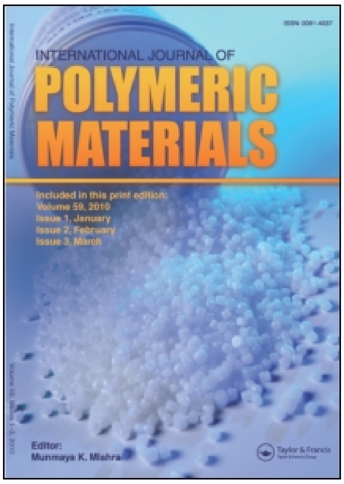

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Mechanical Properties of the Composite Asphalt-Styrene-Butadiene Copolymer at High Degree of Modification

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The morphology and elastic moduli of the composite styrene-butádiene copolymer-asphalt (SBR-A) were obtained at different degrees of modification from 0 to 40% by weight. Even when the 40% of rubber is far above the usual amount of rubber used for asphalt modification, the purpose of this work is to study the composite morphology at high degree of modification and to obtain a prediction for the elastic response of the material.

The morphology of the samples was obtained by scanning and transmission electron microscopy. The mechanical properties of the samples obtained at different chemical compositions were determined at three different strain rates: 5, 50 and 500 mm/min.

For low SBR concentrations, the elastic modulus of the as prepared materials was well modeled by using the Kerner's model, however for concentrations larger than around 20%, the mechanical response of the material is higher than the predicted by this model. By introducing a percolation model that takes into account the connectivity between the discrete domains of the material, it was possible to obtain a good agreement with the experimental data for SBR concentrations up to 40%.

Keywords: Asphalt; styrene-butadiene copolymers; mechanical properties

INTRODUCTION

Composites are a relatively new kind of engineering materials where the polymer precursors are such that they segregate themselves forming small domain in a nano-scale range of one of the components [1–7]. In this way it is possible to obtain a material which combines synergetically the desired properties of the precursors in a single material. For this reason the mixing of polymers which are practically inmiscibles has become very important lately. Several requirements have to be fulfilled in order to have a material with good performance; among them we can mention the adhesion between the phases and the right size of the discrete phase. These, together with the type of the polymers constituents, are the most important requirements to obtain a material with good performance.

Asphalt is an important low-cost thermo-plasic material which is widely used for construction. Asphalt based materials are used in a variety of applications like: roads binders, adhesives, sealants, and water-proof coatings among others. Asphalt, is a building and engineering material with poor mechanical properties, due to this asphalt is usually reinforced with rubber-like materials in order to improve its mechanical properties. This reinforcement is achieved by adding to the asphalt, small amounts of rubbery polymers [8–13]. One of the most popular material used for asphalt modification is styrene-butadiene copolymers; in this case, the incompatibility among polystyrene and poly-butadiene molecules, produces an elastic network which is formed into the asphalt, resulting in a composite with excellent elastic recovery and better mechanical properties.

For this reason, a lot of work has been developed [8–14] in the study of copolymer modified asphalt trying to predict mechanical and physical properties based on the composition and the morphological structure of the composite.

Accordingly, the objective of this work is to model the mechanical behavior of the material in order to predict its behavior and to obtain a correlation between the material morphology of the discrete phase and its mechanical properties.

MECHANICAL MODELS

The SBR-modifyed asphalt shows a phase inversion when the rubber concentration exceed the phase inversion concentration C_{pi} which in this case is around 9 or 10%; this phase inversion modifies drastically the morphology of the material: For concentrations lower than the phase inversion concentration C_{pi} the polymer forms the discrete phase, and for concentrations larger than C_{pi} the asphalt becomes the discrete phase. At certain value of the SBR concentration, (larger than, but near to C_{pi}), the SBR forms a network that connects all the material; this fact produces an increment in the elastic response of the material.

There exist several mathematical models depending on the material's morphology, which can used to predict the mechanical behavior of the composite. The models we are going to use are Kerner's [1–4] and Percolation's [7] models.

Kerner Model

This is a self-consistent approximation model, where the composite structure is modeled as a continuous medium where spherical dispersed particles with same elastic properties as one of the constituents are embedded; these particles are surrounded by shells with the same elastic properties as the other of the constituents, and finally they are in turn surrounded by another second shell with the elastic properties of the whole composite. This model is appropriated for concentrations smaller than the phase inversion threshold. The Kerner's model provides an expression for the shear modulus of the composite G_c given by:

$$\frac{G_c}{G_1} = \frac{\phi_1 G_1 + (\alpha + \phi_2) G_2}{(1 + \alpha\phi_2) G_1 + \alpha\phi_1 G_2} \tag{1}$$

where

$$\alpha = \frac{2(4 - 5\mu)}{(7 - 5\mu)} \tag{2}$$

being G_1, G_2, G_c the shear modulli of the both components and the composite, ϕ_1 and ϕ_2 the volume fraction of the components and μ is the Poisson ratio which for liquids and rubber like materials is 0.5 [9]. The relation between the shear modulus and the Young modulus E_c is through the relationship $E_c = 3G_c$.

Percolation Model

This model has successfully applied to systems which present the property of connectivity. The connectivity will depend on the relative concentration of the phases present in the system; at some critical concentration, the connectivity becomes extremely large, comparable to the size of the system. Above this critical percolation concentration v_c, the system is in a percolated state. The percolation models characterize a transition from a state of local connectivity to one in which the connections are extended indefinitely.

The percolation volume fraction Φ is defined as:

$$\Phi = \begin{cases} 0 & \text{for} \quad v_R < v_C \\ v_R\left(\dfrac{v_R - v_C}{1 - v_C}\right)^{\beta} & \text{for} \quad v_R \geqslant v_C \end{cases} \tag{3}$$

where v_R is the volume fraction of the rigid phase (in this case the PBd) and v_S is the volume fraction of the soft phase (asphalt). The elastic modulus of the composite in a percolated state can be obtained from a series-parallel model which takes into account the long distance connectivity:

$$\frac{G_C}{G_R} = \frac{(1 - \Phi^2 - \Phi v_S)G_S + \Phi v_S G_R}{(1 - \Phi - v_S)G_S + v_S G_R} \tag{4}$$

where G_C, G_R and G_S are the elastic modulli of the composite, the rigid phase and the soft phase respectively.

For concentrations below v_C, practically all the rigid portion is in the discrete phase, producing a modulus that is predicted by classical models like Kerner's or Takayanagy's models. Under these circumstances, the inclusions into the composite practically do not interact with each other. These models are not suitable in cases where nonlinear behavior of the material is present or in the case where these exist interactions between the inclusions.

For concentrations larger than v_C, the molecules of the rigid phase are forming links in such a way that all the material is connected; this situation corresponds to a percolation state in the composite. This connectivity increases substantially the mechanical modulus of the material. For this reason, a mechanical model that takes into account these percolation effects has to be used in order to explain the mechanical behavior of the composite.

EXPERIMENTAL

Composites were obtained by mixing commercial styrene-butadiene copolymer (Solprene S-411 of Industrias Negromex S.A. de C.V. México) with a non-oxidized commercial asphalt (Asphalt 6 of Petroleos Mexicanos S.A. México) at different proportions, from 0 to 40% by weight; the compositions are given in the Table I. The SBR copolymer molecule corresponds to a four-arms star-like nonlinear molecule of high molecular weight. The asphalt was a non-oxidized commercial material. The raw materials were characterized prior the fabrication of the composite, as reported elsewhere [14].

The SBR was previously grounded very finely in order to accelerate the mixing process and to reduce the shear rate of the mixer (Silverson high shear rate mixer); the mixing temperature was kept within the range from 180 to 200°C. The blending was considered complete when under visual inspection, the copolymer particles disappears and no separation of the phases was observed.

The morphology of all samples was determined by scanning electron microscope (SEM) (Carl Zeiss DSM 940A) operated at 20 kV

TABLE I

Sample	*SBR Composition (%)*	*Pressing Temp. (°C)*	*Pressing time (min)*
0	0	25	–
1	6	60	2
2	14	60	2
3	20	67	2
4	25	73	2
5	30	75	2
6	35	78	3
7	40	80	3
8	100	160	5

and in the second electron mode; and by the transmission electron microscope (TEM) (Carl Zeiss EM 910).

The samples for SEM were prepared [15] in the following way: they were cooled with liquid nitrogen and fractured; the fractured samples were placed in a sample holder glued with colloidal silver and stained with osmium tetraoxide vapors for 30 min. Once the sample were stained, they were coated with gold by sputtering.

On the other hand, the samples for TEM were prepared by dissolving the composites in toluene (Baker reactive grade) and evaporating the solvent to produce film with a thickness of around 0.1 microns. These films were stained with osmium tetraoxide vapors to have a good contrast on the micro-graphs for approximately 40 min) [14].

The samples for mechanical testing were prepared by pressing in a hot plate with temperature control to obtain a film of 3.0 mm thick. The compositions and conditions of pressing are given in Table I. The specimens were cut according to ASTM specifications D-638. The mechanical characterization was carried out in an Instron 1125 machine at strain rates of 5, 50 and 500 mm/min, and the corresponding elastic moduli were obtained at these strain rates. All these tests were performed at 25°C.

RESULTS AND DISCUSSION

Transmission Electron Microscopy

Figure 1 shows a SEM micro-graph corresponding to a sample with 6% of SBR; for this concentration the phase inversion has not yet happened and consequently the discrete phase corresponds to the rubber. For SEM micro-graphs the dark zones correspond to asphalt and the lighter to SBR. In this picture it is possible to observe the small quasispherical particles corresponding to rubber, on a soft surface of the asphalt; a fracture on the right hand side is also shown.

In Figure 2 it is possible to observe a SEM micro-graph of a 20% SBR composite. For this concentration the phase inversion has already taken place. The average size of the discrete phase is around 11 microns. The morphology of a sample with 35% of SBR is shown in

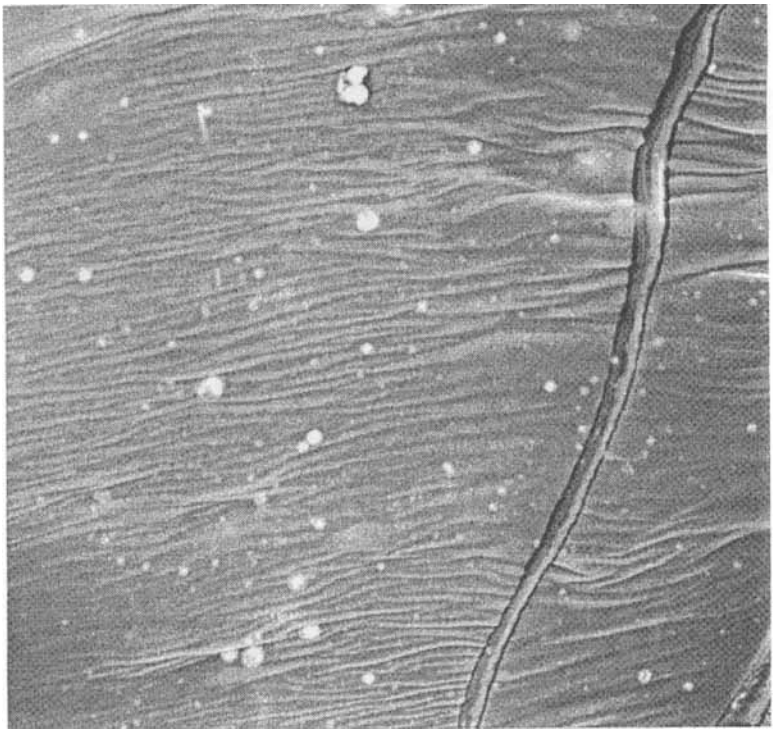

FIGURE 1 SEM micro-graph of a sample with 6% of SBR. The discrete phase (lighter zones) corresponds to the rubber. The amplification factor is 500 x.

Figure 3; this picture was taken at higher amplification in order to see more clearly the domains. We can observe that an increment in the SBR concentration does not change appreciably the morphology of the samples, once the phase inversion has taken place.

In Figure 4 the TEM micro-graph corresponds to the same sample as in Figure 1 i.e., 6% of SBR. Because the samples for TEM were stained with osmium without gold coating, the dark zones correspond, in this case, to the rubbery phase and the lighter to the asphalt.

In Figures 5 and 6 the morphology obtained by TEM of samples with 20 and 30% of SBR is shown; for these samples the rubber modification exceeds the phase inversion concentration and they show similar micro-structure as the corresponding obtained by SEM.

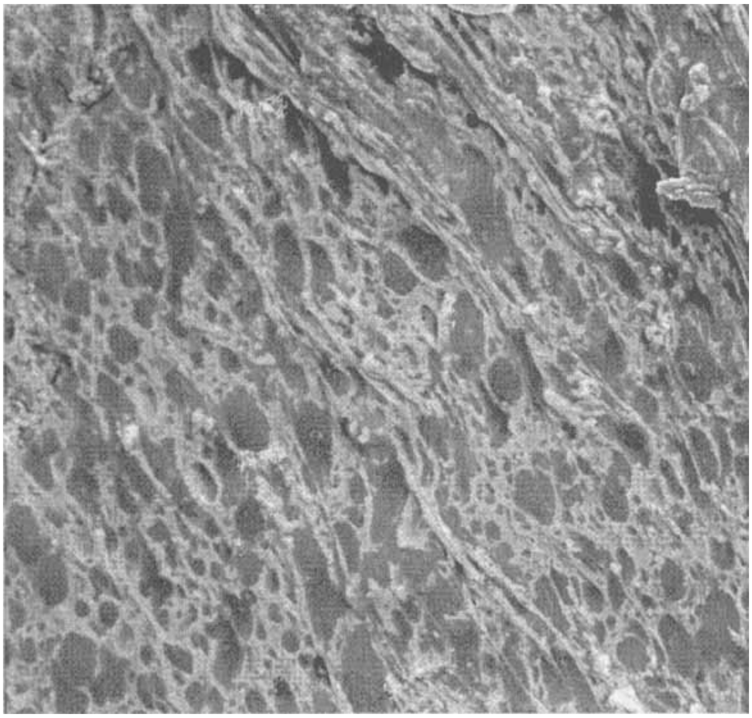

FIGURE 2 Same as Figure 1 but for a sample with 20% of SBR. Here the discrete phase (dark zones) corresponds to the asphalt. The amplification factor is 500 x.

Mechanical Properties

Mechanical tests were performed at three different strain rates: 5, 50 and 500 mm/min. for all compositions. In Figures 7–9 it is possible to see the stress-strain curves for different strain rates. Each of these figures shows an insert where the initial slope of the stress-strain curves are shown. With this information the Young moduli were obtained.

In Figure 10 we are plotting the Young modulus as a function of the volume fraction v_R of SBR for a strain rate of 5 mm/min. In this plot it is possible to see that exist 2 different regimes: for values of v_R lower than around 20%, the rate of change of the Young modulus as a function of the volume fraction has a value of 4.25 MPa, while for values of v_R higher than 20% the Young modulus increases faster

FIGURE 3 Same as Figure 2 but for a composite with 35% of SBR. The amplification factor here was of 2000 x.

respect to the former case, with a slope of 17.6 MPa. As was mentioned before, this effect is due to percolation. For concentrations lower than 20%, the Kerner model fits very well the experimental data, however fails for concentrations larger than this. The percolation model fits well the experimental data from around 10% up to 40%; the fitting produces: $2.01(v_R - 0.124)^{0.247}$, consequently $v_C = 12.4\%$; this expression for Φ is valid only for $v_R > v_C$.

It is interesting to mention that the complete set of data, from 0 to 40% of SBR in the composite, can be well fitted by using the analyti-

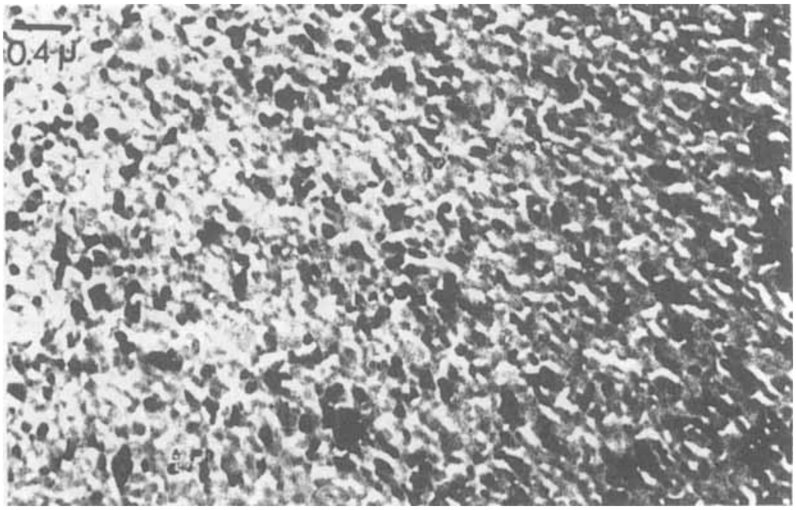

FIGURE 4 TEM micro-graph of the same sample used in Figure 1. The dark zones corres-ponds to rubbery phase while the lighter zones are the asphalt.

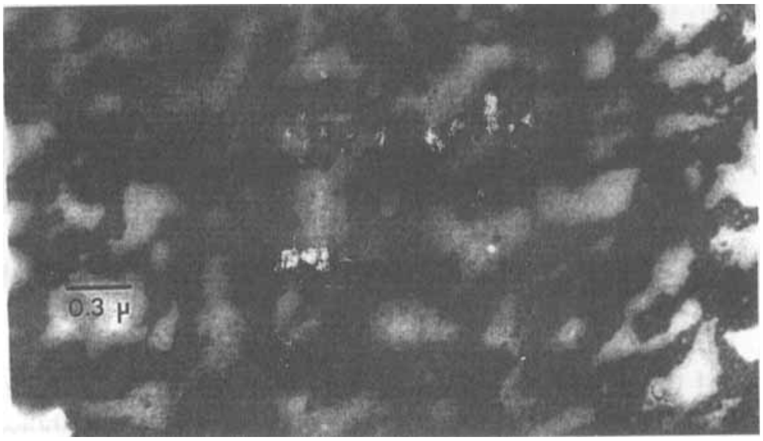

FIGURE 5 Same as Figure 4 but for a composite with 20% of SBR.

cal expression for the percolation volume fraction: $\Phi = \alpha v_R^{\beta}$; using this expression for the experimental data, we have the following numerical results $\Phi = 6.089\ (v_R)^{2.221}$. In Figure 10 the three different fittings are shown for purpose of comparison.

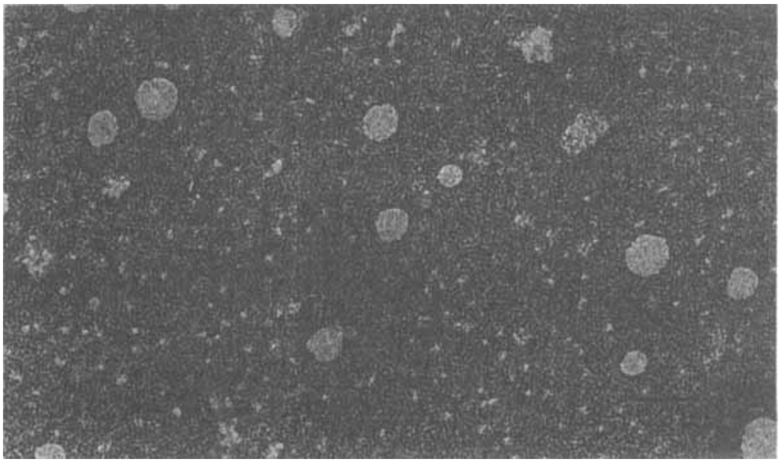

FIGURE 6 Same as Figure 4 but with 30% of the rubbery phase.

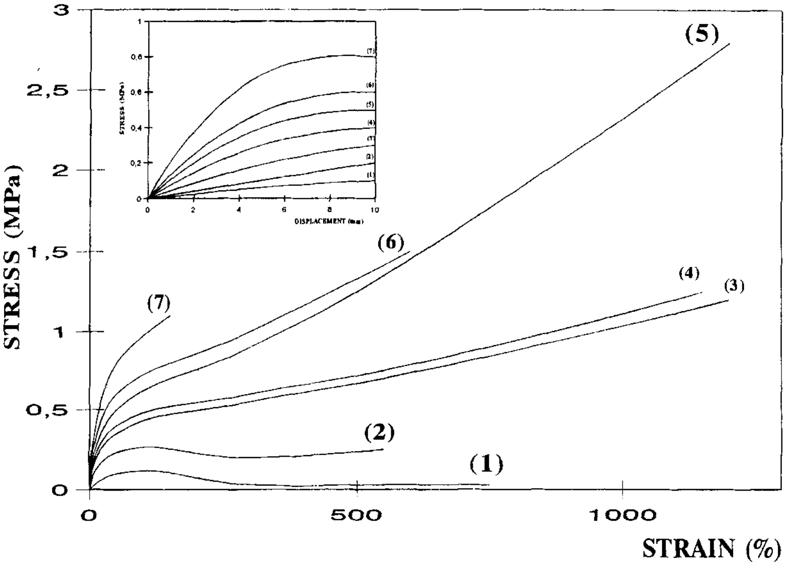

FIGURE 7 Stress-Strain curves obtained for different SBR concentration at a strain rate of 5 mm/min. The insert at the right upper corner is an amplification of the initial slopes of the curves.

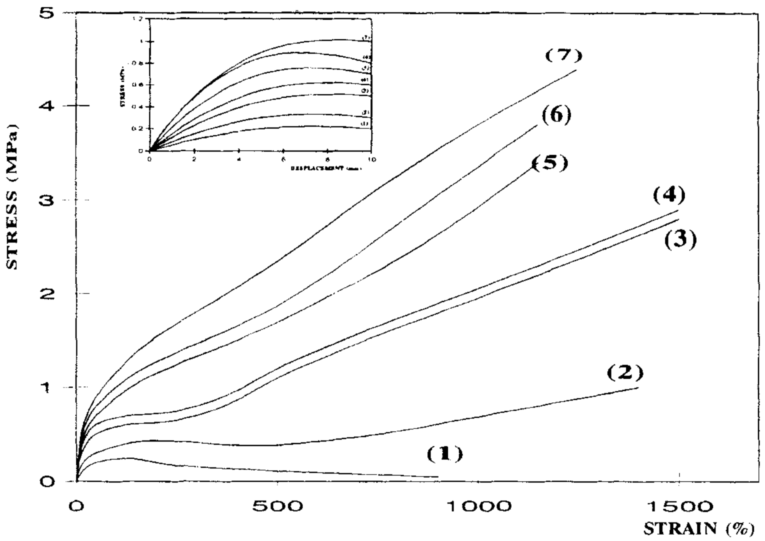

FIGURE 8 Same as Figure 7 but a strain rate of 50 mm/min.

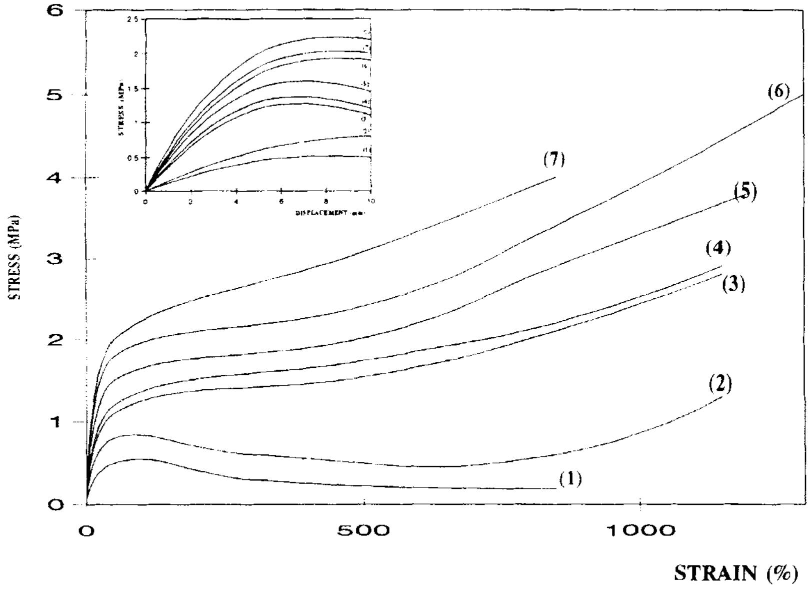

FIGURE 9 Same as Figure 7 but a strain rate of 500 mm/min.

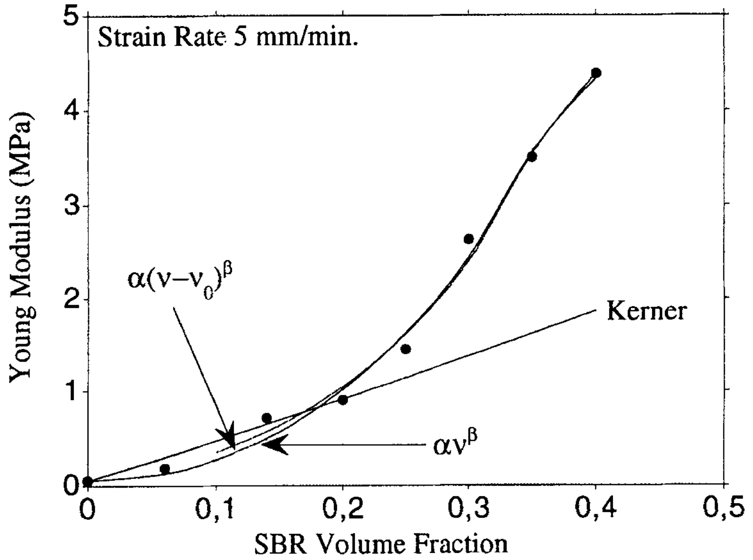

FIGURE 10 Plot of the Young modulus as a function of the SBR composition for a strain rate of 5 mm/min.

Figures 11 and 12 are similar to the Figure 10 but for strain rates of 50 and 500 mm/min respectively. In these cases, the Kerner model and the percolation model with $\Phi = \alpha v_R^{\beta'}$ are shown. The best fittings obtained for the percolation model were: $1.285\ (v_R)^{1.751}$ and $0.462\ (v_R)^{2.091}$.

The coefficients and the exponents for all the strain rates follow a correlation with the strain rate. In Figure 13 a plot of the percolation parameters as a function of the strain rate is shown; these follow a power type relationship with the following results: $11.847\gamma^{-0.455}$ for the coefficient and $4.163\gamma^{-0.341}$ for the exponent, where we have used γ for the strain rate.

The reason why this analystical expression fits the experimental data in the whole range of compositions follows from the definition of Φ and the dependence of the elastic modulus with Φ. It is possible to distinguish two limiting cases: a) for $v_R \ll v_C$ the discrete domains are independent each other i.e., there are not interaction between them, being the Kerner-like models applicable; in this case the elastic modulus is proportional to some power of the volume fraction $(v_R)^{\beta'}$

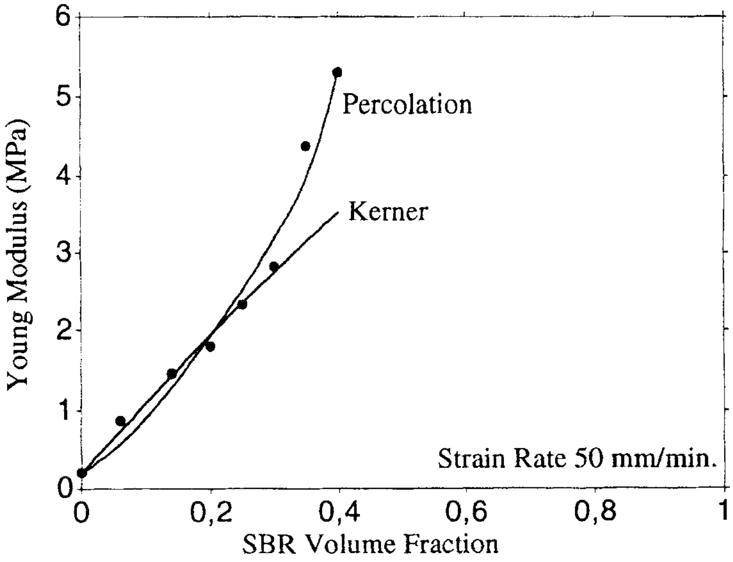

FIGURE 11 Same as Figure 10 but for a strain rate of 50 mm/min.

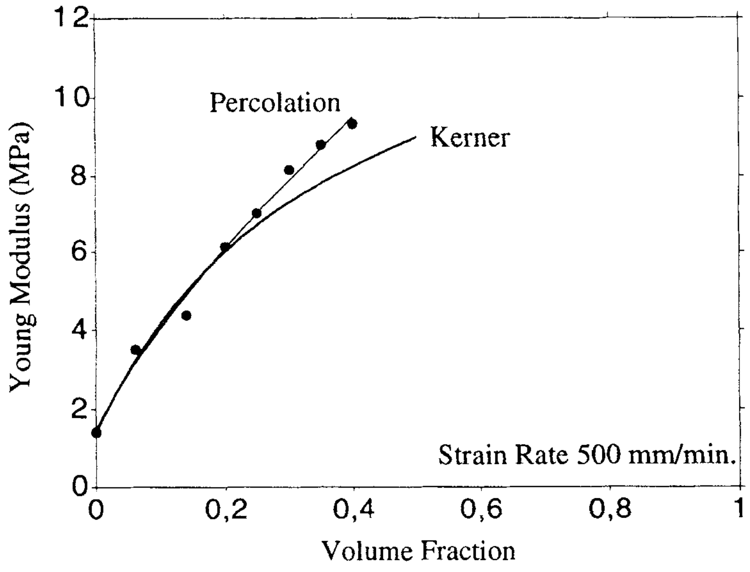

FIGURE 12 Same as Figure 10 but for a strain rate of 500 mm/min.

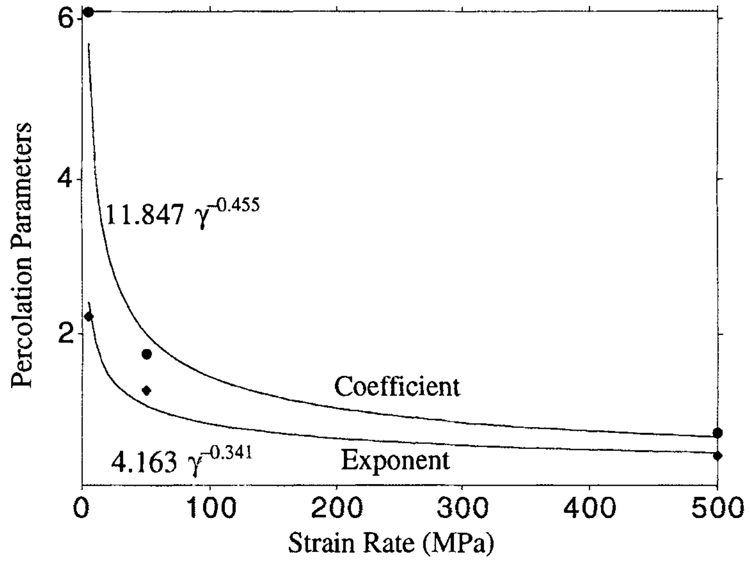

FIGURE 13 Plot of the percolation fitting parameters versus the strain rate.

and then v_R is playing the role of Φ i.e. $\Phi \propto v_R$; in this regime $\beta' = 1.388$ in the expression $\Phi = \alpha v_R^{\beta'}$; b) for $v_R \gg v_C$ we have $\Phi = \alpha(v_R)^{\beta+1}$ from Eq. 3, which corresponds experimentally to $\beta' = \beta + 1 = 2.363$. Then, in both cases Φ follows a power law with the variable v_R with an effective exponent of 2.221 which fit the whole set of data for concentration up to 40% of SBR.

CONCLUSION

Composites prepared at different volume fractions of SBR were used to observe the effect of the chemical compositions on the mechanical response of the material. The morphology of the composite Asphalt-Styrene Butadiene copolymer was obtained by using transmission and scanning electron microscopy. Based on these micro-graphs, analytical models were used in order to predict the mechanical behavior of the material when is subject to external stresses. The experimental data was fitted by using the Kerner's model for lower volume fraction of SBR and by using the percolation model for higher volume fraction. With these two models the complete set of data was well fitted. However, the use of $\Phi = \alpha v_R^{\beta}$ for the percolation volume fraction, allows to fit the complete set of experimental data for all compositions.

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