

# Performance Evaluation of High-cis 1,4-Polybutadienes

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**ABSTRACT:** This article reports the results of a study comparing commercially available high-cis polybutadiene rubbers (BRs) proceeding from different production technologies and bearing distinct structural characteristics. The microstructure of these polymers was characterized by Fourier transform infrared spectroscopy; molecular weight and polydispersity values were characterized by size exclusion chromatography (SEC). The degree of branching was characterized by SEC and dynamic mechanical rheological testing (RPA 2000). Glass-transition temperature was characterized by differential scanning calorimetry, and rheological properties were characterized with an oscillating rheometer rubber process analyzer (RPA 2000). Tire tread formulations were prepared with carbon black HAF N-339 as a reinforcement filler, and we compared the mechanical properties and

performance of the different elastomer compositions. The compositions were characterized by their rheological properties, tensile resistance, resistance to abrasion, resistance to tearing, permanent deformation, resilience, and fatigue properties. The tested compositions obtained from BRs with distinct structural characteristics showed different performances. Neodymium-salt-based catalysts produced BRs with higher cis-1,4 levels and higher linearities. These polymer compositions also showed higher performances in abrasion resistance, fatigue resistance, and resilience tests. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 88–99, 2006

**Key words:** microstructure; polybutadiene; rheology; viscoelastic properties

## INTRODUCTION

Polybutadiene rubber (BR) is the second largest synthetic rubber produced next to styrene-butadiene rubber (SBR), and its consumption is about 1.9 million metric tons per year of the 8.2 million metric tons per year of synthetic rubber consumed worldwide.<sup>1</sup>

Currently, automobile tires are the primary application for BR, a market segment responsible for 67–70% of the world's BR production consumption. A second segment is that of plastic modification, which accounts for 15–20% of the BR production worldwide; the footwear, technical goods, and golf ball segments consume 5–20% of this elastomer's worldwide production.<sup>2</sup>

BR is commercially available in two main forms: one containing 1,4-cis repeating unit levels around 40%, which is called *low-cis BR*, and one with levels that range from 92 to 98%, called *high-cis BR*. The demand for these two products, each with its own distinct properties, comes from major consumption segments, tires and retreads, with high-cis BR being the most appropriate for these applications.

Vulcanized high-cis BR presents high elasticity and resilience, low heat buildup, high resistance to abrasion and to cut growth, good flexibility in low temperatures, and high fatigue cracking resistance. It can take a higher level of carbon black and oil compared to natural rubber (NR). This set of properties makes high-cis BR an excellent elastomer for the tire industry. On the other hand, its compositions do have low skidding resistance and with low resistance to heat and ozone, and it is considered a rather difficult polymer to process. For this reason, high-cis BR is always used in mixtures with other polymers, especially SBR and NR; this mixing enhances some of the properties of vulcanized articles made of these elastomers.<sup>2</sup>

Four different technologies with Ziegler-Natta catalysts can be used in the commercial production of BR with high 1,4-cis repeating unit levels; titanium (Ti), cobalt (Co), nickel (Ni), and neodymium (Nd) are the

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TABLE I  
Microstructures and  $T_g$  Values

Catalyst system metal	Source	Microestructura			$T_g$ (°C)
		Cis (%)	Trans (%)	Vinyl (%)	
Co	A	97.1	0.9	2.0	-108
	B	98.1	0.9	1.0	-109
	C	98.1	0.9	1.0	-109
Ni	D	97.4	1.5	1.1	-106
	E	97.3	1.5	1.2	-109
	F	97.7	1.5	0.8	-109
Nd	G	98.0	1.7	0.3	-109
	H	98.2	1.4	0.4	-109

A, B, and C were BR-Co producers. D, E, and F were BR-Ni producers. G and H (petroflex) were BR-Nd producers.

most commonly used metals in these catalyst systems.<sup>3,4</sup>

The first production run of high-cis BR came off the line in 1960 under the responsibility of Phillips Petroleum Co. with a titanium-based catalyst. Still in the 1960s, high-cis BR started to be produced with cobalt-based catalysts. Goodrich-Gulf was the first company to market this polymer. Bridgestone Tire Co., together with Japan Synthetic Rubber Co., developed the production of this polymer with a nickel-based catalyst, which was marketed in Japan in 1964 by Japan Synthetic Rubber.<sup>5</sup> In that same decade, studies on neodymium-based catalyst systems started to be carried out; however, only in the 1980s did they start to be commercially used by Enichem to produce high-cis BR. Before high-cis BR produced with neodymium-based catalysts, currently the one of greater commercial interest, began to be marketed, the cobalt-based catalysts were the most extensively studied due to the technological and commercial advantages of these systems.<sup>3</sup>

The new economic and technological trends in the automotive and tire industries have had a significant role in BR consumption, as these industries are its bigger market. The tire industry values tire production that prioritizes safety and comfort, low fuel consumption, and the preservation and protection to the environment.<sup>6</sup> Nowadays, tires must obey the three main requirements, which have to do mostly with treads: low rolling resistance, good traction properties on dry or wet surfaces, and high wear resistance. High-cis BR meets all of these requirements except for the traction properties on dry and wet surfaces and has better characteristics in low temperatures due to its low glass-transition temperature ( $T_g$ ). Thus, of the three main elastomers largely used in tire composition, NR (51–52%), SBR (30–31%), and BR (17.5%), BR, especially high-cis BR, is the one that is expected to have the highest growth.<sup>7</sup>

In this study, eight BRs obtained by cobalt (BR-Co), nickel (BR-Ni), and neodymium (BR-Nd) technologies were characterized. For each BR type, BR and BR/SBR compositions were prepared, and their nonvulcanized (noncured) composition properties and their mechanical and dynamic mechanical characteristics were evaluated.

## EXPERIMENTAL

### Materials

The eight high-cis BR samples used in this study were characterized for their molecular weights and microstructures. According to their sources, they were called A [BR-Co: 97.1% cis, number-average molecular weight ( $M_n$ ) =  $65 \times 10^3$ , weight-average molecular weight ( $M_w$ ) =  $228 \times 10^3$ ], B (BR-Co: 98.1% cis,  $M_n$  =  $76 \times 10^3$ ,  $M_w$  =  $251 \times 10^3$ ), C (BR-Co: 98.1% cis,  $M_n$  =  $78 \times 10^3$ ,  $M_w$  =  $243 \times 10^3$ ), D (BR-Ni: 97.4% cis,  $M_n$  =  $54 \times 10^3$ ,  $M_w$  =  $243$

TABLE II  
Rheological and Structural Characteristics

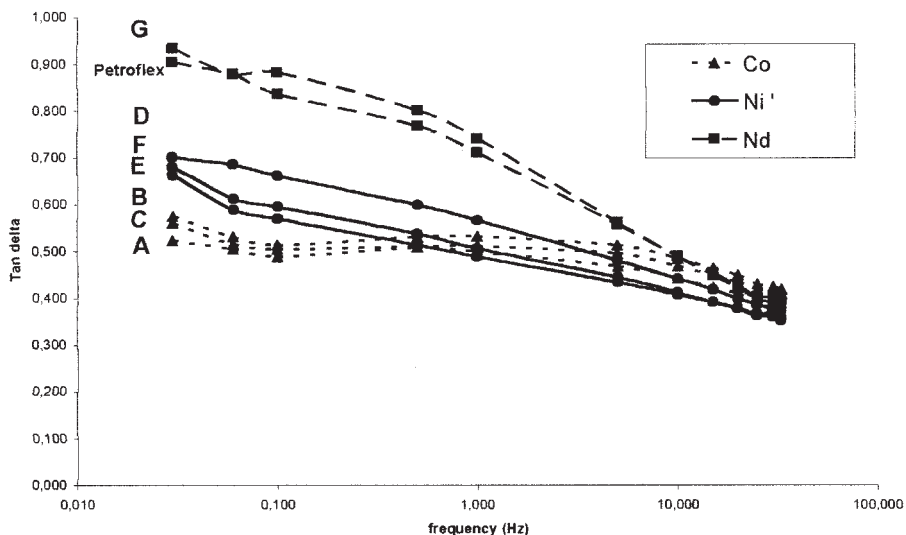
Catalyst system metal	Source	Characteristic molecular weight			ML <sub>4</sub> <sup>a</sup>	Number of branches per 1000 C atoms
		$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	$M_w/M_n$		
Co	A	65	228	3.53	39.8	ND <sup>b</sup>
	B	76	251	3.30	45.9	1.691
	C	78	243	3.13	44.0	1.341
Ni	D	54	243	4.48	39.9	ND <sup>b</sup>
	E	66	286	4.30	43.8	0.915
	F	58	265	4.58	45.8	0.661
Nd	G	82	276	3.35	40.9	0.038
	H	78	278	3.55	40.6	Linear <sup>c</sup>

A, B, and C were BR-Co producers. D, E, and F were BR-Ni producers. G and H (Petroflex) were BR-Nd producers.

<sup>a</sup> Mooney viscosity, ML (1+4) were at 100°C.

<sup>b</sup> ND = not determined.

<sup>c</sup> Petroflex BR was considered a linear reference.



**Figure 1** Evaluation of branching content with rubber process analysis (A, B, and C were BR-Co producers; D, E, and F were BR-Ni producers; and G and Petroflex: were BR-Nd producers).

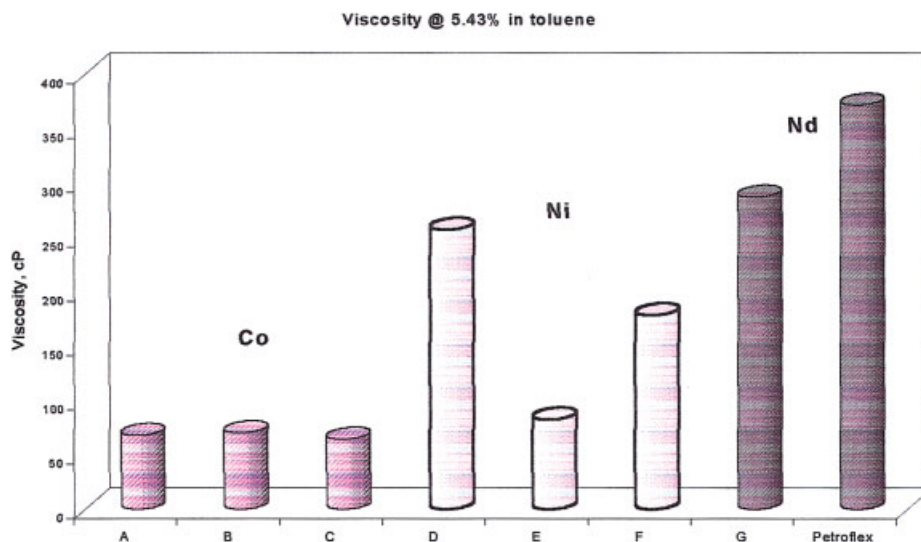
$\times 10^3$ ), E (BR-Ni: 97.3% cis,  $M_n = 66 \times 10^3$ ,  $M_w = 286 \times 10^3$ ), F (BR-Ni: 97.7% cis,  $M_n = 58 \times 10^3$ ,  $M_w = 265 \times 10^3$ ), G (BR-Nd: 98.0% cis,  $M_n = 82 \times 10^3$ ,  $M_w = 276 \times 10^3$ ), and H (98.2% cis,  $M_n = 82 \times 10^3$ ,  $M_w = 278 \times 10^3$ ). Sample H, whose commercial name was Coperflex BRNd-40, and SBR 1712 (10% cis,  $M_n = 132 \times 10^3$ ,  $M_w = 511 \times 10^3$ ) were both produced by Petroflex (Rio de Janeiro, Brazil). The other samples of high-cis BR were obtained on the international market.

Sulfur (Intercuf Ind. e Com. LTDA, São Paulo, Brazil), stearic acid (Barlocher do Brasil, São Paulo, Brazil), zinc oxide (Brasoxido, São Paulo, Brazil), Vulkanox HS (Bayer, Rio de Janeiro, Brazil), Santoflex

6PPD (Flexy's), aromatic oil and naphthenic oil (BR Distribuidora), Vulkacit CZ (Bayer), DPG (Bayer), and carbon black HAF N 339 (Cabot, Billerica, MA) were used in the vulcanized compositions.

### Characterization

The microstructures of the BRs were characterized by Fourier transform infrared spectroscopy in a PerkinElmer Spectrum One Fourier transform infrared spectrometer (PerkinElmer, Norwalk, CT) as films formed on KBr cells and prepared from 2% (w/v) chloroform solutions in the spectral range from 4000 to 450  $\text{cm}^{-1}$ . The contents of the different



**Figure 2** Viscosity of the polymers in solution (A, B, and C were BR-Co producers; D, E, and F were BR-Ni producers; and G and Petroflex: were BR-Nd producers).

**TABLE III**  
ASTM Formulation for BR Evaluation

Raw material	Mass (g)
BR	34.00
Stearic acid	1.020
Carbon black	20.400
Naphthenic oil	5.100
TBBS	0.306
Sulfur	0.510

TBBS, N-t-butylbenzothiazole-2-sulfenamide.

types of repetitive units were obtained with band absorbances at 725  $\text{cm}^{-1}$  (*cis*-1,4), 910  $\text{cm}^{-1}$  (vinyl-1,2), and 965  $\text{cm}^{-1}$  (*trans*-1,4) according to the Kimmmer method, which gives relative values. According to this method, the sum of the isomeric repeating unit proportions corresponds to the total sum of double bonds (100%).<sup>8</sup>

$T_g$  was obtained by differential scanning calorimetry (DSC), with a TA Instruments differential scanning calorimeter (model MDSC 2920) (TA Instruments, New Castle, DE).  $T_g$  was estimated from the inflexion point on the DSC curve, and the analysis was carried out in a  $\text{N}_2$  atmosphere at a heating rate of 5°C/min from -140 to 30°C.

Polymer molecular weight and polydispersity were estimated by size exclusion chromatography (SEC) in a Waters HPLC system (Waters, Milford, MA) with a refractive index detector and with tetrahydrofuran as the solvent (1 mL/min) at 30°C. A universal calibration curve was constructed with monodisperse polystyrene standards.

The degree of polymer branching was determined with two methods: SEC and rheometry (Alpha Technologies, RPA 2000, Akron, OH). The analysis by SEC was carried out with a chromatograph with a Viscotek triple detector array (model 300 TDA) (Houston, TX).

**TABLE IV**  
Tire Tread Formulations (phr) with Different Types of High-*cis* BRs

Raw material	Catalyst system		
	Nd	Co	Ni
SBR 1712	96.25	96.25	96.25
BR Nd 40 (BR-Nd)	30.00		
BR commercial 1 (BR-Co)		30.00	
BR commercial 2 (BR-Ni)			30.00
Stearic acid	1.50	1.50	1.50
Zinc oxide	5.00	5.00	5.00
Vulcanox HS	2.00	2.00	2.00
Santoflex 6PPD	2.00	2.00	2.00
Aromatic oil	4.00	4.00	4.00
Carbon black (HAF N339)	70.00	70.00	70.00
Vulkacit CZ	1.20	1.20	1.20
DPG	0.30	0.30	0.30
Sulfur	1.80	1.80	1.80

**TABLE V**  
Elastomeric Compositions' Cure Characteristics with High-*cis* BRs Obtained from Different Catalyst Systems (BR-Co, BR-Ni, and BR-Nd)

Property	Catalyst system		
	Co	Ni	Nd
ML (dNm)	11.0	11.0	12.5
MH (dNm)	40.5	37.5	48.5
$t_{s1}$ (min)	12.0	16.5	9.8
$t'_{50}$ (min)	22.5	27.5	20.3
$t'_{90}$ (min)	32.0	38.9	29.5

ML, minimum torque; MH, maximum torque;  $t_{s1}$ , minutes to 1 unit rise above ML.  $t'_{50}$ , minutes to 50 units rise above ML.  $t'_{90}$ , minutes to 90 units rise above ML.

This detector was equipped with a differential refractometer, a laser light scatterer, and a capillary viscometer. Tetrahydrofuran was used as the solvent (1 mL/min) at 50°C with 2% (w/v) polymer solutions. Rheometry was carried out with an Alpha Technologies oscillating rheometer rubber process analyzer (model RPA 2000). Branching was determined in crude rubber, according to the variation of  $\tan \delta$  with the oscillation of frequency in the range 0.03–33 Hz under 1° of deformation at 100°C.

Polymer viscosity in solution was measured at 25°C from polymeric solutions at 5.43% (w/v) in toluene in an Ostwald-Fenske capillary viscometer.

The Mooney viscosity of the polymers in melt state [ML(1+4)] was measured according to ASTM D 1646 at 100°C in an Alpha Technologies viscometer (model MV 2000). Analysis was carried out by the placement of two pieces of rubber in the two parts of a compression casting mold. When the mold was closed, a sealed, pressurized cavity was formed, through which a rotor was introduced into the rubber paste. After a preheating period at 100°C, measurement started and lasted 4 min.<sup>9</sup>

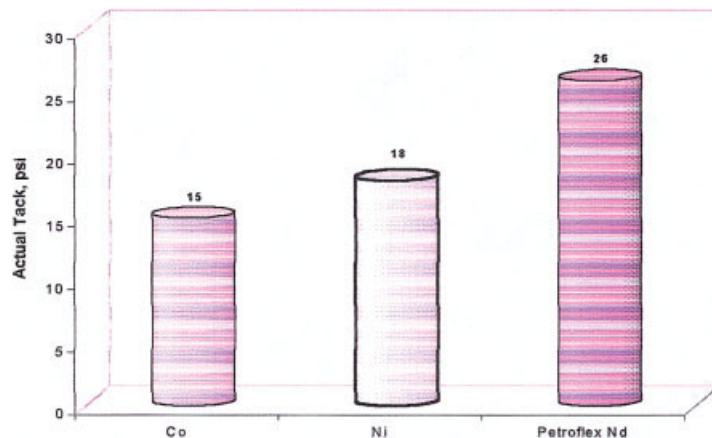
The stress at break, stretching, and modulus tests were run according to ASTM D 1349 at 23°C in a Monsanto T500 tensiometer (Monsanto, Akron, OH).

Shore A hardness was estimated according to ASTM D 2240-97 in a Brasser durometer at 23°C.

The resilience test was carried out according to ASTM D 1054 at 23°C in a Zwick & Co. KG resiliometer (model Z 116) (Hamburg, Germany).

The estimation of abrasion resistance was run according to DIN 53516 at 23°C in Maqtest equipment (Franca, Brazil).

Fatigue testing was conducted according to ASTM D 430 in a De Mattia Maqtest flexometer. The prepared sample was 150 mm long, 25 mm wide, and 6.35 mm thick, with a central longitudinal cavity 2.38 mm of diameter. The sample was submitted to continuous bending deformation until the first crack appeared, at which point the number of bending movements was recorded.



**Figure 3** Actual tack in the elastomeric compositions of high-cis BRs obtained from different catalyst systems.

Resistance to tearing in the vulcanized compositions was estimated according to ASTM D 624-91 at 23°C in a Monsanto T500 dynamometer. In this test, the sample, which was 102 mm long, 19 mm wide, and 2 mm thick, with a 90° central transversal groove, was submitted to elongation strain at a steady speed up to the points when the first crack appeared and when it broke.

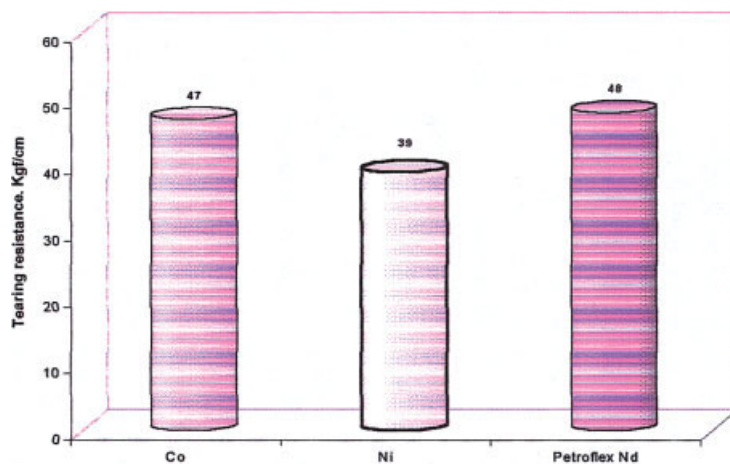
The permanent deformation by compression was measured according to ASTM D 395 Method B. A vulcanized test specimen (a disc 12.5 mm thick and 13 mm in diameter) was compressed to a deformation of 25% in a suitable compression device and maintained at 100°C for 70 h. The residual deformation of the test specimen was measured 30 min after removal from the compression device. After the residual deformation was measured, the compressive set was calculated according to the following equation:

$$C = [(I_0 - I_i) / (I_0 - I_n)]$$

where  $C$  is the compression set,  $I_0$  is original thickness of the specimen,  $I_i$  is the final thickness of the specimen, and  $I_n$  is the thickness of the spacer bar used in the compression device.

Tack estimation was carried out in a Monsanto Tel-Tack tackmeter (Monsanto, Akron, OH) to determine the actual tack. This test consisted of measuring the difference between the necessary strength to separate two rubber sample bodies and the strength that one had to apply to separate a rubber sample from a stainless steel bar; both samples had the same composition, and both tests were run under the same conditions. The sample bodies were cast for 3 min at 100°C. The test was carried out with contact pressure of 16 psi for 5 min.

The vulcanized compositions had their  $\tan \delta$  measured with a Rheometrics dynamic mechanical analyzer (model MK III) (Rheometrics, Piscataway, NJ) in the temperature range -80 to 80°C in a bending mode



**Figure 4** Resistance to tearing.

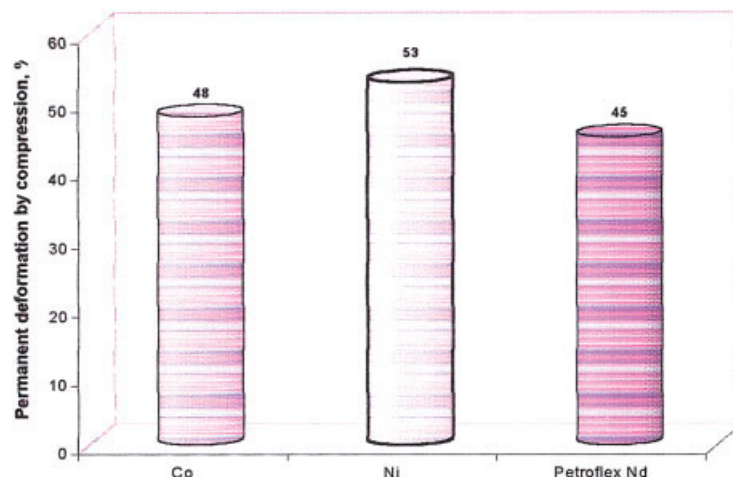


Figure 5 Permanent deformation by compression.

with 0.06% deformation, an oscillating frequency of 1 Hz, and a heating rate of 2°C/min.

#### Preparation of elastomeric compositions

The BR compositions were prepared with the ASTM D 3189 formulation D method conducted in a Haake plastograph internal minimixer (Karlsruhe, Germany) with an 85-mL volume. Cure parameters were found at 145°C in a Monsanto oscillating disc rheometer (ODR-P100) with a  $\pm 1^\circ$  arc for 60 min. The cure times ( $t'_{90}$ 's) for the samples in the tensile resistance test were determined by the rheometric tests of each composition. These times varied according to the catalyst system used in the BR synthesis: 32.0 min for the Co-based system, 38.9 min for the Ni-based system, and 29.5 min for the Nd-based system. As for the rest of the tests, the sample vulcanization time was twice  $t'_{90}$ , that is, 64.0 min for the Co-based system, 77.8 min for the Ni-based system, and 59.0 min for the Nd-based system.

For the BR/SBR compositions, a tire tread formulation for automobiles was used. These formulations were prepared in two stages in two different mixers. At the first stage, the mixing lasted 6 min in a 2-L Banbury internal mixer (Stuttgart, Germany) at an initial temperature of 60°C. At the second stage, sulfur was added in an open-mill mixer (Herman Berstorsff, Hannover, Germany) for 2.5 min.  $t'_{90}$ 's varied according to the catalyst system (Co, Ni e Nd), and were obtained through a similar method to that one used for BR compositions in the ODR rheometer at 150°C and with a  $\pm 1^\circ$  arc for 30 min. The times for the tensile tests were 17.8 min for the Co-based system, 18.0 min for the Ni-based system, and 17.3 min for the Nd-based system. The samples for the other tests were cured in 35.6 min (Co), 36.0 min (Ni), and 34.6 min (Nd).

## RESULTS AND DISCUSSION

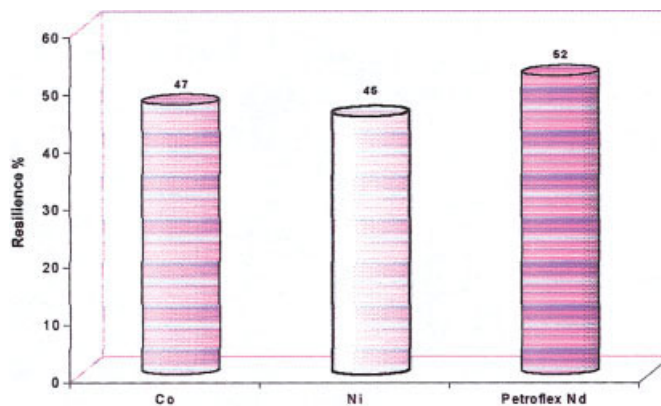
### Characterization of the commercial BRs

The contents of the *cis*-1,4 repeating units found for the eight high-*cis* BR types analyzed and produced from cobalt-, nickel-, and neodymium-based technologies were in the range 97.1–98.2%. These values were slightly different from those found in the literature, which range between 96.97 and 98% *cis*-1,4 units for the BRs obtained from cobalt-, nickel-, and neodymium-based technologies, respectively.<sup>10–13</sup> The BRs produced by the nickel-based technology (BR–Ni) showed a lower average value, whereas the BR–Nd system showed a higher one. There was also a tendency toward lower values for the repetitive vinyl-1,2 unit content for the BR–Nd series and higher values for the BR–Co series (Table I).

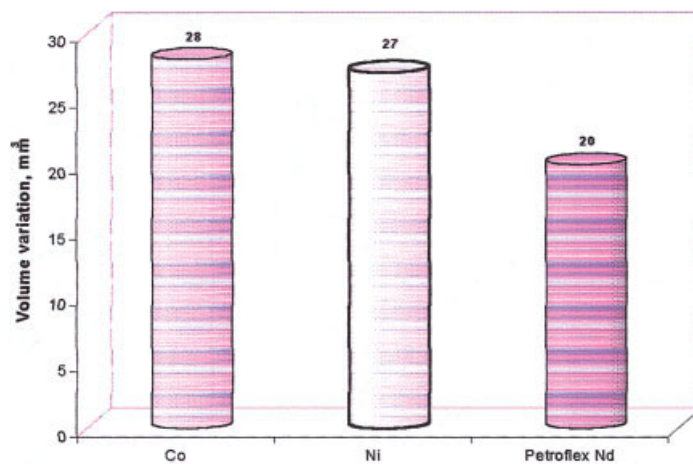
The BR microstructures, especially the *cis*-1,4 content, had an accentuated influence over the physical properties of the pure gum and the vulcanized compositions. In the range 25–80%, the variation in *cis*-1,4 contents did not have a significant effect. However, over 80%, and even more over 96%, the properties suffered a significant change with the least increase in *cis*-1,4 content.<sup>13</sup> That happened because BRs can crys-

TABLE VI  
Evaluation of the Mechanical Properties of the Elastomeric Compositions of High-*cis* BRs Obtained from Different Catalyst Systems (BR–Co, BR–Ni, and BR–Nd)

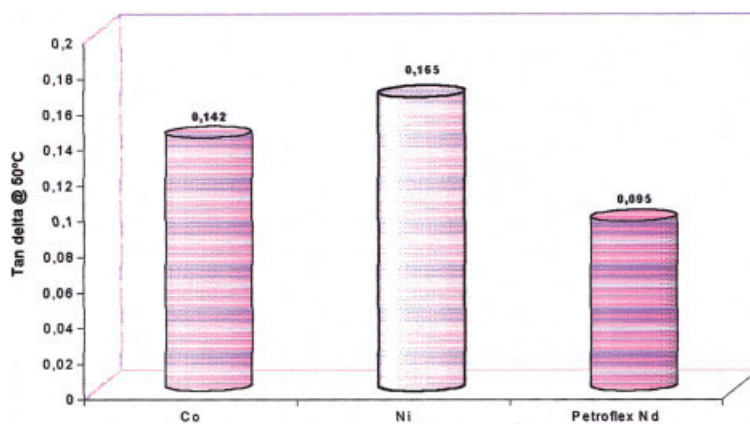
Property	Catalyst system		
	Co	Ni	Nd
Modulus at 300% (Kgf/cm <sup>2</sup> )	68	72	80
Stress at break (Kgf/cm <sup>2</sup> )	127	148	167
Ultimate elongation (%)	470	540	560
Shore A hardness	58	58	63



**Figure 6** Resilience of the elastomeric compositions of high-cis BRs obtained from different catalyst systems (BR-Co, BR-Ni, and BR-Nd).



**Figure 7** DIN abrasion of elastomeric compositions of high-cis BRs obtained from different catalyst systems (BR-Co, BR-Ni, and BR-Nd).



**Figure 8** Tan  $\delta$  of the elastomeric compositions of high-cis BRs obtained from different catalyst systems (BR-Co, BR-Ni, and BR-Nd).

**TABLE VII**  
**Cure Characteristics of BR/SBR Elastomeric**  
**Compositions of High-*cis* BRs Obtained from Different**  
**Catalyst systems (BR-Co, BR-Ni, and BR-Nd)**

Property	Catalyst system		
	Co	Ni	Nd
Viscosity of the ML <sub>4</sub> composition	60.0	59.4	65.5
ML (dNm)	9.5	9.5	9.0
MH (dNm)	36.5	35.6	36.0
$t_{s1}$ (min)	7.5	7.8	7.1
$t'_{50}$ (min)	11.1	11.4	10.8
$t'_{90}$ (min)	17.8	18.0	17.3

tallize under tension, enhancing the polymer's physical properties. This effect becomes more noticeable as the polymer's *cis*-1,4 content gets higher. The *trans*-1,4 units and the vinyl-1,2 ones, especially, which are present in the polymeric chain, act as defects because they make crystallization under tension harder.

The BR molecular weight characteristics had a significant influence on its ability to be processed. A wide polydispersity, as much as high branching content, allowed better polymer processing. On the other hand, this had deleterious effects on physical properties such as resistance to tearing and abrasion. Thus, there must be a balance regarding molecular weight and branching content characteristics in the polymer to assure good processability and good physical properties.

The data presented in Table II show that commercial polymers obtained by nickel-based catalyst systems produced the widest distribution of molecular weights, whereas those obtained by cobalt- and neodymium-based catalysts had narrower and closer polydispersities. The BR-Nd system had a tendency to have a higher molecular weight, especially  $M_n$ , which

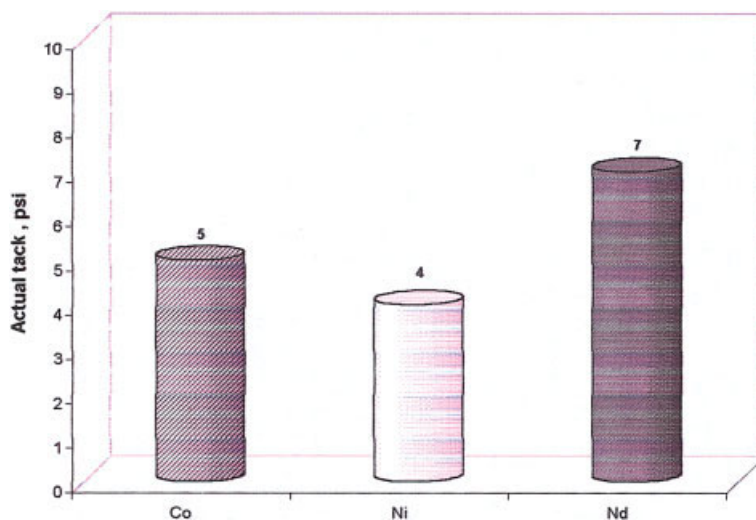
may have had a high influence on the polymer's re-ticulation.<sup>14</sup>

The relative branching content in long chains was estimated through  $\tan \delta$  variation of the crude polymers, which was given by dynamic mechanical thermal tests run under constant deformation temperatures and with frequency variation from very low to very high values. The lower the  $\tan \delta$  variation was with the frequency variation applied, the higher the branching content was. We could distinguish linear polymers, highly or lowly branched,<sup>15</sup> according to Figure 1.

It is possible to distinguish three sets of curves among the eight shown in Figure 1. According to the  $\tan \delta$  variation, the polymers obtained from neodymium-based technologies were the ones that presented higher chain linearity, whereas the BR-Co polymers were the most highly branched, followed by the BR-Ni polymers. This same pattern was if we analyzed the branching content index obtained by viscosimetry analysis (Table II).

Measuring polymer viscosity in solution is another way to comparatively analyze the branching content of polymers. In general, when one considers polymers of the same kind and molecular weight in the same range, the lower the viscosity in solution is, the higher the branching content is. Figure 2 shows the viscosities in solution obtained for the three series of polymers studied. The lower viscosity levels were found in the BR-Co system, which as previously seen, had the highest branching content. The BR-Nd system had the highest viscosity levels, which confirmed their higher linearity compared to the other systems.

The higher polydispersities and branching contents found in the BR-Ni and BR-Co systems made polymer processing easier in relation to the more linear



**Figure 9** Actual tack of the elastomeric compositions with high-*cis* BRs obtained from different catalyst systems (BR-Co, BR-Ni, and BR-Nd).



TABLE VIII

Results of the Tensile and Hardness Tests of Elastomeric Compositions of High-*cis* BRs Obtained from Different Catalyst Systems (BR-Co, BR-Ni, and BR-Nd)

Property	Catalyst system		
	Co	Ni	Nd
Modulus at 300% (Kgf/cm <sup>2</sup> )	82	83	85
Stress at break (Kgf/cm <sup>2</sup> )	178	170	183
Ultimate elongation (%)	540	540	560
Shore A hardness	63	62	64

polymers obtained from the neodymium catalyst systems. On the other hand, these same characteristics, which facilitated processing, influenced in a negative way the mechanical properties of the compositions prepared from such polymers. The higher linearity of the BR-Nd system, associated with higher stereospecificity of the catalyst system in relation to the *cis* unit content and lower vinyl-1,2 unit content, contributed in these polymers to a better performance in their applications.

#### Performance evaluation of the BRs

To comparatively evaluate the performance of the BRs produced from the three different types of catalyst systems (Co, Ni, and Nd) characterized in this study, BR compositions were prepared based on an ASTM formulation (Table III), and BR/SBR compositions were prepared based on formulations for tire treads (Table IV).

We estimated the cure and tack characteristics, mechanical properties (modulus at 300%, elongation and ultimate stress, hardness, tear resistance, and permanent deformation by compression), and dynamic

properties (abrasion resistance, resilience, and  $\tan \delta$  at 0 and 50°C) for these compositions.

The data in Table V show longer  $t'_{90}$ 's for BR-Ni and BR-Co-based catalysts due to higher polydispersities and branching contents in these polymers as compared to BR-Nd-based catalysts, which happened to be more linear polymers. Thus, the use of BR-Nd may have contributed to a decrease in the vulcanization cycle and, consequently, an increase in productivity and power saving.

Tack (adhesiveness) is an important property in the manufacturing of articles obtained from compositions with different constituents. Such characteristics are crucial, for instance, during the assembling of a tire, in which the different nonvulcanized parts are assembled only by rolling pressure and must remain adhered without losing their original shape up to the vulcanization (curing) moment. The compositions prepared with BR-Nd granted higher adhesiveness compared with the rest of the BRs analyzed. This BR-Nd characteristic would grant each one of the several tire parts high dimensional stability during the assembling process (Fig. 3).

Figures 4 and 5 and Table VI show that BR-Nd compositions had better mechanical properties than the compositions of the other types of BR evaluated.

The superiority of the BR-Nd compositions over the ones based on BR-Co and BR-Ni, in relation to resilience and resistance to abrasion, are shown in Figures 6 and 7. The polymeric chains' linearity and high stereoregularity granted the BR-Nd polymers higher elasticity and facilitated the strain-induced crystallization process, which enhanced the aforementioned properties.

The lower  $\tan \delta$  value at 50°C, as shown in Figure 8, indicated that the BR-Nd composition showed a lower heat buildup than the other compositions when

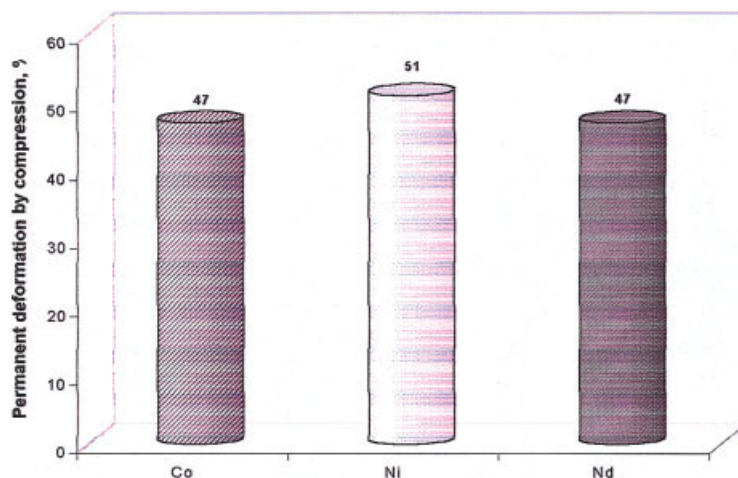
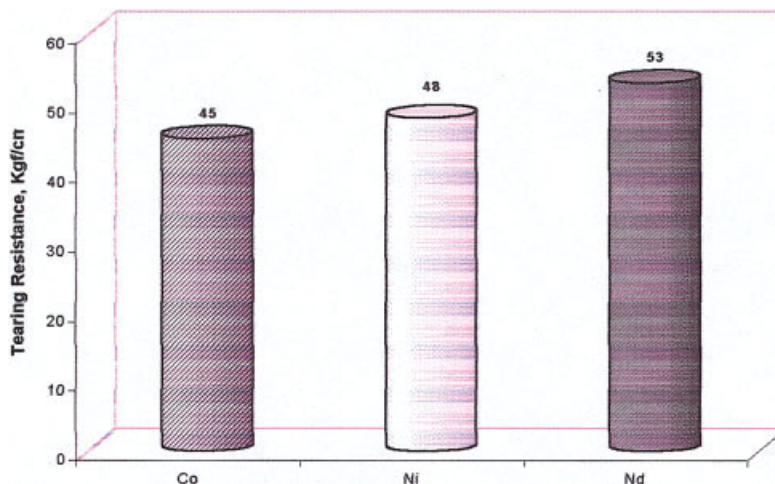


Figure 10 Permanent deformation by compression of the elastomeric compositions of high-*cis* BRs obtained from different catalyst systems (BR-Co, BR-Ni, and BR-Nd).



**Figure 11** Tearing resistance of the elastomeric compositions of high-cis BRs obtained from different catalyst systems (BR-Co, BR-Ni, and BR-Nd).

submitted to continuous deformation. Because elastomers are poor heat conductors, properties such as high resilience and low heat buildup are important, especially in applications in which heat generation is critical, as, for instance, in a tire.<sup>16</sup>

#### Evaluation of the high-cis BR compositions with SBR

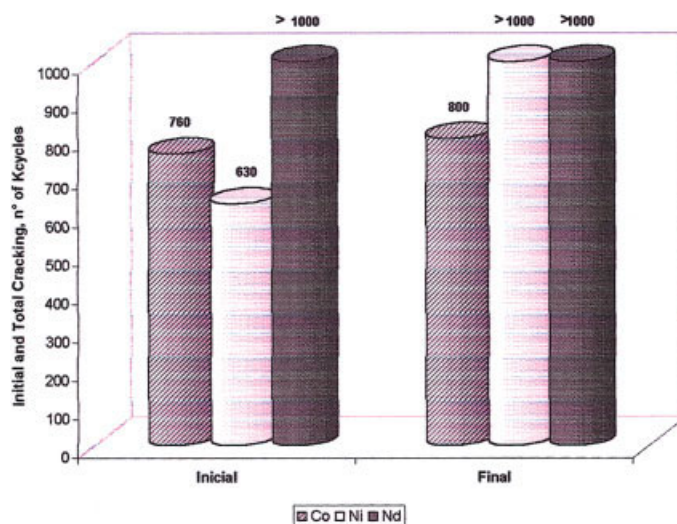
The BRs in this study were mixed with SBR 1712 to evaluate a tire tread formulation's performance (Table IV).

The compositions prepared for the tire tread presented very similar results concerning cure characteristics, except that a minor tendency toward a shorter

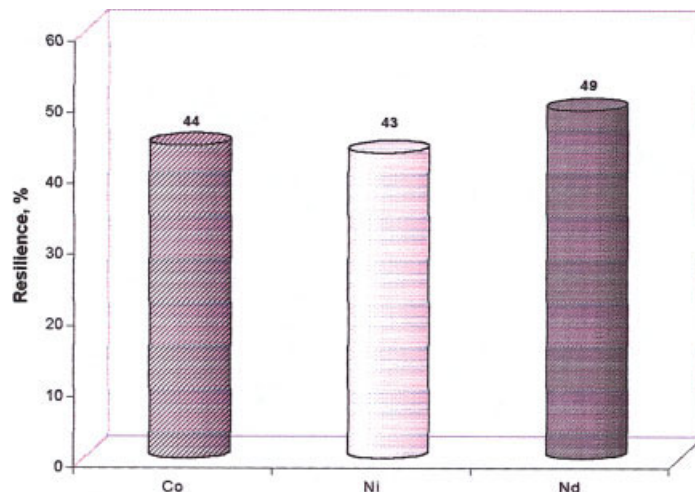
time of cure was observed in BR-Nd-based system (Table VII).

Tack for the BR-Nd-based composition (Fig. 9) was higher than for the other compositions. The tendency observed for the compositions prepared according to the ASTM formulation was the same.

Although the differences observed in the tensile and deformation by compression tests were small, there was still a higher performance in the polymers obtained from the neodymium-based catalyst systems (Table VIII and Figure 10). A more significant difference occurred in the tear test (Fig. 11), in which the BR-Nd-based composition was around 10 and 18% superior to those with the BR-Ni and BR-Co bases, respectively.



**Figure 12** De Mattia bending tests of the elastomeric compositions of high-cis BRs obtained from different catalyst systems (BR-Co, BR-Ni, and BR-Nd).



**Figure 13** Resilience of the elastomeric compositions of high-cis BRs obtained from different catalyst systems (BR-Co, BR-Ni, and BR-Nd).

The major differences in performance occurred when the compositions were submitted to dynamic tests. In the De Mattia bending test, which simulated cyclic deformations imposed to the sides of tires (side-wall), the BR-Nd-based composition was highly resistant to fatigue by bending and completed the test with 1000 K cycles without a single crack appearing. The same did not happen to the other compositions, which started cracking before expected, and the samples of the BR-Co composition tore apart (Fig. 12).

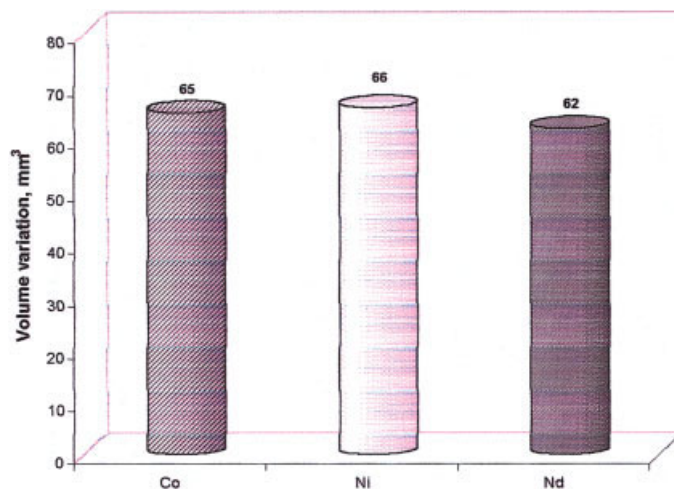
Also, concerning resilience, a property directly connected to heat buildup, the compositions formulated with BR-Nd proved to have the best performance, showing differences of about 11 and 14% compared with the BR-Co- and BR-Ni-based compositions, respectively (Fig. 13).

Resistance to abrasion, defined as the elastomeric compositions' resistance to wear by contact with abra-

sive surfaces in movement, involves the elastomer's plastic and elastic deformation.<sup>17</sup> It is a combination of properties—resilience, stiffness, thermal stability, and resistance to cutting and tearing—that must be optimized to obtain better performance from the formulated compositions. The BR-Nd-based compositions showed a wearing index 5% inferior to the compositions prepared with BR-Ni and BR-Co (Fig. 14).

Two important properties for a tire are rolling resistance, which has good economical and environmental appeal due to fuel saving and the diminishment of the emission of polluting gases, and skidding resistance, which is directly related to car safety and reliability.

The potential tire performance, as for skidding and rolling resistance properties, can be estimated in a laboratory through the values found for  $\tan \delta$  (at 0 and 50°C), under low frequencies (1–10 Hz), of the cured



**Figure 14** Deutsches Institut für Normung abrasion of the elastomeric compositions of high-cis BRs obtained from different catalyst systems (BR-Co, BR-Ni, and BR-Nd).

**TABLE IX**  
**Tan  $\delta$  Values for High-cis BRs Obtained from Different Catalyst Systems (BR-Co, BR-Ni, and BR-Nd)**

Tan $\delta$	Catalyst system		
	Co	Ni	Nd
Tan $\delta$ at 0°C	0.188	0.193	0.174
Tan $\delta$ at 50°C	0.173	0.178	0.155
Tan $\delta$ at 0°C – Tan $\delta$ at 50°C	0.015	0.015	0.019

elastomeric compositions with identical formulations to the ones used in the tire tread. High tan  $\delta$  values at 0°C are favorable to good skidding resistance, whereas low tan  $\delta$  values at 50°C decrease rolling resistance.<sup>18</sup>

The results found for tan  $\delta$  at 50°C (Table VIII) show that the BR-Nd-based composition was the best one to achieve a decrease in rolling resistance because the value obtained was 12 and 15% lower than those ones for tan  $\delta$  at 50°C of the BR-Co- and BR-Ni-based compositions, respectively.

Another important parameter is the difference between the tan  $\delta$  values at 0 and 50°C ( $\Delta$ tan  $\delta$ ), respectively, which indicates it how easy it would be to make the skidding and rolling resistance properties, which are opposite to one another, compatible. The higher the  $\Delta$ tan  $\delta$  is, the more versatile the composition will be to property adjustments. The BR-Nd-based composition showed a  $\Delta$ tan  $\delta$  26% superior to that of the other compositions (Table IX).

## CONCLUSIONS

Among the commercially available high-cis BRs, polymers produced by neodymium-based catalysts bear higher stereopurity and higher linearity, and their polydispersity is considered slightly wide. These characteristics are responsible for the superior mechanical properties of these elastomers, especially the dynamic properties, such as abrasion resistance, resistance to bending, fatigue, resilience, and heat buildup. All of these properties together indicated that BR-Nd is po-

tentially the best high-cis BR for applications that require high performance. In the tire industry, for example, BR-Nd use is highly advisable for the manufacturing of high-performance tires, such as the green tire, which has a low rolling resistance and a high wear resistance.

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