

Properties of a New Synthetic Rubber: High-Trans 1,4-Poly(butadiene-*co*-isoprene) Rubber

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ABSTRACT: A high-trans 1,4-butadiene/isoprene copolymer (TBIP) was synthesized in a 5-L autoclave with hydrogen as an effective molecular weight modifier. The effects of hydrogen on the catalyst efficiency and molecular weight of the copolymers were investigated. The processability and physicochemical properties of TBIP and their relationship to the composition, composition distribution, and molecular weight of TBIP were examined in detail. Increasing the H₂ pressure effectively reduced the molecular weight of TBIP. The optimum Mooney viscosity of TBIP and the 1,4-butadiene molar content in the feed were 30–50 and 5–25%, respectively. No cis–trans isomerization was observed during the roll processing procedure for TBIP. The vulcanization characteristics of TBIP were similar to those of general rubbers, and no reverse vulcanization was observed for

TBIP. A high green strength was the typical characteristic of TBIP. Vulcanized TBIP (TBIR) with an optimum composition and molecular weight presented outstanding antifatigue properties and low heat buildup in comparison with general rubbers. Compared with general sidewall stock [natural rubber (NR)/butadiene rubber (BR) = 50/50], TBIR exhibited a greater than 15-fold increase in its crack-initiation resistance. The other mechanical properties of TBIR were similar to those of 50/50 NR/BR. The heat-aging mechanism of TBIR was crosslinking aging. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2941–2948, 2004

Key words: conjugated polymers; rubber; vulcanization; mechanical properties

INTRODUCTION

With the advancements of the automobile industry and the enhancement of people's safety consciousness, the demands of high-performance tire stocks are becoming more and more urgent from a practical point of view. High-trans 1,4-configuration diene polymers, as new kinds of rubber materials, are attracting much attention. It is generally accepted that a high-trans 1,4-polydiene possesses excellent dynamic properties, including excellent antifatigue properties, low rolling resistance, low heat buildup, and low abrasion loss, which are necessary for high-performance tire stock.^{1–5} Trans 1,4-configuration polymer chains have excellent flexibility, which might contribute to the low-temperature and dynamic properties of the polymers.⁶ In a previous publication,⁷ a new kind of trans 1,4-configuration synthetic rubber [i.e., a high-trans 1,4-butadiene/isoprene copolymer (TBIP)] was reported. The copolymerization of 1,4-butadiene (Bd)

and isoprene (Ip) with supported titanium catalysts was studied in detail. The chemical structure of TBIP was characterized by a high-trans 1,4-configuration: the trans 1,4-content of Ip units was greater than 98%, and the trans 1,4-content of Bd units was greater than 90%. The reactivity of Bd was greater than that of Ip. The melting point and glass-transition temperature of poly(butadiene-*co*-isoprene) were 30–40 and about –74°C, respectively. In this study, the physicochemical properties of the new rubber were investigated. The results indicated that vulcanized TBIP (TBIR) possessed excellent dynamic properties. The antifatigue properties of TBIR were remarkably higher than those of general sidewall stock [50/50 natural rubber (NR)/butadiene rubber (BR)]. Therefore, it appears that TBIR is a promising candidate as sidewall stock for high-performance tires.

EXPERIMENTAL

Materials and agents

Titanium tetrachloride (TiCl₄; >98% purity; Qilu Petrochemical Co., Shandong, China), triisobutyl aluminum [Al(i-Bu)₃; >98% purity; Yanshan Petrochemical Co., Beijing, China], and anhydrous magnesium dichloride (MgCl₂; >98% purity; Beijing In-

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stitute of Chemical Technology, Beijing, China) were used without further purification. Hydrogenation gasoline (polymerization-grade; Qilu Petrochemical) was distilled and stored over molecular sieves under dry nitrogen.

Bd (polymerization-grade; Qilu Petrochemical) was evaporated from a container, dried by passage through a column packed with molecular sieves, and absorbed into a reactor with the proper solvent at about 0°C.

Ip (polymerization-grade; Jinshan Petrochemical Co., Shanghai, China) was refluxed for about 1 h over CaH₂ and then was distilled and stored over molecular sieves under dry nitrogen.

Nitrogen (extrapure-grade; 99.999% purity) was dried through a P₂O₅ column.

Hydrogen (extrapure-grade; 99.999% purity) was used without further purification.

Smoked-sheet 3 NR (NR-RSS3; Malaysia) was kindly supplied by Qingdao Rubber Co. (China).

BR (BR-9000) and styrene-butadiene rubber (SBR; SBR-1502) were supplied by Qilu Petrochemical

The other agents were all chemically pure products.

Preparation of the catalyst and copolymers

The catalyst was prepared in our lab. A milling kettle with a certain number of stainless balls was degassed thoroughly by evacuation and was purged with nitrogen several times under heat before it was used. Prescribed amounts of anhydrous MgCl₂ were added into the milling kettle and were milled for about 24 h, and then a prescribed amount of TiCl₄ was added; the mixture was milled for about 2 days. A supported titanium catalyst (TiCl₄/MgCl₂) was obtained. The titanium content of the catalyst used in this work was 1.8 wt % (unless noted otherwise).

The copolymerization of Bd and Ip was carried out in a 5-L stainless autoclave that was dried thoroughly by evacuation and purging with nitrogen several times under heat before use. Prescribed amounts of the solvent (hydrogenation gasoline), monomers (Bd and Ip) in a consent ratio, Al(i-Bu)₃, and titanium catalyst were added to the reactor successively at certain temperatures for copolymerization. The reaction was terminated with an ethyl alcohol solution containing 1% antiager 264, and the products were coagulated, repeatedly washed with ethyl alcohol, and then dried in an evacuated oven at 30°C.

Sample preparation

The vulcanization mixture formulations were as follows: (1) 100 phr poly(butadiene-*co*-isoprene) (or BR-9000 or NR-RSS3), 2 phr stearic acid, 5 phr zinc oxide, 50 phr carbon black N330, 1 phr accelerator N-cyclo-

hexyl-2-benzothiazole-sulfenamide (CZ), 2 phr sulfur, 7 phr operating oil, and 1 phr antioxidant 264 and (2) 100 phr SBR-1502, 2 phr stearic acid, 5 phr zinc oxide, 50 phr carbon black N330, 1 phr accelerator CZ, 1.75 phr sulfur, 7 phr operating oil, and 1 phr antioxidant 264.

The mixes were milled on a warm 6-in. two-roller mill; the mill opening was 1.4 mm, the front roll rate was 11 m/min, the back roll rate was 13.5 m/min, and the roll temperature was 50 ± 1°C. The vulcanizations were performed on a vulcanizing press using the cure time predicted by the Mooney vulcanometer (the optimum vulcanization time (t_{90}) + mold lag (~ t_{90} + 20%) at 150 ± 1°C.

Measurements

The Fourier transform infrared (FTIR) spectra of TBIP were taken on a Nicolet FTIR spectrophotometer (USA) with films on KBr discs. The microstructure and composition of the copolymers were determined as indicated in the literature.⁸⁻¹⁰ The Mooney viscosity (ML₁₊₄¹⁰⁰) was measured with an EK-2000M Mooney viscometer (Ektron tek, Taiwan) at 100°C according to GB1232-82. The vulcanization characteristics were evaluated with an EK-2000P Mooney vulcanometer (Ektron tek) at 150°C and at a torque angle of 1° according to GB9869-88. The intrinsic viscosity ($[\eta]$) of the copolymers was determined with an Ubbelohde viscometer (Shanghai, China) in toluene at 30 ± 0.5°C.

Mechanical testing

The tensile testing of the copolymers was carried out on an XLL-250 testing machine (Guangzhou, China) with dumbbell-shaped specimens at a cross-head speed of 500 mm min⁻¹ according to GB528-82. The tear strength was tested on the same machine with right-angle-shaped specimens at a cross-head speed of 500 mm min⁻¹ according to GB530-81. The Shore A hardness of the copolymers was determined according to GB531-83. The abrasion resistance was measured on an Acron abrasion tester (Shanghai, China) according to GB1689-82. The heat buildup of TBIR was determined with a compression flexometer according to GB1687-83. The rebound resilience of TBIR was measured according to GB1681-82. The antifatigue data for TBIR were obtained on a Demattia fatigue tester (Beijing, China) according to GB4-836-82. The maximum distance and minimum distance of the clamps were 76 ± 0.5 and 19 ± 0.5 mm, respectively. The crack could be divided into six grades: the first-grade cracks were like pinpricks, and the numbers of the first-grade cracks were less than 10, whereas the sixth-grade crack was longer than 3 mm. The mechanical testing results of the aging samples were

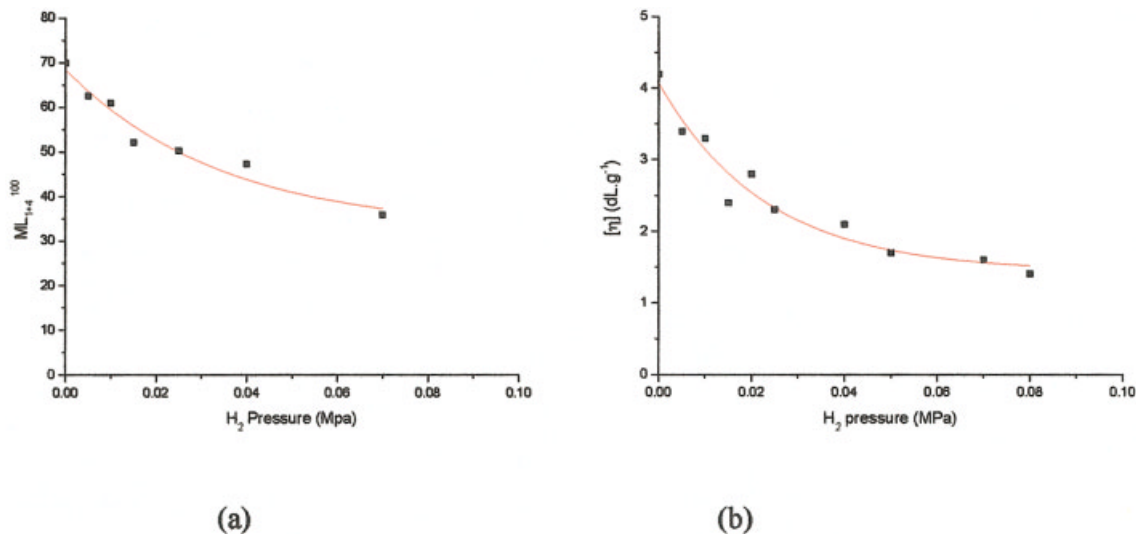


Figure 1 Effect of the H_2 pressure on (a) ML_{1+4}^{100} and (b) $[\eta]$ of the copolymers ($f_1^0 = 15$ mol %, Ti/M molar ratio = 5×10^{-5} , Al/Ti molar ratio = 200, $[M] = 3.5$ mol L^{-1} , temperature = $50^\circ C$, and time = 4 h).

obtained after 2 days of accelerated heat aging at $100^\circ C$ in an aging box. The average values of at least five tests are reported.

RESULTS AND DISCUSSION

Molecular weight regulation of the copolymers

It is generally accepted that the control of the molecular weight is important for synthetic rubbers for the sake of processability. According to previous results,⁷ TBIP synthesized with supported titanium catalyst possesses a relatively high molecular weight ($[\eta] \geq 3.4$ dL g^{-1}), which would be disadvantageous to the processability of copolymers. In this study, hydrogen was used as a molecular weight control agent, and high-trans 1,4-poly(butadiene-co-isoprene)s and high-trans 1,4-poly(butadiene-co-isoprene)s with different molecular weights of different molecular weights were synthesized in a 5-L autoclave through the regulation of the H_2 pressure in the presence of a $TiCl_4/MgCl_2-Al(i-Bu)_3$ catalyst system. The effects of the hydrogen pressure on ML_{1+4}^{100} and $[\eta]$ of the copolymers were investigated, as shown in Figure 1. ML_{1+4}^{100} and $[\eta]$ of the copolymers obviously decreased with an increase in the H_2 pressure. However, when the hydrogen pressure increased to one critical value, ML_{1+4}^{100} and $[\eta]$ of the copolymers decreased slightly with a further increase in the H_2 pressure. The appropriate H_2 pressure allowed us to get copolymers with the desired molecular weight in the range of $[\eta] = 1.3-2.5$ dL g^{-1} . Although an increase in the hydrogen pressure reduced the molecular weight of the copolymers, it also led to a reduced

copolymerization reaction rate (R_p), as shown in Figure 2. The effect of H_2 on the molecular weight of the copolymers and R_p could be explained by the following reaction mechanism:

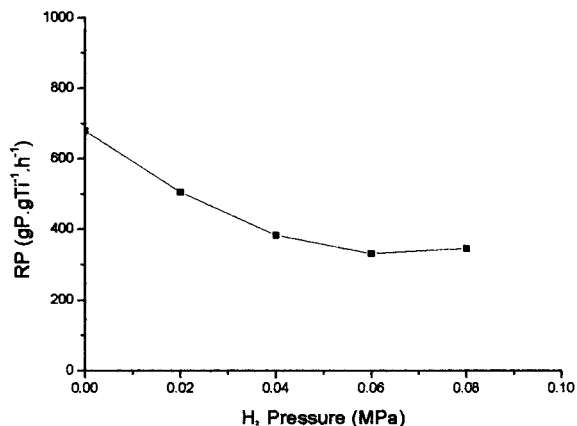
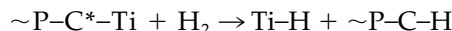


Figure 2 Effect of the H_2 pressure on R_p ($f_1^0 = 15$ mol %, Ti/M molar ratio = 5×10^{-5} , Al/Ti molar ratio = 200, $[M] = 3.5$ mol L^{-1} , temperature = $50^\circ C$, and time = 4 h).

TABLE I
Effect of ML_{1+4}^{100} of the Copolymers on the Mill Behaviors

	ML_{1+4}^{100}			
	60–70	50–60	40–50	30–40
Mill temperature	50–60°C	50–60°C	50–60°C	45–55°C
Plasticization behavior	Mill bagging, shrinkage, poor stickiness	Mill banding, shrinkage, poor stickiness	Mill banding, little shrinkage, good plasticity	Mill banding, no shrinkage, excellent plasticity
Blending behavior	Mill bagging, taking load with difficulty, mill shrinkage, rough surface	Taking load, mill banding, mill shrinkage, smooth surface	Taking load easily, mill banding, no shrinking, smooth surface	Taking load very easily, accepting high filler, mill banding, very smooth surface
Evaluation	Very poor	Poor	Good	Excellent

Polymerization conditions: $f_1^0 = 25 \text{ mol } \%$, Ti/M molar ratio = 1×10^{-4} , Al/Ti molar ratio = 200, $[M] = 3.5 \text{ mol/L}$, 50°C, 4 h.

In this polymerization system, H_2 transferred to Ti—C active centers as a chain-transfer agent, and Ti—H bonds and terminated polymer chains were formed. As we know, the Ti—H bonds were more stable than the Ti—C bonds, and so more energy was needed for the Ti—H bonds to react with the monomer (M) to form the Ti—C bonds. Once the Ti—C bonds were formed, they acted as active centers and initiated monomers to propagate other polymer chains. Therefore, the reduction of the molecular weight of the copolymers accompanied the reduction of the whole polymerization rate.

Processing performances of the copolymers

The processing performance of a synthetic rubber plays an important role in its properties. The mill behaviors of TBIP as a new rubber material were evaluated. The mill behaviors, including the plasticization and blending behaviors, of copolymers with different ML_{1+4}^{100} values are summarized in Table I. ML_{1+4}^{100} of TBIP had a strong influence on the processability. Copolymers with high ML_{1+4}^{100} values showed very poor mill behaviors, such as mill bagging, shrink, poor stickiness, and difficulty in taking up fillers, which might be attributed to the strong entanglements and high viscoelasticity of the macromolecules. With a reduction of ML_{1+4}^{100} , the copolymers presented an gradual improvement in the mill behaviors. The optimum ML_{1+4}^{100} value of the copolymers was 30–50 in view of the mill behaviors.

Cis–trans isomerization was observed during the mill processing procedure for NR,¹¹ and a quantity of cis 1,4-configuration structures of NR were found to transfer to trans 1,4-configuration structures after the mill processing procedure. Undoubtedly, the cis–trans isomerization of NR would have an influence on the vulcanization and subsequent mechanical properties of NR. Table II summarizes the effects of mill processing on the microstructure of TBIP. The results indi-

cated that TBIP with a trans 1,4-configuration had the desired structure stability. The trans 1,4-contents of Bd units and Ip units showed little change after plasticization. No trans–cis isomerization could be observed during the mill processing procedure for TBIP.

Vulcanization characteristics

Vulcanization curves of the copolymers and NR are shown in Figure 3. During the initial vulcanization step, the vulcanization torque values of the copolymers were higher than that of NR, whereas the vulcanization rates of the copolymers were slower than that of NR. The Mooney scorch times (t_{s1}) of the copolymers (3–5 min) were longer than that of NR (2.5 min), and this meant that the copolymers had better vulcanization security. The vulcanization curves of the copolymers were flat, and no distinct decrease could be observed during the final vulcanization step; this indicated that TBIP had no reversion on overcure. However, vulcanization reversion was observed for NR when the vulcanization time was longer than 11 min. TBIP clearly had good reversion resistance. The t_{90} values of the copolymers were about 7–9 min, being very similar to those of general rubbers. As a result,

TABLE II
Effect of Processing^a on the Microstructures of the Copolymers^b

	Microstructure				
	Bd units (%)			Ip units (%)	
	trans 1,4	cis 1,4	1,2	trans 1,4	3,4
Before plasticization	94.1	5.7	0.2	99.5	0.5
After plasticization	94.8	5.1	0.1	99.4	0.6

^a Plasticization conditions: mill temperature = 60°C, plasticization time = 10 min.

^b Microstructures of the copolymers were measured by FTIR spectra.^{8–10}

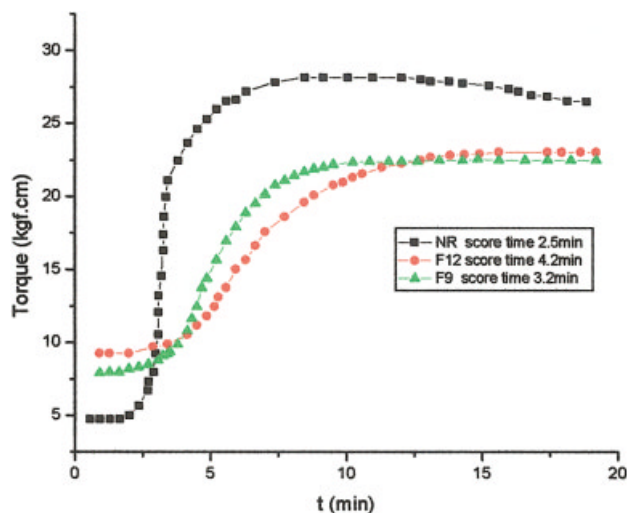


Figure 3 Vulcanization curves of TBIP and NR (vulcanization temperature = 150 ± 0.1°C and torque angle = 1°).

the TBIR copolymers could blend and cocure with general rubbers. It should be pointed out that blending and cocuring properties are vital for new synthetic rubbers

Mechanical properties of the vulcanized copolymers

The mechanical properties of the vulcanized copolymers with the same vulcanization recipe were investigated. The effects of the composition, composition distribution, and ML_{1+4}^{100} values of the copolymers on the vulcanizing properties are discussed in detail.

Table III shows that, for samples F9, F8, F12, F14, and F16, which had approximately the same ML_{1+4}^{100} values, the tensile modulus at 100% elongation, the tensile strength, and the tear strength improved with an increase in the Bd content in the copolymers. The

elongations at break of these vulcanized rubbers were higher than 560% and could reach as high as 790%. However, when the Bd molar content in the feed (f_1^0) was higher than 30%, the properties of the vulcanized rubber obviously deteriorated, and this may have been due to the heterogeneous composition, as reported previously.⁷ Therefore, the f_1^0 value should be kept below 25%.

However, the properties of F7 and F10 were much better than those of F9 and F8. These results reflected that the higher ML_{1+4}^{100} of the copolymers was, the better the properties of the vulcanized rubber were. Copolymers with relatively high ML_{1+4}^{100} values possessed relatively fewer chain ends and consequently achieved more uniformly dispersed crosslinkages in the vulcanized systems; this might have contributed to the enhanced mechanical properties of TBIR.

For F12 and F13 with similar ML_{1+4}^{100} and f_1^0 values, the modulus at 100% elongation, the tensile strength, and the tear strength increased with an increase in the conversion, whereas the elongation at break decreased. Because of the different reactivities of the two monomers, the Ip content in the copolymer increased with an increase in the conversion, and this resulted in the increasing probability of Ip long blocks. Without a doubt, the conversion had a strong influence on the composition distribution and consequent vulcanization properties of TBIR.

Dynamic properties of the vulcanized copolymers

For samples F9, F8, F12, and F14, both the abrasion resistance and rebound of the vulcanized copolymers improved with an increase in the Bd content in the copolymers. As we know, rebound at 23°C represents the wet skid resistance of vulcanized rubber: the lower the rebound value is at 23°C, the higher the wet skid

TABLE III
Mechanical Properties of the Vulcanized Copolymers

	Run							
	F7	F9	F10	F8	F12	F13	F14	F16
f_1^0 (mol %)	10	10	15	15	20	20	25	30
Concentration (wt %)	22	25	42	40	38	24	37	46
$F_1 - (\%)^a$		29.5		33.3	42.7	44	55.1	47
ML_{1+4}^{100}	64.7	28.2	62.2	31.9	28.0	29.2	50	48.7
Tensile modulus (MPa)								
100% elongation	2.5	1.4	2.0	1.7	1.7	1.5	1.9	3.7
200% elongation	4.1	2.4	3.3	2.7	2.9	2.3	3.2	
300% elongation	6.4	3.8	5.4	4.2	4.7	3.1	4.6	
Tensile strength (MPa)	14.9	11.2	15.8	11.4	12.5	11.5	13.7	12.0
Elongation at break (%)	560	702	658	675	690	790	738	300
Permanent set (%)	15	30	20	27	20	22.5	22.5	
Hardness (Shore A)	68	61	67	58	62	57	63	68
Tear strength (KN m ⁻¹)	47.8	36.8	44	37.7	39.3	35.1	43.3	64.4

^a $F_1 -$, the Bd mole constant in the copolymers, was determined by FTIR spectra.

TABLE IV
Dynamic Properties of the Vulcanized Copolymers

	Run						
	F7	F9	F10	F8	F12	F13	F14
F_1- (%) ^a		29.5		33.3	42.7	44	55.1
ML_{1+4}^{100}	64.7	28.2	62.2	31.9	28.0	29.2	50
Rebound							
23°C	42	27	37	29	31.5	33.5	36
70°C	48	31	38.5	30	34	36	38
Heat buildup (°C)	8	—	11	—	9	10	10
Abrasion loss (cm ³ 1.61 km ⁻¹)	0.15	0.26	0.22	—	0.33	—	0.27
Flex fatigue ($\times 10^4$ times)							
First-grade crack	>689	54.8	312.1	78.2	>689	323.8	16.8
Sixth-grade crack		513.7	584.2	263.5		541	134.9

^a F_1- , the Bd mole constant in the copolymers, was determined by FTIR spectra.

resistance is. Rebound at 70°C represents the rolling resistance of vulcanized rubber: the higher the rebound value is at 70°C, the lower the rolling resistance is. The rebound of TBIR in Table IV shows that both the wet skid resistance and rolling resistance of TBIR decreased with an increase in the Bd content in the copolymers. TBIR possessed relatively low heat buildup ($\leq 11^\circ\text{C}$) and excellent antifatigue properties. The crack-initiation resistance was outstanding. Especially for sample F12, first-grade crack was not observed even after 6,890,000-time fatigues.

The effects of ML_{1+4}^{100} on the dynamic properties of TBIR are summarized in Table IV. Rebound at both 23 and 70°C for samples F7 and F10 increased in comparison with that of F9 and F8. These results revealed that both the wet skid resistance and rolling resistance of TBIR obviously decreased with an increase in ML_{1+4}^{100} . The antifatigue properties improved significantly with an increase in ML_{1+4}^{100} . The effect of the molecular weight on the dynamic properties of TBIR could be explained by the chain-tail effect: the free

movements of chain tails result in lagging. The lower the molecular weight is, the more chain tails there are, and the consequent dynamic properties of vulcanized rubber are rather poor, such as an increase in the heat buildup and rolling resistance and a decrease in the antifatigue properties.

Aged properties of TBIR

The aged mechanical properties of TBIR are listed in Table V. The tensile modulus at 100% elongation, rebound, and hardness of aged TBIR increased, whereas the elongation at break decreased, in comparison with pristine TBIR. These results revealed that the heat aging of TBIR could be explained by a crosslinking aging mechanism.

Comparison of the properties between TBIR and general rubbers

Stocks used in different parts of a tire need different properties. The tire tread is the part of the tire in

TABLE V
Aging Properties of the Vulcanized Copolymers

	Run						
	F7	F9	F10	F8	F12	F13	F14
F_1- (%) ^a		29.5		33.3	42.7	44	55.1
ML_{1+4}^{100}	64.7	28.2	62.2	31.9	28.0	29.2	50
Tensile modulus (MPa)							
100% elongation	3.7	2.4	3.2	2.2	2.1	1.6	2.5
200% elongation	5.9	4.2	5.3	4.0	3.6	2.7	3.8
300% elongation	9.6	6.6	9.4	6.9	6.7	4.7	6.4
Tensile strength (MPa)	14.7	11.6	15.9	11.3	13.3	11.4	15.4
Elongation at break (%)	450	450	445	473	460	500	535
Permanent set (%)	26.8	29.8	27.5	28	29	29.4	28.5
Hardness (Shore A)	80	78	75	73	76	70	74
Rebound							
23°C		31.5	38.3	29.7	33.7		
70°C		33.5	42.2	33.8	38		

^a F_1- , the Bd mole constant in the copolymers, was determined by FTIR spectra.

TABLE VI
Comparison of the Properties of TBIR and Other General Rubbers

	Run					
	TBIR F7	TBIR F12	NR-RSS3	BR-9000	BR/NR (50/50)	SBR-1502
ML ₁₊₄ ¹⁰⁰	64.7	28	88.3	44.6		76.0
Green strength (MPa)	10.4	3.4	0.62	0.37	0.22	1.1
Elongation at break (%)	140	400	500	1000	660	700
Compounds (150°C)						
<i>t</i> _{s1} (min)	3.8	4.2	2.5	4.5	4.8	5.9
<i>t</i> ₉₀ (min)	8.6	11.4	6.2	7.7	6.3	16.1
Adherence	8	7	5	12	7	12
Tensile Modulus (MPa)						
100% elongation	2.5	1.7	2.5	1.6	1.7	1.7
200% elongation	4.1	2.9	5.5	3.3	3.2	3.8
300% elongation	6.4	4.7	9.3	5.3	5.2	6.5
Tensile strength (MPa)	14.9	12.5	24.5	17.5	19.4	19.9
Elongation at break (%)	560	690	580	640	770	640
Permanent set (%)	15	20	28	65	23	15
Hardness (Shore A)	68	62	66	63	59	65
Tear strength (KN m ⁻¹)	47.8	39.3	70	39.8	54	48.6
Viscoelasticity	22	22.0	26	38	25	27.8
Rebound						
23°C	42	31.5	37	48	39	37.5
70°C	48	34	49	56	44	41
Heat buildup (°C)	8	9	7	5.5	7	8.5
Abrasion loss (cm ³ 1.61 km ⁻¹)	0.150	0.327	0.369	0.069	0.281	0.098
Flex fatigue (×10 ⁻⁴ times)						
First-grade crack	>689	>689	5.3	160.5	36.6	60.2
Sixth-grade crack	—	—	18	163.5	240	96.8

contact with the road, and so tread stocks should possess high traction and abrasion resistance and low rolling resistance and heat buildup, all of which ensure driving safety and energy savings. The tire sidewall is the part enduring the most alternating stress, and so tire sidewall stocks should have high endurance life as well as high tensile modulus at 100% elongation. During driving, the sidewall stocks of tires suffer dynamic fatigue frequently, and as a result, cracks are generated. It is necessary for sidewall stocks, especially those of radical-ply lorry tires, to possess high antifatigue properties, low heat buildup, and high tensile modulus at 100% elongation. NR, BR, and SBR are the main general rubbers used in industrial tires. BR/NR (50/50) is one of the general sidewall stocks used widely in the tire industry.

The physicochemical properties of typical TBIP and general rubbers are listed in Table VI. TBIP had a high green strength and a low elongation at break in comparison with those of the general rubbers. The green strength of TBIP was about 3 times higher than that of SBR and 6 times higher than that of NR. The green strength of TBIP was related to its relatively high crystallinity. *t*_{s1} and *t*₉₀ of TBIR were similar to those of the general rubbers. The viscoelasticity of TBIP was lower than that of the general rubbers.

The tensile modulus at 100% elongation of TBIR was similar to that of the general rubbers; the tear strength,

rebound, and abrasion resistance of TBIR were between those of NR and BR. The heat buildup was very low and near that of NR/BR (50/50).

Generally, fatigue cracks of materials should undergo the following two stages: the crack-initiation stage and the crack-propagation stage. The results showed that SBR possessed excellent crack-initiation resistance (first-grade crack, 60.2 × 10⁴ times), but its crack-propagation resistance was poor (sixth-grade crack, 98.6 × 10⁴ times). The crack-initiation resistance of NR was rather poor (first-grade crack, 5.3 × 10⁴ times). The antifatigue properties of BR were the best among general rubbers. first-grade cracks were observed for BR after it was flexed 160.5 × 10⁴ times. As shown in Table VI, the antifatigue properties of TBIR (samples F7 and F12) were remarkable; first-grade cracks were not observed for TBIR even after it was flexed 689 × 10⁴ times. The first-grade crack resistance of TBIR was 100 times higher than that of NR, 15 times higher than that of NR/BR (50/50), and 4 times higher than that of BR.

The excellent dynamic properties of TBIR might be explained by the trans 1,4-configuration structures, which would endow the copolymers with better flexibility.

Therefore, trans Bd-Ip copolymers with optimum compositions and molecular weights have distinct dynamic properties, such as outstanding antifatigue

properties and low heat buildup. It appears that TBIR is a promising candidate for use as a sidewall stock for high-performance tires, especially radical-ply tires. TBIR has bright development prospects. Systematic studies of TBIR are being pursued.

CONCLUSIONS

In this research, high-trans 1,4-poly(butadiene-*co*-isoprene) was synthesized with hydrogen as an effective molecular weight control agent in the presence of supported titanium catalysts. The mechanical and processing properties were affected greatly by the composition, composition distribution, and molecular weight of TBIP. TBIR with ML_{1+4}^{100} values of 30–50, synthesized with 5–25 mol % butadiene in the feed, had good processing and mechanical properties. There was no trans–cis isomerization observed during the roll processing procedure for TBIP. The vulcanization characteristics of TBIP were similar to those of general rubbers, and no reversion on overcure was observed for TBIP. TBIP possessed a relatively high green strength. The tensile modulus at 100% elongation of TBIR was similar to that of general rubbers; the tear strength, rebound, and abrasion resistance of

TBIR were between those of NR and BR. The heat-aging mechanism of TBIR was crosslinking aging. TBIR with the optimum composition and molecular weight presented excellent dynamic properties in comparison with general rubbers. The crack-initiation resistance of TBIR was very attractive. Therefore, TBIR is considered a candidate for sidewall stocks of high-performance tires.

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