



## Effect of entanglements in the microstructure of cured NR/SBR blends prepared by solution and mixing in a two-roll mill



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### ABSTRACT

The influence of preparation methodology of vulcanized elastomeric blends of natural rubber (NR) and styrene butadiene rubber (SBR) on the phase morphology and network structure has been studied. Two different compounding methodologies have been applied: (i) mechanical mixing in a two-roll mill and (ii) blending in solution, by dissolving the elastomers in an appropriated solvent.

Samples with different NR/SBR ratios were vulcanized by using a conventional cure system based on sulfur and TBBS (n-t-butyl-2-benzothiazole sulfenamide) as accelerator. The phase distribution of rubber matrices in the blends was investigated by transmission electron microscopy (TEM), identifying differences in the compounds according to the preparation method.

Weak residual dipolar couplings caused by the existence of cross-links and topological constraints in vulcanized samples were characterized by using proton multiple-quantum (MQ) NMR spectroscopy. The structural results obtained by NMR and equilibrium swelling experiments were compared and complemented with viscosity measurements.

It was found that the preparation method has a strong influence on the phase morphology of blends and the molecular network structure of each rubber phase, with an important variation in the entanglements contribution, which is more pronounced when the prepared blends are richer in NR.

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### 1. Introduction

Elastomeric blends are of great industrial interest since blending is a relatively simple fabrication process for elastomers which significantly improves the properties in the material when comparing with compounds made with only the pure elastomers [1].

In order to predict and enhance the mechanical properties for better commercial and industrial applications of elastomeric blends, it is necessary to deeply study the atomic-scale microstructure and interaction between the different phases that constitutes the blend.

Most of the elastomers are immiscible when they are blended because the mixing contribution is endothermic and the entropic factor is small because of the high molecular weights of those matrices [2,3]. Fortunately, miscibility is not a prerequisite for most of the rubber applications.

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The physical properties of immiscible two-phase blends depend on the characteristics of each constituent phase. The morphology, viscosity and stiffness of each phase play a significant role in the properties of the uncured blend. The dispersion of curatives in each phase plays also an important role in the final properties of the vulcanized blend. During vulcanization the creation of cross-links connecting different polymer chains forms a three-dimensional network structure in the compound. In rubber blends, the elastic properties of the sample would depend on the cross-link density inside each rubber phase and additionally on the presence of cross-links that are connecting the phases, i.e. the characteristic of the interphase.

There are many different experimental approaches to analyze cross-linked polymers including osmometry, dynamical mechanical analysis and neutron scattering among others [4–8]. Nowadays equilibrium swelling experiments based on the Flory-Rehner approach [9,10] is the most widely applied methodology to determine the cross-link density in elastomers [11,12], despite the uncertainties associated to the obtained results [13].

NMR spectroscopy has been applied to the study of rubber networks [14,15], being time-domain solid-state NMR experiments one of the most useful and successful tools to investigate the network structure of vulcanized elastomers [16–21]. The central NMR observable is the residual dipolar couplings ( $D_{res}$ ), characterizing local chain order arising from nonisotropic fast segmental motions of the polymer chains, which in turn arise from constraints to the chain motion.

When unfilled elastomers are analyzed, these constraints are imposed by entanglements and in the vulcanized state the cross-links are included. Many NMR experimental procedures have been used to estimate  $D_{res}$  [20–24] and it is in fact well-known that a linear relationship exists between the network parameters determined by equilibrium swelling and by NMR [13,16,19]. These results confirm the direct relationship between the actual NMR observable (an apparent, i.e., averaged residual dipolar coupling,  $D_{res}$ ) and the cross-link density [21] according to the expression:

$$S_b = k \frac{D_{res}}{D_{stat}} = \frac{3}{5} \frac{r^2}{N} \quad (1)$$

where  $S_b$  is the dynamic order parameter of the polymer backbone,  $k$  represents the local coupling topology and intra-segmental motions that should be used to rescale the static coupling constant,  $D_{stat}$ . This expression relates  $D_{res}$  with the ratio of the end-to-end vector to its average unperturbed melt state ( $r^2 = \langle r^2 \rangle / \langle r^2 \rangle_0$ ), and with  $N$ , which represents the number of statistical (Kuhn) segments between constrains.

Proton multiple-quantum NMR (rather than the more common measurement of transverse relaxation times) is the most quantitative and reliable method for the measurement of residual dipolar couplings and hence to obtain local information about the rubber network structure [21]. This technique was used for the determination of the cross-link density and their spatial distribution [18] in different rubber matrices, including vulcanized natural rubber and styrene butadiene rubber [18,19].

During the last years we have studied the mechanical and thermal properties of NR/SBR vulcanized blends considering, in particular, the influence of the fraction of each elastomer on those properties. By means of several experimental techniques, as small-angle X-ray scattering (SAXS), positron annihilation lifetime (PALS), equilibrium swelling experiments, differential scanning calorimetry (DSC) and scanning electron microscopy (SEM), the microstructure of the blends was analyzed [25–30].

In the present work we continue such research topics studying the morphology and network structure (at molecular scale) of NR/SBR vulcanized blends considering, in particular, the influence of preparation method of those compounds: by mechanical mixing and by solution mixing.

## 2. Experimental

The blends studied in the present research are composed by NR (SMR-20) with molecular weight  $M_n$  of 178,800 g/mol and polydispersity of 6.3, and emulsion SBR-1502, Arpol (E-SBR with 23.5% of styrene) provided by Petrobras, with molecular weight of 128,300 g/mol and polydispersity of 3.8, as it was measured by the Gel Permeation Chromatography (GPC) technique. The densities were  $\rho$  (NR) = 0.917 g/cm<sup>3</sup> and  $\rho$ (SBR) = 0.935 g/cm<sup>3</sup>, respectively.

Rubber compounds and NR/SBR blends were prepared according to the proportions showed in Table 1. All the recipes were based on the same vulcanization system composed by 2.25 parts per hundred of rubber (phr) of sulfur and 0.7 phr

**Table 1**

Compound recipes (in parts per hundred of rubber), and optimum cure time  $t_{100}$  at 160 °C for the samples prepared by mixing in solution and in a laboratory two-roll mill.

<i>Solution blending</i>					
SBR1502	0	20	50	80	100
NR (SMR20)	100	80	50	20	0
$t_{100}$ (min)	10.6	16.7	41.6	53.8	87.6
<i>Two-roll mill blending</i>					
SBR1502	0	25	50	75	100
NR (SMR20)	100	75	50	25	0
$t_{100}$ (min)	10.7	17.0	24.8	34.4	42.3

of accelerator TBBS (n-t-butyl-2-benzothiazole sulfenamide) with 2 phr of stearic acid and 5 phr of zinc oxide that act as activators.

The samples were prepared by using two different compounding methods:

(1) Solution blending:

This method consists, in a first step, in dissolving in toluene the NR as received with the aim of removing the impurities by precipitation, then the purified solution was extracted and the solvent was evaporated at room temperature during two days to get a film of purified NR.

To prepare the compounds the relations of elastomer to solvent were 18 g/dm<sup>3</sup> and 20 g/dm<sup>3</sup> for NR (purified) and SBR, respectively. The viscosities of these solutions, measured at room temperature with a Brookfield viscometer, were 55 cP for the NR/toluene and 9.8 cP for SBR/toluene solutions.

To prepare each blend, both solutions were mixed with the chosen proportions of each elastomer and the required chemicals according to the recipe. The mixture was further homogenized by mechanical stirring and by ultrasonic treatment in a bath. Finally, the solvent was evaporated at room temperature for 3 days until obtaining a constant weight.

(2) Laboratory two-roll mill blending:

The pure elastomers and blends were compounded in a two-roll mill at 50 °C, following conventional procedures in rubber technology. Firstly the elastomers were mixed to prepare a master batch where the other ingredients were added and mixed until they were completely dispersed in the rubber matrices.

In order to study the influence of the preparation method on the viscosity of NR and SBR, the Mooney viscosity (ML 1 + 3 100 °C) was measured in an Alpha MV2000 Mooney viscometer, following ASTM D1646-04 standard.

The rheological characterization of these samples prepared by both methods was described in previous works of our research group [27,28]. From this information, the rheometer curves at 160 °C were obtained and the optimum vulcanization time,  $t_{100}$  (time to achieve the maximum degree of vulcanization), for each compound was obtained and summarized in Table 1.

All samples were vulcanized at 160 °C at their respective  $t_{100}$  time in a hydraulic press. At the end of the vulcanizing cycle, samples were cooled down in an ice-water mixture. Compounds prepared by the solution method were vulcanized in disks of 17 mm diameter and 2 mm thickness, whereas vulcanized sheets of 150 × 150 × 2 mm<sup>3</sup> were obtained for samples prepared in two-roll mill.

TEM images for cured samples were obtained with a Philips Tecnai 20 TEM apparatus using an accelerating voltage of 200 kV. Specimens for TEM characterization were prepared by using a LEICA EM UC6 ultracryomicrotome with a thickness of 40–50 nm. It was not necessary to perform a previous treatment on the samples.

In recent works [28,29], the molecular weight of the network chain between chemical cross-links  $M_{cs}$  was determined from swelling experiments using the relationship [9,10]:

$$M_{cs} = - \frac{\rho(1 - 2/\phi)V_1 v_{2m}^{1/3}}{\ln(1 - v_{2m}) + \chi v_{2m}^2 + v_{2m}} \quad (2)$$

where  $\rho$  is the density of the rubber network,  $\phi$  the functionality of the cross-links,  $v_{2m}$  the polymer volume fraction at equilibrium (maximum) degree of swelling and  $V_1$  the molar volume of solvent.  $\chi$  is the Flory-Huggins interaction parameter between the polymer and the swelling agent. Sulfur cured elastomers are usually considered as a 4-functional network and  $\phi = 4$  was used in Eq. (2).

Double-quantum NMR experiments were performed at 80 °C to ensure fast enough dynamics to complete the segmental averaging over all possible chain conformations on the time scale imposed by the NMR experiment [18,19] on a Bruker minispec mq20 spectrometer operating at 0.5 T with 90° pulses of 3 μs length and dead time of 11 μs. Normalization procedure applied to the double quantum intensity ( $I_{ndQ}$ ) effectively separates the effect of temperature dependent dynamics from the time-independent effect of network structure. The subsequent analysis of  $I_{ndQ}$  by using a numerical inversion procedure based on a modified Fast Tikhonov Regularization [31], has been used to obtain a quantitative picture of the actual distribution function of residual couplings. Regularization procedure and data analysis for NR and SBR samples were widely explained in a cursory way elsewhere [16–19,21,31].

### 3. Results and discussion

#### 3.1. Effect of the mixing procedure on the morphology of NR/SBR blends

A first point to mention when comparing the compounds prepared with both methods is that the optimum cure times  $t_{100}$  measured by rheometer at 160 °C shift to higher values when the samples are richer in SBR, as it can be appreciated in Table 1.

The sulfenamide class accelerators, as TBBS, present a delayed action as well as a faster cure rate during the vulcanization of rubber compounds. TBBS is soluble in toluene and this fact improves their dispersion in the compound when it is prepared by our solution method. Then, the delayed would be more efficient in the case of the compounds prepared by this method. The less reactivity of SBR compared with NR does that the delayed effect was more evident in this one.

Fig. 1 shows TEM micrographs of vulcanized SBR/NR blends prepared by both the solution approach and the traditional mechanical mixing technique in a two-roll mill. These pictures reveal that the obtained phase morphology depends on the preparation method and the composition of the binary blend. All pictures are given with the same magnification in order to compare the obtained structures. Two domains are present: the dark one corresponds to SBR phase and the clear one to NR domains, respectively. By means of EDAX technique it was found that the remaining zinc oxide was well distributed in both phases.

The NR phase is identified by the presence of small particles, as grey dots, inside it in all the TEM pictures. However, these particles are in much less quantity in the samples prepared by solution. The size of these particles was not big enough to be analyzed and identified by EDAX, however we have a strong suspicion that these particles could be (i) impurities and non-rubber components from the NR matrix, being partially removed during purification treatment or (ii) they could be some fraction of high molecular weight NR that were not dissolved in toluene (swollen gel fraction) and eliminated in the purification of the raw NR. In this sense, it has been described that the non-rubber components (mainly proteins and phospholipids) of NR can interact at the molecular chain ends of the polymer, forming a tree-dimensional pseudo end-linked network, contributing to the outstanding physical properties and characteristics of the un-vulcanized NR [32].

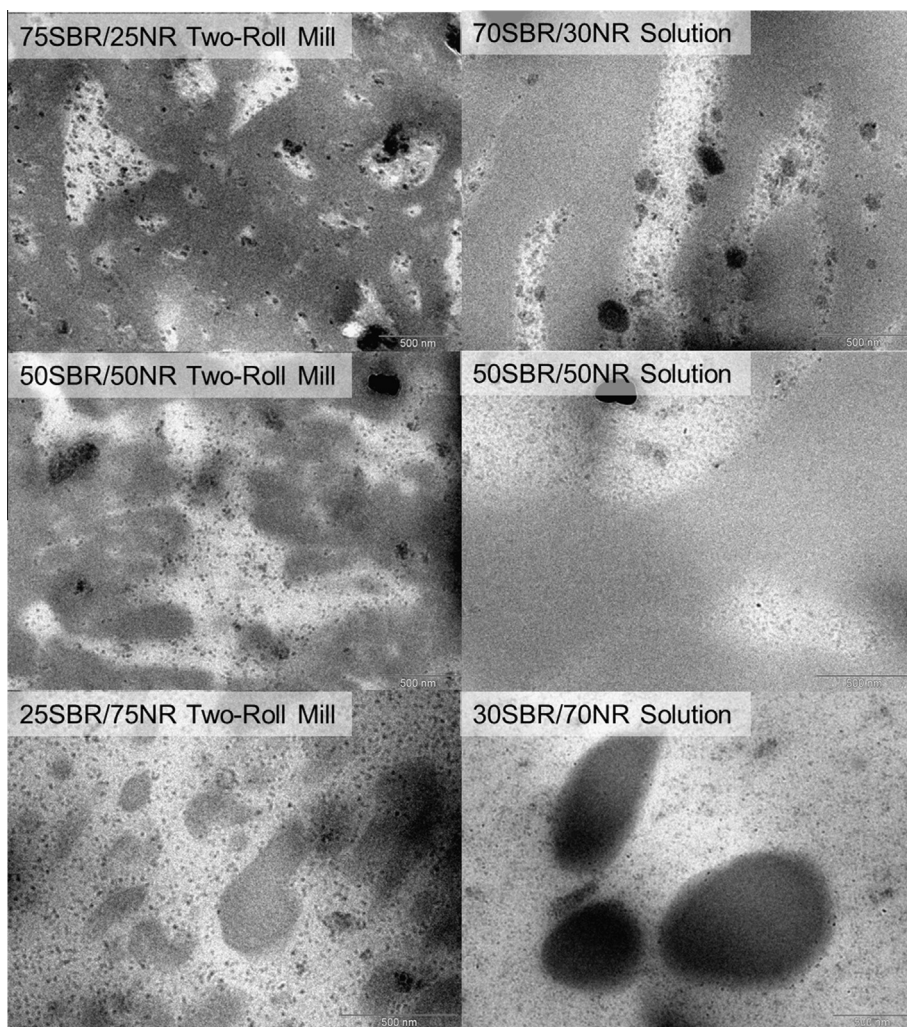


Fig. 1. TEM micrographs of vulcanized SBR/NR blends at different compositions and different mixing procedure. SBR is the dark phase and NR is the clear one.

Depending on the composition of the blend and the initial viscosity of each elastomer, it is obtained a continuous phase with an encapsulated second phase or a co-continuous structure. Fig. 1 shows several different microstructures obtained in this research.

The Mooney viscosity  $\eta$  of the pure elastomers used to prepare the binary blends are represented in Fig. 2. When the compound were prepared by two-roll mill blending, the initial Mooney viscosities of the elastomers were  $\eta(\text{NR}) = 87 \text{ Mu}$  and  $\eta(\text{SBR}) = 56.5 \text{ Mu}$  and the viscosity ratio was  $[\eta(\text{NR})/\eta(\text{SBR})]_{\text{mechanical}} = 1.54$ .

In the case of the compounds prepared by solution blending, initially the elastomer were dissolved in toluene and the viscosities measured were 55 cP for the NR/toluene and 9.8 cP for SBR/toluene solutions. Then  $[\eta(\text{NR})/\eta(\text{SBR})]_{\text{solution}} = 5.65$ . The difference in the viscosity ratios in both preparation methods implies that the morphology and phase distribution in the blends should be different.

If the compound is richer in SBR, this is the continuous phase in samples prepared by both methods (samples 75SBR/25NR and 70SBR/30NR) as it is shown in Fig. 1. Usually, for a blend where the viscosities of the components are unequal, the low viscosity component encapsulates the high viscosity component and becomes the continuous phase [33]. This fact is in accordance with the observed in these compounds.

The situation of a co-continuous phase is observed in the samples 50NR/50SBR regardless the preparation method (Figs. 1 and 3).

However, the situation is more complex for the compounds richer in NR. For both preparation methods, the continuous phase is that of higher viscosity (NR). This result would indicate that there are other factors that are influencing the phase distribution in these compounds. To elucidate this point more research must be done.

It can also be observed in Fig. 1 that the size of the encapsulated regions is bigger when the samples are prepared by solution, and the interphase between both phases is notoriously more diffuse than in the case of samples compounded via two-roll mill. To stress this point, Fig. 3 shows micrographs obtained for the compound 50SBR/50NR prepared with both methods where the differences in the interphase are evident. This can be interpreted as evidence of an interpenetration of NR and SBR chains at the interphase, generating a region with different properties than in the pristine phases.

As shown in Fig. 2, viscosity of the raw rubbers decreases dramatically after the solution treatment, reaching a drop in the viscosity value of 62% in the case of NR and 23% in SBR matrix. The variation of viscosity after the solvent dilution treatment of both rubber samples could be related with the molecular reorganization, in terms of entanglements and topological constraints, promoted by the slow evaporation of the solvent. It should mean that disentanglement process during the solvent dilution treatment and the subsequent re-entanglement phenomenon of the polymer chains during the elimination of the solvent does not provide the same polymer structure, releasing some of the topological constrains present in the raw materials.

Thermodynamically, the miscibility in polymer-solvent mixtures or polymer-polymer blends can be predicted if the values of the Hildebrand solubility parameters,  $\delta$ , of their components are similar [34–36]. At room temperature, the solubility values of NR, SBR and toluene are:  $\delta_{\text{NR}} = 16.6 \text{ MPa}^{1/2}$ ,  $\delta_{\text{SBR}} = 17.3 \text{ MPa}^{1/2}$  and  $\delta_{\text{toluene}} = 18.3 \text{ MPa}^{1/2}$ , respectively [37]. This fact implies a higher compatibility for SBR/toluene system than NR/toluene solution. However, the dissolution process creates a greater drop in the NR viscosity as it observed in Fig. 2. It seems to indicate that dissolution process produces a higher variation in the entanglement structure of NR as compared to the SBR [38] because the reduction of the impurities and some of the non-rubber components which act as natural branching points in NR.

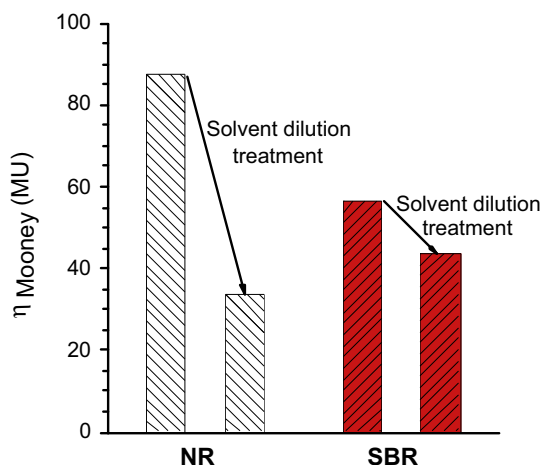
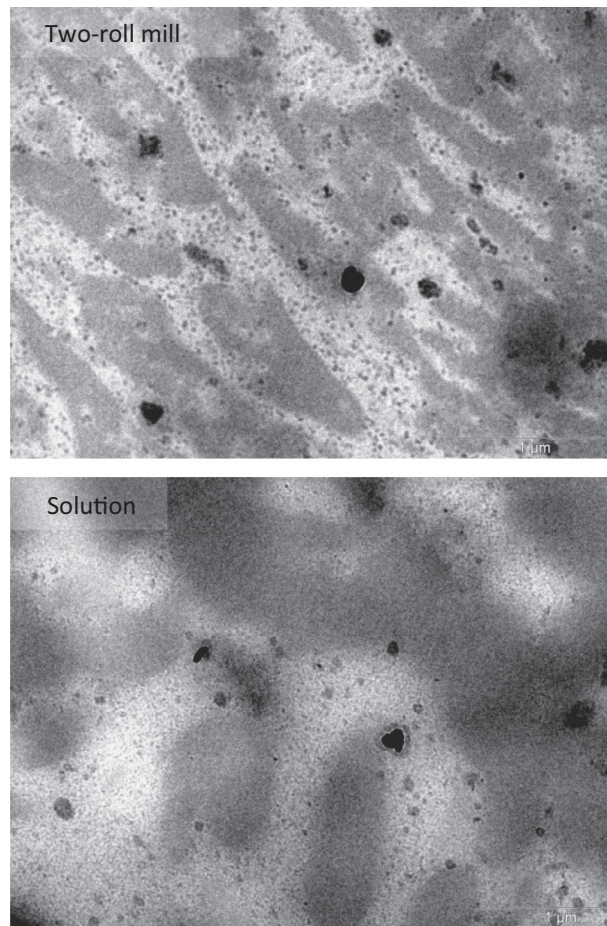


Fig. 2. Mooney viscosity for pure elastomers (NR and SBR) as received and after the solution treatment.



**Fig. 3.** TEM micrographs of vulcanized 50NR/50SBR blends with both preparation methods. SBR is the dark phase and NR is the clear one.

### 3.2. Network structure in vulcanized rubber blends

The network structure of vulcanized samples has been studied by equilibrium swelling and MQ-NMR experiments, respectively. From the equilibrium swelling experiments in toluene, the molecular weight between cross-links  $M_{cs}$  was obtained using Eq. (2). Then, assuming 4-functional networks the total cross-link density  $\mu_{cs}$  could be defined by the following equation [9]:

$$\mu_{cs} = \frac{\rho}{2} \left( \frac{1}{M_{cs}} - \frac{1}{M_n} \right) \quad (3)$$

For blends, this equation can be used as a first approach considering a mixture law for the molecular weights. In Fig. 4 the so-obtained cross-link density values are shown, demonstrating that  $\mu_{cs}$  is lower in mixtures made by solution than those prepared by mechanical mixing. The biggest difference in the cross-link density according to the compounding method is showed by the pure compound of NR, whereas this difference is almost negligible for SBR samples. As consequence, the differences in the cross-link density according to the preparation method scale with the amount of NR in the blend.

At this point it is important to take into account that once the polymer matrix is vulcanized, the elastic force that balances the osmotic pressure of the solvent in equilibrium swollen networks is defined by the cross-links and the elastically active entanglements that could be not relaxed under the swollen conditions [38,39]. Consequently, swelling test does not distinguish between cross-links and the elastically active trapped entanglements. Previous works [40,41] assert that the presence of trapped entanglements in vulcanized materials is significant and they exert an important effect on the mechanical properties of elastomers [42]. Therefore the differences observed on the swelling experiments according to the blending method have to be attributed to the variation in both the cross-link density and the entanglement constraints, being more important the last contribution when the NR content is higher in the sample.

According to the previously discussed effect of solution blending related to the extraction of the impurities and non-rubber component of NR, it could be expected a reduction in the topological restrictions as compared to the blends

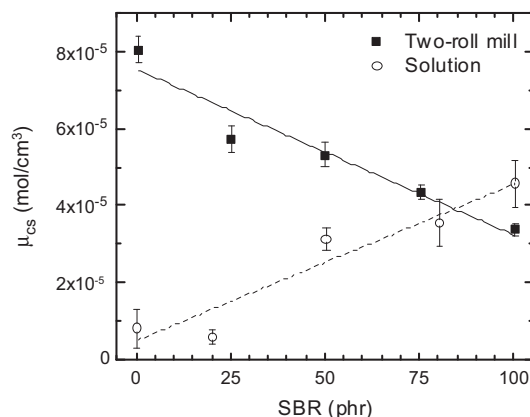


Fig. 4. Total cross-link density as function of the SBR content, for the blends prepared by solution and in a laboratory mill. Lines are for visual guide.

mechanically prepared in the two-roll mill. The significant increase in the swelling capacity of those samples should be additionally linked to a decrease in the cross-link density. The importance of non-rubber components on the sulfur vulcanization of NR has been studied, demonstrating that proteins and nitrogenous compounds act as natural accelerator for the sulfur vulcanization process. Consequently, the purified samples show slower vulcanization rates and cross-link densities as compared to raw NR counterparts [43]. This effect was observed in a previous work of some of the authors where the cure rate was analyzed [44].

On the other extreme, SBR samples show similar swelling behavior independently of the processing approach (Fig. 4). Assuming that vulcanization reaction (and hence the cross-link density) is not affected for SBR compounds, the supposed variation in the entanglement structure according to the decrease in the Mooney viscosity on un-vulcanized SBR sample after its dilution treatment does not provoke an observable effect on the equilibrium swelling degree.

Opposite to the swelling experiments,  $^1\text{H}$  MQ-NMR experiments provide direct evidences about the dipolar couplings that depend on the constraints to the segmental polymer motions, independently of their nature [18,19,21,45,46]. According to this statement, the NMR observable depends on the rubber network structure and it contains quantitative information of both cross-links and entanglements without any model dependence [21] and completely free of the uncertainties associated to the complex thermodynamic of the swelling process in rubber networks [13]. Additionally, MQ-NMR experiments provide information about the distribution of the dipolar couplings, which supposes a step forward in the characterization of the rubber network structure. Fig. 5 shows the distributions obtained after the numerical inversion procedure of  $I_{HDQ}$  for pure samples based on NR and SBR, respectively. This regularization analysis is able to discriminate between located network heterogeneities with phase separated morphology and randomly (homogeneously) distributed network heterogeneities as it has been demonstrated [31]. The studied rubber blends show a phase separated morphology (see TEM images in Fig. 1) and consequently, a bimodal spatial distribution of dipolar couplings, corresponding to the network structure for the two rubber phases, would be expected in the NMR experiments. Unfortunately the dipolar coupling distribution for the

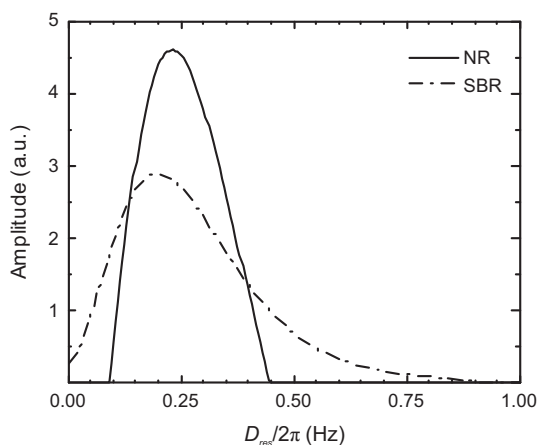


Fig. 5. Distribution of residual dipolar couplings obtained by the regularization method for the pure samples of NR and SBR vulcanized at 160 °C until their optimum times.

individual networks (NR and SBR, respectively) is very similar in average and they clearly overlap as it is showed in Fig. 5. This fact prevents the differentiation between different blend morphologies by using the NMR data, but they are quite useful to analyze (without any additional uncertainty) some of the structural parameters that define the network structure in polymer blends.

In the case of NR sample, the distribution of dipolar couplings is very narrow because this rubber is a homo-polymer from isoprene monomer. It means that any variation in the spatial distribution of cross-links will implicate an important and obvious variation in the measured distribution of dipolar couplings. At the other extreme, we have a random co-polymer of styrene and butadiene (SBR), characterized by a broader distribution of dipolar couplings because of the chemical structure of the polymer backbone, so the weaker effects resulting from heterogeneities in the network structure will be diluted in those samples.

It is possible to characterize the average value ( $D_{res}$ ) and the standard deviation ( $\sigma$ ) that defines the distribution of dipolar couplings extracted from the regularization procedure. The standard deviation is normalized with respect to the mean value of the distribution ( $\sigma/D_{res}$ ) in order to be able to compare the broadness of different distributions. These values are shown in Fig. 6a and b, depending on the amount of SBR in the composition of each blend.

It is quite important to mention that increasing residual dipolar couplings with the addition of SBR to the blend would not be directly ascribed to the cross-link density because in each case the scaling factor  $D_{stat}/k$  would be different (see Eq. (1)). Only in those samples with the same NR/SBR content, differences on the measured residual dipolar coupling could be directly related with changes in the network structure. In this sense, it is important to point out the reduction in the averaged residual dipolar coupling observed in the NR compound prepared by solution method compared to the mechanically mixed counterpart. To avoid any error in the NMR measurements, the pure NR samples prepared by both methodologies have been measured on several occasions showing similar results. These results confirm the decrease in the constrain density (cross-links and entanglements) observed in the equilibrium swelling experiments caused by the dissolution of NR. The presence of non-rubber components in the raw NR (prepared in the two-roll mill) not only increases the cross-link density, but also promotes some slight broadening of the spatial distribution of cross-links.

The next step in this study was the simulation of theoretical residual dipolar coupling distributions that should have the NR/SBR blends according the network structure of pure NR and SBR elastomers by applying a mixture law. This approach has been demonstrated to be valid for samples with phase separated morphologies [31]. Consequently, a metadata set for each rubber blend was obtained by averaging experimental data for pure elastomers according the known weight fractions of

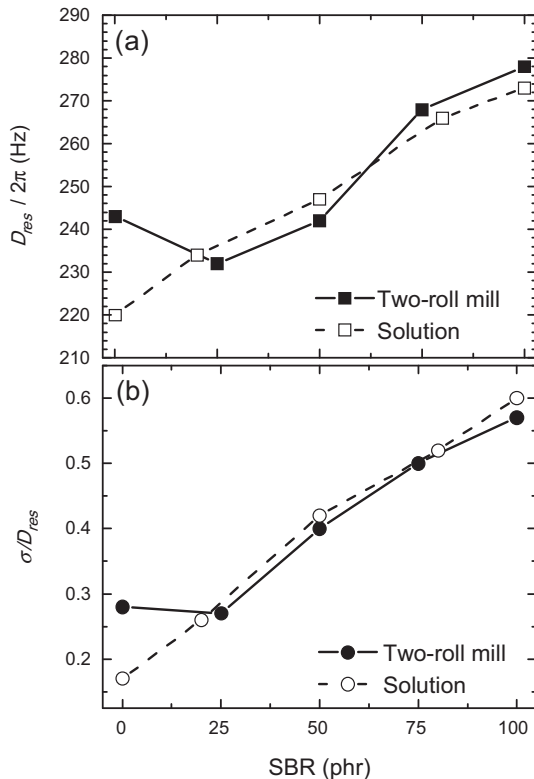
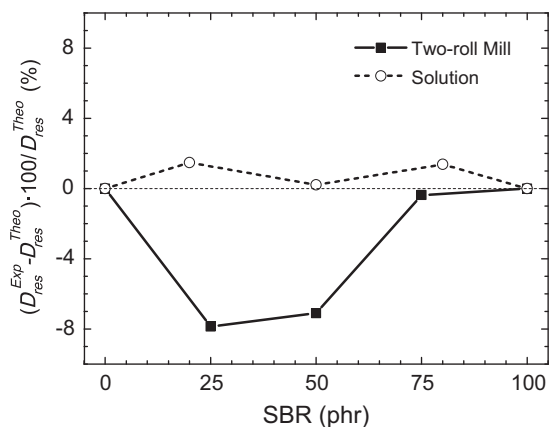


Fig. 6. (a) Variation of the dipolar coupling constant and (b) the normalized standard deviation of the distribution as function of the SBR content in the blend samples.





**Fig. 7.** Percentage deviation between experimental values of the dipolar coupling (related with the cross-link density) and theoretical ones, obtained from a mixture law using the pure compounds, as function of the SBR content.

each component. The so-obtained build-up curves were analyzed by using the regularization procedure. Fig. 7 shows the comparison between theoretical distributions (based on the metadata set) and the experimental results obtained from the NMR measurements of different blends.

The biggest differences between the experimental and theoretical values are obtained in those blends compounded in two-roll mill with a higher content of NR. In the case of the samples prepared by mechanical mixing, the addition of 25 phr of SBR to the NR matrix causes a decrease of approximately 8% in the averaged dipolar coupling constant with respect to the expected value according to the mixing law. Assuming that all sulfur atoms are involved in the formation of cross-links (or at least a similar concentration) for all the studied samples, the preferential migration of the vulcanization system to one phase suppose the decrease in the sulfur concentration in the opposite rubber matrix. According to the higher residual dipolar couplings showed by the pure SBR with respect the NR matrix, the decrease in the experimental dipolar couplings can be attributed to the under-curing degree of the SBR phase [27], which correspond to lower cross-link density for these SBR domains.

Differences between theoretical and experimental values are minimized when the fraction of SBR in blends increases as it can be observed in the sample 25NR/75SBR where the dipolar coupling value obtained experimentally are equal to the theoretical one. The different behavior between these two complementary samples can be attributed to the migration of curatives, that in the pair NR-SBR occurs from SBR towards NR [42]. So in the blend 25NR/75SBR the over-cured NR phase (according to the vulcanization curve obtained from the rheometer) is receiving additional curatives from SBR matrix, making possible to compensate the degraded cross-links caused by the reversion phenomenon [27].

Opposite to the mechanically mixed samples, the rubber blends prepared by solution show a network structure that exhibits the expected behavior according to the mixture law applied to the pure samples. These results seem to indicate a greater interaction of the chains of NR and SBR at the interphase, i.e. NR chains could be present in the SBR domains and vice versa.

To give a relative weight to this analysis is necessary to consider the uncertainties. Usually, the  $D_{res}$  value is assumed (in a conservative estimation) to have an experimental error of 5%, although the experimental variability is generally lower [31]. Secondly, NR has a narrower distribution of dipolar couplings than SBR due to the chemical structure of this homopolymer. This fact provokes that slight variations in the network structure for NR are clearly reflected in the distribution of dipolar couplings, so this technique is much more sensitive to small changes in NR than in SBR. According to this issue, the sensitivity for detecting variations in the spatial distribution of cross-links in the NR phase decreases in blends where the fraction of SBR is higher.

#### 4. Conclusions

The differences in the microstructure of NR/SBR vulcanized at 160 °C, produced by two type of sample preparation are presented. Two manufacturing methods were used: by mixing in solution and in two-roll mill, which are based on different initial viscosities in each of the used elastomers. This starting point determines the differences in the blend morphology according to the preparation method. Immiscible blends are obtained in both manufacturing methods; however, TEM observations show a smooth contrast on the interfaces in the case of the samples prepared by solution. This fact could indicate a better compatibility between the two phases. The obtained results reflect that the dilution process produces disentanglement effects in the polymeric chains, generating the different behaviors observed in the two sets of blends.

The analysis of the vulcanized compounds by means of equilibrium swelling experiments and proton multiple-quantum NMR show pronounced differences between the samples prepared by the two methods mainly when the blends are richer in NR. In the case of samples prepared by the solution technique, a mixture law can be applied to adjust the residual dipolar

coupling as functions of the elastomer composition in the blend, demonstrating an enhanced interface between both separated phases. Opposite to this behavior, the rubber blends prepared by mechanical procedure show the preferential migration of the vulcanization system to NR phase as it has been showed by the NMR analysis.

The preparation method strongly affects the network structure of NR whereas the SBR samples seem to be almost unaffected. This fact has to be ascribed to the additional purification process of NR matrix during the dilution process. Elimination of impurities and non-rubber components provokes the drop of Mooney viscosity and the reduction in the cross-link and entanglement density in NR because they act as branching points in the un-vulcanized samples and they behave as accelerators during the sulfur vulcanization. This fact is more important in those blends that are richer in NR phase.

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## References

- [1] D. Mangaraj, *Elastomer blends*, *Rubber Chem. Technol.* 75 (2002) 365–427.
- [2] W.M. Hess, C.R. Herd, P.C. Vegvari, Characterization of miscible elastomer blends, *Rubber Chem. Technol.* 66 (1993) 329–375.
- [3] S. Datta, in: J.E. Mark, B. Erman, F.R. Eirich (Eds.), *Science and Technology of Rubber*, third ed., Elsevier Academic Press, 2005, pp. 529–554.
- [4] D.J.P. Harrison, W.R. Yates, J.F. Johnson, Techniques for the analysis of cross-linked polymers, *J. Macromol. Sci.-Pol.* R 25 (1985) 481–549.
- [5] Z. Tan, R. Jaeger, G.J. Vancso, Cross-linking studies of poly(dimethylsiloxane) networks: a comparison of inverse gas chromatography, swelling experiments and mechanical analysis, *Polymer* 35 (1994) 3230–3236.
- [6] S.K. Patel, S. Malone, C. Cohen, J.R. Gillmor, R.H. Colby, Elastic modulus and equilibrium swelling of poly(dimethylsiloxane) networks, *Macromolecules* 25 (1992) 5241–5251.
- [7] Y. Han, J. Zhang, Q. Yang, L. Shi, S. Qi, R. Jin, Novel polymethoxysiloxane-based cross-linking reagent and its *in-situ* improvement for thermal and mechanical properties of siloxane elastomer, *J. Appl. Polym. Sci.* 107 (2008) 3788–3795.
- [8] N. Vennemann, K. Bökamp, D. Bröker, Cross-link density of peroxide cured TPV, *Macromol. Symp.* 245–246 (2006) 641–650.
- [9] P.J. Flory, J. Rehner, Statistical mechanics of cross-linked polymer networks. I. Rubberlike elasticity, *J. Chem. Phys.* 11 (1943) 512–520.
- [10] P.J. Flory, J. Rehner, Statistical mechanics of cross-linked polymer networks. II. Swelling, *J. Chem. Phys.* 11 (1943) 521–526.
- [11] A.J. Marzocca, C.A. Steren, R.B. Raimondo, S. Cerveny, Influence of the cure level on the monomeric friction coefficient of natural rubber vulcanizates, *Polym. Int.* 56 (2004) 646–655.
- [12] A.J. Marzocca, M.A. Mansilla, Analysis of network structure formed in styrene-butadiene rubber cured with sulfur/TBBS system, *J. Appl. Polym. Sci.* 103 (2008) 1105–1112.
- [13] J.L. Valentín, J. Carretero-González, I. Mora-Barrantes, W. Chassé, K. Saalwächter, Uncertainties in the determination of cross-link density by equilibrium swelling experiments in natural rubber, *Macromolecules* 41 (2008) 4717–4729.
- [14] M. Mori, J.L. Koenig, Solid-state C-13 NMR studies of vulcanized elastomers XIII. TBBS accelerated, sulfur-vulcanization of carbon black filled natural rubber, *Rubber Chem. Technol.* 68 (1995) 551–562.
- [15] L. Pelliccioli, S.K. Mowdood, F. Negroni, D.D. Parker, J.L. Koenig, Solid state <sup>13</sup>C NMR applied to styrene-butadiene rubbers study of the rubber vulcanized network structures, *Rubber Chem. Technol.* 75 (2002) 65–76.
- [16] A. Vieyres, R. Pérez-Aparicio, P.-A. Albouy, O. Sanseau, K. Saalwächter, D.R. Long, P. Sotta, Sulfur-cured natural rubber elastomer networks: correlating cross-link density, chain orientation, and mechanical response by combined techniques, *Macromolecules* 46 (2013) 889–899.
- [17] K. Saalwächter, B. Herrero, M.A. López-Manchado, Chain order and cross-link density of elastomers as investigated by proton multiple-quantum NMR, *Macromolecules* 38 (2005) 9650–9660.
- [18] J.L. Valentín, P. Posadas, A. Fernández-Torres, M.A. Malmierca, L. González, W. Chassé, K. Saalwächter, Inhomogeneities and chain dynamics in diene rubbers vulcanized with different cure systems, *Macromolecules* 43 (2010) 4210–4222.
- [19] J.L. Valentín, I. Mora-Barrantes, J. Carretero-González, M.A. López-Manchado, P. Sotta, D.R. Long, K. Saalwächter, Novel experimental approach to evaluate Filler-Elastomer interactions, *Macromolecules* 43 (2010) 334–346.
- [20] V.M. Litvinov, EPDM/PP thermoplastic vulcanizates as studied by proton NMR relaxation: phase composition, molecular mobility, network structure in the rubbery phase, and network heterogeneity, *Macromolecules* 39 (2006) 8727–8741.
- [21] K. Saalwächter, Proton multiple-quantum NMR for the study of chain dynamics and structural constraints in polymeric soft materials, *Prog. Nucl. Magn. Reson. Spectrosc.* 51 (2007) 1–35.
- [22] P.T. Callaghan, E.T. Samulski, Molecular ordering and the direct measurement of weak proton-proton dipolar interactions in a rubber network, *Macromolecules* 30 (1997) 113–122.
- [23] E. Fischer, F. Grinberg, R. Kimmich, S. Hafner, Characterization of polymer networks using the dipolar correlation effect on the stimulated echo and field-cycling nuclear-magnetic resonance relaxometry, *J. Chem. Phys.* 109 (1998) 846–854.
- [24] D.E. Demco, S. Hafner, C. Fülber, R. Graf, H.W. Spiess, Two-dimensional proton magnetization-exchange NMR spectroscopy in cross-linked elastomers, *J. Chem. Phys.* 105 (1996) 11285–11296.
- [25] M.A. Mansilla, A. Ghilarducchi, H. Salva, A.J. Marzocca, Alpha (Vitrea) transition in vulcanized natural rubber/styrene butadiene rubber blends prepared by mechanical and solution mixing, *Solid State Phenom.* 184 (2012) 405–410.
- [26] W. Salgueiro, A. Somoza, A.J. Marzocca, I. Torriani, M.A. Mansilla, A SAXS and swelling study of cured natural rubber/styrene-butadiene rubber blends, *J. Polym. Sci. Polym. Phys.* 47 (2009) 2320–2327.
- [27] W. Salgueiro, A. Somoza, L. Silva, G. Consolati, F. Quasso, M.A. Mansilla, A.J. Marzocca, Temperature dependence on free volumen in cured natural rubber and styrene-butadiene rubber blends, *Phys. Rev. E* 83 (051805) (2011) 1–8.
- [28] M.A. Mansilla, L. Silva, W. Salgueiro, A.J. Marzocca, A. Somoza, A study about the structure of vulcanized natural rubber/styrene butadiene rubber blends and the glass transition behavior, *J. Appl. Polym. Sci.* 125 (2012) 992–999.
- [29] A.J. Marzocca, W. Salgueiro, A. Somoza, in: P.M. Visakh, S. Thomas, A.K. Chandra, A.P. Mathew (Eds.), *Advances in Elastomers II*, Springer, 2013, pp. 399–426.
- [30] M.A. Mansilla, A.J. Marzocca, C. Macchi, A. Somoza, Influence of vulcanization temperature on the cure kinetics and on the microstructural properties in natural rubber/styrene-butadiene rubber blends prepared by solution mixing, *Eur. Polym. J.* 65 (2015) 50–61.
- [31] W. Chassé, J.L. Valentín, G.D. Genesky, C. Cohen, K. Saalwächter, Precise dipolar coupling distribution analysis in proton multiple quantum NMR of elastomers, *J. Chem. Phys.* 134 (044907) (2011) 1–10.

- [32] S. Toki, C. Burger, B.S. Hsiao, S. Amnuaypornsi, J. Sakdapipanich, Y. Tanaka, Multi-scaled microstructures in natural rubber characterized by synchrotron X-ray scattering and optical microscopy, *J. Polym. Sci., Part B: Polym. Phys.* 46 (2008) 2456–2464.
- [33] G.N. Avgeropoulos, F.C. Weissert, P.H. Biddison, G.G.A. Böhm, Heterogeneous blends of polymers. Rheology and morphology, *Rubber Chem. Technol.* 49 (1976) 93–104.
- [34] M.M. Coleman, C.J. Serman, D.E. Bhagwagar, P.C. Painter, A practical guide to polymer miscibility, *Polymer* 31 (1990) 1187–1203.
- [35] D.J. David, T.F. Sincok, Estimation of miscibility of polymer blends using the solubility parameter concept, *Polymer* 33 (1992) 4505–4514.
- [36] K.K. Chee, Temperature dependence of solubility parameters of polymers, *Malay. J. Chem.* 7 (2005) 057–061.
- [37] J. Brandrup, E.H. Immergut, E.A. Grulke, *Polymer Handbook*, Wiley-Interscience, 2003.
- [38] C.C. Wang, Y. Gao, A.P. Shreve, C. Zhong, L. Wang, K. Mudalige, H.L. Wang, M. Cotlet, Thermochromic of a poly(phenylene vinylene): untangling the roles of polymer aggregate and chain conformation, *J. Phys. Chem. B* 113 (2009) 16110–16117.
- [39] J.M. Chenal, L. Chazeau, L. Guy, Y. Bomal, C. Gauthier, Molecular weight between physical entanglements in natural rubber: a critical parameter during strain-induced crystallization, *Polymer* 48 (2007) 1042–1046.
- [40] S. Ceveny, A.J. Marzocca, Analysis of variation of molecular parameters of natural rubber during vulcanization in conformational tube model, *J. Appl. Polym. Sci.* 66 (1997) 1085–1092.
- [41] A.J. Marzocca, S. Goyanes, An analysis of the influence of the accelerator/sulfur ratio in the cure reaction and the uniaxial stress-strain behavior of SBR, *J. Appl. Polym. Sci.* 91 (2004) 2601–2609.
- [42] M.A. Mansilla, *Influencia de la microestructura en las propiedades mecánicas y térmicas de mezclas de caucho natural y caucho estireno butadieno* PhD Thesis, University of Buenos Aires, Argentina, 2012.
- [43] K. Suchiva, T. Kowitteerawut, L. Srichantamit, Structure properties of purified natural rubber, *J. Appl. Polym. Sci.* 78 (2000) 1495–1504.
- [44] M. Mansilla, A.J. Marzocca, About the cure kinetics in natural rubber/styrene Butadiene rubber blends at 433 K, *Physica B* 407 (2012) 3271–3273.
- [45] J.L. Valentin, D. Lopez, R. Hernandez, C. Mijangos, K. Saalwachter, Structure of poly(vinyl alcohol) cryo-hydrogels as studied by proton low-field NMR spectroscopy, *Macromolecules* 42 (2009) 263–272.
- [46] M.A. Malmierca, A. González-Jiménez, I. Mora-Barrantes, P. Posadas, A. Rodríguez, L. Ibarra, A. Nogales, K. Saalwächter, J.L. Valentin, Characterization of network structure and chain dynamics of elastomeric ionomers by means of <sup>1</sup>H Low-Field NMR, *Macromolecules* 47 (2014) 5655–5667.