Effect of Mica Addition on the Properties of Natural Rubber and Polybutadiene Rubber Vulcanizates

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ABSTRACT: The rheometric, mechanical, and dynamic mechanical properties as well as fracture surfaces of natural rubber–mica and polybutadiene rubber–mica vulcanizates were studied. Mica was used in the range of 0–30 phr and the rheometric study was carried out at 160°C. The results indicate that the mechanical properties are improved as filler addition increases. Dynamic mechanical testing was used to analyze the observed mechanical behavior. The two elastomers showed different fracture behaviors. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 2156–2162, 2003

Key words: blends; elastomers; filler; crosslinking; electron microscopy

INTRODUCTION

Fillers are finely divided powders that have been used since the early days of the rubber industry, mainly to promote reinforcement and thus making rubber compounds useful for a variety of applications. Fillers are also used to reduce cost or to impart certain characteristics such as modulus, abrasion resistance, tear resistance, and tensile strength.[1–3] Another consequence of incorporating a filler into a polymer is the considerable change in the dynamic properties one can achieve in the final composites.[4]

Carbon black is unquestionably the universal reinforcing filler, even though silicas are also often used. Other fillers are extensively used where a high degree of reinforcement is not essential as, for example, silicates, clays, calcium carbonate, and other so-called mineral fillers.[5] However, in the search for cheaper vulcanizates, new materials have been considered as potential fillers, whether for mere economical reasons or rather to impart some desirable characteristics.[6] Mica has been considered as a useful filler because of its low cost, availability, and outstanding electrical, heat, and chemical resistance.[7]

In addition to the effect of the presence of filler, physical properties of sulfur vulcanizates of diene rubbers also depend on the network structure, which is a function of the degree of crosslinking, crosslink structure, and main chain modification. Of these the most important determining factor concerning physical properties is crosslink density.[8]

In this study, the influence of mica in natural rubber (NR) and polybutadiene rubber (BR) vulcanizates was investigated by comparing their mechanical and dynamic mechanical properties. These two elastomers are frequently combined in the tire industry, so the behavior of each one separately is of great interest.

EXPERIMENTAL

Preparation of vulcanizates

The formulations used for this study are shown in Table I. Mica was used as the filler in a range varying from 0 to 30 phr.

NR and BR compositions were prepared on a Berstorff two-roll mill, operating at 50°C and friction rate of 1 : 1.25. The sheeted compounds were then conditioned at 27°C for 24 h, before testing.

The curing parameters were determined on an oscillating disk rheometer (TI-100; Tecnología Industrial) according to ASTM D 2084-81,[9] at 160°C and 3° arc. The results are shown in Table II. The compositions were then vulcanized at 160°C during the respective optimum cure times, under pressure (3.0 MPa), on an electrically heated press.

Determination of mechanical properties

The tensile properties and tear resistance of vulcanizates were determined according to ASTM D 412 and

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TABLE I
Formulation of Rubber Vulcanizates

Component	phr
NR[a] (or BR[b])	100
Zinc oxide	3.0
Stearic acid	2.5
Aminox[c]	2.0
PVI[d]	0.3
Mica	Variable
Sulfur	2.5
TBBS[e]	0.6

[a] Mooney viscosity, $ML_{(1+4)}$ at 100°C = 102.6.
[b] 97.5% 1,4(*cis*); Mooney viscosity, $ML_{(1+4)}$ at 100°C = 41.7.
[c] Reaction product between diphenylamine and acetone, obtained at low temperature.
[d] N-Cyclohexylthiophthalimide.
[e] *tert*-Butyl-2-benzothiazolsulfenamide.

ASTM D 624, respectively. These tests were carried out at room temperature on a Instron universal testing machine (Model 1101; Canton, MA), with a crosshead speed of 500 mm/min. The tensile specimens were die cut from vulcanized rubber plates and at least five specimens for each composition were tested and the stress and strain at break determined.[10,11] Hardness measurements were performed according to ASTM D 2240 on a Shore A hardness tester.[12]

Crosslink density

Vulcanized samples (5.0 × 2.5 × 0.2 cm) were weighed and allowed to swell in an excess of toluene at room temperature, in the dark, until equilibrium was achieved. The swollen samples were then weighed, the solvent removed under vacuum, and weighed again. The volume fraction of the rubber in the swollen vulcanizates (V_r) was calculated using the following equation:

$$V_r = \frac{(m_1/\rho_r) - V_f}{(m_1/\rho_r) - V_f + (m_2 - m_3)/\rho_s}$$

where m_1 is the initial weight of specimen, m_2 is the weight of swollen specimen, m_3 is the weight of specimen after equilibrium, V_f is the volume of filler, ρ_r is the density of rubber, and ρ_s is the density of solvent (0.8669 for toluene).[13]

V_r was substituted in the Flory–Rehner equation, as follows:

$$\nu = \frac{\ln(1 - V_r) + V_r + \mu V_r^2}{V_0(V_r^{1/3} - V_r/2)}$$

where ν is the crosslink density, V_r is the volume fraction of the rubber in the swollen vulcanizates, μ is the parameter characteristic of interaction between the rubber network and the swelling agent, and V_0 is the molar volume of toluene (V_0 = 106.2 cm^3/mol).[14]

The polymer–solvent interaction parameters[15] used were μ_{NR} = 0.42, μ_{BR} = 0.34, and μ_{NR-BR} = 0.38.

Dynamic mechanical testing

The dynamic mechanical properties were measured using a Rheometric Scientific DMTA analyzer (Model MK III; Polymer Laboratories, Poole, UK) under the following conditions: frequency, 1 Hz; heating rate, 2°C/min; single-cantilever bending mode, and temperature ranging from −130 to 20°C.

Scanning electron microscopy

A scanning electron microscope (JEOL JSM 5800LV, Peabody, MA) was used to examine the fracture aspects of the rubber compounds. The study of the failure mechanisms was carried out by direct observation of the sample topography of samples cryofractured after being immersed for at least 10 min in liquid nitrogen. All samples were sputter-coated with gold in a vacuum chamber before examination.

RESULTS AND DISCUSSION

Curing characteristics

The cure characteristics are detailed in Table II. The NR compositions show, in comparison to BR, shorter scorch times (t_{s2}) and higher overall reaction rates [cure rate index (CRI)].

For each set of compositions the optimum cure times (t_{90}) increase with the addition of mica, which means that a retardation effect occurs in the vulcanization process.

Minimum torque (M_L) values can be related to the viscosity of the unvulcanized compounds. NR compositions show higher M_L values compared to those of BR. The addition of mica slightly decreases M_L values

TABLE II
Cure Characteristics of Vulcanizates[a]

Rubber	Mica (phr)	t_{90}	M_L	M_H	t_{s2}	CRI
NR	0	10.79	8.25	49.95	5.94	20.61
	10	11.12	8.5	50.15	6.22	20.41
	20	13.46	6.05	49.9	6.67	14.72
	30	15	7.8	52.65	7.32	13.02
BR	0	35.7	12.7	49.35	13.5	4.5
	10	35.7	11.8	44.35	13.2	4.44
	20	42.3	11.2	42.85	15.3	3.7
	30	42.6	11.3	43.4	15.6	3.7

[a] t_{90}, optimum cure time (min); M_L, minimum torque (lb. · in.); M_H, maximum torque (lb. · in.); t_{s2}, scorch time (min); CRI, cure rate index (min^{-1}).

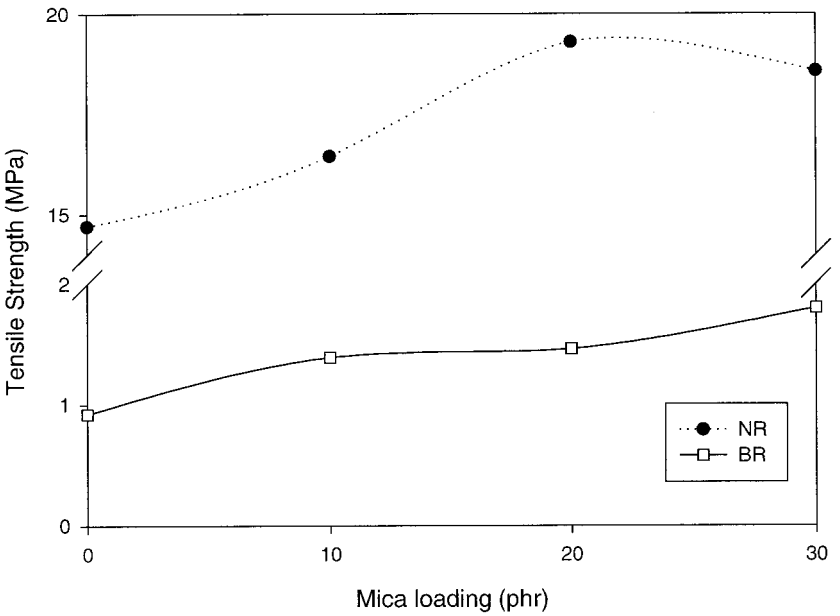


Figure 1 Effect of mica loading on tensile strength.

of BR–mica compositions, whereas in the case of NR–mica compositions a clear tendency cannot be drawn, except for the 20 phr composition, which shows a significant reduction of this parameter. Thus, mica-filled compounds are easier to process, given that lower viscosities are involved.

The maximum torque (M_H) can be taken as a measure of crosslinking density, and the gums (NR and BR, without mica) show similar values. Nevertheless, although NR vulcanizates present a discrete increase in M_H with mica addition, vulcanizates with BR show decreased values. These results suggest that NR is more susceptible than BR to crosslinking.

Physicomechanical properties

Physicomechanical properties are illustrated in Figures 1, 2, and 3. As expected, the mechanical performance of the NR vulcanizates was significantly superior.

Figures 1 and 2 show the tensile strength and the elongation at break for all compositions. The results show the superiority of NR, compared to BR, in the entire range of mica loading. In general, mica increases the tensile strength of both NR and BR. In the case of NR vulcanizates, by increasing the filler content the tensile strength also increases until a maximum value is reached at 20 phr. Further addition of

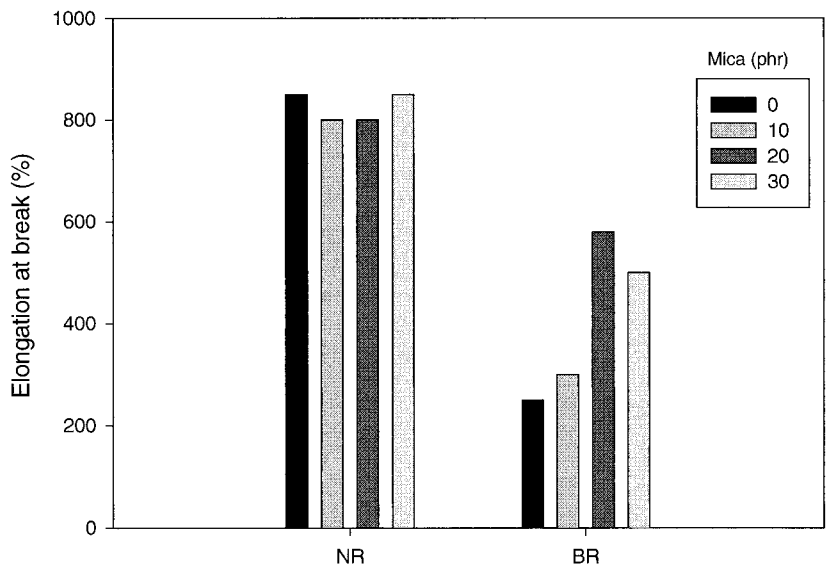


Figure 2 Effect of mica loading on elongation at break.

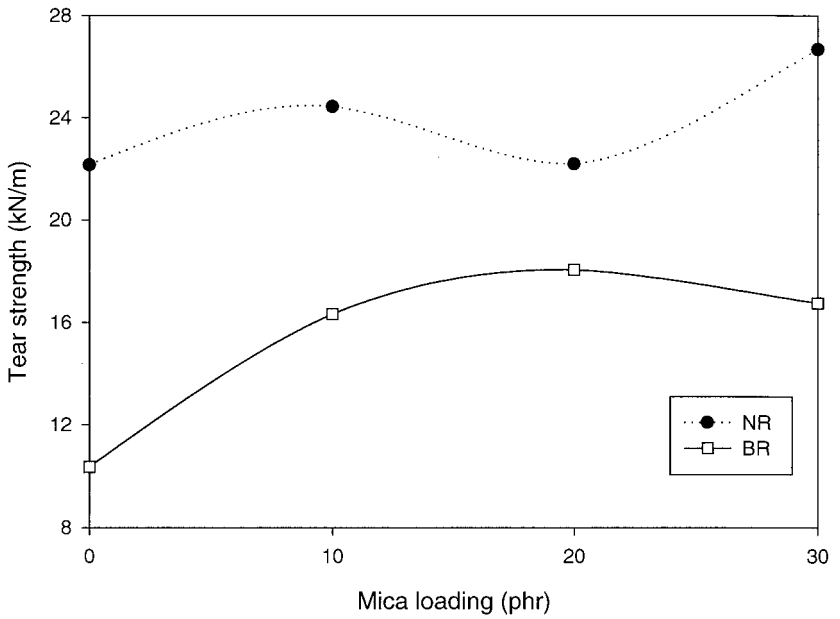


Figure 3 Effect of mica loading on tear strength.

the filler reduces the tensile strength. In the case of BR vulcanizates, the increase in tensile strength upon addition of mica is gradual over the entire range studied.

Figure 2 shows that the behavior of the elongation at break for the two rubbers is not the same. Although for the NR compounds a more or less constant value is observed, independent of mica loading, for BR a positive effect is obtained. The BR compositions containing 20 and 30 phr of mica show elongation values that are twice as high as that for the unfilled BR. The presence of mica in these compounds shows that for NR, the tensile strength increases without having a deteriorating effect on elongation, whereas for BR, both properties increase over the entire range of filler used.

The effect of mica on tear strength is shown in Figure 3. It can be seen that this effect is more pronounced in the case of BR vulcanizates, although both rubbers experience a positive effect. Figure 3 also shows that, considering the range of mica loading studied, a critical content is detected, around 20 phr, for the BR vulcanizates, whereas for NR compositions, the property has not yet achieved the limit of saturation.

Hardness values presented in Figure 4 show that, as expected, both sets of compositions have increased results with increasing filler loading.

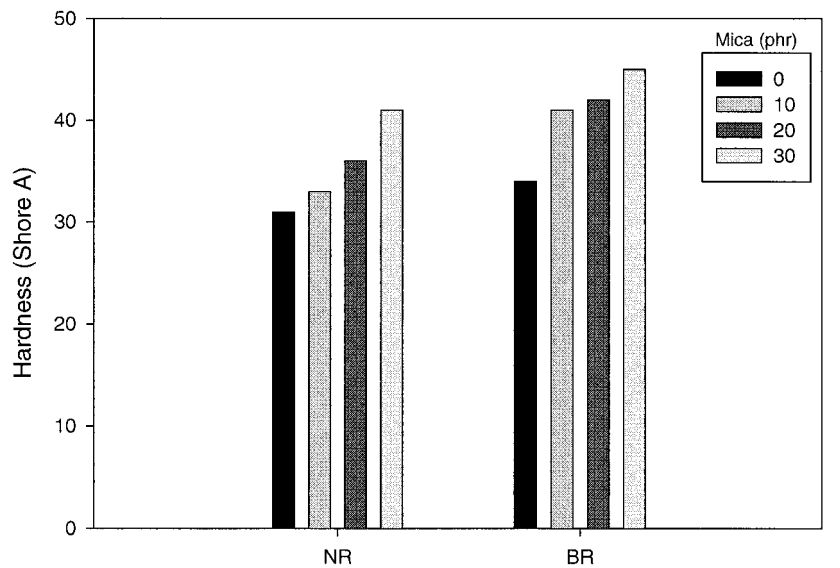


Figure 4 Effect of mica loading on hardness.

TABLE III
Crosslink Density of Vulcanizates

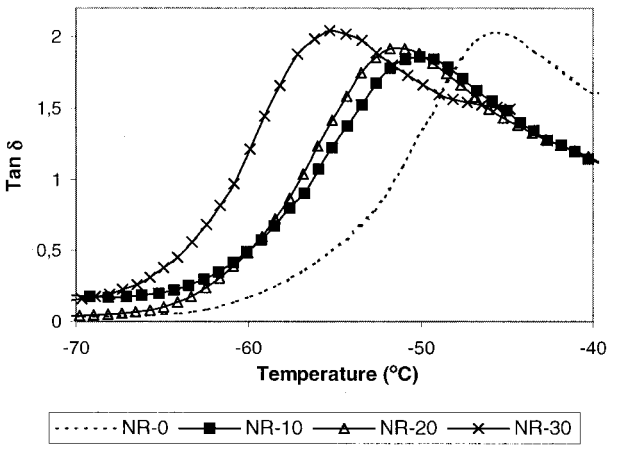
	Mica content[a]/(phr)							
	0		10		20		30	
Rubber	V_r	ν (10^5)	V_r	ν (10^5)	V_r	ν (10^5)	V_r	ν (10^5)
NR	0.1537	8.64	0.1787	12	0.1944	14.5	0.2001	15.5
BR	0.1356	6.61	0.1804	12.3	0.1728	11.1	0.1598	9.4

[a] ν, the crosslink density; V_r, the volume fraction of the rubber in the swollen vulcanizates.

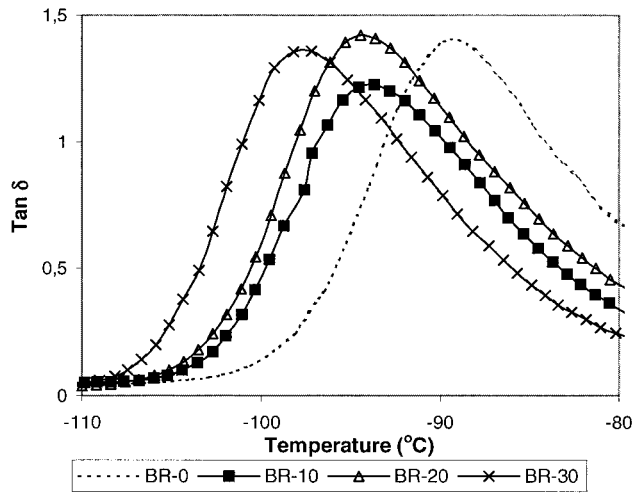
Determination of crosslink density

Values of V_r and ν are presented in Table III, showing the variation of ν for each composition.

In the compositions without filler the crosslink density of NR is higher than that of BR. This fact, in addition to the better properties shown by NR, known to be able to crystallize under stress, resulted in improved mechanical properties, compared to those of BR. The addition of 10 phr of mica increases the crosslink density of both rubbers, but further addition causes an opposite effect in each of the rubbers. For BR these values decrease whereas for NR values of ν increase with these higher contents of mica. Generally speaking, crosslink densities for NR are superior to the

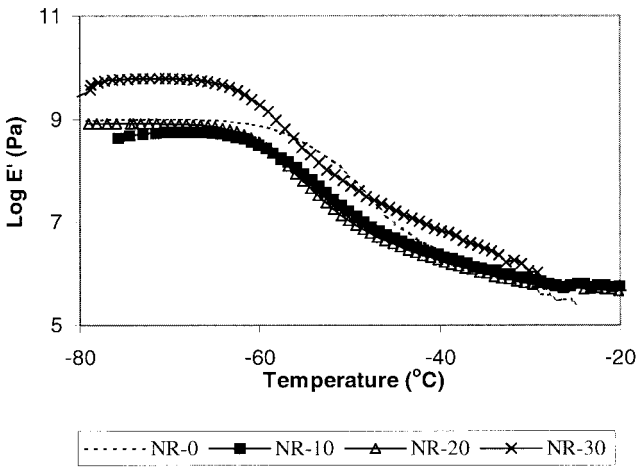


(a) Natural rubber

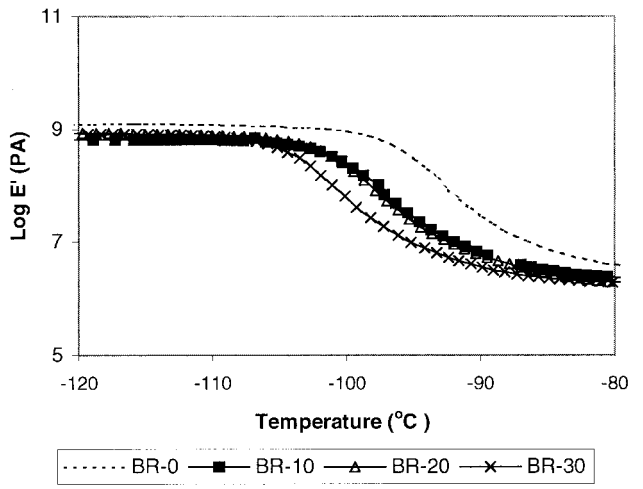


(b) Polybutadiene rubber

Figure 5 Variation of tan δ for (a) NR and (b) BR vulcanizates as a function of mica loading.



(a) Natural rubber



(b) Polybutadiene rubber

Figure 6 Variation of log E' for (a) NR and (b) BR vulcanizates as a function of mica loading.

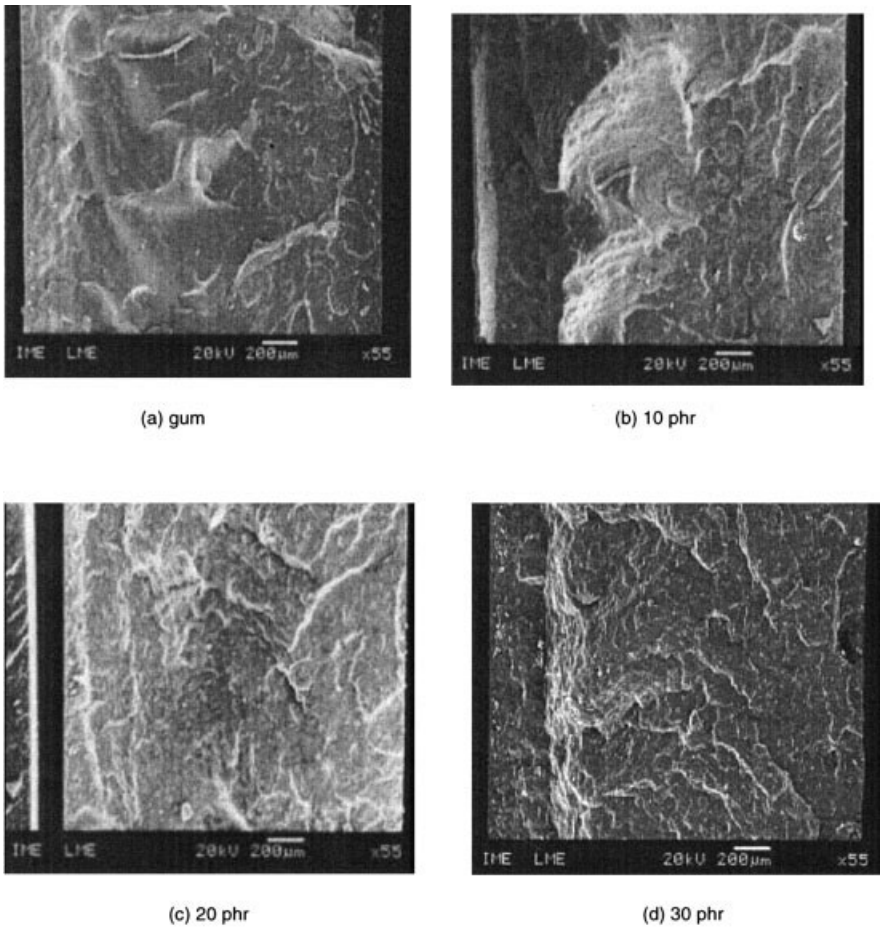


Figure 7 SEM microphotographs of various NR/mica compositions.

values obtained for BR, which is in agreement with maximum torque data.

Dynamic mechanical properties

The variation of the damping (tan δ) with temperature for NR and BR with different filler contents is shown in Figure 5. The tan δ versus temperature curve for NR gum [Fig. 5(a)] shows a peak, related to the glass-transition temperature (T_g), at a higher temperature (−45°C) than that for BR gum (−89°C) [Fig. 5(b)]. In both cases, T_g decreases with increasing filler loading, thus suggesting a higher mobility of the polymeric chains; this result in combination with the better tensile strength observed suggest a good dispersion of the filler in the elastomeric matrix. Because NR and BR are formed by chains that interact by weak Van der Waals forces and considering that mica is formed by a laminar structure, these two characteristics may be acting to promote a good dispersion of the filler between the rubber chains. Figure 6(a) and (b) show the variation of storage (or elastic) modulus (E') with temperature. Considering the NR compositions in the rubbery region, the one with 30 phr of mica presents lower stability compared to that of compositions with 10 and 20 phr, despite its higher crosslink density, which suggests the presence of physical entanglements. For BR vulcanizates the behavior observed is in accordance with crosslink density, decreasing upon filler addition.

Scanning electron microscopy

Figures 7 and 8 present the microphotographs of the fracture surfaces of NR and BR vulcanizates, respectively, with and without filler. The materials show fracture surfaces with different topographic aspects. The fracture surfaces of NR vulcanizates, independently of mica content, show similar microscopic features of surface roughness and tearing patterns, characterizing a ductile fracture mechanism, thus indicating that mica addition has no significant influence on the plasticity of NR vulcanizates. The BR vulcanizates present flat regions with many cracks, characterizing a fragile behavior compared to that of NR. The presence of tearing patterns indicates that in the range used, mica addition will improve the plasticity of BR. These SEM observations agree with the tensile test results.

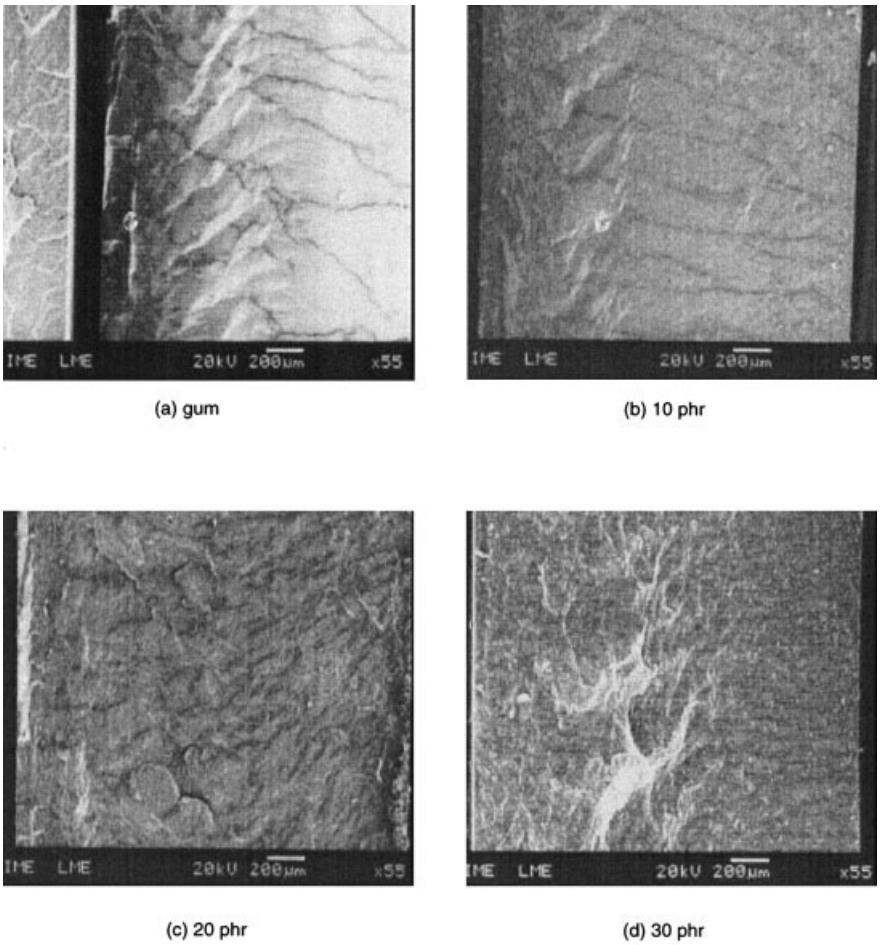


Figure 8 SEM microphotographs of various BR/mica compositions.

CONCLUSIONS

- The addition of filler improves the mechanical and dynamic mechanical properties for both sets of vulcanizates, which indicates the reinforcing effect of mica as filler.
- The crosslink density of natural rubber increases with mica addition, a result that suggests a filler–rubber interaction in this case.
- From dynamic mechanical analysis, for both sets of elastomeric compounds, the displacement of T_g toward lower temperatures is thought to be attributed to a good dispersion of the filler.

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