crystallizability, higher green strength, good compatibility with NR, for they can determine the evolution of filler networks in the vulcanizates,[37,38] and then endow the NR/TBIR vulcanizates with outstanding flexural fatigue resistance when the molecalar weight is not too low.

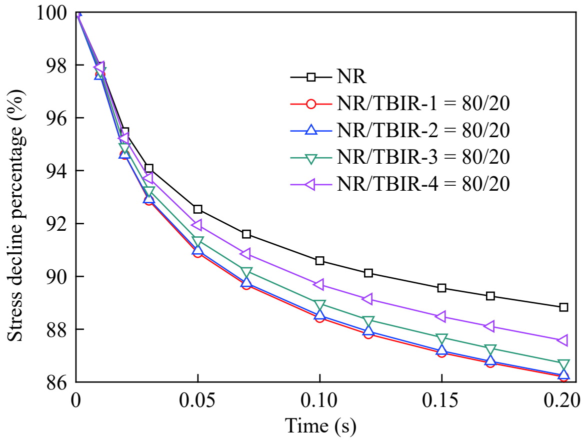

Fig. 7 The stress relaxation of NR and NR/TBIR vulcanizates

CONCLUSIONS

TBIR with different molecular weights were high *trans*-1,4-copolymers of butadiene and isoprene with the similar chain sequence distribution and crystalline *trans*-1,4-polyisoprene (TPI) blocks. The green strength and modulus of TBIR increased with the increasing molecular weight, which are higher than those of NR. The NR/TBIR vulcanizates with 40 phr carbon black filling showed increased tensile strength, hardness, modulus, rebound, abrasion resistance, and flexural fatigue properties with the increasing TBIR molecular weight. Compared with NR vulcanizate, all the NR/TBIR vulcanizates with different molecular weights showed outstanding flexural fatigue resistance (1.8 to 9.3 times higher). The unique features of TBIR, such as moderate crystallizability, higher green strength, and good compatibility with NR, contribute to the unique network structure of the NR/TBIR vulcanizates including higher rubber matrix strength and modulus, faster stress relaxation, more stable polymer network structure under flexural fatigue test and much better filler dispersion. The TBIR with a wide range of molecular weight are ideal rubbers for high performance tires with much longer fatigue serving life.

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REFERENCES

1 Castellano, M.; Conzatti, L.; Costa, G.; Falqui, L.; Turturro, A.; Valenti, B.; Negroni, F. Surface modification of silica: 1. Thermodynamic aspects and effect on elastomer reinforcement. *Polymer* **2005**, *46*, 695−703.

2 Prasertsri, S.; Rattanasom, N. Fumed and precipitated silica reinforced natural rubber composites prepared from latex system: Mechanical and dynamic properties. *Polym. Test.* **2012**, *31*, 593−605.

3 Wang, Y. X.; Ma, J. H.; Zhang, L. Q.; Wu, Y. O. Revisiting the correlations between wet skid resistance and viscoelasticity of rubber composites *via* comparing carbon black and silica fillers. *Polym. Test.* **2011**, *30*, 557−562.

4 Ismail, H.; Suzaimah, S. Styrene butadiene rubber/epoxidized natural rubber blends: Dynamic properties, curing characteristics and swelling studies. *Polym. Test.* **2000**, *19*, 879−888.

5 Mathew, N. M.; De, S. K. Scanning electron microscopy studies in abrasion of NR/BR blends under different test conditions. *J. Mater. Sci.* **1983**, *18*, 515−524.

6 Wu, W. L.; Chen, D. J. Silica-modified SBR/BR blends. *J. Appl. Polym. Sci.* **2015**, *120*, 3695−3700.

7 Wang, Y. X.; Wu, Y. P.; Li, W. J.; Zhang, L. Q. Influence of filler type on wet skid resistance of SSBR/BR composites: Effects from roughness and micro-hardness of rubber surface. *Appl. Surf. Sci.* **2011**, *257*, 2058−2065.

8 Rattanasom, N.; Saowapark, T.; Deeprasertkul, C. Reinforcement of natural rubber with silica/carbon black hybrid filler. *Polym. Test.* **2007**, *26*, 369−377.

9 Arrighi, V.; Mcewen, I. J.; Qian, H.; Prieto, M. B. S. The glass transition and interfacial layer in styrene-butadiene rubber containing silica nanofiller. *Polymer* **2003**, *44*, 6259−6266.

10 Stöckelhuber, K. W.; Svistkov, A. S.; Pelevin, A. G.; Heinrich, G. Impact of filler surface modification on large scale mechanics of styrene butadiene/silica rubber composites. *Macromolecules* **2011**, *44*, 4366−4381.

11 Yatsuyanagi, F.; Suzuki, N.; Ito, M.; Kaidou, H. Effects of secondary structure of fillers on the mechanical properties of silica filled rubber systems. *Polymer* **2001**, *42*, 9523−9529.

12 He, A. H.; Huang, B. C.; Jiao, S. K.; Hu, Y. L. Synthesis of a high-*trans*-1,4-butadiene/isoprene copolymers with supported titanium catalysts. *J. Appl. Polym. Sci.* **2003**, *89*, 1800−1807.

13 Jiang, X. B.; Zhang, Q. F.; He, A. H. Synthesis and characterization of *trans*-1,4-butadiene/isoprene copolymers: Determination of sequence distribution and thermal properties. *Chinese J. Polym. Sci.* **2015**, *33*, 815−822.

14 Zhang, Q. F.; Jiang, X. B.; He, A. H. Synthesis and characterization of *trans*-1,4-butadiene/isoprene copolymers: Determination of monomer reactivity ratios and temperature dependence. *Chinese J. Polym. Sci.* **2014**, *32*, 1068−1076.

15 He, A. Synthesis of high *trans*-1,4-butadiene-isoprene copolymers by supported titanium catalysts. *Acta Polymerica Sinica* (in Chinese) **2002**, 19−24.

16 Niu, Q. T.; Jiang, X. B.; He, A. H. Synthesis of the spherical *trans*-1,4-polyisoprene/*trans*-1,4-poly(butadiene-*co*-isoprene) rubber alloys within reactor. *Polymer* **2014**, *55*, 2146−2152.

17 Niu, Q. T.; Zou, C.; Liu, X. Y.; Wang, R. G.; He, A. H. Isothermal crystallization fractionation and fraction characterization of *trans*-1,4-poly(isoprene-*co*-butadiene). *Polymer* **2017**, *109*, 197−204.

18 Wang, H.; Zou, C.; He, A. H. Characterization of *trans*-1,4-poly(butadiene-*co*-isoprene) copolymer rubber and its application as hump strip stocks in PCR tires. *Acta Polymerica Sinica* (in Chinese) **2015**, 296−305.

19 He, A. H.; Yao, W.; Huang, B. C. Properties of a new synthetic rubber: High-*trans*-1,4-poly(butadiene-*co*-isoprene) rubber. *J. Appl. Polym. Sci.* **2004**, *92*, 2941−2948.

20 Wang, H.; Cui, H. H.; Ma, Y. S.; Zhang, J. P.; Song, L. Y.; He, A. H. The study of *trans*-1,4-poly(butadiene-*co*-isoprene) copolymer rubbers as tire belts stocks. *Polym. Bull.* **2016**, 61−67.

21 Wang, H.; Song, L. Y.; Ma, Y. S.; Wang, R. G.; He, A. H. The structures and properties of high performance PCR tire tread stock modified with *trans*-1,4-poly(butadiene-*co*-isoprene) copolymer rubber. *Acta Polymerica Sinica* (in Chinese) **2018**, 419−428.

22 Zhang, X. P.; Cui, H. H.; Song, L. Y.; Ren, H. C.; Wang, R. G.; He, A. H. Elastomer nanocomposites with superior dynamic

mechanical properties *via trans*-1,4-poly(butadiene-*co*-isoprene) incorporation. *Compos. Sci. Technol.* **2018**, *158*, 156−163.

23 Wang, H.; Zhang, J. P.; Wang, R. G.; He, A. H. Properties of nature rubber/high *trans*-1,4-poly(butadiene-*co*-isoprene) rubber blends. *China Rubber Ind.* **2018**, *65*, 167−172.

24 Zhang, Z. P.; Wang, H.; Ren, H. C.; Wang, R. G.; He, A. H. Rubber nanocomposites with nano-scale phase structures and kinetically inhibited filler flocculation for enhanced integrated performances *via* reactive multi-block copolymer incorporation. *Ind. Eng. Chem. Res.* **2019**, *58*, 917−925.

25 Wang, H.; Zhang, X. P.; Nie, H. R.; Wang, R. G.; He, A. H. Multi-block copolymer as reactive multifunctional compatibilizer for NR/BR blends with desired network structures and dynamical properties: Compatibility, *co*-vulcanization and filler dispersion. *Comps. Part A* **2019**, *116*, 197−205.

26 Boochathum, P.; Prajudtake, W. Vulcanization of *cis*- and *trans*-polyisoprene and their blends: Cure characteristics and crosslink distribution. *Eur. Polym. J.* **2001**, *37*, 417−427.

27 Niu, Q. T.; Li, W. T.; Liu, X. Y.; He, A. H. *Trans*-1,4-stereospecific copolymerization of isoprene and butadiene catalyzed by $TiCl_4/MgCl_2$ type Ziegler-Natta catalyst II. Copolymerization kinetics and mechanism. *Polymer* **2018**, *143*, 173−183.

28 Li, W. T.; Nie, H. R.; Shao, H. F.; Ren, H. C.; He, A. H. Synthesis, chain structures and phase morphologies of *trans*-1,4-poly(butadiene-*co*-isoprene) copolymers. *Polymer* **2018**, *156*, 148−161.

29 Marigo, A.; Marega, C.; Causin, V.; Ferrari, P. Influence of thermal treatments, molecular weight, and molecular weight distribution on the crystallization of β-isotactic polypropylene. *J. Appl. Polym. Sci.* **2010**, *91*, 1008−1012.

30 Benedetti, E.; D'Alessio, A.; Bertolutti, C.; Vergamini, P.; Fanti, N. D.; Pianca, M. Influence of molecular weight on the crystallization of poly(vinylidene fluoride). *Polym. Bull.* **1989**, *22*, 645−651.

31 Shao, H.; Wang, S.; He, A. The influence of molecular weight on high shear rate macroscopic rheological properties of polybutene-1 melts through rubber-processing analyzer. *Polym. Bull.* **2016**, *73*, 3209−3220.

32 Yuan, M.; Galloway, J. A.; Hoffman, R. J. Influence of molecular weight on rheological, thermal, and mechanical properties of PEEK. *Polym. Eng. Sci.* **2011**, *51*, 94−102.

33 Jordens, K.; Wilkes, G. L.; Janzen, J.; Rohlfing, D. C.; Welch, M. B. The influence of molecular weight and thermal history on the thermal, rheological, and mechanical properties of metallocene-catalyzed linear polyethylenes. *Polymer* **2000**, *41*, 7175−7192.

34 Zuiderduin, W. C. J.; Homminga, D. S.; Huétink, H. J.; Gaymans, R. J. Influence of molecular weight on the fracture properties of aliphatic polyketone terpolymers. *Polymer* **2003**, *44*, 6361−6370.

35 Nunes, R. W.; Martin, J. R.; Johnson, J. F. Influence of molecular weight and molecular weight distribution on mechanical properties of polymers. *Polym. Eng. Sci.* **2010**, *22*, 205−228.

36 Ismail, H.; Freakley, P. K.; Sutherland, I.; Sheng, E. Effects of multifunctional additive on mechanical properties of silica filled natural rubber compound. *Eur. Polym. J.* **1995**, *31*, 1109−1117.

37 Liu, X.; Zhao, S. H.; Zhang, X. Y.; Li, X. L.; Bai, Y. Preparation, structure, and properties of solution-polymerized styrene-butadiene rubber with functionalized end-groups and its silica-filled composites. *Polymer* **2014**, *55*, 1964−1976.

38 Huneau, B.; Masquelier, I.; Marco, Y.; Saux, V. L.; Noizet, S.; Schiel, C.; Charrier, P. Fatigue crack initiation in a carbon black-filled natural rubber. *Rubber Chem. Technol.* **2016**, *89*, 126−141.