

Different Preparative Modes for the Incorporation of Additives in NR/SBR Blends

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ABSTRACT: Rubber goods usually require a combination of properties that cannot be provided by one elastomer only and then two or more polymer components have to be mixed to meet specific requirements. In such cases, the additives normally employed in rubber formulations are unevenly distributed, depending on the affinity of each compound to each polymeric phase. Thus, the dispersion of each one of these ingredients in the different rubbers will influence the rate and degree of vulcanization and, in consequence, the performance of the final composite. In this work, natural rubber (NR) and styrene butadiene rubber (SBR) were mixed in a 1 : 1 ratio. The compositions were obtained according to ASTM D 3182, by using four different prepar-

ative modes for the incorporation of the additives. After vulcanization, morphological, and dynamic mechanical thermal analysis, tensile strength, hardness, and tear resistance of each composition were investigated. The results show that the best properties were found when the NR/SBR mixture was prepared in such a way as to favor the vulcanization of the SBR phase while preserving the NR phase from excessive vulcanization. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 483–489, 2004

Key words: blends; elastomers; mechanical properties; morphology

INTRODUCTION

Natural and synthetic rubbers are not used very often in an isolated form. To have practical application, several ingredients are incorporated, the choice of which is based on the set of properties required for that particular use. Moreover, for many of these applications, all the suitable characteristics cannot be accomplished with the use of one rubber alone and then mixtures of two or more rubbers have to be employed.

An elastomer is mixed to another one for three main reasons: to improve the properties of the original material, to improve processibility, and/or to lower costs. Any elastomer is deficient in a given aspect so the combination of two or more can be a suitable way to get a good balance of properties.¹ The resulting blend will be composed of distinct high molecular weight polymers with different chemical structures and will, in consequence, be partially or completely incompatible.

A number of techniques are used to prepare polymer mixtures but the mechanical one is the most common. In the case of rubber mixes, there is an additional difficulty due to the differences in solubility each ad-

ditive shows in relation to each polymer, which may result in a nonuniform dispersion of the ingredients in the rubber phases. This means that each additive will migrate preferentially to that phase with which it has more affinity and this will certainly lead to differences in the final behavior. The affinity of additives toward the various elastomers has been extensively discussed in the literature.^{2–6}

In this work, mixtures with the two mostly used rubbers were investigated. Natural rubber (NR) is known for its excellent stress strength, even in the absence of reinforcing fillers such as carbon black, because of its capability to crystallize under stress. Styrene butadiene rubber (SBR) is not crystallizable and its properties are far lower than those for NR. It is, however, the general purpose rubber mostly used when no specific performance is required, due to the low price.^{7,8}

These two elastomers were mixed in a 1 : 1 (w/w) ratio. The mixing of the two rubbers as well as the incorporation of the additives were carried out according to four different modes and the effect of the preparation mode on the vulcanizates properties was evaluated.

EXPERIMENTAL

Materials used in this work were as follows: NR from Braslátex Indústria e Comércio de Borrachas Ltda.

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(São Paulo, Brazil), GEB1 type, Mooney viscosity $ML(1 + 4)(100^\circ\text{C}) = 102.6$; and SBR 1502 from Petroflex Indústria e Comércio S.A. (Rio de Janeiro, Brazil). 23.5% styrene, Mooney viscosity $ML(1 + 4)(100^\circ\text{C}) = 52.0$.

The composites were prepared following the formulation (in phr): NR (50); SBR (50); zinc oxide (3.0) (Uniroyal Química S.A., Greenville, Santa Catarina, Brazil); stearic acid (2.0) (Cho Indústria e Comércio Ltda., São Paulo, Brazil); octylated diphenylamine (2.5) (Uniroyal Química S.A.); sulfur (1.5) (Vetec Indústria Química S.A., Duque de Caxias, Rio de Janeiro, Brazil); *t*-butyl-2-benzothiazol sulfenamide (TBBS; 1.1) (Bayer do Brasil S.A., Belford Roxo, Rio de Janeiro, Brazil). Mixing was carried out in a two-roll mill, at 50°C , according to the four following preparation modes:

- G1: all the additives except the accelerator were incorporated into NR and, after homogenizing, SBR was added. To the resulting mixture, the accelerator was added;
- G2: all the additives except the accelerator were incorporated into SBR. After homogenizing, NR was added. To the resulting mixture, the accelerator was added;
- G3: the two rubbers were previously mixed, before incorporation of the additives;
- G4: each rubber was mixed with one-half the amount of each additive, except for the accelerator. The two composites were then combined and the accelerator was added.

The vulcanization parameters were determined on an oscillating disk rheometer, model TI-100 from Tecnologia Industrial, operating at 160°C and 3° arc.

Stress and tear strength were carried out on an Instron universal machine, model 1101, according to ASTM D 412 and D 624, respectively, at room temperature and 500 mm/min deformation rate.

Equilibrium swelling was carried out at room temperature in toluene. Small specimens ($2.5 \times 5.0 \times 0.2$ cm) dried to constant weight were allowed to swell in the dark, in sealed bottles until no further swelling occurred. The swollen samples were weighed after removal of excess swelling agent and dried to constant weight. The volume of imbibed toluene was calculated from the difference between the weights of swollen and deswollen samples. The crosslink density was calculated by using eq. (1), developed by Flory-Rehner⁹ and based on the swelling at

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

where ν is the crosslink density; V_R is the reduced volume of the sample, equal to the ratio between the

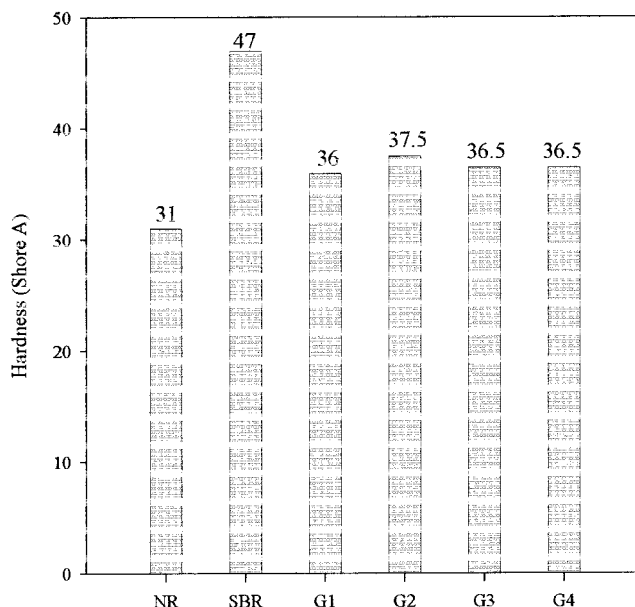


Figure 1 Shore hardness of NR/SBR blends.

volumes of the dried and swollen samples; μ is the polymer-solvent interaction parameter; and V_0 is the molar volume of the solvent ($\text{cm}^3/\text{g mol}$).

A Rheometric Scientific, model MK III, DMTA analyzer was used for the dynamic mechanical thermal analysis, under the following conditions: frequency, 1 Hz; heating rate, $2^\circ\text{C}/\text{min}$; single cantilever bending and temperature, -80 to 10°C .

Morphology was investigated on a JEOL scanning electron microscope, model JSM 5800 LV, through the observation of cryoscopically fractured surfaces covered with a thin layer of gold.

RESULTS AND DISCUSSION

Results of mechanical properties for all the compositions studied are presented in Figures 1 and 2.

Figure 1 shows that hardness values for all mixes are intermediate between those for the pure rubbers and, as expected, do not significantly vary with the preparation mode.

From Figure 2, it can be seen that the behavior of the mixtures, concerning stress and tear resistances, is not the same. Mixes G1 and G3 have values of tear strength similar to NR, while G4 showed the worst result. The best one was that for G2, even superior to NR. As for the stress resistance, this rubber is indeed much more resistant than SBR and, when these two very different rubbers are mixed together, the resulting compositions present values of stress strength that are in between those for the pure rubbers. The magnitude of this property, however, depends on the preparation mode. It is higher for G2 than for G1, and lowest for G3. Both G1 and G4 show practically the

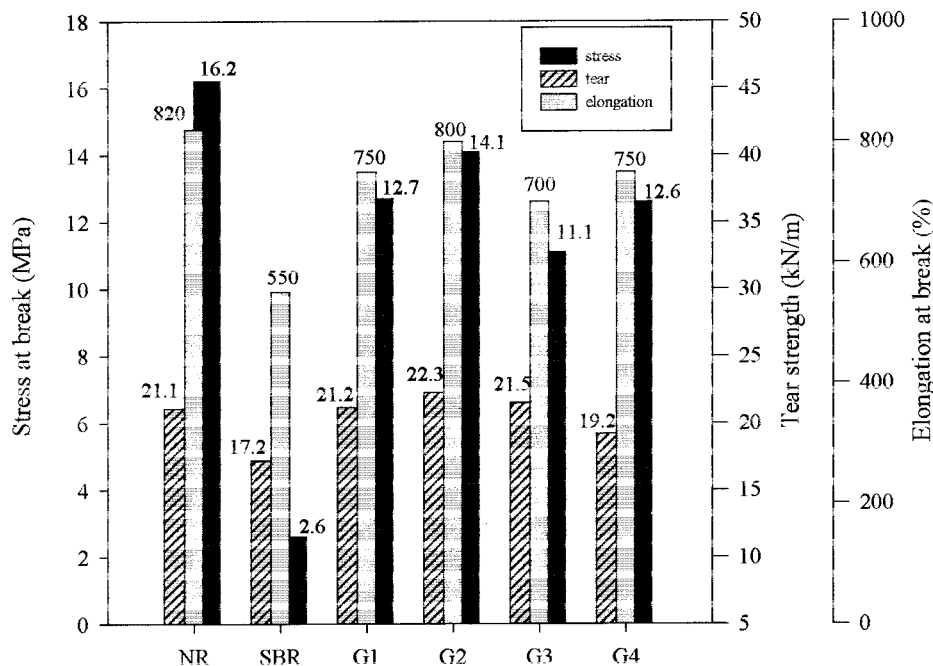


Figure 2 Mechanical properties of NR/SBR blends.

same result, which means that by increasing the concentration of the vulcanizing system, the vulcanization process is not necessarily favored in the sense of improving the stress resistance. The compositions with either NR or SBR show a large difference in the value of this property. So, by mixing these two rubbers, the main challenge is to somehow improve the poorer rubber while preserving the good features of the other.

Table I shows the rheometric parameters for the mixes.

When comparing NR and SBR compositions, it can be seen that, because of the chemical structure, NR is more susceptible to undergo crosslinking reactions than SBR. This turns out to be the case as, for this composition, the value of maximum torque, which is related to the degree of crosslinking, is higher than for SBR composition. In opposition to this, among the

four mixes, no significant variation in the rheometric parameters was detected, except for G4.

The rheometric curves are shown in Figure 3. It can be seen that the vulcanization system used in this work¹⁰ (i.e., zinc oxide and stearic acid as the activators), and TBBS as the accelerator, under the conditions described in the experimental part, gave rise to a curve of maximum torque for NR, which goes through a maximum, followed by a reversion process.

The thermooxidative degradation of rubbers can occur through two mechanisms.⁷ In the first one, the scission or depolymerization takes place and the elastomer becomes gradually softer and sticky. In the second mechanism, the oxidation of the carbon-carbon double bond gives rise to free radicals that can

TABLE I
Rheometric Parameters of NR/SBR Blends

Material	t_{90}^a (min)	M_t^b (lb in.)	M_{II}^c (lb in.)	$t_s 1^d$, min
NR	5.25	8.0	41.3	1.25
SBR	21.5	6.0	30.8	2.0
G1	17	5.5	46	2.25
G2	17.5	5.0	46.5	1.25
G3	17	5.5	46	1.0
G4	18.5	4.5	46	1.0

^a Time to 90% of full cure.
^b Minimum torque.
^c Maximum torque.
^d Scorch time.

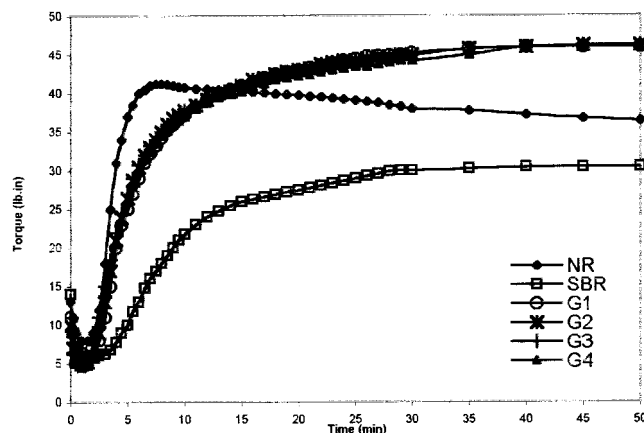


Figure 3 Rheometric curves of NR/SBR blends.

TABLE II
Crosslink Density of NR/SBR Blends

Material	Crosslink density ($\nu \times 10^5$) (mol/cm ³)
NR	5.89
SBR	3.77
G1	7.47
G2	7.32
G3	7.40
G4	7.30

then attack the polymer chains, leading to an increase in the number of crosslinks. In such a case, the resulting material is stiff and brittle.

Figure 3 also shows that NR vulcanizes faster than the rubber mixtures and much faster than SBR. However, the method is not sensitive enough to detect any difference from one mixture to the others. From Figure 3, it is seen that NR reaches a maximum torque followed rapidly by a reversion process, in opposition to SBR, which shows a constant value for this parameter. It is known from the literature¹¹ that, upon aging, NR depolymerizes, becoming softer and sticky. SBR, on the other hand, becomes stiffer due to an increase in the number of crosslinks. In the case of the four mixtures, no reversion was found. Moreover, the values of maximum torque are even higher than that for SBR. This may suggest that the vulcanization system used in this work favors SBR and that its presence in the mixtures somehow gives NR some sort of protection,

thus helping to prevent NR degradation. As NR degradation normally follows the first mentioned mechanism, one can assume that if NR is being overcured, the formed scission products might be assisting the vulcanization of SBR. However, if NR is excessively vulcanized, a high degree of degradation for this rubber may occur, leading to an endangering of the mechanical performance of the mixture. Thus, the least one favors the vulcanization of the NR phase, and the best will be the mechanical results.

Another point to be considered is the different affinity of the additives, which is higher toward NR, so that this phase becomes richer in curatives due to the preferential dispersion of the ingredients in this phase. Thus, in G3, prepared by incorporating the additives to the rubbers previously mixed, mechanical properties have been impaired due to the possibility of having a higher concentration of curatives in the NR phase, as well as because of the high value of t_{90} , then favoring a high degree of vulcanization of this rubber and its consequent degradation.

The results of the crosslink density, which were obtained from the swelling at equilibrium, are presented in Table II. The solubility parameters used for the calculations were based on the literature.¹² It can be observed that NR has higher crosslink density than SBR. This fact confirmed the larger susceptibility of NR to undergo crosslinking reactions and the higher affinity of the additives toward it, as discussed earlier. Besides, the higher crosslink densities of the mixtures

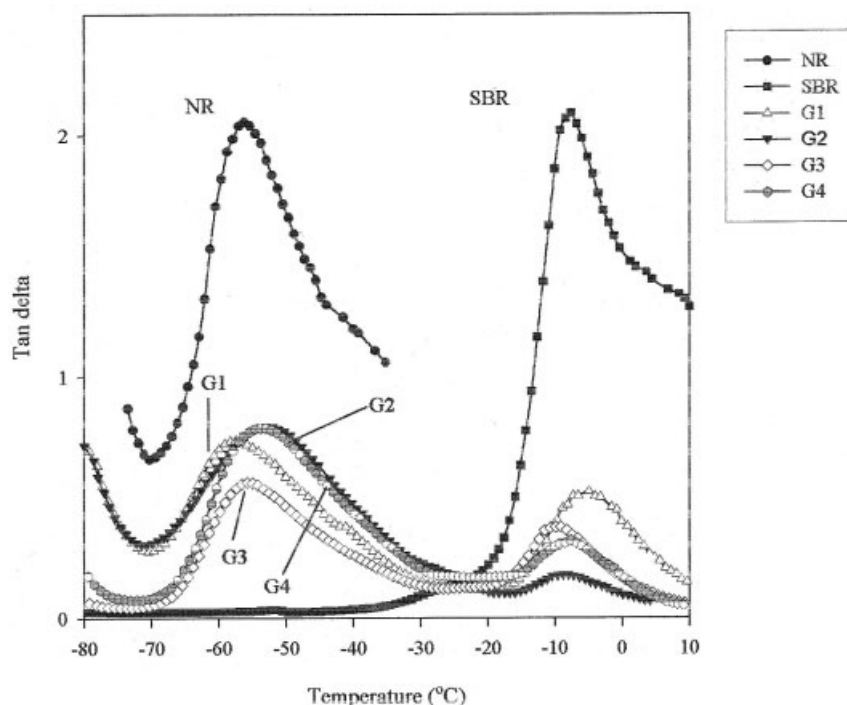


Figure 4 Tan δ versus temperature of NR/SBR blends.

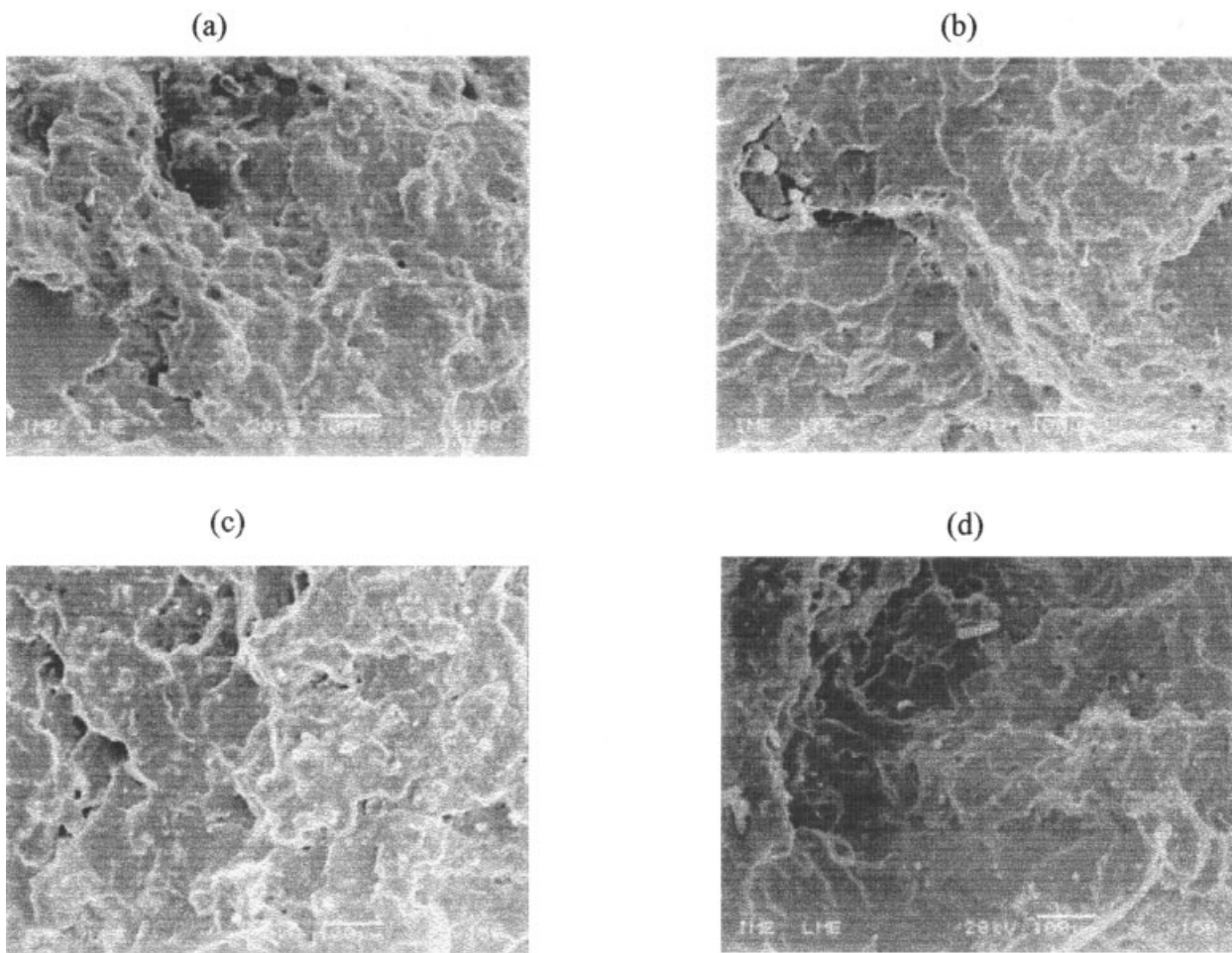


Figure 5 Photomicrographs of NR/SBR blends, 20 kV, $\times 150$: (a) G1; (b) G2; (c) G2; (d) G4.

in comparison to pure rubbers corroborate the maximum torque values shown in Table I, once this parameter is related to the number of crosslinks formed in the absence of filler. G1 and G3 showed the higher crosslink densities because of the higher concentration of curatives in the NR phase. G2 and G4 presented similar results because, in both cases, as SBR vulcanization was favored, NR phase was less vulcanized.

The incorporation of NR into SBR can be considered worthwhile from the point of view of mechanical properties because tear strength was not worsened (even though there had been a small decrease in stress strength), but mainly because of the rheometric properties, as seen before. In addition, there is the economical aspect, as the developed compositions have more competitive prices, due to lower cost of SBR as compared to NR, and better processibility.

The results of $\tan \delta$ from DMTA can be seen in Figure 4, which presents the regions where the transitions corresponding to NR (at lower temperatures) and to SBR phases occur.

According to the literature,¹³ increasing degrees of vulcanization lead to a decrease in $\tan \delta$.

The values of stress strength have shown that the mix G3 presented the worst result. As in this mix, the additives were incorporated to the two rubbers already mixed; they were allowed to preferentially migrate to the phase with which they had more affinity, namely NR, and thus, most of the curatives were consumed in the NR vulcanization. So, considering the NR phase, this would explain why G3 presents the lowest value of $\tan \delta$ among all mixes. Also, the low value of glass transition temperature (T_g) for the NR phase is related to its degradation, occurring due to the long time needed to vulcanize the mix. The same behavior of T_g is found for G1, prepared by adding all the ingredients into the NR phase, thus causing this phase to be excessively cured. Considering G2 and G4, as SBR vulcanization was favored, better results of mechanical properties were obtained because the NR phase was fairly preserved (it was not too vulcanized). This is suggested by the values of $\tan \delta$, the highest ones and close to each other, as well as by the highest values of T_g for the NR phase.

Looking now at the region corresponding to SBR, the lowest vulcanization degree of this phase is pre-

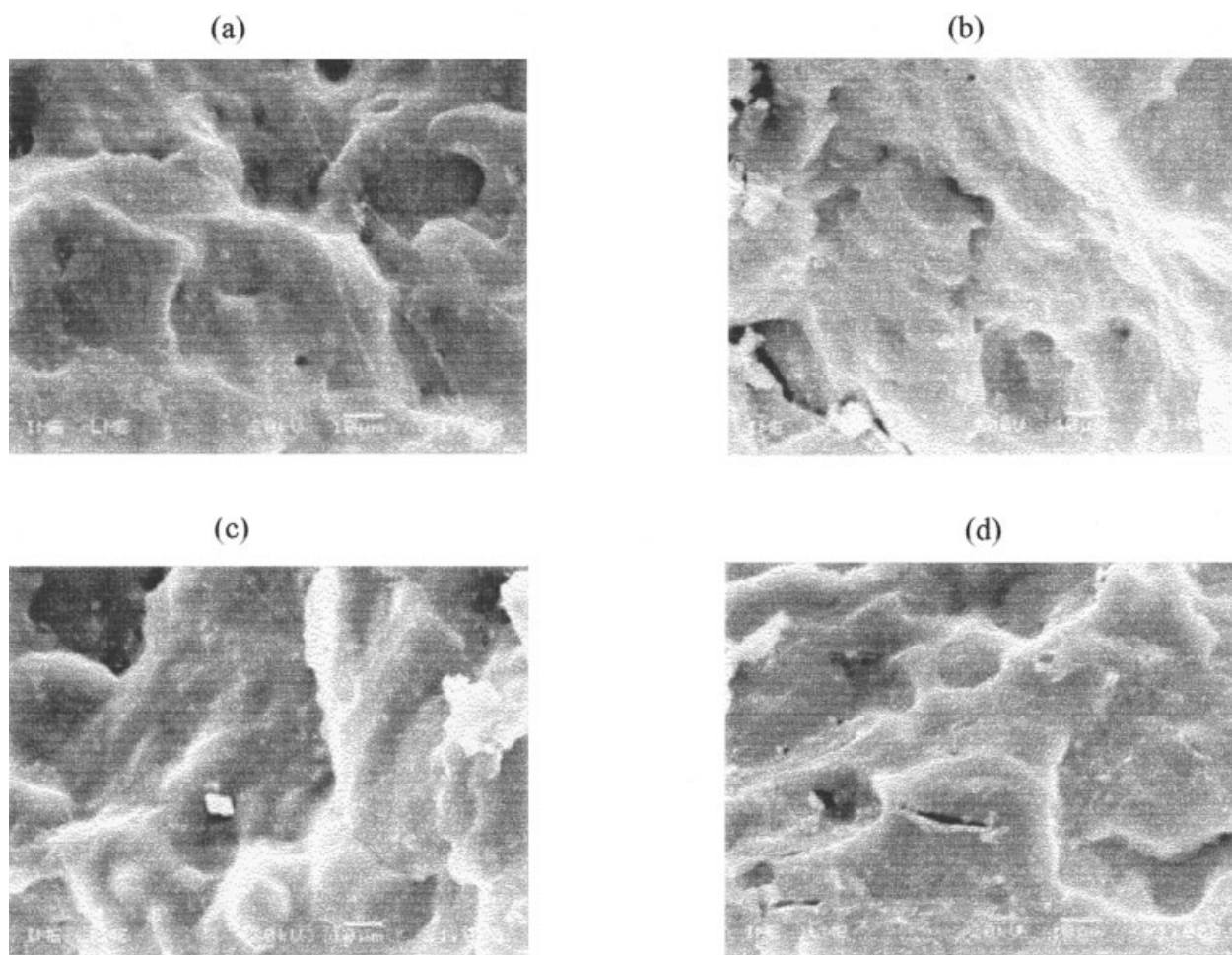


Figure 6 Photomicrographs of NR/SBR blends, 20 kV, $\times 1000$: (a) G1; (b) G2; (c) G3; (d) G4.

sented by G1, whereas for G2, this phase was more vulcanized.

Dynamic mechanical properties of polymeric materials are strongly sensitive to composition and the interactions present in the compound.^{14,15} In incompatible mixtures of two or more polymers, DMTA peaks corresponding to the distinct phases can easily be distinguished. However, depending on the degree of incompatibility (or compatibility), the phases will sense differently the presence of the other ones and this will be reflected on the viscoelastic behavior of the compound as a whole.

Rubber vulcanizates are very complex systems because, in addition to the polymeric matrix, there are always a number of additives and almost always the presence of high amounts of fillers. The way these ingredients are dispersed in the matrix will result in properties which are a consequence of the built morphology. DMTA technique is suitable for this type of investigation as $\tan \delta$ is sensitive to these morphological changes. So, the differences in $\tan \delta$ resulting from blending show that rubber compounds, in which the phases are differently susceptible toward vulcaniza-

tion, can be conveniently prepared by modifying the way the additives are incorporated in the rubber matrix.

Figures 5(a-d) and 6(a-d) show the photomicrographs of the cryofractured samples at different magnifications. In Figure 5(a-d), it is observed that for all photomicrographs a similar morphology, compact and homogeneous, was found. At higher magnification [Fig. 6(a-d)], small particles distributed in the matrix could be detected. These particles are more visible in G3 and G4 and probably resulted from a dispersion not so efficient of the additives in the rubbers. These particles can act as factors of stress concentration, reducing the mechanical strength of the material, as seen in Figure 2. The existence of tearing zones can also be observed, indicating that these mixtures present more plasticity. From Figure 2, the higher degree of plasticity for G2 can be seen, as well as the decrease in this property for G3, due to an inhomogeneous distribution of the additives, as mentioned earlier.

This work was meant to be part of a series of articles covering the full range of NR/SBR ratios.

CONCLUSION

The way the additives of a formulation are incorporated into a rubber mixture does play an important role concerning the mechanical properties of the resulting compositions. The four modes used in this work to prepare NR/SBR vulcanizates showed that specific properties can be enhanced by properly changing the way the additives, in particular the curatives, are incorporated. As the elastomeric components have very different characteristics, better properties are obtained when one favors the vulcanization of that rubber which, when unblended, presents poorer properties while, at the same time, the good features of the other rubber are kept, as much as possible, unchanged.

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