

Morphology and Tensile Properties of Styrene–Butadiene Copolymer Reinforced Asphalt

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SYNOPSIS

Morphology and tensile properties of several styrene–butadiene copolymer reinforced asphalts have been investigated. In all cases, the raw materials were commercial samples; for the styrene–butadiene copolymer, a branching (nonlinear) block polymeric chain of high molecular weight was used. On the other hand, the asphalt was a nonoxydized commercial sample. The raw materials were characterized prior to making the composite. The morphology and mechanical properties of composites obtained at different chemical compositions were determined, and a comparison of these experimental results to different models, according to the composite morphology, is shown. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Many of the novel engineering polymeric materials are obtained by mixing two or more practically immiscible polymers which have the properties required for the new material. The mixing of polymers which are practically immiscible has become very important, because an inhomogeneous material can be obtained; when the miscibility of polymers is restricted, the polymer that appears in small proportion usually segregates into small regions (in a mesoscopic scale), which are called the discrete phase; these are occluded in the continuous matrix, formed by the other polymer; these kind of materials are called composites. In this way it is possible to improve substantially the properties of original materials and to obtain a novel material which combines synergetically the properties of the precursors materials. In order to have a new material with good performance, it is also required, among other things, to have a good adhesion between phases, and a right size for the particles of the discrete phase. These are, together with the type of the polymer

constituents, the most important requirements to obtain a good engineering material.

Asphalt is an important low-cost thermo-plastic material which is widely used for construction. Asphalt-based materials are used in a variety of applications such as road binders, adhesives, sealants, and waterproof coatings among others. Asphalt, as a building and engineering material, is exposed to a wide range of load and weather conditions; however, this material does not have good mechanical properties because it is hard and brittle in cold weather and soft and fluid in a hot environment, besides that it has a small elastic recovery. Due to this, asphalt is usually reinforced with rubber in order to improve its mechanical properties. This reinforcement is achieved by adding small amounts of rubbery polymers to the asphalt.^{1–5} Lately, the asphalt has also been reinforced by using styrene–butadiene copolymers (SBC). In this case, the incompatibility among these two polymers produces an elastic network into the asphalt, resulting in an excellent elastic recovery and increasing substantially its mechanical properties.

For this reason, a lot of work has been developed^{1–5} in the study of copolymer-modified asphalt, trying to predict mechanical and physical properties based on the composition and morphological structure of the composite.

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Table I Characterization of Asphalt A-6

Asphalt	Saturates (%)	Aromatics (%)	Resins (%)	Asphaltenes (%)	Tensile Modulus
6	11.4	39	39.2	9.7	0.13 MPa

EXPERIMENTAL

The raw materials were characterized prior to fabrication of the composite. Composites were obtained by mixing commercial styrene-butadiene copolymer (Solprene S-411 of Industrias Negromex S.A. de C.V., México) with a nonoxydized commercial asphalt (Asphalt 6 of Petroleos Mexicanos S.A., México). In Tables I and II the characterization of the raw materials is reported, while in Table III the standard ASTM properties of the composite are shown; these results are plotted in Figures 1 and 2. In Figure 3, a set of strain-tensile stress curves is shown for composites at different compositions.

It is important to mention that the copolymer material used here is obtained by coupling four styrene-butadiene linear block copolymer molecules. This chain morphology improves the formation of an elastic network structure into the asphalt.^{1,2}

The composites were prepared by mixing the asphalt with grounded copolymer under very slow agitation in order to avoid high shear rates. The mixing temperature was kept within the range 180–200°C. The blending was considered complete when, under visual inspection, the copolymer particles disappeared and no separation of the phases was observed when sieved (300 mesh).

The morphology of the composite was obtained by using a transmission electron microscope (JEOL 100-CX analytical machine). The samples were prepared by dissolving the composite in toluene (Baker, reactive grade) and evaporating the solvent to produce a film with a thickness of around 0.1 μm .⁶ These films were stained with OsO_4 vapors to have a good contrast in the micrographs. The original and modified asphalts were subjected to mechanical and physical properties for comparison.

THEORETICAL MODELS

For inhomogeneous materials like composites, the dynamical response is related to molecular relaxation processes characteristic of each constituent that forms the material; however, this is strongly influenced by the composition and morphology of the composite and also by the adhesion between the phases. There exist several mathematical models⁷ depending on the material's morphology which can predict the mechanical behavior of the composite. In this study two models will be used because the morphology of the composite depends on the concentration of the constituents; for this particular material, when the concentration of the copolymer is in the range between 6 and 8%, there appears a phase inversion which changes drastically the morphology of the material. For concentration lower than the phase inversion concentration C_{pi} the polymer forms the discrete phase which are small particles with a quasi-spherical shape. On the other hand, for concentration larger than C_{pi} the asphalt becomes the discrete phase with a morphology different to the former case.

The models used here are the Kerner's model⁷ and the Ashby-Gibson's model.⁸ In both cases the models are dependent on the morphology of the composite. These models will be discussed briefly.

Kerner Model

This model is a self-consistent approximation model, where the composite structure is modeled as a continuous medium where spherical dispersed particles with the same elastic properties as one of the constituents are embedded; these particles are surrounded by shells with the same elastic properties

Table II Properties of Styrene-Butadiene Copolymer S-411

Copolymer	Butadiene/Styrene	Density	Tensile Modulus
Solprene 411	70/30	0.94 g/cm ³	3.3 MPa

Table III Properties of the SBC–Asphalt Composite

Blend (%) A-6/S-B	Softening Point (°C) ASTM: D-36, E-28	Penetration (mm/10) ASTM: D-5	Brookfield Viscosity (cp) ASTM: D-1084
0	50	94	800
96/4	68	80	980
96/6	84	64	1600
92/8	90	58	2200
90/10	92	42	5420
86/14	98	38	12000

as the other the constituents, and finally they are in turn surrounded by another second shell with the elastic properties of the whole composite. In this particular case, when the concentration of the modifier is less than 6%, the material has not suffered, yet the phase inversion and its morphology is appropriated to apply the Kerner’s model (see Figs. 4, 5, and 6). The Kerner’s model provides an expression for the shear modulus of the composite G_c given by:

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

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

with G_1, G_2, G_c being the shear moduli of asphalt, SBC and the composite, respectively, 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 Young’s modulus E_c is through the relationship:

$$E_c = 3G_c \quad (3)$$

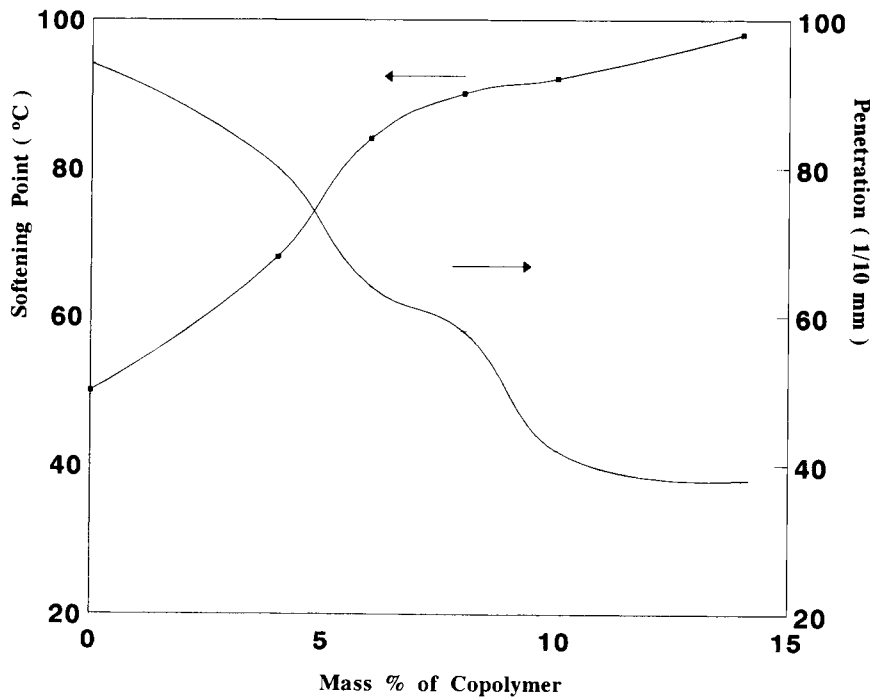


Figure 1 Penetration and softening point of the composite as a function of the copolymer concentration.

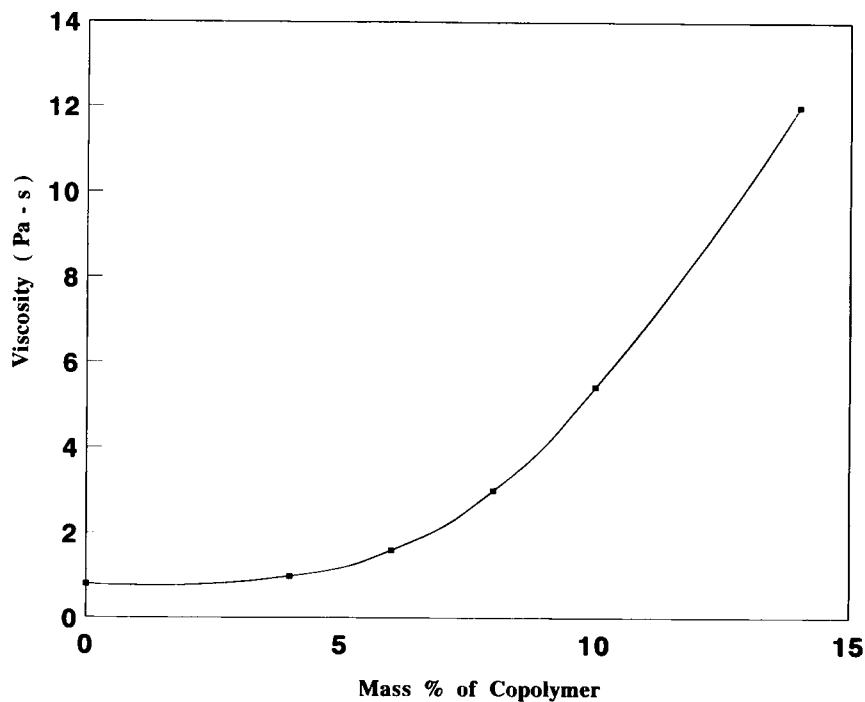


Figure 2 Brookfield viscosity as a function of the composite composition (test temperature: 160°C).

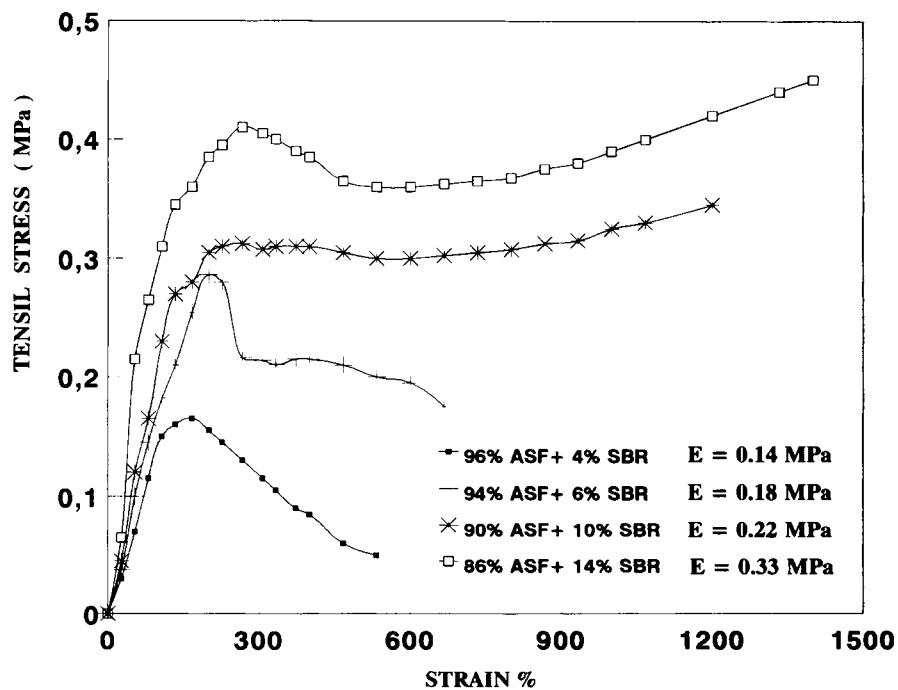
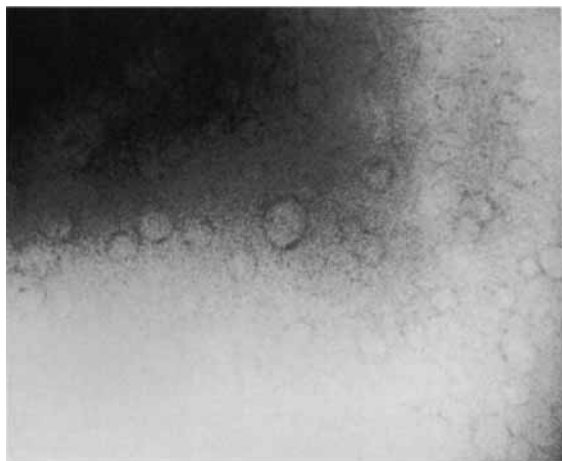
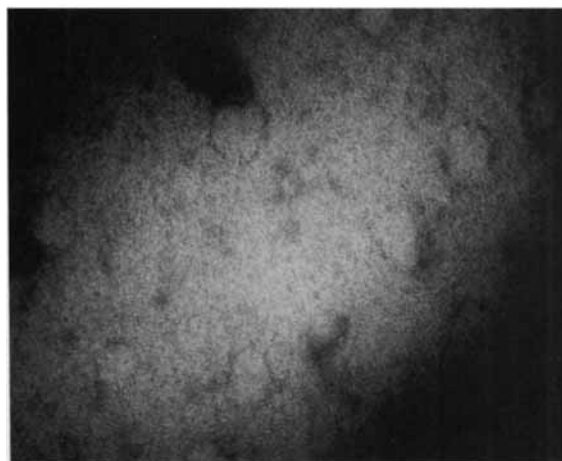


Figure 3 Tensile stress-strain curves at different asphalt-SBC compositions.



200 nm



100 nm

Figure 4 Micrograph showing the composite containing 4% copolymer. (Copolymer is the discrete phase.)

Ashby–Gibson Model

This model is applicable to cellular materials, i.e., those which have a structure like a honeycomb. For this composite, when the modifier material appears in a concentration larger than 8%, a phase inversion occurs, and the morphology looks like a honeycomb where the empty space is filled with asphalt (refer to Figs. 7, 8, and 9). The linear elastic response of the honeycomb structures is primary caused by the bending of the cell walls (in this case, by bending of the rubbery copolymer). Each wall is modeled as a beam of length l , thickness t , depth b , and Young’s modulus E_C . The analytical expression for the composites’ Young’s modulus is given by:

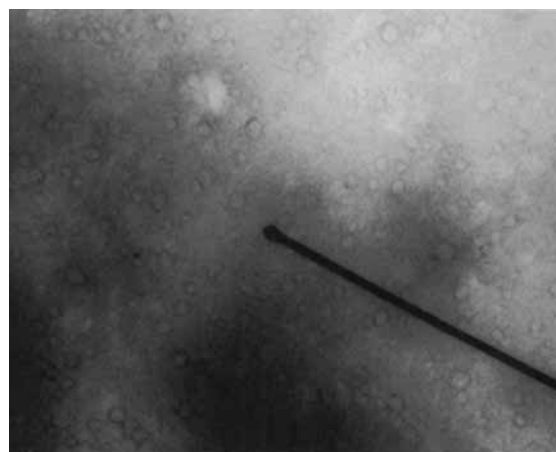
$$E_C = \frac{12E_s I \cos \theta}{(h + l \sin \theta) b l^2 \sin^2 \theta} \tag{4}$$

where θ is the angle subtended by half of a side in the hexagon and I is the moment of inertia of the beam with respect to its neutral axis.

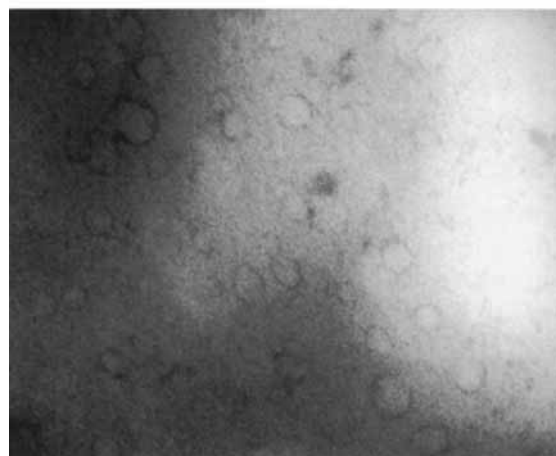
Each hexagon only has four side walls associated (the other two are associated to a neighboring hexagon); then the volume associated to each cell is given by:

$$V_T = 2.598 b l^2 + 4 l t b \tag{5}$$

and the volume fraction of rubber per cell is given



500 nm



200 nm

Figure 5 Micrograph showing the composite containing 6% copolymer. (Copolymer is still the discrete phase.)

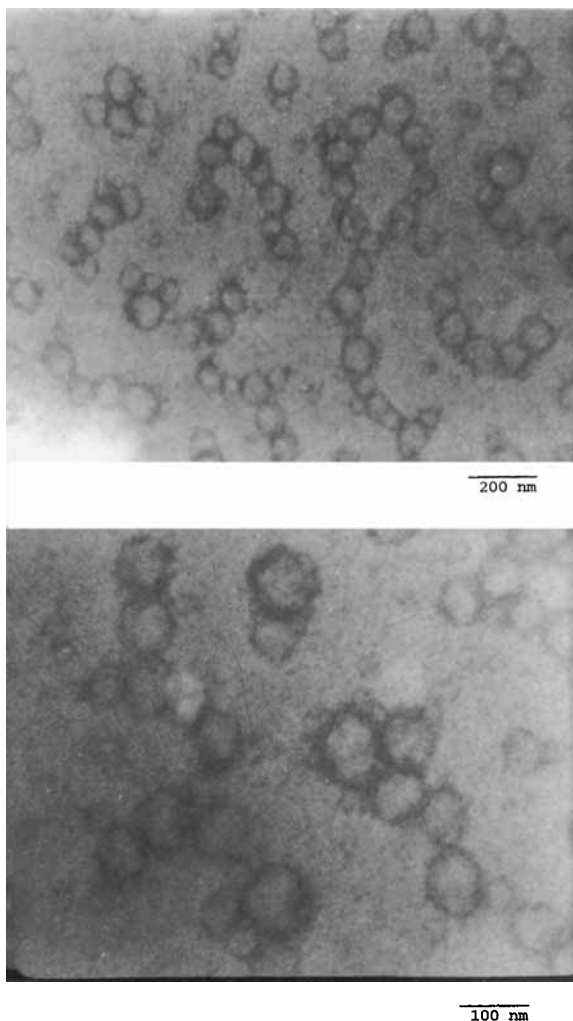


Figure 6 Micrograph showing the composite containing 8% copolymer. (Phase inversion has started.)

by:

$$\Phi_{\text{rubber}} = \frac{4ltb}{2.598bl^2 + 4ltb} \quad (6)$$

By using this equation, it is possible to obtain the thickness the cell wall should have in order to reproduce the composition of the composite. These values are different from those obtained from the micrographs.

From the micrographs obtained for the composite, the particle size and the cell wall geometry (length, thickness, etc.) can be obtained. Table IV shows the mean values and the standard deviation, measured for the cell geometry. Based on these experimental data, and by assuming that a way to take into account the fact that the cells in the cellular material

are not empty but filled with asphalt, the values for the Young's modulus can be evaluated, and the results are shown in Figure 9.

RESULTS AND DISCUSSION

In Figure 2 the Brookfield viscosity is plotted as a function of the composition of the material. It is possible to see that the phase inversion occurs at a composition between 6 and 8%, where a change of regime of the viscosity profile is observed. In Figure 3 it is possible to observe the strain–tensile stress behavior for composites of different composition. When the asphalt is modified with the copolymer,

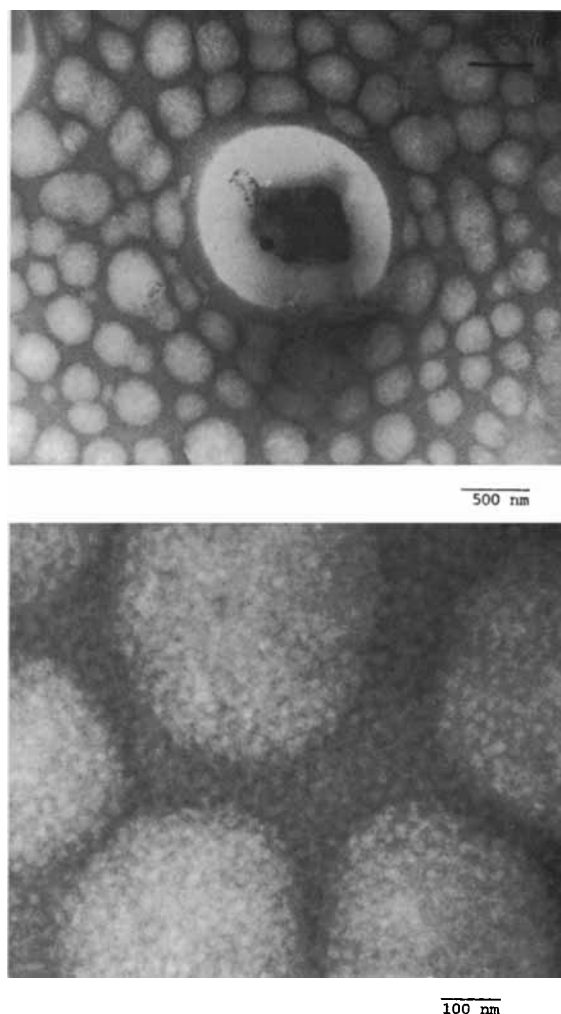


Figure 7 Micrograph showing the composite containing 10% copolymer. (Phase inversion has taken place and the asphalt is now the discrete phase.)

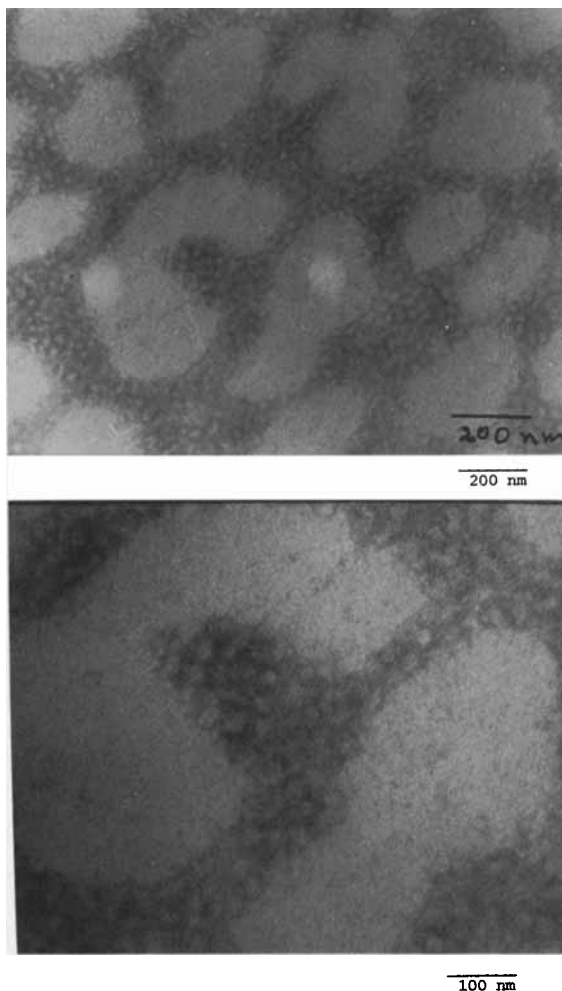


Figure 8 Micrograph showing the composite containing 14% copolymer.

the Young’s modulus increases gradually as a function of the amount of copolymer. The moduli are plotted in Figure 9 as a function of the concentration of constituents.

Figure 4 shows a micrograph of the composite corresponding to a 4% copolymer composition. Here, it is possible to see that the discrete phase is the copolymer which is forming small quasi-spherical particles embedded in the asphalt. Figures 5 and 6 are similar to this one and correspond to compositions of 6 and 8% of copolymer, respectively; in these micrographs it is also possible to observe again that the copolymer is forming small quasi-spherical particles included in the continuous phase.

On the other hand, in Figures 7 and 8 it is possible to see the micrographs corresponding to concentrations of 10 and 14% of copolymer. In these cases, the phase has been inverted and the copolymer be-

comes the continuous matrix, while the asphalt is playing the role of the discrete phase. In these micrographs, it is possible to notice a resemblance between this morphology and a cellular material (honeycomb). For these composites, the Ashby–Gibson model was applied modifying the elastic properties of the beams because the honeycomb is not empty, but filled with asphalt. In Figure 9 it is possible to see the comparison between the experimental data for the Young’s modulus obtained from Figure 3 and the data obtained from the Kerner and Ashby–Gibson models discussed here. As can be seen, there is good agreement between the experimental and fitted data. In this figure, both models are shown, and it is possible to see how the assumption used in the Ashby–Gibson model works. From this plot it is possible to observe that there is a change in the rate of change of the Young’s modulus at the phase inversion: for concentrations less than C_{pi} , the rate of change of the modulus as a function of concentration is approximately 2 MPa, while for the high concentration regime this rate of change is of 2.75 MPa, this being considerable larger than the other.

CONCLUSION

For the composite Styrene–butadiene copolymer asphalt the morphology of the material was obtained by using transmission electron microscopy. Based on these micrographs, analytical models were used in order to predict the mechanical behavior of the material when subjected to external stresses. For low copolymer concentrations (where the discrete phase is the copolymer), the Kerner model was used, and good agreement was obtained between the experimental data and the model. On the other hand, when the copolymer concentration exceeds the phase inversion concentration (in this case 8%), the material resembles cellular material. In such case, the Ashby–Gibson model was applied, and a good agreement between the experimental data and the model was obtained.

Table IV Characteristic Geometry of the Composite Obtained from the Micrographs

Concentration (%)	Radius (nm)	Length (nm)	Thickness (nm)
10	155 ± 34	165 ± 28	59 ± 23
14	123 ± 28	152 ± 28	61 ± 19

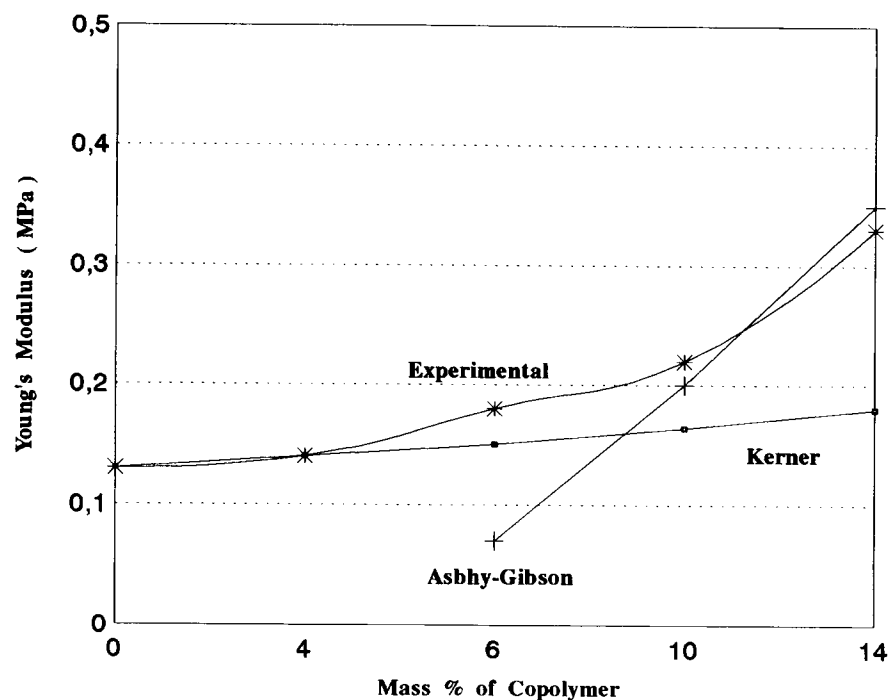


Figure 9 Comparison of Young's modulus and the prediction obtained from the Kerner and Ashby-Gibson models.

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