Rheological Properties of Styrene–Butadiene Copolymer-reinforced Asphalt

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SYNOPSIS

Rheological properties of styrene–butadiene copolymer-reinforced asphalt were investigated. A percolation-like model was used to fit dynamical experimental data, and a comparison with the Kerner–Takayanagi model is presented. In addition, a frequency-composition-temperature correspondence principle is proposed. This correspondence principle allows the prediction of the rheological behavior of an asphalt-based composite within a wide range of compositions, provided a narrow composition range at different frequencies and temperatures is previously known. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

In terms of the annual volume produced, asphalt composites constitute one of the most popular materials, for their applications span from construction, road binders, adhesives and sealants, to water-proofing coatings, and several others. Asphalts themselves have poor mechanical performance because they are hard and brittle in cold weather and soft in hot environments, in addition to their small elastic recovery capabilities. Therefore, these materials ought to be modified, in low proportions to maintain their own advantages, with other materials to improve the property or properties desired.

The most widely used modifiers for asphalt are different types of rubber-like polymers or copolymers.[1-5] Among these, the most common are polybutadiene-based materials, due to their very low T_g and relatively low cost. Several attempts have been reported to physically and/or chemically modify the asphalt to produce a material with good enough mechanical properties. In this regard, one example is the oxidation of the material to increase the molecular weight and, consequently, the corresponding viscosity. However, by this method, the mechanical properties are only slightly improved. More recently, it was found that the styrene–butadiene (SB) block copolymer molecules are suitable for an adequate morphology modification in the resulting materials. The main advantage of this modifying technology is the fact that the two polymers are immiscible to each other. This allows the three-block molecules (SBS) to form a physical network (thus providing the material with a good elastic recovery), the styrene blocks being those areas which are forming the physically reticulated regions and the polybutadiene blocks being the elastic component of the resulting network. Even provided that SBS materials are expensive, they are used only in small proportions (between 8 to 10% vol), which makes their use profitable in terms of the cost-benefit relationship.

In general, these composites present a complicated spatial structure which, when adequately handled, allows to control, to a large extent, their final mechanical properties. In this sense, extensive work has been dedicated in the last few years to obtain good correlations between the morphology of the material and the corresponding mechanical performance.[6-8] In a previous contribution,[7] Kerner–Takayanagi and Ashby–Gibson models were employed to explain the elastic modulii experimentally obtained for asphalt–nrubber composites at zero

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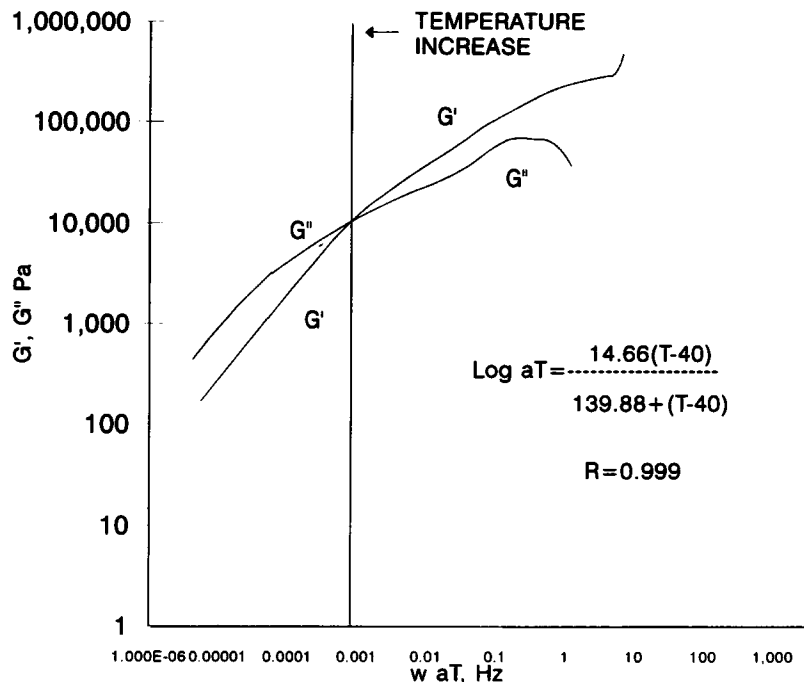
Figure 1 Master curve of G' and G'' versus frequency for a composite with a 10 wt % copolymer.
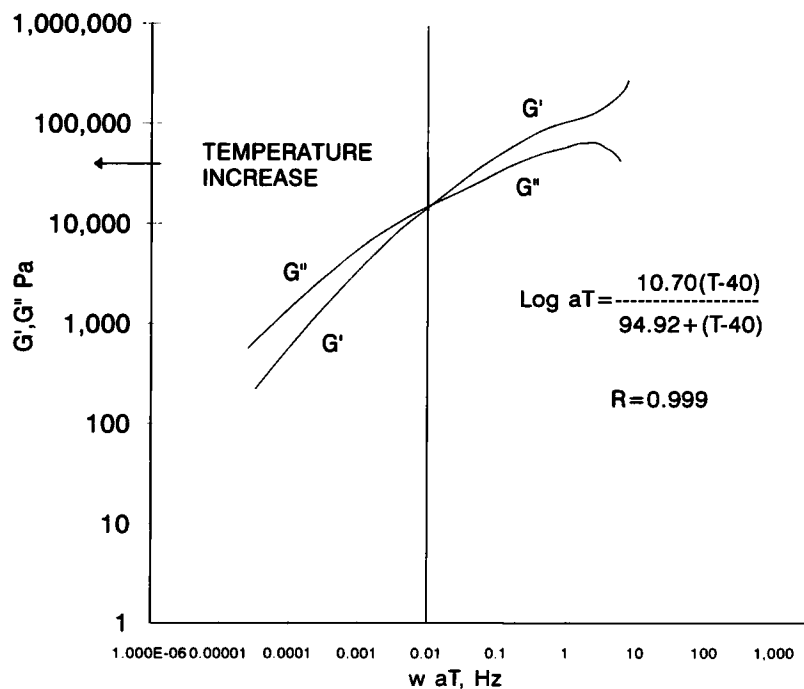
Figure 2 Master curve of G' and G'' versus frequency for a composite with an 8 wt % copolymer.
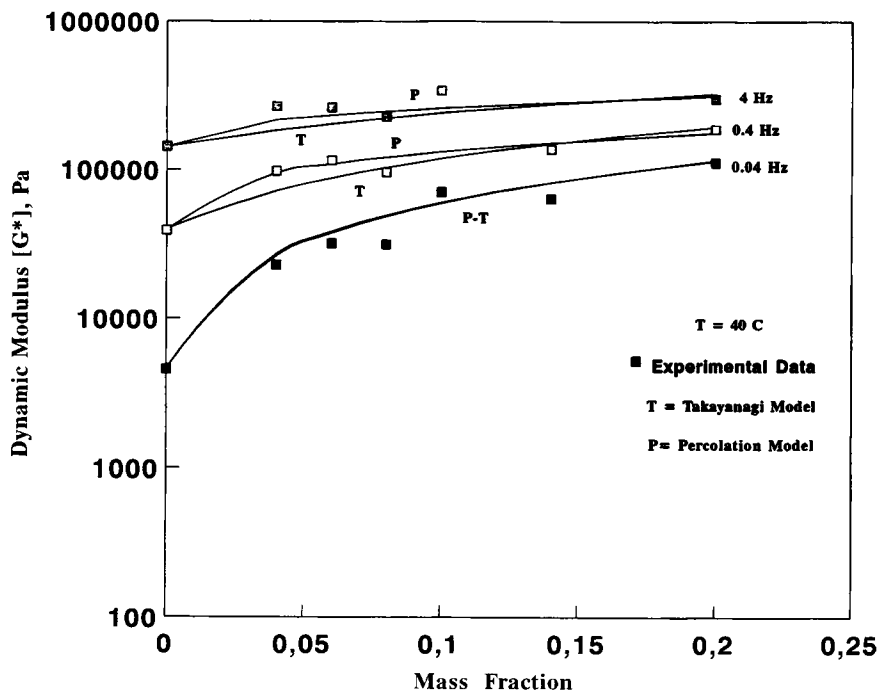
Figure 3   Dynamic modulus versus composition for various frequencies at 40°C.

frequency in a range of compositions from 0–14%. Accordingly, in the present article, a study of the rheological properties of asphalt–butadiene copolymer blends with different compositions is carried out. The results, as will be explained, allow to propose a frequency-composition-temperature correspondence principle for these materials.

THEORETICAL MODELS

For nonhomogeneous materials, such as composites, the dynamic response is related to molecular relaxation processes characteristic of each constituent of the material. In addition, this is also strongly influenced by the composition and morphology of the composite and by the interfacial adhesion. There exists a number of mathematical models,[6–8] depending on the particular morphology, which attempt to predict the mechanical behavior of the composite. In this article, two different models will be used to predict the rheological properties, namely, the Kerner–Takayanagi models and the percolation model.[6] A brief review of these models follows.

Kerner–Takayanagi

These are really a family of models originally proposed by Kerner and then modified by Takayanagi,

which allow estimation of the mechanical properties by modeling the spatial structure of the composite. In the original Kerner model, the composite is regarded as quasispherical particles with elastic behavior, dispersed in a continuous medium with viscous behavior. Takayanagi's modification consists in considering the spatial structure as an arrangement of blocks (each representing one of the components of the composite) connected in series and in parallel, depending on what property that particular block (component) represents, either with elastic or with viscous behavior. In both approaches, the shear modulus G_c of the composite is given by

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

where G_1 and G_2 are the modulii of each component of the composite; ϕ_1 and ϕ_2, the corresponding volume content; and α, a characteristic parameter.

The difference between the two approaches lies on the parameter α, which is fixed and equal to 0.67 for the original Kerner model; whereas it becomes an adjustable parameter for Takayanagi's approach.

Percolation

This is a widely used and useful concept in materials science, and it is related to a property (the perco-
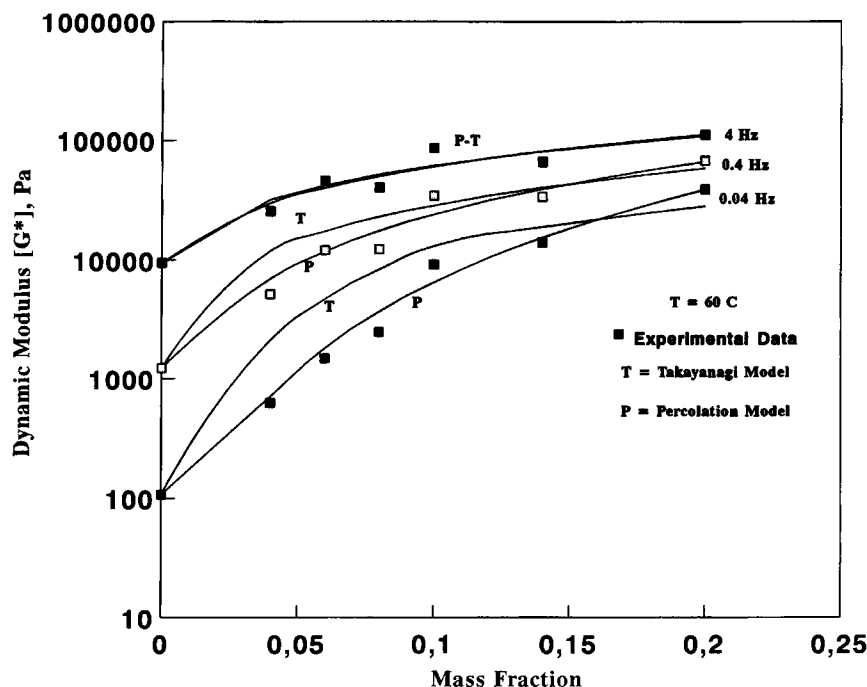
Figure 4 Dynamic modulus versus composition for various frequencies at 60°C.

lation threshold) of a given system, which depends, generally speaking, on the topology of the materials' phases. It has been proven[6] that a percolation approach can be adapted also for the dynamic case by using the concept of corresponding states. In this case, the shear modulus is given by

$$
\frac{G_c}{G_2} = \frac{\begin{array}{c}[(1 - \alpha\phi^\beta) + (\alpha\phi^\beta)\phi]G_m \\ + [(\alpha\phi^\beta)(1 - (\alpha\phi^\beta) - \phi)]G_2\end{array}}{\phi G_m + [(1 - (\alpha\phi^\beta) - \phi)]G_2}
$$

where the meaning of the symbols are the same as above, and β is the percolation characteristic exponent.

EXPERIMENTAL

Nonoxydized commercial asphalt from Petroleos Mexicanos, S.A. (Asphalt No. 6) fully characterized in terms of its aromatics, resins, and asphaltenes contents (39, 39, and 9.7%, respectively) as was reported previously[7,11] along with a characterization of the commercial styrene–butadiene copolymer employed (Solprene S-411 from Industrias Negromex, S.A. de C.V.). This copolymer is the result of coupling four styrene–butadiene linear block copol-

ymer molecules, which provides an interesting molecular structure to the material.

The blending was achieved by mixing, under slow agitation to prevent damaging from high shear rates, the asphalt as-received, with the grounded copolymer at 180–200°C, with compositions ranging from pure asphalt to a 20 wt % copolymer. The resulting material was sieved with a 300 mesh. Rheological properties of these composites were obtained at three different temperatures (40, 60, and 80°C). The experimental dynamical modulus [i.e., $G'(\omega)$ and $G''(\omega)$] was obtained in each case in a Bholin rheometer.

RESULTS AND DISCUSSION

As mentioned, asphalts are modified with different types of rubber to improve their rheological properties. More specifically, perhaps the most important property is the elastic recovery. This is why it is so important to be able to predict the rheological behavior of an asphalt-based composite at different rubber concentrations and temperatures. In this regard, the so-called time–temperature principle[10] allows one to obtain the elastic modulus of a viscoelastic material in a wide time (or frequency) range, provided a narrow time (or frequency) interval is
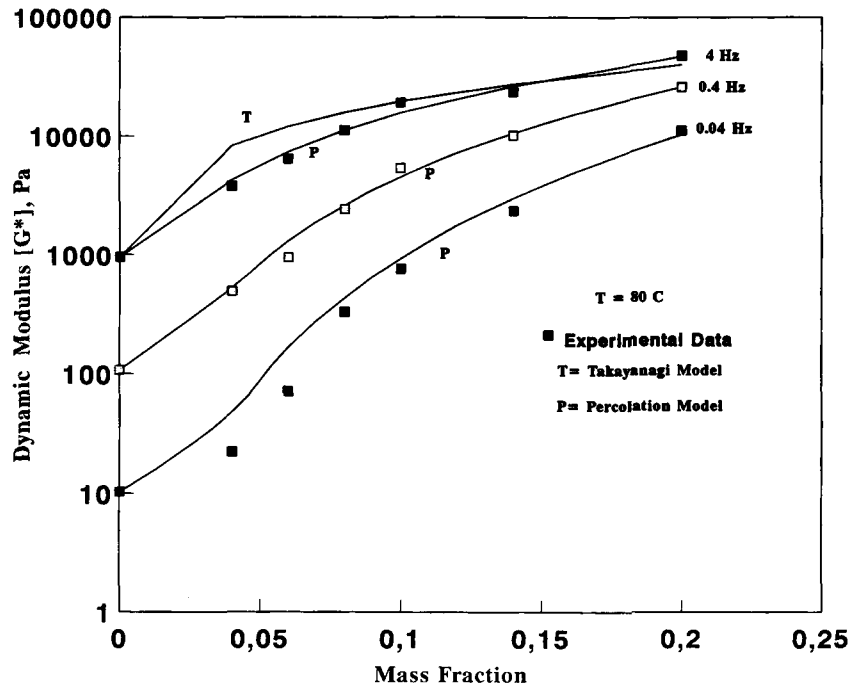
Figure 5 Dynamic modulus versus composition for various frequencies at 80°C.

already known at different temperatures. This is achieved through the WLF (Williams–Landel–Ferry) Equation,[10] which is basically a superposition principle in which a shifting factor is calculated for each temperature. Figures 1 and 2 show the so-called master curves for composites with 8 and 10% copolymer content. Moreover, when the shifting factors at different temperatures are fitted with the aid of the WLF equation, information can be obtained either about the free volume of the polymer (in a
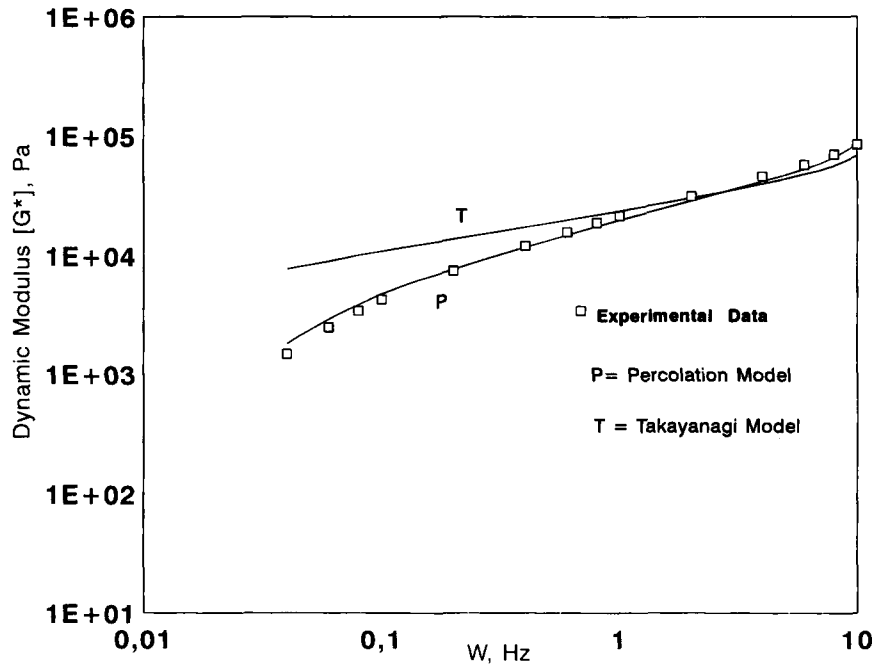

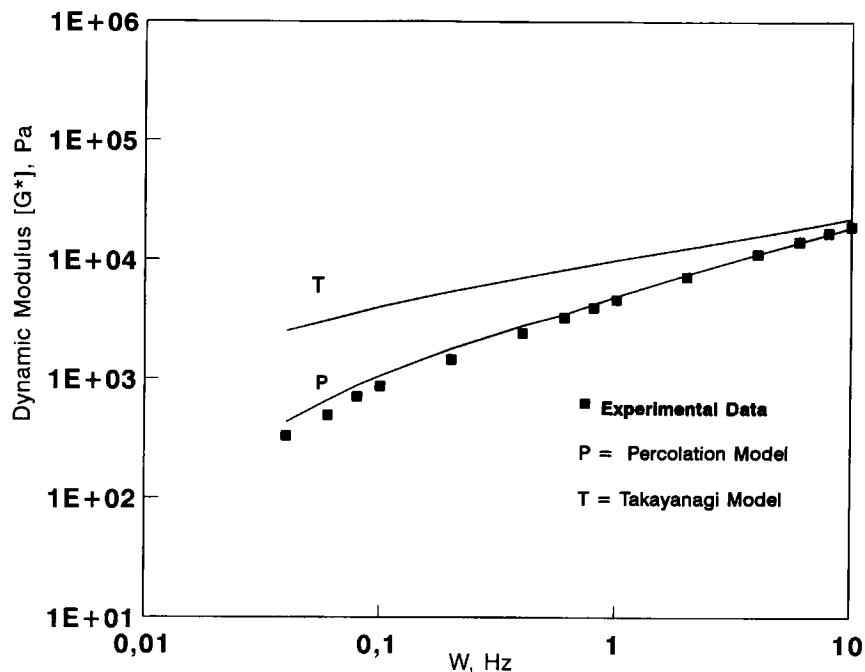**Figure 6** Dynamic modulus versus frequency for the 6 wt % composite at 60°C.

Figure 7 Dynamic modulus versus frequency for the 8 wt % composite at 80°C.

pure polymeric sample, of course) or about some type of averaging (for the case of composites).

In this regard, the standard Principle of Correspondence was extended to also include the volume fraction of the discrete phase of the composite. In other words, with the modification to the standard principle, it is possible to predict the rheological behavior of an asphalt composite in a wide range of
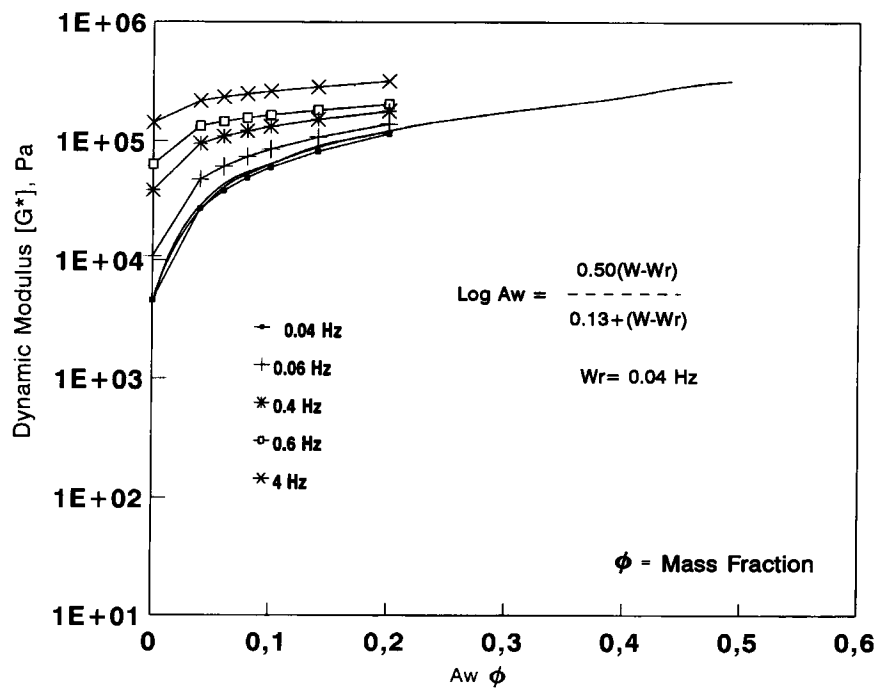

Figure 8 Dynamic modulus versus composition for different frequencies at 40°C.
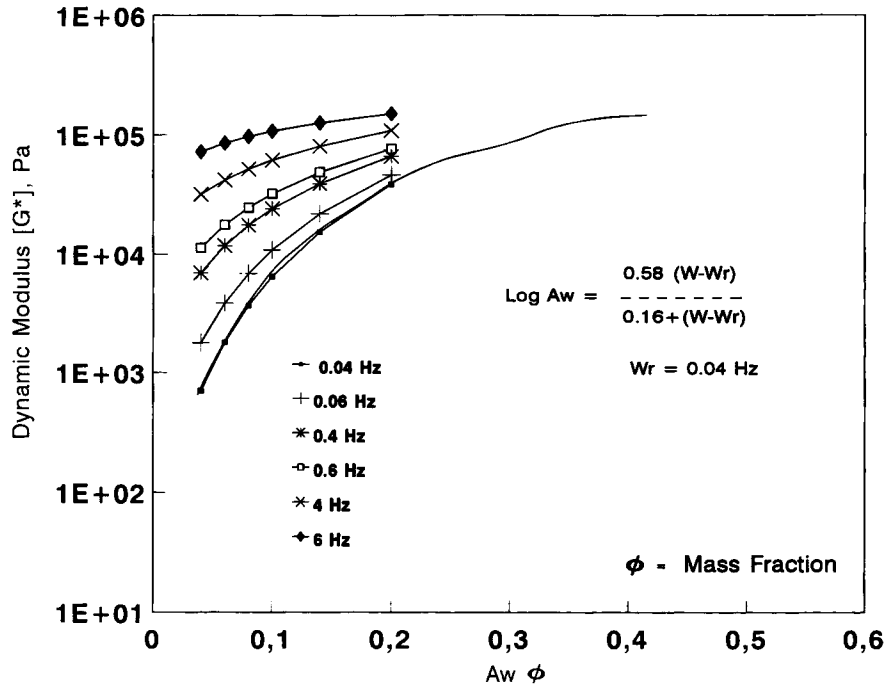
Figure 9   Dynamic modulus versus composition for different frequencies at 60°C.

compositions, provided a narrow range of compositions is known at some frequencies, as it will be demonstrated in the following discussion.

As was mentioned before, a recent work[7] showed the excellent fitting of a numerical modeling of the modulus of asphalt–rubber composites but zero fre-
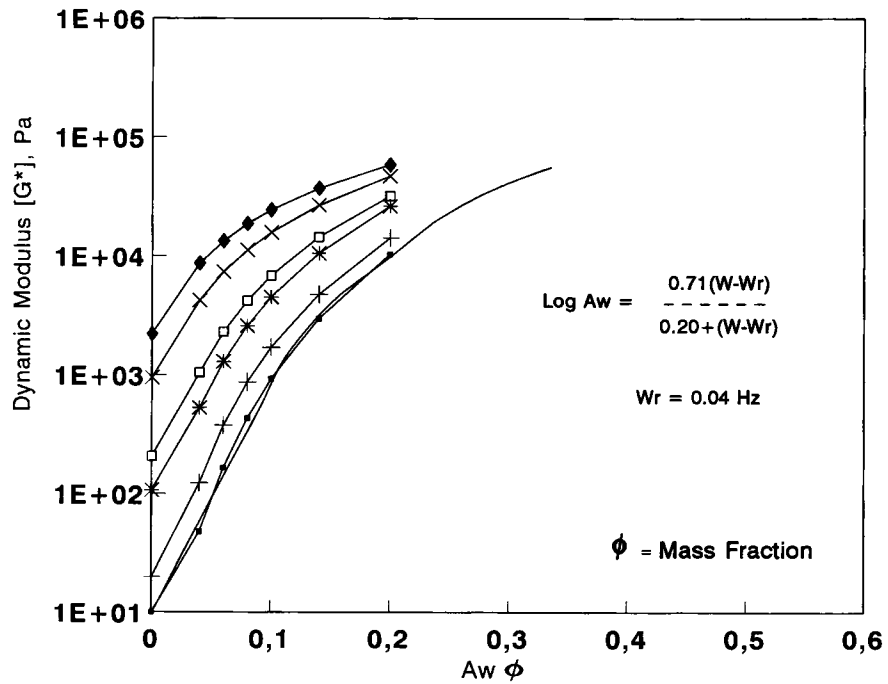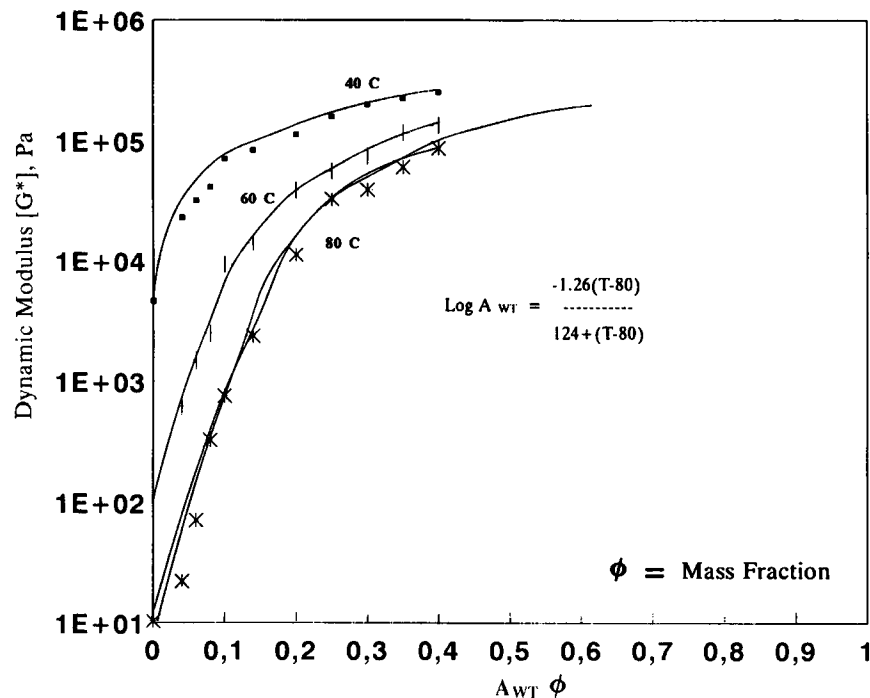

Figure 10   Dynamic modulus versus composition for different frequencies at 80°C.

Figure 11   Super master curve of the dynamic modulus versus composition for all temperatures and frequencies studied.

quency conditions (i.e., the static modulus). Now, by using the generalized correspondence principle, it will be demonstrated that is possible to also obtain the dynamical modulus of the composite as a function of composition. The experimental data were, in each case, fitted by using both the Kerner–Takayanagi and the percolation models. Figures 3, 4, and 5 show the experimental dynamical moduli plotted as a function of the composition as well as a comparison between the percolation and Takayanagi models, for 40, 60, and 80°C, respectively. As observed there, the percolation model fits the best the experimental data. Similarly, Figures 6 and 7 show the dynamic modulus as a function of frequency for given compositions (6 and 8 wt %), along with the corresponding predictions by both theoretical models, for 60 and 80°C, respectively. Again, the Takayanagi model represents only a very poor approximation to the experiment, whereas the percolation model shows a remarkable agreement.

Figures 8, 9, and 10 show plots of G' versus relative composition ϕ for some selected frequencies for 40, 60 and 80°C, respectively. The continuous curve corresponds to a master curve. This master curve was obtained in a similar way to the WLF master curves. In this last case, however, the reference curve was chosen as that of the lowest frequency tested

(i.e., 0.04 Hz). With the master curves, it is indeed possible to predict the behavior of the composite for all frequencies as a function of composition. Obviously, there exists one master curve for each temperature. The shifting factors, A_ω, were fitted by using a WLF-like relationship but with the variables ω (frequency) and ϕ (relative composition); whereas in the original WLF relation, the variables are t (time or, conversely, frequency) and T (temperature) by using the following relation.[10]

$$\log(A\omega) = \frac{B(\omega - \omega_r)}{C(\omega - \omega_r)}$$

where ω_r is the reference frequency, which, for the present case, was arbitrarily chosen as 0.04 Hz, as mentioned. The adjustable parameters B and C have, for example, the values of $B = 0.59$ and $C = 0.16$ for the 40°C master curve; those for the other temperatures are indicated in the corresponding curves (Figs. 8, 9, and 10 for 40, 60, and 80°C, respectively).

By taking as reference the master curve corresponding to 40°C, a super master curve was built, as shown in Figure 11. This curve, which includes all master curves obtained previously, can be conveniently used to cover the whole range of experimental data obtained in the present work and to

predict those points not experimentally obtained yet. In addition to the practical relevance of this super master curve, it also indicates a universal scaling behavior in the properties of this system, which is certainly worth exploring in detail because its possible fundamental consequences toward the understanding of the characteristics of these composites.

CONCLUSION

Percolation and Kerner-Takayanagi models were employed to fit the dynamic moduli of asphalt-elastomer composites as a function of the relative composition. The fitting obtained was very good, in particular with the percolation model, which implies that the observed improvement in mechanical response of those materials is basically due to the spatial connectivity of the segregated elastomer and asphalt phases. Additionally, a WLF-like equation was obtained from the analysis of the data, in such a way that the whole dynamical behavior of these composites can be adequately predicted, provided the frequency of operation and the composition are specified. These results not only represent a step toward the understanding of the specific characteristics of this particular system but also open interesting possibilities in the area of studying micro-

structure properties relationships in systems with complex topologies.

REFERENCES

1. M. Bouldin and A. Collins, "Rheology and Microstructure of Polymer Asphalt Blends," Mtg. Rubber Div., ACS, Las Vegas, Shell Devel. Co., 1990.
2. G. Krauss, *Rubber Chem. Tech.*, **55,** 1389 (1982).
3. *Kraton Thermoplastic Rubber in Asphalt Products,* Shell Chem. Co. Tech. Bull., 1987.
4. *Finaprene Rubber for Bitumen Modification,* Fina Co. Tech. Bull., 1980.
5. *Use of Finaprene Blockcopolymers to Modify Asphalts from Different Crude Sources,* Fina Co. Tech. Bull., 1980.
6. R. A. Dickie, *J. Appl. Polym. Sci.,* **17,** 45 (1973).
7. R. Blanco, R. Rodríguez, M. Garcia-Garduño, and V. M. Castaño, *J. Appl. Polym. Sci.,* **56,** 57 (1995).
8. L. J. Gibson and F. Ashby, *Proc. Roy. Soc. London,* **382,** 25 (1982).
9. D. Paul and S. Newman, *Polymer Blends,* Academic Press, New York, 1982.
10. J. D. Ferry, *Viscoelastic Properties of Polymers,* Wiley, New York, 1980.
11. R. Blanco, M.Sc. Thesis (Chemical Engineering), Universidad Autónoma Metropolitana Iztapalapa, Mexico City, 1995.