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Natural rubber (NR) is poly(isoprene), a polymer essentially made by *cis*-1,4 repeating units with regular head-to-tail enchainment (refs. 1 and 2). NR has unmatched properties such as building tack and strength in the uncured state, and tensile strength and crack growth resistance in the crosslinked state. These properties make NR the most important rubber, with worldwide consumption that amounts at present to more than 12 million metric tons per year (ref. 3). NR on the commercial scale is obtained almost exclusively from the *Hevea brasiliensis* tree (HNR), and nowadays faces major issues: Shortage is envisaged, plantations are located in relatively small geographic areas and diseases could lead to significant crop loss. Research efforts are thus increasing on alternative sources for natural rubber. *Parthenium argentatum*, also known as guayule (refs. 4-11), a flowering shrub grown in semi-arid regions, typically in Mexico and in the southern United States, is an alternative crop for natural rubber (GR) since the early 20th century.

A typical feature of poly(1,4-*cis*-isoprene) from natural sources is the presence, together with the polymer, of non-rubber components. NR samples provide a cocktail of chemicals that can affect the samples' properties, and whose composition (types and amounts) depends on the type of rubber, plant or shrub, crop and extraction process (refs. 10-12). It is already reported in the literature that natural rubber from guayule contains a remarkable amount of non-rubber components, larger than the amount usually detected in NR. Research on natural rubber from alternative sources cannot leave out of consideration the role of non-rubber components.

This work was focused on the sulfur-based vulcanization of HNR and GR, and of synthetic poly(1,4-*cis*-isoprene) from Ziegler-Natta catalysis (IR). Detailed characterization of HNR, GR and IR samples was performed: Main molecular features of the polymers, and type and amounts of most non-rubber components are reported. Vulcanization was performed in the absence of fillers. Rheometric curves were taken, and crosslinking density and the nature of the crosslinking network (the distribution of sulfur bridges length) were assessed. Reactivity of low molecular mass chemicals present in GR-R was investigated by performing model reactions between such chemicals and a sulfur-containing reagent such as 1-dodecane-thiol.

Experimental section

Materials

Rubber samples included:

- Synthetic poly(1,4-*cis*-isoprene) (IR) (Nizhnekamskneft-echim Export) had the trade name SKI3 and 70 Mooney units

(MU) as Mooney viscosity ($M_L [1+4] 100^\circ\text{C}$).

- Natural poly(1,4-*cis*-isoprene) (NR) (EQR-E.Q. rubber, BR-THAI, Eastern GR. Thailandia - Chonburi) had the trade name STR20 and 73 Mooney units (MU) as Mooney viscosity ($M_L [1+4] 100^\circ\text{C}$).

- Natural poly(1,4-*cis*-isoprene) (TKS) (NovaBioRubber Green Technologies Inc.) had 76 Mooney units (MU) as Mooney viscosity ($M_L [1+4] 100^\circ\text{C}$).

Natural poly(1,4-*cis*-isoprene) (GR) was extracted with solvent from latex of Yulex Corporation. GR 'raw' (GR-R) had 35 Mooney units (MU) and GR 'purified' (GR-P) had 102 Mooney units (MU) as Mooney viscosity ($M_L [1+4] 100^\circ\text{C}$).

Isolation of GR-R from rubber latex involved the following steps: In a 15 cm diameter flat beaker were poured 30 mL of guayule rubber latex that formed a 2 mm thick continuous layer which was dried for 48 hours in a hood at room temperature in the absence of light. The quantity of GR-R obtained was 15 g.

For the preparation of GR-P, GR-R (10 g) was finely sliced and placed into a brown laboratory glass bottle (Duran GL 45) provided with a cap, and 500 mL of ethyl acetate were added. The suspension was left 24 hours without stirring, in the absence of light. The solvent was poured off and the operation was repeated twice. The pure solid rubber was dried for 12 hours at 30°C under nitrogen atmosphere. Eight g of pure rubber were eventually obtained.

The following ingredients were used as received: ZnO (Zincol Ossidi), stearic acid (Sogis), N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) (Crompton), sulfur (Solfotecnica), N-tert-butyl-2-benzothiazolesulfenamide (TBBS) (Flexsys), and dicumylperoxide (DCP) with a concentration of 40% by weight (Arkema).

Characterization of poly(1,4-*cis*-isoprene) samples

The amount of non-rubber components was determined by thermal gravimetric analysis (TGA), performed with a Mettler TGA SDTA/851 instrument in a flowing N₂ (flow rate 60 ml/minute) from 30°C to 300°C with a heating rate of 10°C/minute.

For extraction of non-rubber components from poly(1,4-*cis*-isoprene), samples were extracted with a Soxhlet apparatus in refluxing acetone for 16 hours, using the ISO 1407 procedure. The extracts were characterized by ¹³C-NMR experiments.

For determination of fatty acids present in poly(1,4-*cis*-isoprene) samples, content and type of fatty acids were determined by GC-MS analysis. In a 100 mL conical flask equipped with a condenser were poured in sequence 2 g of solid rubber and 40 ml of a solution 4% (w/v) of H₂SO₄ in methanol. The reaction was carried out under reflux for one hour. Upon cooling the suspension to room temperature, solid NaHCO₃ was added to achieve a neutral solution. Salts were removed by

Table 1 - amount and type of non-rubber components in poly(1,4-*cis*-isoprene) samples from natural sources^a

	HNR	GR-R	GR-P
Non-rubber components (mass %) ^a	1.7	8.9	1.5
Nitrogen content (mass %) ^{b, c}	0.28	0.04	0.03
Fatty acids, total amount (mass %) ^b	1.53	0.6	0.91
Saturated - unsaturated	0.65-0.88	~0-0.58	~0-0.79
Terpenes	N.F. ^d	7.9	N.D. ^e

^afrom TGA analysis; ^bon the total mass of the sample; ^cmass % of nitrogen is taken as indication of protein content; ^dnot found; ^enot determined

filtration, performed using a filter paper and a funnel. The liquid was brought to 100 mL by adding methanol into a volumetric flask. Five ml of such solution were put into a 30 mL test tube and mixed with 5 ml of heptane. The organic phase was washed with 5 ml of brine. The upper phase was removed, dried on Na₂SO₄ and analyzed by GC-MS analysis.

For NMR analysis, one-dimensional ¹H- and ¹³C-NMR spectra were measured at 400 and 100 MHz, respectively, using a Bruker AV 400 equipped with a 5 mm multinuclear probe with reverse detection (Bruker, Rheinstetten, Germany). The solvent was deuterated chloroform and the temperature was 27°C. The experimental time for ¹³C-NMR spectra was typically 12 hours (corresponding to more than 10,000 scans). Data were processed using Topspin 1.1 or MestReNova.

Composites preparation by melt blending

A Brabender type internal mixer with 50 mL mixing chamber was used for the preparation of composites. The following standard procedure was adopted: The rubber was introduced into the mixer at 80°C and 60 rpm and masticated for one minute, vulcanization ingredients were added and mixing was carried out for five minutes. Composites were finally homogenized by passing them five times on a two-roll mill operating at room temperature. Formulations of composites are reported in tables 3 and 6.

Table 2 - characteristics of poly(1,4-*cis*-isoprene) samples

	HNR	GR-R	GR-P	IR
M _w ^a 10 ⁻⁶ (Da)	1.5	N.D.	2.5	1.1
M _w /M _n ^a	3.2	N.D.	3.2	3.4
Mooney units ^b	73	35	102	70
T _g ^c (°C)	-64.4	-64.6	-64.9	-65.3
1,4- <i>cis</i> units ^d (mol %)	98.8	N.D. ^f	99.2	98.3

^afrom GPC analysis; ^bfrom Mooney measurements; ^cfrom DSC; ^dfrom ¹³C-NMR 100 MHz; ^fnot performed

Composites characterization

Crosslinking reaction was studied at 151°C for 30 minutes and at an oscillation frequency of 1.67 Hz with a Monsanto oscillating disc rheometer (MDR 2000) (Alpha Technologies, Swindon, U.K.). The following parameters were determined: The minimum modulus M_L, the maximum modulus M_H, the modulus M_{final} at the end of the crosslinking reaction, the time t_{s1} required to have a torque equal to M_L + 1, the time t₉₀ required to achieve 90% of the maximum modulus M_H (i.e., to achieve the optimum of crosslinking) and the so-called reversion, i.e., the relative decrease of the modulus at the end of the crosslinking reaction: (M_H - M_{final})/(M_H - M_L) • 100.

Results and discussion

Purification and characterization of poly(1,4-*cis*-isoprene) samples

Purification of a GR-R sample was performed by extracting the non-rubber components at room temperature with an eco-friendly solvent such as ethyl acetate, as described in the experimental part, obtaining the GR-P sample. Table 1 shows the amount and type of non-rubber components of poly(1,4-*cis*-isoprene) samples from natural sources.

It is widely acknowledged that non-rubber components in natural rubber samples depend on the type of tree or shrub, crop and extraction method. However, data in table 1 that are only representative of the investigation samples are substantially in line with what is reported in the literature. The highest nitrogen content, about 0.3 mass %, can be observed in the HNR sample and is appreciably lower in GR-R. Nitrogen content in solid rubber of 0.4% (ref. 13) has been reported for HNR. The nitrogen content for the GR ASTM 2227 grade 5 and for a FEMA specification grade (refs. 14 and 15) was reported to be ≤0.6 mass %.

A larger amount of fatty acid was found in HNR. It is worth observing that fatty acids in GR were essentially only unsaturated. In an HNR sample containing about 6% by mass of non-rubber chemicals, neutral lipids were about 2%, and glycol lipids and phospholipids about 1% (refs. 16 and 17).

The content of terpenes in GR-R shown in table 1 is remarkable indeed. The maximum amount of resins (extracted with acetone) was found to be about 8% in GR from two-year-old guayule plants grown in Arizona (ref. 18) and from three to four-year-old plants from Yulex (ref. 19).

¹³C-NMR characterization was performed on the terpene mixture, detecting the presence of sesquiterpenes. Most abundant terpenes were found to be argentatines, guayuline A and guayuline B: Mass % were 43, 31 and 19, respectively.

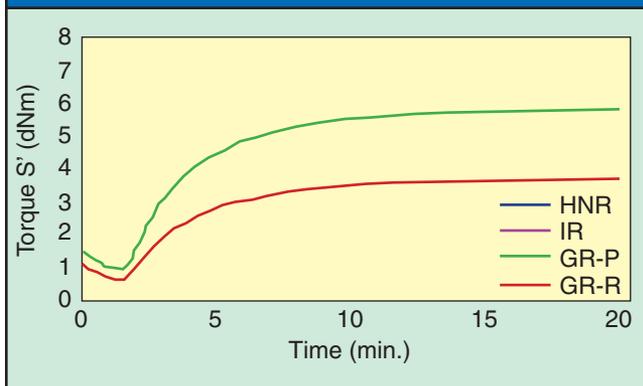
Table 2 shows the main molecular characteristics of the poly(1,4-*cis*-isoprene) samples. All of the poly(isoprene)s have high molecular mass (M_w higher than 10⁶ Da) and com-

Table 3 - formulation of composites based on poly(1,4-*cis*-isoprene) samples, crosslinked with DCUP

Ingredients	phr
Rubber ^a	100.0
DCUP	1.4

^aHNR, IR, GR-R, GR-P

Figure 1 - rheometric curves of composites based on different poly(1,4-cis-isoprene) samples crosslinked with DCUP



parable molecular mass distribution (M_w/M_n equal to about 3). Glass transition temperature (T_g) was found at about -65°C . Steric purity was assessed through ^{13}C -NMR analysis. All of the poly(isoprene)s have high 1,4-cis content; about 99% for the polymers from natural sources, slightly lower (about 98%) for the IR sample.

Crosslinking of poly(1,4-cis-isoprene) samples with peroxide
Crosslinking of poly(1,4-cis-isoprene)s from different sources was performed with dicumyl peroxide at 151°C . Formulations are reported in table 3.

The rheometric curves are shown in figure 1. Data derived from the rheometric curves are shown in table 4, and composites crosslinking density is shown in table 5.

Data in table 4 reveal similar induction time for composites based on the different poly(1,4-cis-isoprene) samples, in spite of the different chemical composition. Composites based on GR have lower vulcanization rate (higher t_{90}), and GR-R shows the lowest M_H value. These results suggest that the peroxide is able to initiate the radical process that propagates creating bridges responsible for the modulus enhancement, both in the absence and in the presence of non-rubber components, such as the terpenes in the case of GR-R. The lower M_H value observed for the composite based on GR-R can be attributed to the plasticizing effect of terpenes, as well as to the lower crosslinking density. Data obtained with GR-P-based composites show that, upon extracting non-rubber components from GR-R, M_H and M_H-M_L values, as well as the crosslinking density, become similar to those of NR and IR based composites.

Vulcanization of poly(1,4-cis-isoprene) samples with sulfur-based system

Vulcanization with a sulfur-based system was performed on composites based on poly(1,4-cis-isoprene) samples using the standard ASTM D 3184-89 formulation, shown in table 6.

The rheometric curves are shown in figure 2. Data derived from the rheometric curves are in table 7, and data from the analysis of the crosslinking network are shown in table 8. Analysis of the crosslinking density was performed according

Table 4 - data from the rheometric curves of composites based on different poly(1,4-cis-isoprene) samples crosslinked with DCUP

Parameter	Poly(1,4-cis-isoprene) samples			
	HNR	IR	GR-P	GR-R
t_s (1), min.	2.3	2.3	2.4	2.7
t (90), min.	3.5	3.3	5.0	5.0
M_H (dNm)	6.1	6.1	5.8	3.7
$(M_H - M_L)$ (dNm)	4.4	4.5	4.9	3.1

to the so-called thiol-amine decomposition method. Crosslinking density was first determined through swelling measurements by applying the Flory-Rehner equation. Swollen samples were then reacted with propanethiol to assess the number of polysulfidic bridges whose scission is supposed to occur as a consequence of the reaction with the thiol.

Curves in figure 2 show that poly(1,4-cis-isoprene)s from different sources have quite different behavior in sulfur-based vulcanization. Differences are definitely more pronounced than in the case of peroxide-based crosslinking. GR-R promotes the fastest vulcanization, showing the lowest t_{s1} and t_{90} values. The removal of by-products from GR-R makes the vulcanization appreciably slower, with t_{s1} and t_{90} time values higher than those of the composite based on HNR. The slowest kinetics are shown by the composite based on IR. As observed in the case of crosslinking promoted by peroxide, the GR-R based composite has the lowest M_H modulus. Values of M_H and M_H-M_L appear to be in line with data arising from the analysis of the crosslinking network. In particular, it appears in table 8 that the composite based on GR-R has lower crosslink-

Table 5 - crosslink density of composites based on different poly(1,4-cis-isoprene) samples crosslinked with DCUP

Poly(isoprene)	Total crosslink [mol/g $\times 10^{-5}$]
HNR	2.6
GR-P	2.0
GR-R	1.5
IR	2.2

Table 6 - ASTM D 3184-89 formulation of composites based on poly(1,4-cis-isoprene) samples crosslinked with sulfur-based system

Ingredients	phr
Rubber ^a	100.0
ZnO	6.0
Stearic acid	0.5
Sulfur	3.5
TBBS	0.7

^aHNR, IR, GR-R, GR-P

Table 7 - data from the rheometric curves of composites based on different poly(1,4-cis-isoprene) samples crosslinked with sulfur-based system

Rubber	t_{s1}	t_{90}	$\Delta S'$
HNR	6.0	9.1	6.0
GR-P	8.4	12.2	5.6
GR-R	4.2	6.5	3.6
IR	17.1	21.4	4.8

Figure 2 - rheometric curves of composites based on different poly(1,4-cis-isoprene) samples crosslinked with sulfur-based system

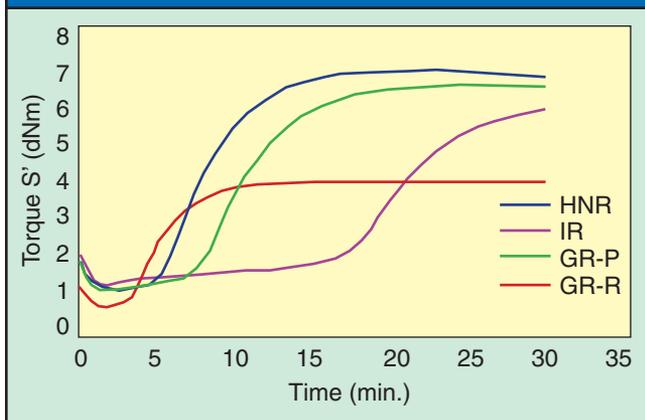


Figure 3 - rheometric curves of composites based on GR-R and different amounts of sulfur - reference composite is with 3.5 phr of sulfur (formulation is in table 6)

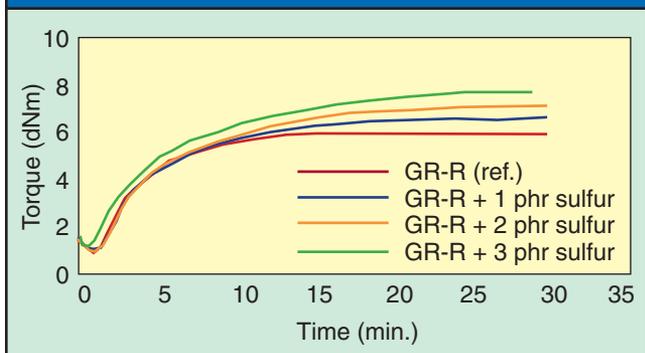
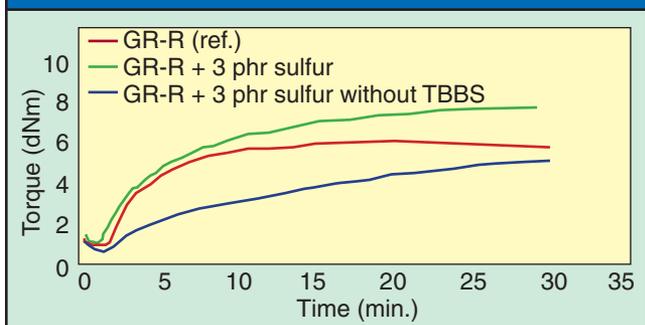


Figure 4 - rheometric curves of composites based on GR-R, in the presence and in the absence of sulfenamide (formulation is in table 6)



ing density and becomes soluble after the reaction with the thiol. The removal of by-products from GR-R makes the GR-P based composite similar to the HNR-based one: Similar values of M_H and M_H-M_L can be observed in table 7 and figure 2, and similar structure of the crosslinking network can be observed in table 8.

Table 8 - crosslinking density and length of sulfidic bridges for composites based on different poly(1,4-cis-isoprene) samples crosslinked with sulfur-based system

Poly(isoprene)	Total crosslink [mol/g ($\times 10^{-5}$)]	Mono and di-sulfide [% (wt./wt.)]	Poly-sulfidic [% (wt./wt.)]
HNR	2.5	28	72
GR-P	2.1	32	68
GR-R	1.4	-	-
IR	1.9	32	68

Table 9 - crosslinking density and length of sulfidic bridges for composites based on different poly(1,4-cis-isoprene) samples crosslinked with sulfur-based system

Amount of sulfur in the composite (phr) ^a	3.5	4.5	5.5	6.5
Total crosslink [mol/g ($\times 10^{-5}$)]	0.8	1.5	2.8	3.4
Mono and di-sulfide [mass %]	-	24	22	24
Poly-sulfide [mass %]	-	76	78	76

^aFormulation is in table 6.

Data arising from the sulfur-based vulcanization reveal that GR-R promotes fast vulcanization and, at the same time, low crosslinking density. Both these findings were verified by vulcanizing GR-R composites in the presence of larger amounts of sulfur. Besides the formulations shown in table 8, three more composites were prepared with 4.5, 5.5 and 6.5 phr of sulfur. Rheometric curves are shown in figure 3, and data about the structure of the crosslinking network are shown in table 9.

The addition of sulfur leads to the substantial increase of M_H modulus and of the crosslinking density. By adding 1 phr of sulfur, the composite becomes insoluble, and by adding 2 phr of sulfur, it acquires the same crosslinking density as the HNR-based composite. It is definitely worth observing that vulcanization remains fast, with almost undetectable differences in the induction time values.

To verify the ability of GR-R to promote fast vulcanization reactions, composites were prepared by modifying the formulation reported in table 6 with 6.5 phr of sulfur, with and without the sulfenamide as accelerator. Rheometric curves are shown in figure 4.

It appears that the fast vulcanization reaction is also obtained in the absence of the accelerator. However, both vulcanization rate and M_H modulus are lower.

Data discussed so far seem to suggest that chemicals present in GR-R, namely terpenes, are able to react efficiently with sulfur and sulfur-based systems, promoting fast activation of the vulcanization process and at the same time, preventing, to different extents, the reaction of sulfur with the polymer chains.

Table 10 - data from the rheometric curves of composites based on either HNR or GR-R, prepared with 1 phr of ZnO (formulation is in table 6)

	HNR	GR-R
t_{s1} min.	3.3	2.4
t_{90} min.	5.5	4.0
M_H (dNm)	6.4	4.5
M_L (dNm)	1.3	0.8
% reversion	13.9	32.0

To verify the ability of the by-products present in the GR-R sample to preferentially interact with sulfur, hindering the traditional pathway of the vulcanization reaction, composites were prepared with reduced amounts of ZnO. The same formulation reported in table 6 was used, but the amount of ZnO was reduced to 3 phr and to 1 phr. HNR and GR-R were used as the natural rubber samples. Very similar results

were obtained with 3 phr of ZnO. Figure 5 shows the rheometric curves observed for composites based on 1 phr of ZnO.

Also in figure 5, it is possible to observe the fast vulcanization promoted by GR-R and, at the same time, the remarkably lower modulus and higher reversion, as confirmed by the values reported in table 10.

These data seem to confirm the efficient reaction of the non-rubber components in guayule rubber, namely terpenes, with sulfur and sulfur-based systems. A lower amount of sulfur is thus available for the formation of the active sulfurating species based on Zn and the aromatic moiety of the sulfenamide (ref. 20).

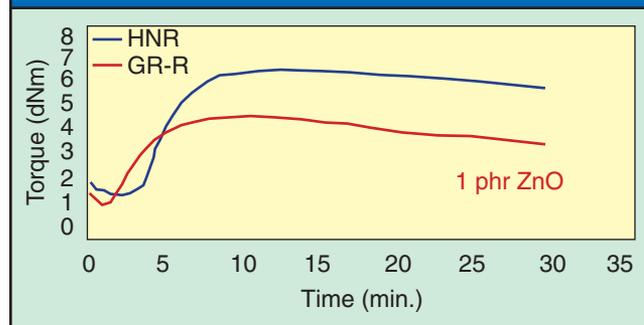
To verify the reactivity of terpenes with a sulfur-based chemical, the reaction of guayuline A with 1-dodecanethiol was studied. Preliminary results indicate the reactivity of the double bond of the terpene ring with the thiol.

Conclusions

Poly(1,4-*cis*-isoprene) samples were studied, from *Hevea brasiliensis* (HNR) and *Parthenium argentatum* (GR), and from Ziegler-Natta catalysis. The GR sample was coagulated from latex (GR-R); non-rubber components were then extracted with solvent, obtaining the purified GR-P sample. Poly(1,4-*cis*-isoprene)s from natural sources had comparable molecular features, such as molecular mass, molecular mass distribution, steric purity and glass transition temperature. Remarkably different was the amount and the composition of non-rubber components. In particular, a large amount of terpenes was found in GR-R. Crosslinking was performed with dicumyl peroxide and with a sulfur-based system. Differences observed when the latter system was used have to be ascribed to the effect of terpenes. Quick start of the vulcanization reaction even in the absence of accelerator, lower crosslinking density that can be recovered to higher values by adding sulfur, and remarkable reversion when a low amount of ZnO is used, appear to be clear indicators of the reactivity of terpenes with sulfur and sulfur-based chemicals. Addition of 1-dodecanethiol to guayuline A was used as the model reaction to demonstrate such reactivity.

This article is based on a paper presented at the 186th Technical Meeting of the Rubber Division, ACS, October 2014.

Figure 5 - rheometric curves of composites based on either HNR or GR-R, prepared with 1 phr of ZnO (formulation is in table 6)



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