Progress of Synthesis and Application of *trans*-1,4-Polyisoprene

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ABSTRACT: A new technology to synthesize *trans*-1,4-polyisoprene (TPI) with bulk precipitation polymerization in the presence of a supported Ti catalysts was introduced. The termination of polymerization, stabilization of the polymer, and the adjustment of the molecular weight of TPI and its quality index are discussed. The blending and covulcanization of TPI with natural rubber (NR), styrene butadiene rubber (SBR), and butadiene rubber (BR) were studied. The blending compounds had outstanding dynamic mechanical properties, especially the rolling resistance, heat buildup, and wet skid resistance. Tread and sidewall compounds that contained TPI had a higher modulus, longer fatigue life, better abrasion resistance, lower rolling resistance, and lower buildup, which indicates that TPI is suitable for high-performance tire. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 81–89, 2001

Key words: *trans*-1,4-polyisoprene; bulk precipitation polymerization; dynamic mechanical properties; tread stock; high-performance tire

INTRODUCTION

High *trans*-1,4-polyisoprene (TPI), which is also called synthetic Gutta-percha rubber or Balata rubber, is a thermoplastic crystalline polymer at room temperature with a melting point (T_m) of 60°C. The TPI can be cured by the general vulcanization method of unsaturated rubber. With different crosslinking densities, TPI has different properties and purposes.[1,2] With low crosslinking density, TPI, whose molecular chain can still be crystalline, is a kind of heat-stimulated shape memory material.[3] When the crosslinking density increases to a critical point, the molecular chain becomes difficult to crystallize because of the restriction of the crosslinking network. Then, TPI becomes a kind of elastomer with excellent dynamic mechanical properties. TPI is widely used in medical materials, golf ball covers, electrical insulated materials, shape memory materials, and so on. Blends of TPI with natural rubber (NR), styrene butadiene rubber (SBR), and butadiene rubber (BR) have excellent processability and mechanical properties; in particular, the dynamic properties, such as flex fatigue resistance, are improved.[4] Tread and sidewall stocks have a higher modulus, longer fatigue life, better abrasion resistance, and lower heat buildup, which indicates that TPI may be used for high-performance tire.[4,5] Therefore, TPI is a promising new synthetic rubber.

EXPERIMENTAL

Synthesis of TPI

Materials

Commercially available isoprene (obtained from Shanghai Petro-Chemical Co. (Shanghai, China) by separation of carbon-5 hydrocarbon, the purity was no less than 99.5%) was used after it was dried by molecular sieves and purified by distillation. A supported Titanium (Ti) catalyst was prepared by ball grinding in our laboratory. Triisobutylaluminum, pure hydrogen, and antioxidant 2,6-bi-*tert*-butyl-4-methyl-phenol (BHT) were commercial products.

Procedures

Bulk precipitation polymerization of isoprene in the presence of the supported Ti catalysts was carried out in a sealed, replaced with pure N_2, 5-L reactor. The ingredients were added in the following sequence: isoprene, triisobutylaluminium, and Ti. Hydrogen as chain transfer agent was kept at a given pressure during polymerization. After polymerization for a given time, the polymerization was terminated with quantitative water, and antioxidant BHT was added in the reactor afterward at about 1 wt % of the product. After the unpolymerized monomer was distilled, powder polymer was obtained.

Rubber Characteristics

The high TPI in this study was synthesized in 140-L polymerization reactor with the supported Ti catalyst by bulk precipitation polymerization. The Mooney viscosity was 66. Both 1,4-unit and 3,4-unit contents were measured with ^{13}C-NMR and IR spectroscopy. The glass-transition temperature (T_g) and T_m were determined with differential scanning calorimetry. The natural rubber used was China national standard rubber No. 5. SBR1500 was commercially produced with an emulsion method with 23.5% styrene content. BR9000 had a high *cis*-1,4-content and was a commercial product from China Petro-Chemical Corp. (Zibo, China). Other ingredients were commercial products.

Mixing

All compounds were mixed with a laboratory internal mixer and a two-roll mill in accordance with ASTM D3182. Rubber processibility was

Table I   Standard Testing Method

Property	Standard
Vulcanization characteristics	ASTM D2084-81
Tension properties	ISO 34
Shore A hardness	ASTM D2240-86
Tear strength	ISO 34
Rebound	ISO 4662-86
Flex fatigue life	ASTM D518
Akron abrasion	BS903/A9-57
Tension fatigue	ASTM D4482
Heat air aging	ASTM D573-81

measured with a Mooney viscometer according to ASTM D1646. All compounds were cured to t_{90} + appropriate mold lag.

Property Test

The vulcanization characteristics, mechanical properties, dynamic properties, and aging resistance were determined according to related standard methods as shown in Table I.

SYNTHESIS OF TPI

Since the 1960s, British Dunlop Co., Canadian Polysar Co., and Japan Kuraley Co. have commercially produced TPI. The production mainly occurs by a solution polymerization process with vanadium (V)[6,7] or V—Ti[8,9] catalysts in aromatic hydrocarbon or fatty solvents. Because of the comparatively low efficiency of the catalyst, the sophisticated process, and the small production scale, the production cost of TPI is very high. Therefore, the price of TPI is as much ten times as that of NR or isoprene rubber (IR), which hinders the application of TPI, especially in the rubber and tire industries.

Bulk Precipitation Polymerization of Isoprene with a Supported Ti Catalyst

Isoprene can be polymerized with a supported Ti catalyst to obtain TPI whose *trans*-1,4-unit content is more than 98%.[10] The solution polymerization of isoprene has been carried out.[11] The kinetics of solution polymerization has also been studied.[11,12] Despite 5 years of research, the catalytic efficiency of solution polymerization with a supported Ti catalyst was not much higher than that with V or V—Ti catalysts, and it has the same shortcoming of too high a kinetic viscosity,
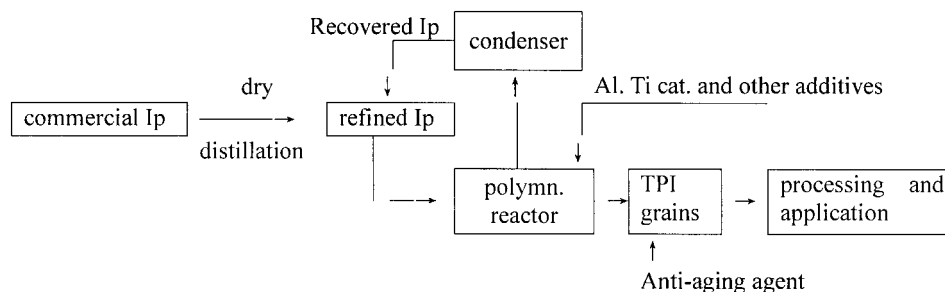
Figure 1 Schematic diagram of technological process.

which makes heat transfer, mass transfer, and power transmission very difficult. Because a large amount of solvent and monomer must be recycled and the products must be treated with complicated aftertreatment processes such as deashing, coacervation, drying, and so on, the production cost of TPI is still very high.

Fortunately, the bulk precipitation polymerization of isoprene was put into effect by controlling the conditions of polymerization according to the characteristics on which TPI is difficult to dissolve in isoprene.[11,13] The TPI grains are swollen by its monomer and are easy to adhere. So, how to prevent the TPI grains from adhering is key technology. The effects of catalyst preparation and polymerization conditions on the microstructure of polymer, catalytic efficiency, molecular weight, and its molecular weight distribution have been studied.[11] The kinetics of bulk precipitation polymerization has also been studied.[14] The schematic diagram of the technological process is shown in Figure 1.

The advantages of this method are as follows:

1. The catalytic efficiency can exceed 50 Kg of TPI/g of Ti higher than V catalyst by 20–30 times.
2. The viscosity of the polymerization system is very low, which is in favor of heat transfer, monomer diffusion, and stirring. Therefore, it is favorable to operate.
3. The *trans*-1,4-unit content of the TPI is more than 98%, and the properties of TPI can reach the level of a like product.
4. The polymerisate has grains about 1–5 mm and can be used directly as a powder rubber.
5. The technological process is very simple because of the avoidance of the solvent and aftertreatment; therefore, the production cost is much lower.
6. It causes no environmental pollution.

We estimate that the price of TPI synthesized by this method will decrease to close that of NR, which makes the use of TPI in the general purpose rubber and tire industries advantageous.

The experimental results of 3000-mL, 10-L, and 100-L reactors showed that the bulk precipitation polymerization process is feasible and effective.

Termination of Polymerization and Stabilization of Polymer[15]

It is necessary for active centers in coordination polymerization to be terminated. If unterminated TPI is exposed directly in air, active centers will react with oxygen to produce peroxide and initiate autoxidation.[16] TPI produced by bulk precipitation polymerization is in the form of loose grains. Attempts have been made to terminate the active centers with air directly, but TPI degrades rapidly and severely and becomes yellow during storage.

TPI, containing many double bonds, is unstable to oxygen, ozone, light, mechanical shear, and so on. A suitable antioxidant should be added. The effects of aftertreatment patterns and aging of TPI on its molecular weight and properties have been studied.[15]

The untreated TPI became worse because of aging. Its molecular weights decreased rapidly during storage. The crystal forms of TPI changed during aging, the high melting peak gradually disappeared, and the crystallinity decreased, but the microstructure of the TPI did change.

The ideal and cheap aftertreatment manner is termination with quantitative water and the addition of 1 wt % antioxidant BHT, which can guarantee the purity of the recycled monomer and stability of TPI during storage.

Table II   Main Structure and Properties of TPI

Appearance	Milky white particle
Content of *trans*-1,4-unit, (%)	≥98
Money viscosity ($ML_{3+4}^{100°C}$)	30–90
T_g (°C)	−53
Density (g/cm^3)	0.94–0.96
Crystallinity at 15°C (%)	≥30
Melting point (°C)	57–63
Yield strength (MPa)	5.6
300% modulus (MPa)	19.8
Tensile strength (MPa)	35.4
Elongation at break (%)	430
Tear strength (kN/m)	90
Hardness (shore A)	94

Adjustment of Molecular Weight of TPI[17]

The molecular weight of TPI prepared in the laboratory is usually very high, whereas TPIs with fairly high molecular weights has very bad processing properties and even cannot be processed. Although the molecular weight of TPI can be decreased through oxidation or mechanical shear, the process is uncontrollable, and the properties of the TPI become worse.

A common practice to reduce the average molecular weight is to introduce a chain-transfer agent. Hydrogen has been used on many occasions. The experimental results showed that hydrogen as a chain-transfer agent can adjust the molecular weight of TPI effectively.

STRUCTURE AND PROPERTIES OF TPI

According to the results of IR and ^{13}C-NMR spectra, the *trans*-1,4-unit content of the TPI synthesized in the presence of a supported Ti catalyst with bulk precipitation polymerization was more than 98%. The main structure and properties of TPI reached or exceeded those of the same kind of products, as shown in Table II.

PROCESSIBILITY AND VULCANIZATION OF TPI

It is difficult for TPI to process at temperatures below 60°C because of its crystallizability. However, between 70 and 90°C, TPI has better processibility. It may be blended, mixed, strained, extruded, and injected. Its rollability is similar to that of NR and superior to that of BR and SBR.

TPI can be vulcanized with a conventional sulfur/accelerator system, and its vulcanizability is similar to that of NR. The properties of vulcanizates of TPI, NR, BR, and SBR are listed in Table III.

It can be seen from Table III that TPI can be vulcanized to a rubbery elastomer with the vulcanizing recipe of general rubber, but the levels of sulfur and accelerator are slightly higher. TPI is a crystalline polymer with a high strength and hardness (as shown in Table II). When TPI is vulcanized, with the increase of sulfur content,

Table III   Properties of Vulcanizates of TPI, NR, BR, and SBR[4]

	Rubber									
	TPI							NR	BR	SBR
Sulfur content (phr)	2.0	2.5	3.0	4.0	5.0	7.0	10.0	2.0	2.0	2.0
Accelerator content (phr)	1.0	1.25	1.5	2.0	2.5	3.5	5.0	1.0	1.0	1.0
100% modulus (MPa)	9.71	3.76	3.98	2.18	3.21	3.63	6.62	1.59	1.55	1.49
200% modulus (MPa)	12.2	5.83	8.14	5.19	9.10	—	—	5.98	3.49	4.83
300% modulus (MPa)	17.7	11.2	13.6	11.8	—	—	—	11.8	7.15	9.76
Tensile strength (MPa)	20.6	16.3	18.3	17.3	13.1	11.0	7.38	23.8	14.2	23.6
Elongation at break (%)	468	490	440	430	260	190	110	530	455	530
Set (%)	16	18	20	16	6	5	4	30	4	16
Hardness (shore A)	90	84	80	63	66	72	76	63	60	64
Tensile fatigue at 100% strain (10^3 Kc)	0.28	0.09	0.08	0.12	0.17	0.47	—	0.35	1.23	0.185
Goodrich heat buildup	17	16	12.5	9.2	8.4	7.8	10	14	8.4	15

The TPI was synthesized by bulk precipitation with the supported titanium (Ti) catalysts.

Recipe: 100 phr rubber, 5 phr ZnO, 2 phr stearic acid (SA), 2 phr antiaging agent, 50 phr high abrasion furnace black N339 (HAF), and 8 phr softener.

Vulcanizing temperature = 150°C for 25 min.

Table IV   Properties of Blend Vulcanizates of TPI and NR[4]

	100	80	60	40	20	0
TPI (phr)	100	80	60	40	20	0
NR (phr)	0	20	40	60	80	100
100% modulus (MPa)	9.7	6.0	3.2	1.8	1.5	1.6
200% modulus (MPa)	12.2	8.1	6.1	4.7	4.1	5.9
300% modulus (MPa)	17.7	14.1	10.9	10.0	8.4	11.8
Tensile strength (MPa)	20.6	20.0	20.5	23.8	23.6	23.8
Elongation at break (%)	468	470	510	550	600	530
Set (%)	16	12	16	20	24	30
Tear strength (kN/m)	92.9	60.3	52.1	49.1	47.1	65.4
Hardness (shore A)	90	91	81	61	60	63
Tension fatigue at 100% strain (10^3 kC)	0.28	0.15	1.27	1.25	1.29	0.35
Heat buildup (°C)	17.0	12.2	10.2	8.2	8.2	14

Recipe: 2.0 phr sulfur and 1.0 phr accelerator; the others ingredients are the same as listed in Table III.

the crystallinity of TPI decreases dramatically, so the modulus and strength of TPI decrease rapidly. When the content of sulfur is 3.0–4.0 phr, the crosslinking density of TPI is high enough that TPI cannot crystallize; therefore, when the hardness of TPI vulcanizate is the lowest, the TPI shows elastic materials with better properties. When the content of sulfur is over 5.0 phr, the hardness of the TPI vulcanizate increases, and the elongation at break decreases like conventional vulcanized rubber. When the content of sulfur is 5.0–7.0 phr, the tension fatigue resistance and dynamic heat buildup are very excellent.

BLENDING AND COVULCANIZATION OF TPI WITH NR, BR, AND SBR

It is easy for TPI to be blended and covulcanized with other unsaturated rubbers. The suitable processing condition is to make TPI plasticize at the temperature of 70–80°C first and then add another rubber to it. The properties of blend vulcanizates are listed in Tables IV–VI.

It is shown in Table IV that the blend vulcanizates of TPI and NR possess excellent comprehensive properties. When the content of TPI in blends is less than 50%, the vulcanizate almost keeps the excellent properties of NR; meanwhile, the dynamic performance is improved. The tension fatigue resistance increases 5.3 times, whereas heat buildup decreases greatly.

The results in Tables V and VI show the same rule as in Table IV. BR blending with TPI can improve the processability, Green strength, and modulus of the blend vulcanizate. Although the tension fatigue resistance of BR is very excellent, the blends of BR and TPI (the levels of TPI are 20–40 phr) have better tensile fatigue resistance when the tension strain is 100%. The fatigue breaking times can get 4×10^3 kC.

As shown in Table VI, the SBR blend with TPI can improve its dynamic fatigue resistance and heat buildup greatly. When the level of TPI in blends is 20 phr, the tension fatigue resistance is improved nearly 8 times, whereas the heat buildup is decreased by 4 °C.

STUDY OF HIGH TPI RUBBER APPLICABLE TO HIGH-PERFORMANCE TIRE

The most important quality for high-performance tire is the comprehensive balance among higher wet skid resistance, lower rolling resistance, and better abrasion resistance. Particularly, more and more new kinds of synthetic rubbers were developed in the past to meet the needs of high-performance tire. The latest studies[2,4,18] have shown that pure TPI elastomer has a high modulus, low deformation, and low rolling loss, and blends of TPI with NR, SBR1500, and BR9000 had excellent processability and mechanical properties; in particular, the dynamic properties, such as flex fatigue resistance, can be improved, which made us investigate the feasibility of replacing conventional tire stocks such as NR/SBR1500 and NR/BR9000 with NR/TPI/SBR1500 and NR/TPI/BR9000 blends in the laboratory.

Table V   Properties of Blend Vulcanizates of TPI and BR[4]

TPI (phr)	100	80	60	40	20	0
NR (phr)	0	20	40	60	80	100
100% modulus (MPa)	9.7	7.0	4.1	3.1	2.1	1.6
200% modulus (MPa)	12.2	9.4	7.0	5.7	4.8	3.5
300% modulus (MPa)	17.7	15.6	12.4	10.0	9.1	7.2
Tensile strength (MPa)	20.6	19.8	18.4	11.7	12.5	14.2
Elongation at break (%)	468	465	460	370	410	455
Set (%)	16	13	12	8	6.6	4
Tear strength (kN/m)	92.9	58.7	48.6	38.6	38.1	37.2
Hardness (shore A)	90	91	82	76	67	60
Tension fatigue at 100% strain (10^3 kC)	0.28	0.13	1.23	4.32	4.75	1.23
Heat buildup (°C)	17.0	14.4	12.2	13.2	11.5	8.4

The recipe is the same as listed in Table IV.

The experimental results in the laboratory showed that the use of 20 phr as a partial replacement of natural rubber afforded tread and sidewall stocks with a higher modulus, longer fatigue life, better abrasion resistance, and lower heat buildup, which indicates that TPI may be used for high-performance tire.

Vulcanization Characteristics

As shown in Table VII, he scorch time (t_{10}) and cure time (t_{90}) were slightly increased with 20 phr of TPI used as a partial replacement of NR. It is thought that the cure reaction activity of TPI is lower than that of NR with the same vulcanization conditions. On the other hand, the cure rate $(t_{90} - t_{10})^{-1}$ of the stock with TPI was decreased, whereas its better processing safety can be obtained.

Mechanical Properties

The basic mechanical properties of typical and improved tread & sidewall stocks are given in Table VIII. It is shown that the stocks replaced by TPI had an increased modulus, Shore A hardness, rebound at room temperature or higher temperatures, and aging resistance but decreased tensile strength, elongation at break, set, and tear strength. It is shown in #1A and #1B in Table VIII that the NR/TPI/SBR stock had a higher rebound than a typical NR/SBR tread.

Table VI   Properties of Blend Vulcanizates of TPI and SBR[4]

TPI (phr)	100	80	60	40	20	0
SBR (phr)	0	20	40	60	80	100
100% modulus (MPa)	9.71	4.15	2.27	1.74	1.58	1.49
200% modulus (MPa)	12.2	6.77	4.61	3.48	4.02	4.83
300% modulus (MPa)	17.7	12.9	9.66	7.66	8.88	9.76
Tensile strength (MPa)	20.6	22.3	21.3	20.3	24.4	23.6
Elongation at break (%)	486	530	560	580	570	530
Set (%)	16	26	24	20	18	16
Tearing strength (kN/m)	92.9	—	47.9	49.1	39.9	44.9
Hardness (shore A)	90	86	75	59	62	64
Tension fatigue at 100% strain (10^3 kC)	0.28	0.18	1.17	1.50	1.60	0.185
Heat buildup (°C)	17.0	19	15	14	11	15

The recipe is the same as listed in Table IV.

Table VII   Vulcanization and Characteristics of Compounds

Formulation Characteristics and Vulcanization Properties	Tread					Sidewall	
	#1A	#1B	#2A	#2B	#2C	#3A	#3B
Natural rubber, SCR 5	70	50	70	50	50	50	40
SBR 1500, emulsion, 23.5% styrene	30	30			15		
BR 9000, 96% *cis*-1,4-unit			30	30	15	50	40
TPI, 98% *trans*-1,4-unit		20		20	20		20
Monsanto rheometer at 150°C							
t_{10} (min)	6.72	6.97	6.60	6.33	6.63	6.88	6.88
t_{90} (min)	15.10	16.15	12.58	13.02	13.82	12.87	13.47
$(t_{90} - t_{10})^{-1}$ (min^{-1})	0.12	0.11	0.17	0.15	0.14	0.17	0.15

Recipe: 100 phr rubber, 5 phr zinc oxide, 2.5 phr stearic acid, 1 phr Flectol H, 1 phr Microwax, 2 phr Uop 688, 1 phr Uop 788, processing aid, 2 phr T-78, 2 phr sulfur, 0.9 phr accelerator CZ, 7 phr aromatic oil, 25 phr carbon black N234 (only in tread stock), 25 phr carbon black N339, 25 phr carbon black N539 (only in sidewall stock).

Dynamic Properties

The flex fatigue resistance, tension fatigue, abrasion resistance, and cut growth of typical and improved formulation compounds were compared, as shown in Table IX.

As shown in Table IX, the improved tread and sidewall stocks with TPI had more excellent flex and tension fatigue resistance, better rolling loss resistance, lower dynamic deformation, and temperature rise, whereas the cut-growth resistance decreased and the abrasion resistance increased slightly. Although the tensile strength of TPI stocks decreased after 100 kC of tension fatigue, the modulus maintained higher values, and the set reduced significantly. The result showed that improved tread and sidewall stock had comprehensive, excellent dynamic properties, which can meet the needs of high-performance tire.

Table VIII   Basic Mechanical Properties of Compounds

Mechanical Property	Tread					Sidewall	
	#1A	#1B	#2A	#2B	#2C	#3A	#3B
Initial properties at 23°C							
Shore A hardness	64	65	62	64	64	61	62
Tensile strength (MPa)	26.7	24.0	26.2	22.0	23.5	21.6	17.3
100% modulus (MPa)	2.3	2.6	2.0	2.4	2.8	2.1	2.4
300% modulus (MPa)	11.4	13.0	9.6	11.9	13.2	10.6	11.7
Tear strength (kN/m)	58.3	53.3	63.2	54.0	53.4	52.8	50.6
Elongation at break (%)	571	481	600	494	472	525	580
Set (%)	21	12	17	12	12	11	8
After Aging, 100°C × 48 h							
Shore A hardness	72	73	67	69	70	65	67
Tensile strength (MPa)	21.0	20.0	22.1	19.5	21.0	18.6	13.8
Elongation at break (%)	360	319	401	341	350	356	268
Aging coefficient	0.50	0.55	0.56	0.61	0.66	0.58	0.51
Tear strength (kN/m)	51.8	52.2	56.1	51.7	52.8	50.2	50.8
Rebound (%)							
At 23°C	40	44	53	49	48	56	55
At 60°C	48	52	59	56	55	64	64
At 80°C	56	59	63	62	61	69	68
At 100°C	56	62	66	66	65	72	71

Table IX   Dynamic Properties of Formulations

Formulation Type and Dynamic Property	Tread					Sidewall	
	#1A	#1B	#2A	#2B	#2C	#3A	#3B
Natural rubber, SCR 5	70	50	70	50	50	50	40
SBR 1500, emulsion, 23.5% styrene	30	30			15		
BR9000, 96% *cis*-1,4-unit			30	30	15	50	40
TPI, 98% *trans*-1,4-unit		20		20	20		20
Flex fatigue at 23°C							
kc/1 Grade crack	123	360	220	5150	360	>5890	5280
kc/4 Grade crack	150	400	750	>5890	420	>5890	5500
kc/6 Grade crack	420	950	1240	>5890	570	5890	5710
Tension fatigue at 23°C, 100% strain							
kc/cracked	526	1184	1766	>3110	2720	1976	3110
After 100 kc of tension fatigue							
Shore A hardness	63	64	61	61	62	61	62
Elongation at break (%)	532	443	582	416	422	515	414
Tensile strength (MPa)	27.5	22.6	28.0	20.0	22.7	22.2	18.7
Tension fatigue coefficient	1.03	0.94	1.07	0.91	0.97	1.03	1.08
100% modulus (MPa)	2.4	2.7	2.2	2.7	2.8	1.9	2.3
300% modulus (MPa)	13.8	14.3	11.6	13.2	14.9	10.9	12.9
Set (%)	20	8	14	8	8	10	6
Dunlop rotation power loss							
Rolling loss (relative)	2.75	2.35	2.10	1.95	2.25	1.70	1.65
Dynamic deformation (in.)	0.0375	0.0360	0.0405	0.0355	0.0365	0.0360	0.0345
Temperature rise	18	14	12	10	10	8	8
Cut-growth at 23°C							
mm at 50 kc	10.0	12.5	9.7	16.0	16.9	5.0	9.7
mm at 100 kc	11.1	—	10.0	17.2	17.8	5.7	10.6
mm at 200 kc	14.2	15.7	—	18.1	18.5	5.9	10.9
mm at 500 kc	—	19.3	11.6	20.1	20.2	6.1	11.2
Akron abrasion volume at 23°C (cm^3/1.61 km)	0.142	0.138	0.138	0.123	0.135	—	—

Processibility of Mixing Compounds

The experimental results for the mixing process showed that the TPI stocks had better rollability, but the rollability decreased when the NR level was less than 50 phr (as seen in #3B in Table VII.). The use of TPI as a 20-phr replacement for NR in tread compounds significantly increased the Brabender extruding rate of TPI stocks. The extrudate surface was much smoother than those of typical tread stocks. However, the extrusion swell behavior was slightly increased because TPI stocks have higher resilience.

CONCLUSIONS

A new synthetic method of TPI in the presence of a supported Ti catalyst system with bulk precipitation polymerization process was put into effect, which made the production cost of TPI much lower than before because of higher catalytic efficiency, lower energy consumption, and a simpler technological process. The *trans*-1,4-unit content of the TPI was more than 98%. The main structure and properties of TPI reached or exceeded those of the same kind of product. Because of its outstanding dynamic mechanical properties, TPI

can be used to develop high-performance tire. Consequently, synthesized TPI made by bulk precipitation polymerization in the presence of a Ti catalyst is a new type of general purpose synthetic rubber with a bright future.

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