

Influence of Mixing Procedures and Mica Addition on Properties of NR/BR Vulcanizates. I

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ABSTRACT: Elastomeric compositions of natural rubber (NR) and polybutadiene rubber (BR) in a 1 : 1 ratio (w/w), with mica in the range 0–30 phr, were investigated. For all compositions the same formulation was used but two different additives incorporation sequences were followed. The results of the tests showed that the mechanical performance is sequence-dependent, as the two elastomers have very different rheometric characteristics. It was also observed that mica, when present in amounts of 20 and 30 phr, improves the mechanical properties. Scanning electron microscopy

(SEM) permitted the observation of the fracture behavior of each composition, and dynamic mechanical thermal analysis (DMTA) suggested different migration tendencies of the additives in each phase, thus corroborating the differences found for the mechanical properties. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1575–1585, 2004

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

INTRODUCTION

The utilization of polymeric mixtures to achieve a desired combination of properties has obvious attraction given the economical and technical uncertainties associated with synthesizing new polymeric materials.¹ Elastomeric materials frequently do not have the desired properties, showing deficiencies in one or more aspects, and so are often blended with other elastomers during processing.^{2,3} Blending of elastomers allows for optimum all-round performance, so this practice is widely employed to achieve improved processing characteristics and physicomachanical properties and also to reduce the cost of compounds.^{4–7}

The technical and economic interest of mica as polymer filler is now widely recognized. Its advantages are, essentially, low cost; availability; outstanding electrical, heat, and chemical resistances; reinforcing properties; and isotropy.^{8,9}

However, the effect of filler loading on rubbers is not the same for all rubbers. Different physical properties have their optimum value associated with different optimum filler loadings. In blends of rubbers, these effects are even more complex.¹⁰ Cure characteristics of filled rubber compounds depend on content

and kind of rubber, fillers, curatives, and other ingredients. In general, competitive vulcanization occurs due to different rates of vulcanization and/or rates of diffusion of curatives (sulfur, accelerators) in each polymeric phase.^{11–13} Properties of filled rubber compounds and their vulcanizates also vary with the mixing conditions.¹ The final properties can be influenced by the distribution of the additive in the discrete polymer phases and by the interfacial compatibility between the components.^{4,11–13}

In this study, the influence of mica and two different sequences to incorporate the additives into NR and BR blends were investigated by comparing their mechanical and dynamic mechanical properties with the fracture surface analysis.

EXPERIMENTAL

Preparation of NR/BR/mica compositions

The compositions were prepared on a Berstorff two-roll mill (Hannover, Germany), with friction ratio of 1 : 1.25 at 50°C, and the uncured sheets were stored for 24 h at 25°C. The formulation of the mixtures is presented in Table I. The curing parameters were determined according to ASTM D 2084,¹⁴ using an oscillating disk rheometer (TI-100; Tecnología Industrial, Buenos Aires, Argentina) and 3° arc (Table II). Vulcanization was carried out at 160°C during the respective optimum cure time of composition, t_{90} , in an electrically heated press.

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TABLE I
Formulation

Component	phr
NR	50
BR	50
Zinc oxide	3.0
Stearic acid	2.5
Aminox ^a	2.0
PVI ^b	0.3
Mica	0–30
Sulfur	2.5
TBBS ^c	0.6

^a Reaction product between diphenylamine and acetone, obtained at low temperature.

^b N-cyclohexylthiophthalimide.

^c T-butyl-2-benzothiazolsulfenamide.

The following procedures were used for additives incorporation:

- M1. The additives (except the accelerator) were introduced into NR, then BR was added. The accelerator was incorporated after complete homogenization of the mixture;
- M2. The additives (except the accelerator) were introduced into BR, then NR was added. The accelerator was incorporated after complete homogenization of the mixture.

Determination of crosslink density by equilibrium swelling

Vulcanized samples (5.0cm × 2.5cm × 0.2cm) were weighed and allowed to swell in excess of toluene (Vetec, Rio de Janeiro, RJ, Brazil) at room temperature, in the dark, until equilibrium swelling was achieved. The swollen samples were then weighed, the solvent removed under vacuum, and the dried pieces were weighed again. The volume fraction of the rubber in the swollen vulcanizates (V_r) was then calculated through the equation,

$$V_r = \frac{(m_1/\rho_r) - V_f}{(m_1/\rho_r) - V_f + (m_2 - m_3)/\rho_s} \quad (1)$$

where: m_1 is the initial weight of the specimen; m_2 is the weight of the swollen specimen; m_3 is the weight of the specimen after solvent evaporation; V_f is the volume of the filler; ρ_r is the density of rubber; and ρ_s is the density of the solvent (0.8669 for toluene).¹⁵

V_r was then substituted in the Flory–Rehner equation:

$$v = -\frac{\ln(1 - V_r) + V_r + \mu V_r^2}{V_o(V_r^{1/3} - V_r/2)} \quad (2)$$

where v is the crosslink density; V_r is the volume fraction of the rubber in the swollen vulcanizates; μ is the polymer–solvent interaction parameter; and V_o is the molar volume of toluene ($V_o = 106.2 \text{ cm}^3/\text{g.mol}$).¹⁶

The polymer–solvent interaction parameters used were: $\mu_{NR} = 0.42$; $\mu_{BR} = 0.34$; and $\mu_{NR-BR} = 0.38$.¹⁷

Mechanical testing

Tensile properties and tear strength were determined in an Instron Universal Testing machine (model 1101) (Massachusetts), at a crosshead speed of 500 mm/min, according to ASTM D 412 and ASTM D 624, respectively.^{18,19}

The hardness of the vulcanizates was expressed in Shore A units and determined according to ASTM D 2240.²⁰

Dynamic mechanical testing

The dynamic mechanical properties were measured on a Rheometric Scientific DMTA analyzer, model MK III (London, UK). The single cantilever bending mode of deformation geometry was used in the temperature range of -130° to 20°C at a heating rate of $2^\circ\text{C}/\text{min}$ and frequency of 1 Hz.

Scanning electron microscopy

A scanning electron microscope (Jeol JSM 5800LV) (Massachusetts) was used to examine the fracture aspects of the rubber compounds. The study of the failure mechanisms was carried out by direct observation

TABLE II
Cure Characteristics of Vulcanizates

	Material	t_{90}	M_L	M_H	t_{s2}	CRI
Gum	NR	10.79	8.25	49.95	5.94	20.61
	BR	35.7	12.7	49.35	13.5	4.50
	M1	14.59	6.6	52.9	6.81	12.85
	M2	11.29	7.7	54.6	6.66	21.59
10 phr mica	NR	11.12	8.5	50.15	6.22	20.41
	BR	35.7	11.8	44.35	13.2	4.44
	M1 blend	17.13	7.3	50.4	8.35	11.38
	M2 blend	15.92	10.15	50.5	8.89	14.22
20 phr mica	NR	13.46	6.05	49.9	6.67	14.72
	BR	42.3	11.2	42.85	15.3	3.7
	M1 blend	22.8	6.3	49.8	12	9.26
	M2 blend	22.5	9.2	51.2	11.4	9.00
30 phr mica	NR	15	7.8	52.65	7.32	13.02
	BR	42.6	11.3	43.4	15.6	3.7
	M1 blend	24.3	7.45	55	10.8	7.40
	M2 blend	18.3	9.85	55.65	10.2	12.34

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}).

TABLE III
Crosslink Density of Vulcanizates

Mica*	0 phr		10 phr		20 phr		30 phr	
	Vr	ν (10^5)	Vr	ν (10^5)	Vr	ν (10^5)	Vr	ν (10^5)
NR	0.1537	6.7	0.1787	9.4	0.1944	11.5	0.2001	12.3
BR	0.1356	8.2	0.1804	14.8	0.1728	13.5	0.1598	11.5
M1 blend	0.1544	8.7	0.1860	13.2	0.1926	14.2	0.1954	14.6
M2 blend	0.148	7.9	0.1863	13.2	0.1888	13.5	0.2019	15.8

*filler content.

ν -the crosslink density.

Vr-the volume fraction of the rubber in the swollen vulcanizate.

of the topography of samples cryofractured after being immersed for at least 10 min in liquid nitrogen. All the samples were sputter-coated with gold in a vacuum chamber before examination.

RESULTS AND DISCUSSION

Curing characteristics

Table II shows the curing characteristics for all compositions.

The shorter values of t_{90} and t_{s2} and the higher values of CRI for NR compounds observed by comparing the isolated rubbers, confirm the higher reactivity towards crosslinking formation of this rubber in comparison to BR. The optimum cure time (t_{90}) remains nearly constant with the addition of 10 phr of mica, but additional filler (20 and 30 phr) increases this parameter, indicating that mica has a retardation effect on the vulcanization process. The maximum torques for the unfilled rubbers are very close, but the

addition of mica makes these values decrease in the case of BR while for NR, no effect is observed up to 30 phr.

In comparison with the isolated rubbers, the blends present intermediate values of t_{90} independently of the filler loading. The results, however, have different tendencies depending on the preparation mode. Employing the M2 sequence, t_{90} reaches a maximum when the amount of mica in the blend is 20 phr, while through the M1 sequence this parameter increases as mica loading also increases. Data of maximum torque for the blends are higher than those for the isolated rubbers and present similar behaviors, decreasing on the addition of 10 and 20 phr and increasing with 30 phr of mica.

Crosslink density

The results of crosslink density and volume fraction of the rubber in the swollen vulcanizates are presented in Table III.

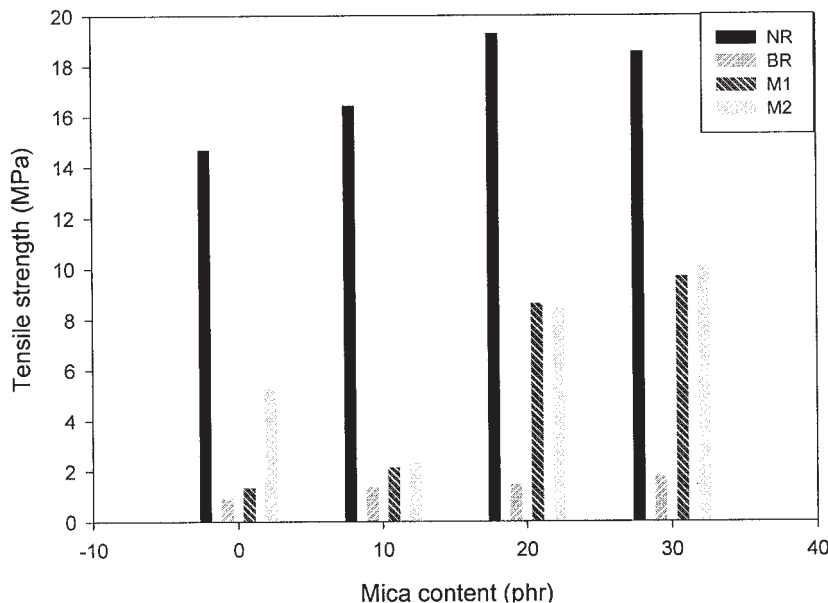


Figure 1 Tensile strength of vulcanizates.

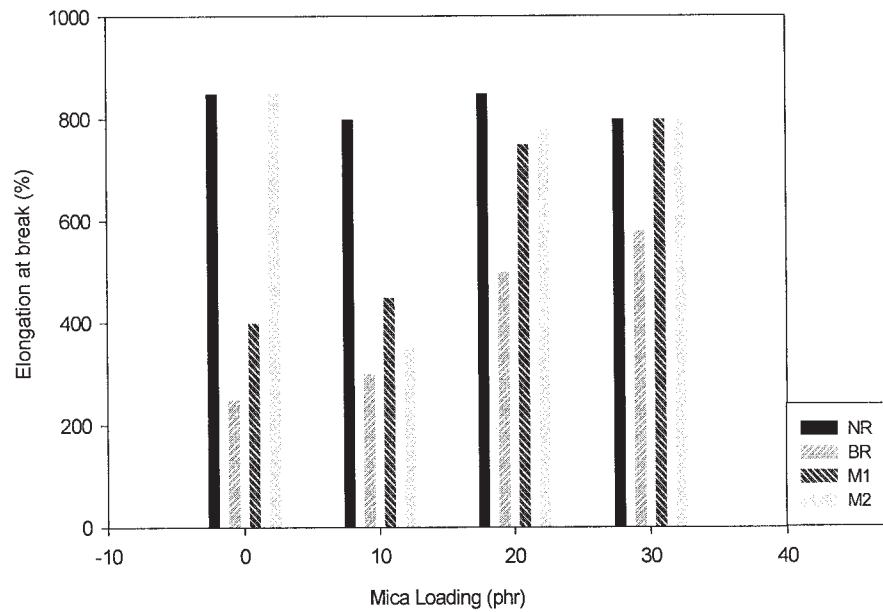


Figure 2 Elongation at break of vulcanizates.

The crosslink density for BR gum is higher than that for NR. The addition of 10 phr of mica increases this parameter for both rubbers, but if more filler is added, the crosslink density decreases in the case of BR and increases for NR, suggesting a mica–NR interaction.

The crosslink densities for unfilled blends are similar to BR and higher than NR. The unfilled blends have similar crosslink densities. The addition of filler increases this parameter in both cases, with the highest value given by the M2 blend with 30 phr of mica.

Mechanical testing

The NR vulcanizates show, as presented in Figures 1 to 4, a better mechanical performance as compared to BR ones. The blended compositions have intermediate behavior and the values were dependent on the preparation mode.

The tensile strength and the elongation at break for all compositions are shown, respectively, in Figures 1 and 2. In general, mica has a positive effect on tensile strength. In the case of BR vulcanizates, a gradual

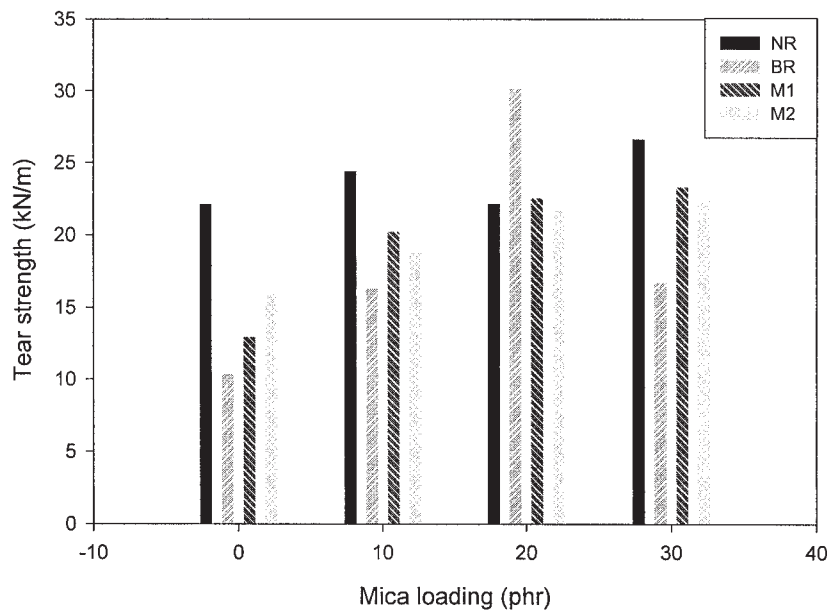


Figure 3 Tear strength of vulcanizates.

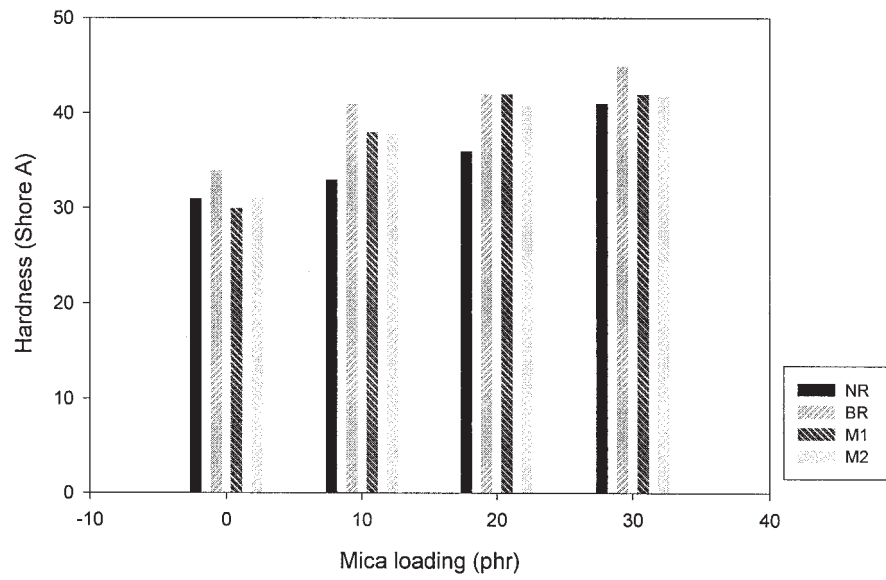
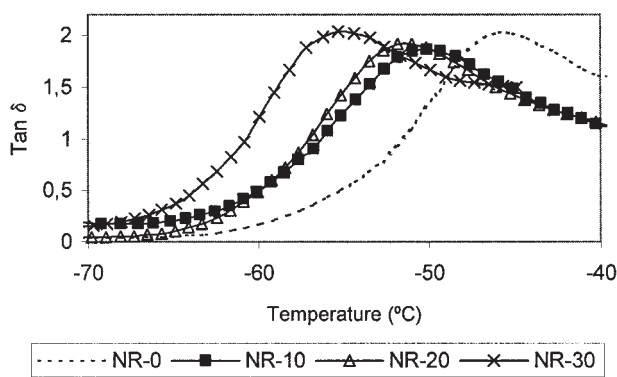
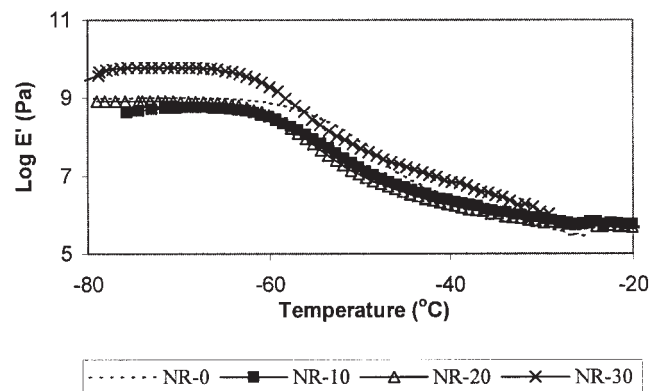


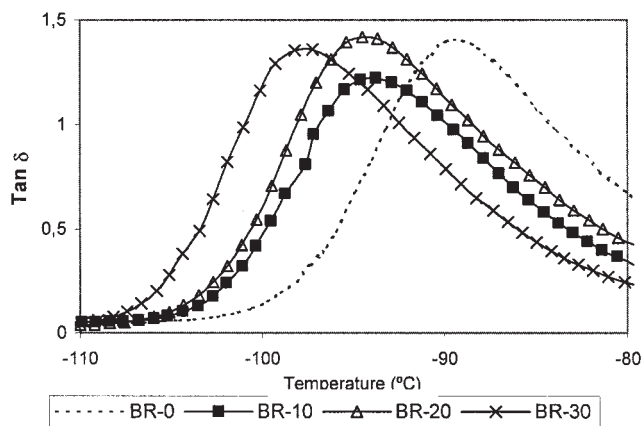
Figure 4 Hardness of vulcanizates.



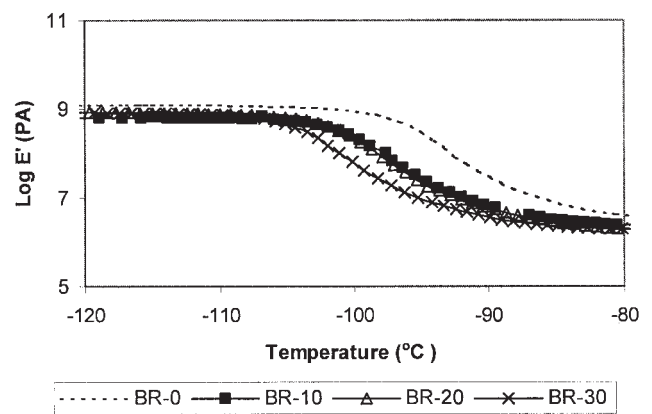
(a) NR



(a) NR



(b) BR



(b) BR

Figure 5 Variation of $\tan \delta$ of (a) NR and (b) BR vulcanizates.

Figure 6 Variation of $\text{Log } E'$ of (a) NR and (b) BR vulcanizates.

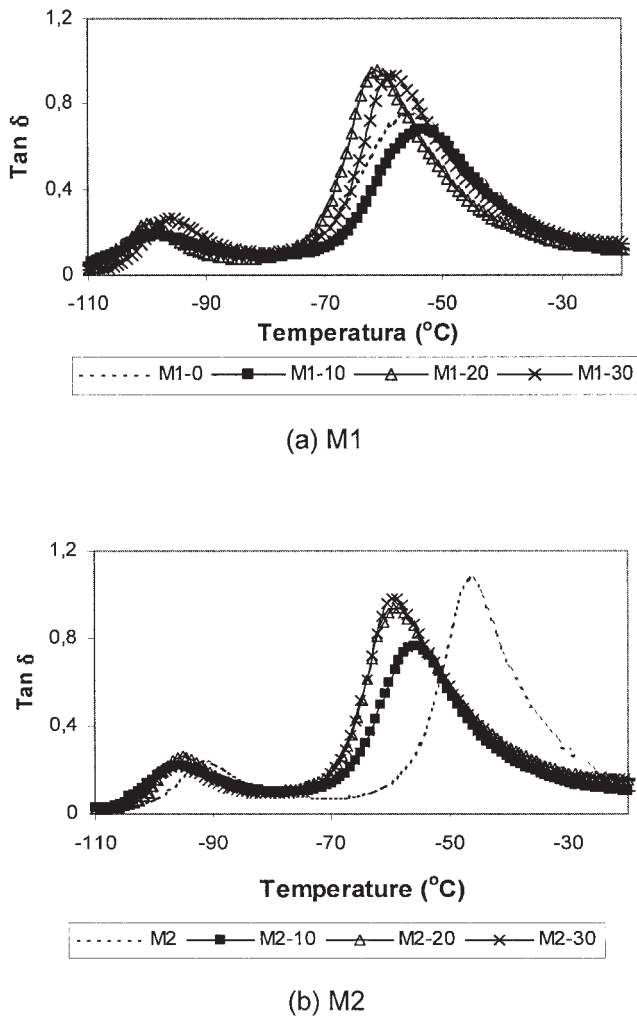


Figure 7 $\tan \delta$ for (a) M1 and (b) M2 blends.

increase in this property upon addition of mica is observed over the entire range studied. For NR vulcanizates, by increasing the filler content the tensile strength also increases until a maximum value is reached at 20 phr.

The unfilled blends shows that the one prepared through the M2 mode has a higher value of tensile strength than M1 blend. In the M2 sequence all the additives are incorporated in the BR phase, stimulating the vulcanization of this phase. In addition, the comparatively low value of t_{90} resulted in a relative protection of the NR phase against excessive cure; as a consequence, a good mechanical response was achieved. The incorporation of the additives into the NR phase, as in M1 mode, in opposition to this, led to an excessive cure of this phase and to an under-cure of the BR phase. Thus, degradation of the NR phase has to be considered, and the net result was the poorer mechanical performance shown by this blend.

The increasing mica loading has a different influence on the tensile strength according to the preparation mode. For the M1 blends the addition of mica improved tensile strength over the entire range investigated, while for the M2 blends a minimum was found on the addition of 10 phr of mica.

The behavior of the elongation at break is different for NR or BR compounds. Independently of the mica loading, the NR compounds present a more or less constant value. For the polybutadiene compositions a positive effect is observed, and the compositions with 20 and 30 phr of mica show elongation values that are twice as high as that for the unfilled composition. The unfilled M2 blend has an elongation at break value similar to NR, but the addition of 10 phr of mica decreases it to half the original value. Additional filler incorporation, as in the case of 20 and 30 phr, causes a new increase in this parameter. As for the M1 blends, the addition of 20 and 30 phr of mica has a positive effect, and these compositions show elongation values that are twice as high as that for the unfilled one,

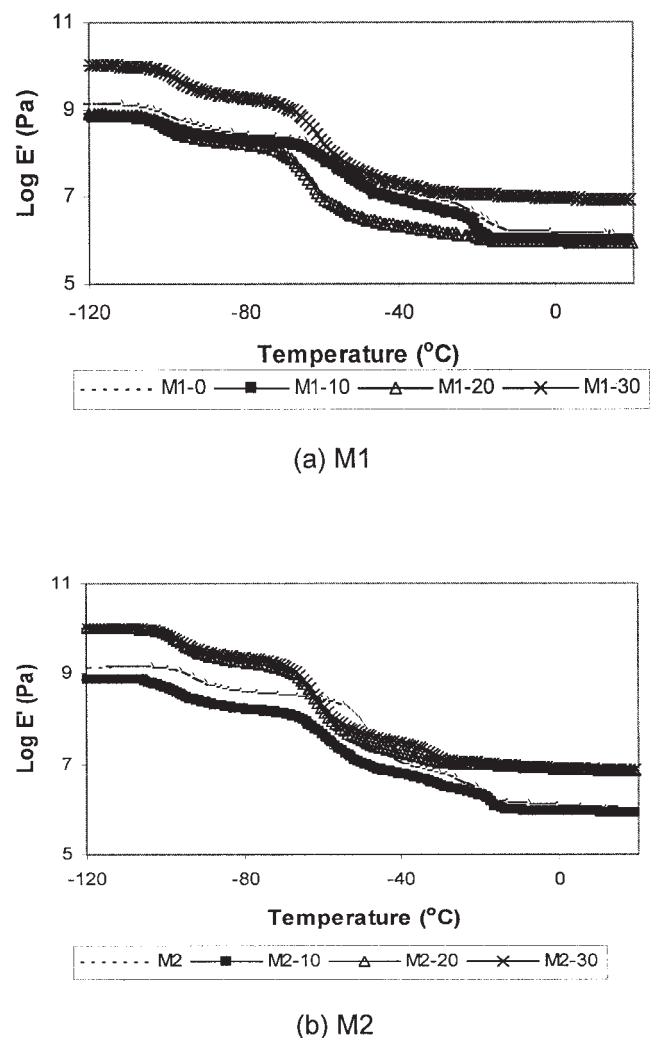


Figure 8 Storage modulus for (a) M1 and (b) M2 blends.

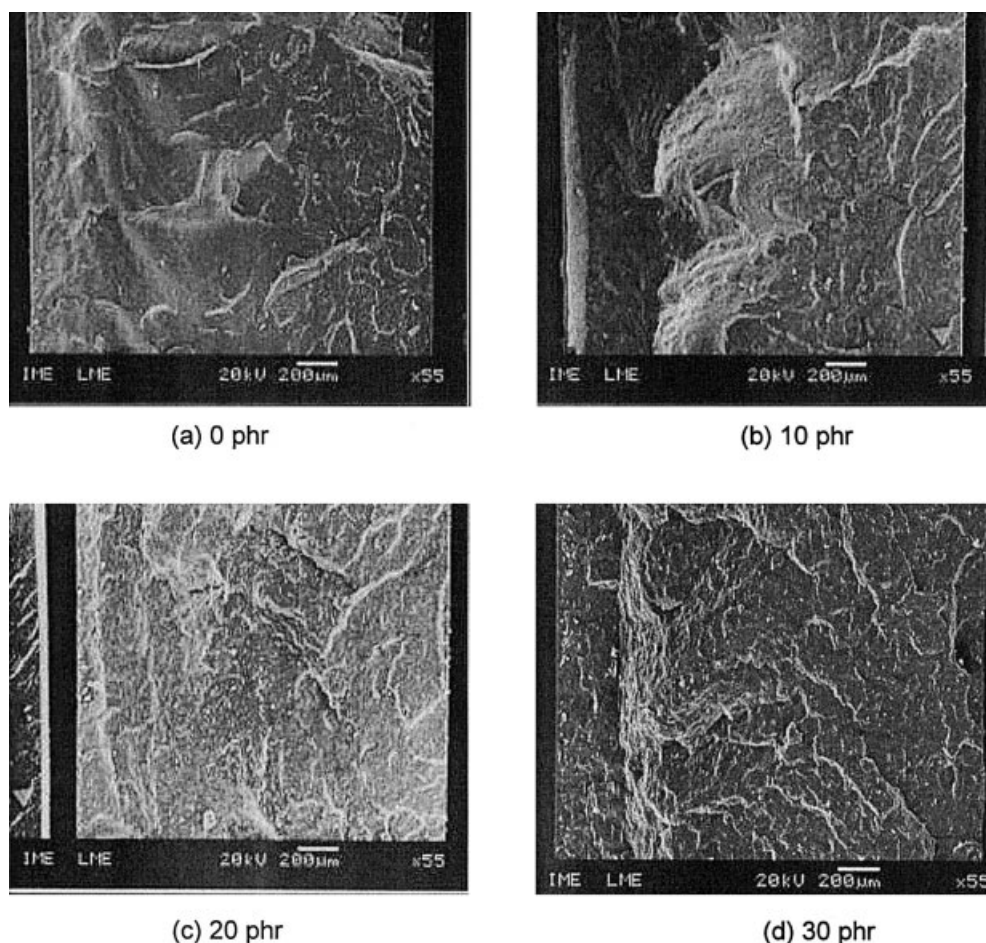


Figure 9 SEM photomicrographs of NR/mica compositions: (a) 0 phr; (b) 10 phr; (c) 20 phr; and (d) 30 phr.

without decreasing the tensile strength. With 30 phr of mica, both M1 and M2 blends show elongation at break of the same magnitude as NR composition with the same filler content.

The higher performance of NR compounds, over the entire range of mica loading, in relation to tear resistance, as compared to BR ones, can be seen in Figure 3. Although having a positive influence on both rubbers, the effect of mica is more pronounced for the BR vulcanizates. Considering the range of mica loading studied, NR has not yet achieved the saturation stage concerning this property, while BR reaches it with 20 phr.

For the unfilled blends, with regard to tear strength, Figure 3 shows that, as expected, values in between those for the isolated rubbers were found. The M2 mode provided the best performance, which may be the result of the short t_{90} used to vulcanize this mixture, thus contributing to a lower level of NR degradation.

Hardness values, presented in Figure 4, were, as expected, increased as mica loading also increased, but did not show significant variation with the preparation mode.

Dynamic mechanical testing

The dynamic mechanical properties, damping ($\tan \delta$) and storage modulus (E'), of BR, NR, and NR/BR blends are shown in Figures 5–8.

The $\tan \delta$ curve for NR gum (Fig. 5a) shows a peak at -45°C due to the α -transition arising from segmental motion. This corresponds to the glass transition temperature (T_g) of this rubber. For BR gum the glass transition appears at -89°C in the $\tan \delta$ versus temperature curve (Fig. 5b). It can be observed from these figures that NR has higher T_g and higher damping as compared to BR.

The variation of $\tan \delta$ as a function of the temperature for different filler contents is shown in Figure 5. It can be seen that, for both rubbers, T_g decreases with increasing filler loading, thus suggesting a higher mobility of the polymeric chains, probably due to a good dispersion of the filler in the elastomeric matrix. Considering that NR as well as BR are formed by chains that interact with each other by the weak Van der Waals forces and that mica has a laminar structure, these two characteristics may be acting to promote a good dispersion of the filler in between the rubber chains.

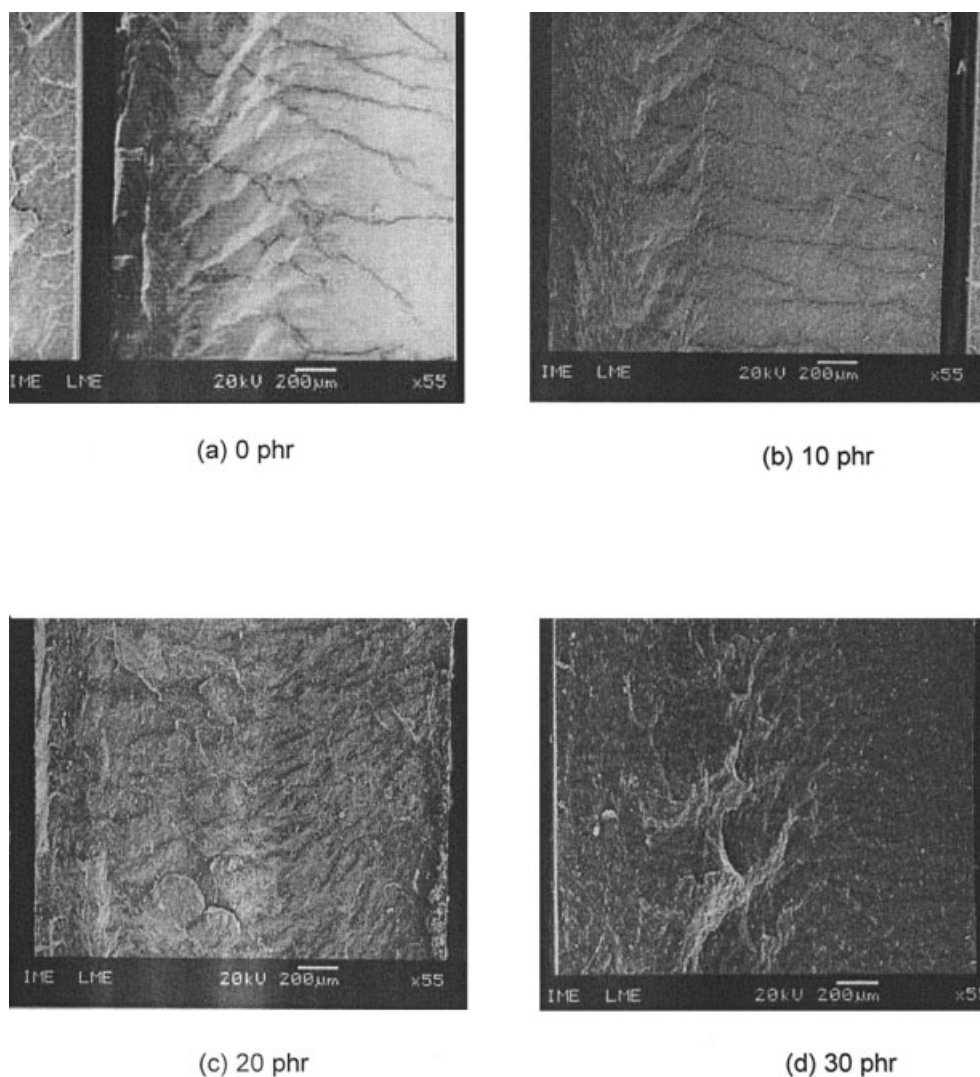


Figure 10 SEM photomicrographs of BR/mica compositions: (a) 0 phr; (b) 10 phr; (c) 20 phr; and (d) 30 phr.

The variation of the storage modulus, E' , of NR and BR compounds, as a function of the temperature, is shown in Figure 6. The observed behavior for BR vulcanizates shows a decrease upon mica addition, in accordance with the observed results of crosslink density. From the observation of NR vulcanizates, it can be seen that, in the rubbery region, the compositions with 30 phr of mica present lower stability compared to the compositions with 10 and 20 phr, despite its higher crosslink density, which may suggest the presence of physical entanglements.

As seen in Figure 7 (a and b), in both blends, the two peaks corresponding to the T_g 's of NR and BR are well separated, which indicates that the blends are not compatible. Figures 7 and 8 show that the T_g values for the blends depend on both the preparation mode and the filler content. Considering the unfilled blends, the one prepared through M1 mode was found to present the worst result of tensile

strength, which was credited to its high value of t_{90} . This long vulcanization time would cause degradation of the NR phase, resulting in scission of the macromolecular chains, thus affecting T_g . This can be seen in Figure 7 as the value of T_g for the NR phase in this blend is shifted to a lower temperature. It is known from the literature²¹ that overcure also affects $\tan \delta$ since the higher the degree of vulcanization, the lower will be the magnitude of $\tan \delta$, which is also seen in Figure 7a. These results confirm that when the additives are all incorporated into NR, even though they would preferentially migrate to BR, they still are present in the NR phase in amounts that are high enough to cause overcure.

The highest values of T_g for the NR phase were found for the M2 blend, suggesting that the mixing sequence used to prepare this compound caused less deterioration of this phase, in agreement with the better mechanical properties shown before.

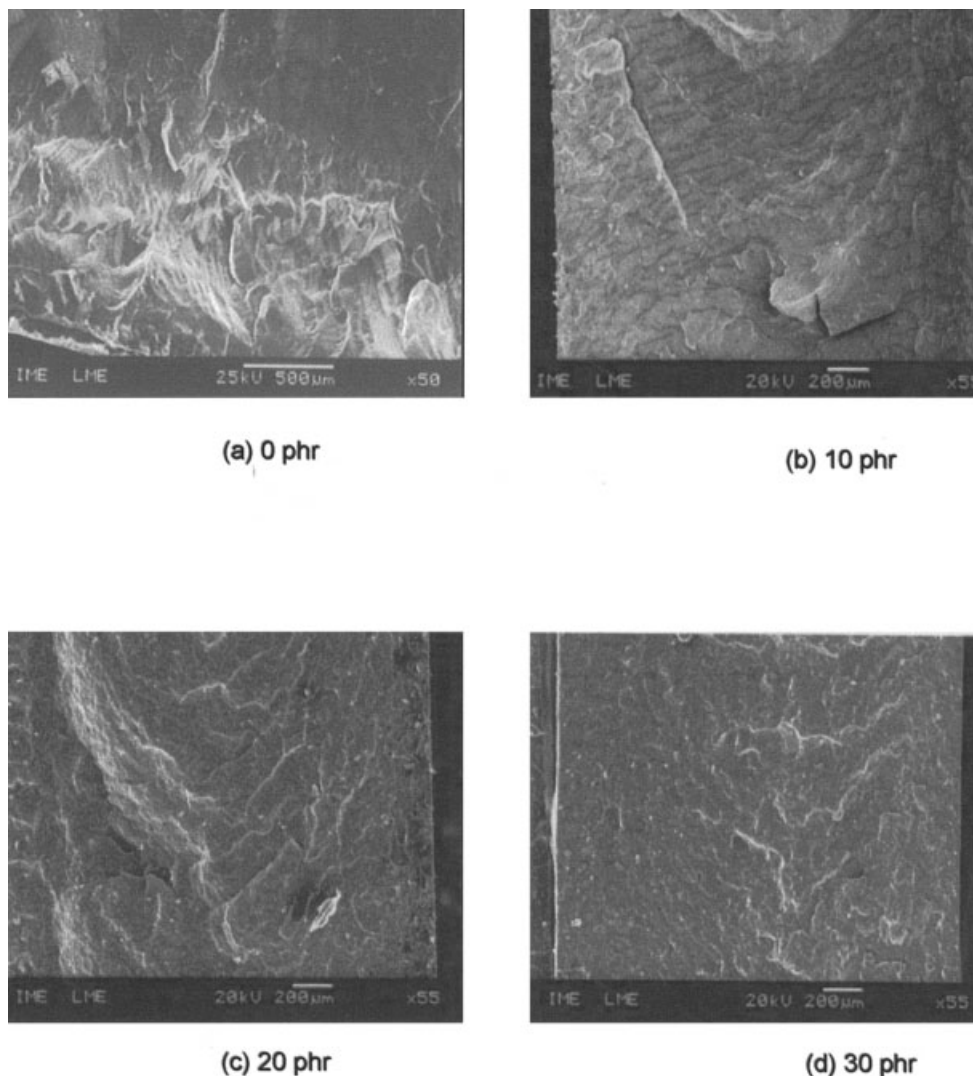


Figure 11 SEM photomicrographs of M1/mica compositions: (a) 0 phr; (b) 10 phr; (c) 20 phr; and (d) 30 phr.

Regarding the filled blends, the temperature at which the transition occurs depends on the preparation mode and the filler content.

The T_g values for blends prepared through M1, in which the additives are added to NR, show a displacement towards the lower temperature region, as the amount of mica increases. This may be associated to a good dispersion of the filler and/or to the possibility of NR degradation. Good filler dispersion would increase chain mobility. However, the blend with 30 phr of mica has higher values of t_{90} and T_g than the blend with 20 phr. Mica is a good thermal insulator, and this property may be acting to protect NR from overcure during the vulcanization. So the NR phase would vulcanize slower as more content of mica is present, resulting in a minor degradation, and allowing for the higher tensile strength presented by this mixture. The T_g of the BR phase for the blends with 20 and 30 phr are higher than that for unfilled composition, and this

may be credited to the higher degree of BR vulcanization in these mixtures, favored by longer T_{90} values.

Figure 7b also presents $\tan \delta$ curves of M2 blends with different contents of mica, as a function of the temperature. According to this preparative mode, the additives are added to the BR phase to which the vulcanization system has more affinity. So it is expected that the BR phase would achieve a vulcanization index very close to the ideal value and that the NR phase would be less susceptible to overcure. In relation to the BR phase, the blends show a similar behavior to the BR–mica compositions. The increase in mica content does not promote significant change in T_g or $\tan \delta$ of this phase. On the other hand, it does promote expressive changes in these parameters for the NR phase, suggesting that in spite of mica being added to BR, it shows more affinity for NR.

Figure 8a does not show expressive differences in the modulus behavior of the blends with 10 and 20 phr

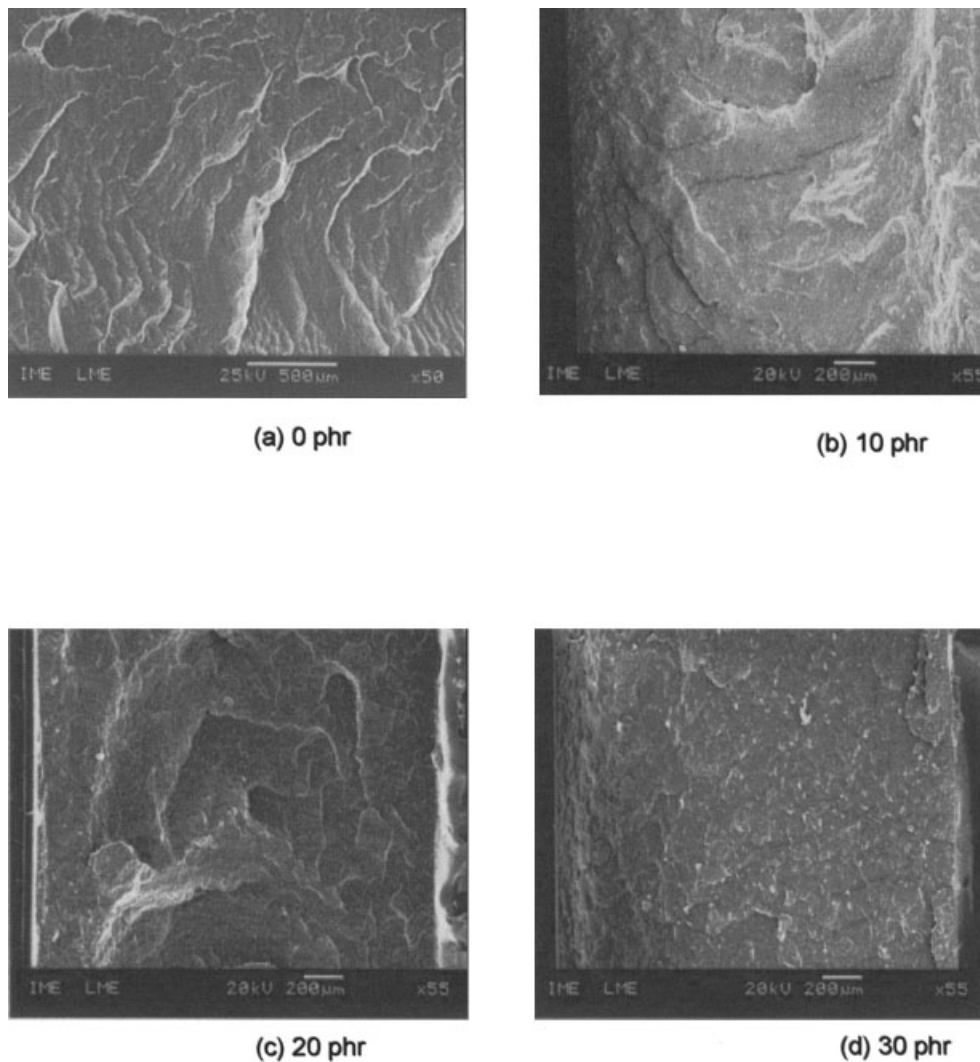


Figure 12 SEM photomicrographs of M2/mica compositions: (a) 0 phr; (b) 10 phr; (c) 20 phr; and (d) 30 phr.

in comparison with the unfilled one. The bigger storage modulus in the rubbery region found for the blend with 30 phr of mica is in agreement with the higher crosslink density of this mixture.

As for the storage modulus, Figure 8b shows that filled M2 blends behave very much like NR–mica compositions.

Scanning electron microscopy

Figures 9–12 present SEM photomicrographs of the fracture surfaces of cryofractured samples. The materials show different topographic aspects in the fracture surfaces.

The samples of NR vulcanizates (Fig. 9), independently of mica content, show similar microscope features, with surface roughness and tearing patterns characterizing a ductile fracture mechanism, thus indicating that mica addition has no great influence upon the plasticity of NR vulcanizates.

The BR vulcanizates show, as compared to NR, a more brittle behavior (Fig. 10). The fracture surfaces are characterized by many cracks. In the blends of higher mica content (Fig. 10d), the presence of tearing patterns indicates that, in the used range, mica can improve the plasticity of BR.

Figures 11 and 12 present the photomicrographs of the fracture surfaces of NR/BR blends. The observed fractures indicate that the fracture behavior of these blends can be affected by the processing conditions and by the addition of mica.

The fracture behavior of unfilled blends is affected by the processing conditions. The M1 blend presents characteristic elements of a mixed fracture mechanism, with flat regions associated to localize plastic strain areas and tearing patterns (Fig. 11a). The fracture surfaces of the M2 sample show (Fig. 12a) low surface roughness and the presence of striations characterizing a more ductile fracture mechanism.

The addition of mica to the blends does not produce a high effect in the fracture behavior as compared with unfilled compositions (Figs. 11b–d and 12b–d). It is observed that both blends present a surface with a low roughness fracture surface. Blends with 10 phr of mica present a network of surface cracks, especially that obtained through M1, indicating that this content of filler produces a material with lower plasticity, more brittleness. The M1 and M2 samples with 20 and 30 phr present tearing patterns, showing that the fracture occurs by a stick-slip mechanism, resulting in an improvement of plasticity and roughness of the material.

These SEM fractures are in agreement with the tension test results.

CONCLUSION

In spite of the lower properties of the blends of NR/BR in relation to natural rubber gum, these properties are nevertheless better than those presented by BR alone. The blends have, in addition, improved processability given by the lower values of minimum torque, as compared to BR compositions. These two factors make NR/BR blends interesting materials, taking into account that BRs are rather expensive.

In general, the addition of mica increased the tensile strength of compositions, with no effect on the elongation, especially at higher contents (20 and 30 phr).

Micrographs of unfilled blends show a variation of fracture morphology depending on the sequence of ingredients addition. The presence of mica did not produce any important changes compared to the unfilled blends, but the crack propagation was affected by the filler content.

Good properties are achieved when the NR/BR blends are prepared in such a way as to favor the vulcanization of the BR phase and, at the same time, preserve NR from excessive cure.

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