Study on Rubber Blends: Influence of Epoxidation on Phase Morphology and Interphase

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ABSTRACT: A discussion about phase morphology and interphase is presented taking into account the influence of the epoxidation on NR/SBR blends. Unfilled blends were examined in a broad composition range to investigate the morphology by TEM (transmission electron microscopy) and to estimate the volume fraction of the interphase by means of DMA (dynamic mechanical analysis). It was observed that the domain sizes and the volume fraction of the interphase depend on the difference in polarity of rubbers caused by the presence of the epoxidized phase and the polarizability caused by the difference on the vinyl content. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 2377–2384, 2007

Key words: blends; compatibility; interphase; phase morphology; epoxidation; elastomers

INTRODUCTION

Blending of two or more polymers has been used to obtain compounds with desirable properties combinations as an alternative route to the synthesis of new polymers. Chemical modification of polymeric materials is widely used to produce new materials that cannot be easily prepared by conventional polymerization reaction. Among the numerous possibilities for the chemical modification of polydienes, epoxidation is a simple and efficient method of introducing a reactive group into the polymer chain, leading to new and useful properties.[1,2] The reaction can be performed by means of the action of peroxides in the presence of a catalyst[3] or peracids, which could be added to the polymer solution[4,5] and regenerated *in situ*.[6–9] In previous works, the epoxidation reaction strategy was described for solution SBR [6] and BR-grades[10] with different microstructure.

The chemical structure is crucial for understanding and tailoring properties relevant for practical applications. It is known that the presence of the vinyl groups[11] and the epoxide groups[12] has a very significant influence on the phase morphology and final properties of the blends.

Different techniques have been used for investigation of phase morphology, such as dynamic mechanical measurements,[13–16] thermal analysis,[16,17] electron microscopy,[18–23] and inverse gas chromatography.[24,25]

The objective of this article is to investigate the phase morphology and interphase as a function of polymer constitution and microstructure.

THEORETICAL BACKGROUND

Compatibility is a more general term with a wider diversity of meanings than miscibility, which is consistently defined by thermodynamic criteria.[17,18,26]

The necessary condition for any blend system to be miscible is derived from the free energy of mixing as a function of composition.[27,28,29] The Gibbs and Helmholtz free mixing energy ΔG is one important criteria for miscibility considering the thermodynamic equilibrium.[30,31] A miscible system is achieved for a known temperature when the difference of the free mixing enthalpy is negative.

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \qquad (1)$$

The mixing enthalpy decreases with increasing temperature. When the mixing enthalpy is small enough, the contribution of the entropy of mixing is dominating and leads to a negative value of ΔG_{mix}, which means that the miscibility is achieved.

Some factors controlling the phase morphology are the viscosity of the components, the thermodynamic interactions between the blend constituents and the share rate employed during mixing. Thus, the interfa-

cial tension controls the morphology development. For dispersed phase morphology, the resulting domain sizes can be described as follows:[32]

$$\overline{d} = c(\gamma/\eta_m) \times f(\eta_m/\eta_d)dV_x/d_y \qquad (2)$$

where γ is the interfacial tension; η_m, viscosity of the matrix; η_m, viscosity of the dispersal phase; and dV_x/d_y is the share rate.

The interfacial tension arises mainly from the disparity between the polarities of the two phases. It is already known for BR with a higher amount of vinyl groups that the solubility parameter decreases increasing the vinyl content as has been shown in previous work.[25] The introduction of vinyl groups into the chains leads to a decrease in the polarity of the polymer conducting to values of solubility parameter (δ_2) similar to the natural rubber (i.e., BR 95 wt % of vinyl groups $\delta_2 = 8.08$ and NR $\delta_2 = 8.11$). Taking into consideration the differences between the solubility parameters of the two polymers the miscibility will be better if the $\Delta\delta$ tends to zero.[33,34]

If the interaction between the components of the system deteriorates and the difference between the solubility parameters of the two rubbers ($\Delta\delta$) rises, the interfacial tension increases. Even in the case of stronger polymer incompatibility a finite interphase is built in any case by entropic gain and enthalpic contribution.[35,36] Whereas the interdiffusion coefficient is limited by the critical interaction parameter for phase separation,[37,38] the equilibrium thickness of the interphase a_{IPH} is shown to be inversely proportional to the solubility parameter difference:

$$a_{IPH} \approx \frac{1}{\sqrt{\chi}} \approx \frac{1}{|\delta_1 - \delta_2|} \qquad (3)$$

The phase bonding nature performed by the interphase has a great influence on the physical properties of the rubber blends, as it has been shown on a blend system of EPDM and polybutadiene (BR)[39] and on blends of cis-BR.[40]

Increasing the degree of compatibility, the volume fraction ϕ_{IPH} and the thickness of the interphase increase; however, the interphase thickness of variable blend increases inversely proportional to $\Delta\delta$.[41,42]

Estimation of the interphase

For an estimation of the interphase volume fraction in rubber blends from dynamical mechanical data, it is first necessary to analyze the impact of blend ratio on the $G''(T)$ in the glass transition region of unfilled blend systems. The experimentally loss modulus of an unfilled blend establish the sum of relaxation of all phases presented in blend. The phase contribution to the overall loss modulus can be separated by means of

a fitting procedure that takes into account the separation of the temperature-dependent loss modulus curve into the contributions of the different phases using a parameter-modified spline-fit function of the single polymers. The spline parameters considered here are the amplitude, the broadness, and the temperature shift of the damping maximum. The parameters of both splines are modified for the best fit of their sum to the experimental test curves. The deviations of the obtained fit indicate a third contribution to the blend loss modulus, i.e. the signal of the interphase, which reaches its maximum in the region between the glass temperatures of the blend constituents.

EXPERIMENTAL ASPECTS

Materials

In this study were used different commercially available rubbers without further purification. The chemical characteristics of these rubbers are shown in Table I. The amount of vinyl and styrene units in the solution styrene butadiene rubber is displayed in brackets [i.e., SBR with 25 wt % vinyl and 25 wt % styrene is solution SBR (25 : 25)].

Epoxidation

Epoxidation was carried out in toluene solution (7%, w/v) using as epoxidation agent hydrogen peroxide. The performic acid, which will react with the double bonds, was generated in situ through the reaction between hydrogen peroxide and formic acid. The chemistry of the epoxidation reaction has been discussed in previous work.[6]

The epoxidized rubber was analyzed for its epoxide content using ^{1}H NMR spectroscopy (NMR device Varian XL-20). The secondary reactions were controlled by the Fourier transform infrared spectroscopy (FTIR) in an FTIR Mattson: films were cast from THF on NaCl plates. The glass transition temperature anal-

TABLE I
Matrix Rubbers Used

Rubbers	Trade name	Microstructure (wt %)	T_g (°C) *
NR	SMR CV50	cis-1,4-Isoprene : 100	−62
SBR (50 : 25)	Buna VSL 5025-0	Vinyl : 50, Styrene : 25	−18
SBR (25 : 25)	Buna VSL 2525-0	Vinyl : 25, Styrene : 25	−44
SBR (8 : 25)	Buna VSL 25-0	Vinyl : 8, Styrene : 25	−63
		Epoxidation grad (mol %)	
ENR	ENR50	50	−17
EpSBR**	Buna VSL 2525	30	−28

* Data from DSC measurements.
**Epoxidized in laboratory.

ysis was carried out using DSC polymer laboratory thermal equipment at a heating rate of 10°C/min.

The epoxidation degree used in this work was 30 mol %. Until this value of epoxidation, it was shown that there is the reaction, mainly of the *cis*- and *trans*-1,4 butadiene units and the vinyl units do not react, as presented in the literature.[6]

Preparation of blends

The blends were mixed for 16 min using an internal mixer (Thermo Haake PolyLab System) equipped with a 50-mL mixing chamber at a temperature of 60°C, with a rotor speed of 50 rpm. The vulcanization system was S/CBS (1.6/2.5 phr). Vulcanization of all compounds was performed at 160°C in a press machine (J. Wickert and Söhne), using a slab with 2 mm × 8 cm × 18 cm. The vulcanization time was chosen in view of an almost complete crosslinking procedure up to 90% of the maximum torque (t_{90}) found in vulcameter measurements.

Swelling

For the determination of the swelling degree it was used solvents with different solubility parameter. A range of solubility parameter was used by chosen the solvents considering its solubility parameter, i.e., hexane, toluene, xylene, acetone, etc. The swelling equilibrium was reached after 4 days. The weight of initial sample was measured before immersing in the solvent. The weight of swollen sample was determined after removing the solvent from the surface of the sample by blotting with filter paper.

Morphology investigations

Morphological analyses were performed on ultrathin cuts (70 nm) obtained on Ultra Cut FC4 (Reichert-Jung) microtome. The micrographs were taken using the electron spectroscopy imaging–transmission electron microscopy (ESI–TEM) technique on an EM 902 (Zeiss) machine. By making use of energy filters the inelastically scattered electrons were removed. The micrographs provided by the elastically scattered electrons only show a good contrast based on the differences in carbon densities in the phases under consideration.

Dynamical mechanical analysis

Test specimens were employed for temperature sweeps in the glass transition of the rubber. The measurements were performed in torsion by dynamic analyzer (ARES 3A5 Rheometric Scientific), the frequency used was 1 Hz, the strain 1% and the temperature was varied with a heating rate of 1°C/min.

RESULTS AND DISCUSSION

Epoxidation

The epoxidation reaction of the butadiene units could be monitored using ^{1}H NMR spectroscopy, through the disappearance of the double bonds ($\sim$ 5.4 ppm) and the appearance of the signal of epoxide group ($\sim$ 2.4–2.7 ppm), as can be seen in Figure 1.

In the ^{1}H NMR spectrum of EpSBR (30%), two new peaks appear at δ = 2.45 and 2.70 ppm, which correspond to the methine (in trans and cis position) resonance of the epoxide groups. The degree of epoxidation, X, has been calculated considering the normalized area of the peaks using eq. (4):

$$X\% = \left(\frac{A_{\mathrm{epox}} - A_{\mathrm{Hst}}}{(A_{\mathrm{epox}} - A_{\mathrm{Hst}}) + A_{1,4} + A_{1,2}} \right) \times 100 \quad (4)$$

where A_{epox} is the normalized proton area intensities for the epoxidized peaks at δ = 2.45 and 2.70 ppm, A_{Hst} the normalized area intensities for methylene bonded to the styrene ring, $A_{1,4}$ and $A_{1,2}$ the normalized area for the unsaturated 1,4-butadiene peak at δ = 5.25 and unsaturated 1,2-butadiene peak at δ = 4.9 ppm. The normalized proton intensity is defined as the integrated area of the peak divided by the number of hydrogen associated with that isomeric structure.

Phase morphology

The investigation of the phase morphology of rubbers is made through the ESI–TEM.

Considering the NR/SBR blends [Fig. 2(a–c)], it was observed that increasing the content of vinyl groups the domains of NR phase become smaller. From the images analysis, it was estimated the average diameter of the domain size of NR phase ($\bar{d}$) that decreases from 447 nm for 20NR/80SBR (8 : 25), 382 nm for 20NR/80SBR (25 : 25) to 355 nm for 20NR/80SBR (50 : 25).
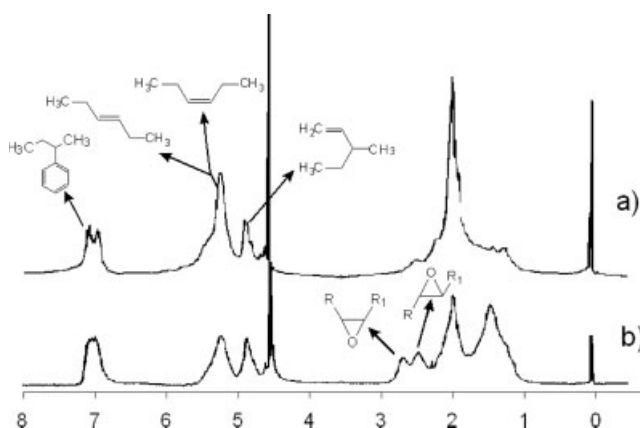

Figure 1 ^{1}H NMR spectra of (a) SBR (25 : 25) and (b) EpSBR (30 mol % epoxidised SBR (25 : 25)).
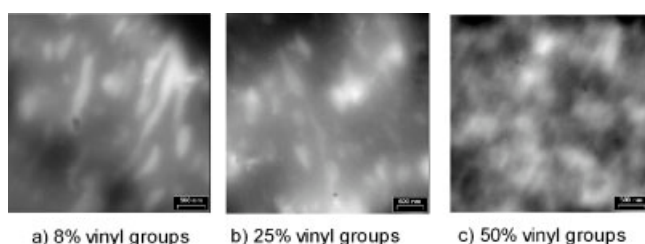
Figure 2 TEM micrographs of 20NR/80SBR blend for different vinyl content. The bright domains represent the NR phase and the dark matrix is SBR phase.

This demonstrates an increase of the compatibility due to the interaction of the vinyl with the isoprene units. This is based on the polarizability of these groups. Basically the interaction energy for nonpolar molecules is proportional to the product of the polarizability,[43] which gives an account of the interaction parameter χ, determined by the magnitude of the interaction energy and it is an approach for the calculation of difference of the solubility parameter. Based on the solubility parameters for the polymers it has been shown that the exchange enthalpy between isoprene and butadiene becomes more endothermic (reduced miscibility) as the concentration of 1,4-units in the latter increases.[44]

Considering the NR/SBR blend it was noticed that as the concentration of vinyl units in SBR increases, there is a large increase in miscibility with NR that suggests a near equivalence in polarizability between the respective vinyl and isoprene units.

Influence of polarity on compatibility

The polarity is a determinant factor in the compatibility of rubber blends, $\Delta\delta$ and interfacial tension. With increase in the differences in the polarities by introducing epoxide groups into the chain the compatibility degree of rubbers decreases. The general trend of compatibility enhancement by decreasing of the solubility parameter can be observed analyzing the TEM micrographs presented in Figure 3.

Comparing the TEM micrographs [Fig. 3(a,c)] of the 20NR/80EpSBR and 20NR/80SBR blends, respectively, it was noticed that for the blend 20NR/80EpSBR the domains are large with a broad distribution due to presence of the epoxide groups. However, for 20NR/80SBR blend there is a narrow distribution
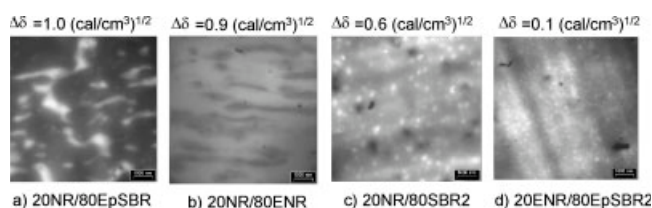

Figure 3 TEM micrographs of various blend systems.

of the domains, this indicates a more compatible blend and this is in good agreement with the values of the differences of solubility parameter obtained by swelling measurements. It is know that the higher the difference in the solubility parameter the higher the interfacial tension and the domain size leading to a decrease of the compatibility of the rubber blends.

Considering the four systems presented in Figure 3(a–d), it is observed that the difference between the polarities of both rubbers has a great influence on domains size. Large domains can be noticed for the system presented in Figure 3(a) with a formulation 20NR/80EpSBR. Considering the nonpolar system 20SBR/80NR [Fig. 3(c)], the bright domains become smaller. When both phases are polar as can be seen in Figure 3(d) (20ENR/80EpSBR) there is no big difference in polarity between the phases and due to this there is a better compatibility showed through the dispersion of the domains. The introduction of the epoxide group into the rubber chains leads to a better interaction of the chains influencing the size of the domains and favoring the dispersion of the epoxidized NR into the epoxidized SBR phase.

The influence of the difference in the solubility parameter on the compatibility of rubber blends can be clear seen in Figure 3. As the difference in solubility parameter decreases there is an increase in the compatibility of the rubber blends, what can be seen trough the decreasing in the domain size of the TEM pictures in Figure 3(a–d). Even a small difference in the solubility parameter, as showed to the systems presented in Figure 3(a) (20NR/80EpSBR) to Figure 3(b) (20NR/80ENR) causes pronounced changes in the size of the domains leading to changes in the blends compatibilities.

The introduction of functional groups into the main-chain and the microstructure of polydienes rubbers invariably results in some changes in the glass transition temperature (T_g) for those polymers.

Figure 4 shows the influence of the epoxidation degree on the T_g of three different types of SBR, where the vinyl units content was varied and the styrene content was kept constant (SBR 50 : 25 contains 50 wt % of
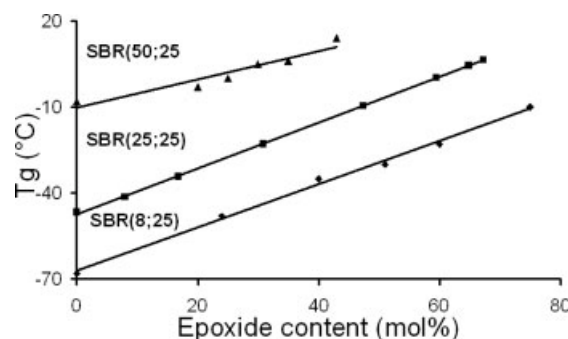

Figure 4 Influence of the epoxide content in the main chain of the rubber on the glass transition temperature.
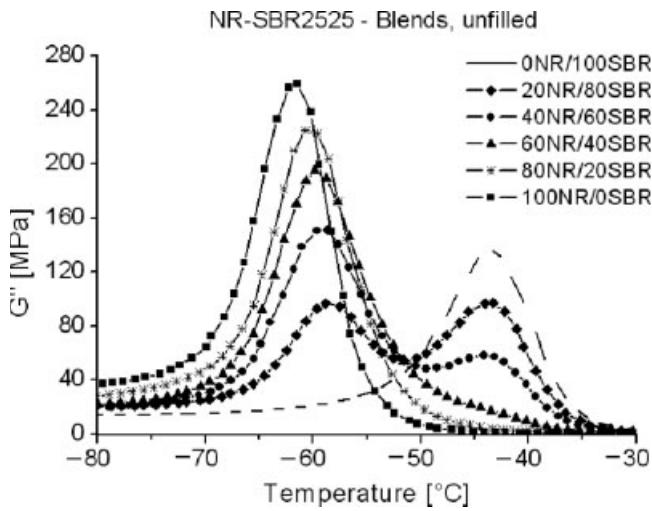
Figure 5 Loss modulus vs. temperature for NR/SBR blend 25 wt % vinyl groups.

vinyl units and 25 wt % of styrene units, SBR 25 : 25 contains 25 wt % of vinyl units and 25 wt % of styrene units and SBR 8 : 25 contains 8 wt % of vinyl units and 25 wt % of styrene units).

It can be observed a linear relationship between the degree of main-chain rubber epoxidation and the increase in T_g (Fig. 4). This behavior occurs because incorporating epoxide groups into SBR phase, leads to a considerable change in the phase structure.[45] This behavior can be explained due to the reduced rotational freedom of modified repeating units and a very pronounced change in the chain polarity, which causes a higher interaction between the rubber chains leading to an increase in the T_g values.

Dynamic mechanical investigations

The NR/SBR blends, where the SBR phase presents 25 or 50 wt % vinyl groups, were analyzed by means of dynamic mechanical measurements.
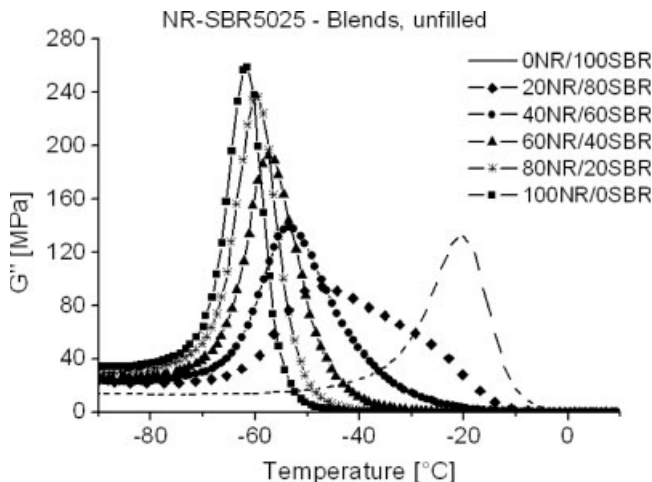

Figure 6 Loss modulus vs. temperature for NR/SBR blend 50 wt % vinyl groups.

Figure 5 can be discussed as follow: considering the pure rubbers (100NR/0SBR and 0NR/100SBR) it can be seen that the loss modulus shows one single peak. The maximum of the loss modulus is considered as the glass transition temperature. Varying the temperature there is an increase of G'' until a maximum (T_g) is reached and after that there is a decrease until zero. Taking into account the blends, a similar behavior is observed until 80NR/20SBR blend. Increasing the SBR content (from 40 to 80 phr) a new peak arises around $-45°C$ due to the SBR phase. The broadness of the peaks of the NR (about $-60°C$) and SBR (about $-43°C$) phases increases and the height of the peaks decreases as the content of the NR decreases indicating a formation of an interphase between the two rubbers.

Figure 6 illustrates a similar behavior as discussed in Figure 5. The maximum of loss modulus is shifted, the broadness and the height of the peaks are changed as the blend ratio is varied.

In the case of NR/SBR 25 wt % vinyl groups blends (Fig. 5), the maximum loss modulus for the blend ratio 20NR/80SBR has the same height for both phases (95 MPa), but for a higher content of vinyl groups NR/SBR 50 wt % vinyl groups blends, for the same blend ratio 20NR/80SBR (Fig. 6) it is observed a peak with a shoulder that can be related to the SBR phase.

Figure 7 shows the dynamical mechanical analysis for a blend between two epoxidized rubbers (ENR/EpSBR).

The broadening of the transition region can be estimated by evaluation of the half width of the peaks. Analyzing the loss modulus curves presented in Figure 7 it is possible to see the following: just one maximum for loss modulus of the blends, the maximum of G'' is shifted to higher temperatures as the content of ENR increases. Taking into account the half width of the peaks it is possible to see that the broadness of the peaks starts at a minimum value for the pure rubbers, increases until reach a maximum value for ENR/
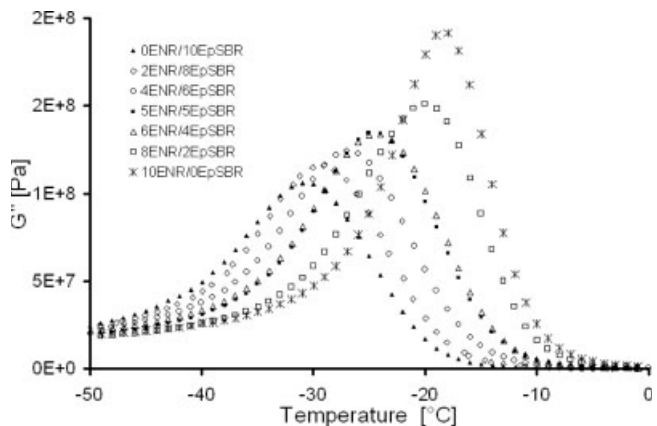

Figure 7 Loss modulus vs. temperature for ENR/EpSBR blends varying the blend ratio.
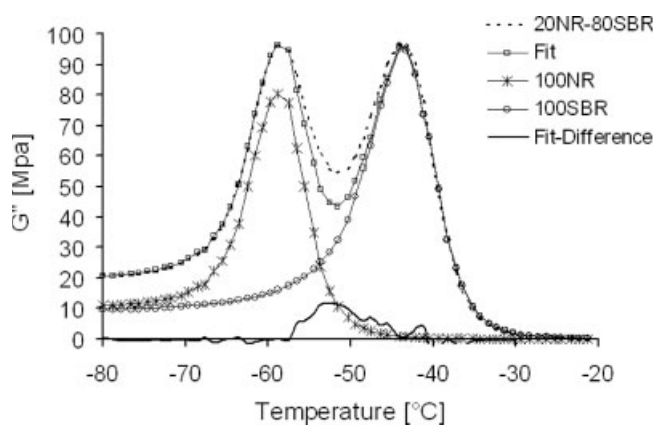
Figure 8 Fitting procedure for 20NR/80 SBR blend 25 wt % vinyl groups.

Figure 10 Maximum values of interphase signal vs. SBR-volume fraction for NR/SBR blends.

EpSBR (50 : 50 blend ratio) and after that decrease. These results indicate the formation of an interphase in the blends.

Interphase

To evaluate the interphase it has been considered the systems presented in Figures 10 and 11. According to the literature,[13] the experimentally measured loss modulus of the blend components, constitutes the sum of the relaxations of all phases present in the blend. Further on, the fitting procedure[13] was applied to the 20NR/80SBR 25 wt % of vinyl groups (Fig. 8) and the 20NR/80SBR 50 wt % of vinyl groups (Fig. 9) for the evaluation of the interphase taking into account the three spline parameters: the amplitude, the temperature shift and the broadness of the damping maxima.

Analyzing Figure 8, it was taken into consideration the damping signal of the two pure rubbers. The fitting procedure used to describe the loss modulus as a function of the temperature has been done modifying
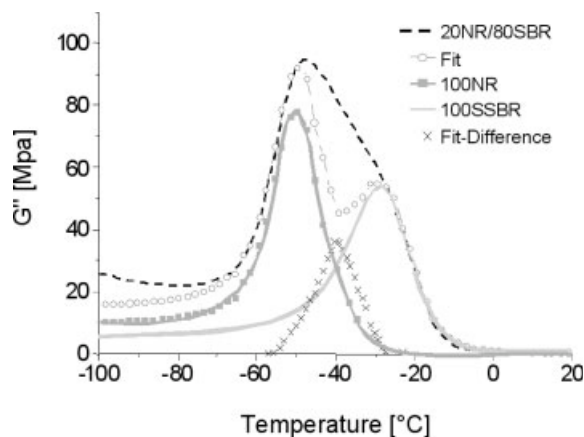
the parameters of the two components of the blend for the best fit to the experimental curves. The difference of the blends signal and the two phase fit gives the signal of the interphase.

Estimation of the interphase of 20NR/80SBR blend 50 wt % of vinyl groups (Fig. 9) has been done in the same manner as discussed for Figure 8. As can be observed the interphase signal shown in Figure 9 is higher than that in Figure 8 indicating that there is a better interaction between the two rubbers. To evaluate the amount of interphase in NR/SBR blends with different vinyl content at different ratios, the interphase volume fraction ϕ_i as a function of volume fraction ϕ_i SBR was considered (Fig. 10).

Figure 10 shows that the volume fraction of the interphase ϕ_i starts from zero, going trough a maximum value and decreases to zero again as the volume fraction ϕ_i of SBR increases.

It can be seen that in the case of NR/SBR (50 : 25) blend, the fitting curve has a symmetrical aspect, the maximum value of the interphase signal is achieved at $\phi_{SBR} \approx 0.5$ while at the NR/SBR (25 : 25) blend this
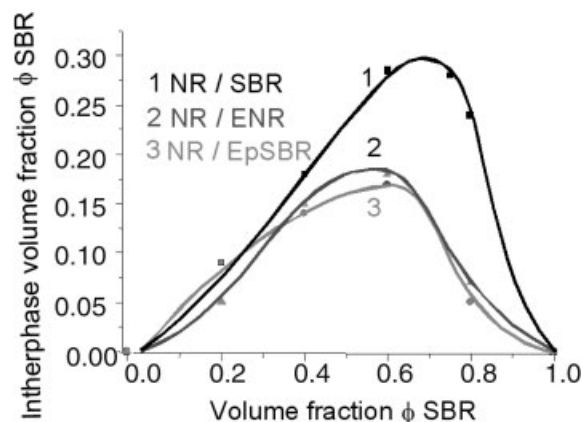

Figure 9 Fitting procedure for 20NR/80 SBR blend 50 wt % vinyl groups.

Figure 11 Interphase signal vs. SBR-volume fraction for blends of NR with different rubbers.
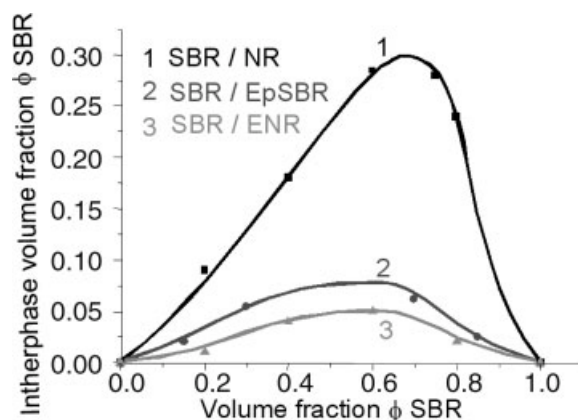
Figure 12 Interphase signal vs. SBR-volume fraction for blends of SBR with different rubbers.

maximum is shifted to the right side, has lower amplitude and occurs at $\phi_{SBR} \approx 0.75$. This behavior is attributed to the changing on the conformation of the vinyl groups of the SBR that interact with the isoprene units of the NR. The interaction between the isoprene and vinyl units occurs due the very similar structure and polarizabity of these units. That means as the vinyl content increases there is a better interaction between vinyl groups of the SBR and the isoprene units of NR leading to a more compatible blend.

It is already known[24,25] that vinyl groups exert a higher endothermic contribution than the styrene groups, which leads to a decreasing of the solubility parameter. By increasing the amount of vinyl groups the compatibility between SBR with NR is improved because the $\Delta\delta = |\delta_1 - \delta_2|$ decreases.[35]

As can be seen in Figure 10, the maximum of interphase volume fraction of NR/SBR (50 : 25) blend is higher compare to NR/SBR (25 : 25) blend. The presence of vinyl groups determines an increase of the interphase volume fraction in blends of SBR and NR.

Studies of interphase have been done for blends of NR (epoxidized and nonepoxidized) with SBR (epoxidized and nonepoxidized) to predict the compatibility degree of these rubbers.

Figures 11 and 12 show an estimation of the amount of interphase of NR blends with different rubbers (Fig. 11) and SBR blends with different rubbers (Fig. 12).

The compatibility of blends is related to the polarity of rubbers.

Figure 11 displays a higher value of the interphase volume fraction that point a better compatibility for NR/SBR blends compare with NR/ENR and NR/EpSBR blends. For the blend NR/SBR the maximum of the volume fraction of the interphase is reached at a value about 0.3, for NR/ENR and NR/EpSBR blends the maximum is near the same value, ~ 0.17. This gives an indication of the compatibility of those blends. In Figure 12 can be seen that the maximum of the volume fraction of the interphase varies from 0.3

for SBR/NR blend, 0.07 for SBR/EpSBR blend to 0.05 respectively, for SBR/ENR blend.

This difference on value of the maximum of the volume fraction of the interphase occurs because of the interaction between the rubber chains owing to the polarity of epoxidized rubber. For nonpolar rubbers (SBR/NR blend) the interaction between the chains is more favorable compare to a polar/nonpolar system. This can be explained considering the difference in solubility parameter of the rubbers, as discussed before (Fig. 3).

CONCLUSIONS

The results presented in this work show that the presence of vinyl and epoxide groups has a great influence on phase morphology. Increasing the amount of vinyl groups of SBR phase, a better compatibility in blend with NR is achieved because the interaction between the vinyl and isoprene units is preferable. Taking into account the presence of the epoxidized rubber it was demonstrated that the compatibility and the interphase of the blend depend on phase polarity. Systems with high difference in solubility parameter showed a small value of the interphase volume fraction.

The compatibility increases in the following sequence: NR/EpSBR < NR/ENR < NR/SBR < ENR/EpSBR.

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