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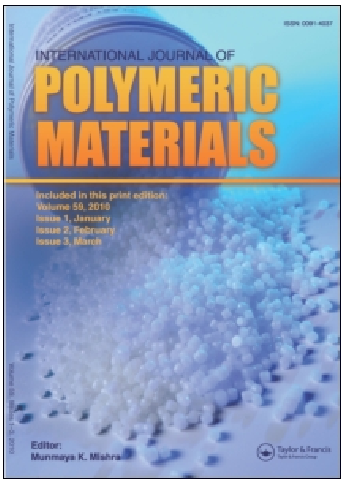

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RHEOLOGICAL PROPERTIES OF SBS-ASPHALT COMPOSITES AT HIGH DEGREE OF MODIFICATION

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Rheological properties of Styrene-Butadiene-Styrene (SBS)-Asphalt composites were studied as a function of the SBS concentration, frequency, and temperature. The experimental data were fitted by using the percolation model, aiming to predict the rheological behavior of this composite at any specific composition, temperature, and frequency. This was achieved through a WLF-type relationship that has been extended to allow composition to be considered. This extended WLF is conceptually supported by a free volume theory, allowing to generate master curves with shifts in temperature (Log aT) and in concentration (Log aC). The temperature-concentration displacements (Log aTC) and the concentration-temperature displacements (Log aCT) were well fitted, producing practically the same super-master curve, demonstrating that this model applies well to both types of shifts.

Keywords: rheology, asphalt, SBS copolymer, modified asphalt, WLF model, master curve, super-master curve, shift factor

INTRODUCTION

The poor properties of asphalt make this material a good candidate to be modified in order to improve its properties to fulfill the tough requirements needed for highway construction. In this sense, much effort has been dedicated to improve its properties by modifying asphalt with Styrene-Butadiene block copolymers (SBS) to improve its

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performance, forming a type of molecular composite material [1–3]. The properties achieved by this modification are especially relevant for pavements and waterproofing applications. A current program has been developed in the USA, starting approximately 10 years ago, known as SHRP (Strategic Highway Research Program), aimed precisely to obtain a rheological characterization of asphalt and modified asphalt to determine the so-called Performance Grade (PG) of this material during practical use. A great effort has been invested to obtain a scientifically based classification of the asphalt. However, three questions remain to be properly addressed: (1) What type of asphalt does one need for a particular use?; (2) What kind of asphalt is available on the market?; and (3) How does one produce or modify the asphalt that is needed for the specific use?

The first two questions can be answered from the available literature; [4] however, the last question still requires some basic research mainly due to the complex morphology the raw and the modified asphalt already have. Accordingly, in this work some results on the rheological properties of SBS-modified asphalt at high degree of modification are shown. A percolation model was used to predict the dynamical behavior of the composite as a function of the temperature, frequency, and chemical composition. A WLF-type relationship, where the concentration effects were taken into account, was used to generate the master curves by shifting in both temperature and concentration. Combined displacements: temperature-concentration (Log aTC) and concentration-temperature (Log aCT) were also employed to generate the super-master curve, which contains the general dependence of the elastic modulus on temperature, frequency, and concentration.

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THEORETICAL BACKGROUND

Free Volume Considerations

The Williams, Landel, and Ferry [5] (**WLF**) model provides an analytical relationship for the shift factor aT that allows obtainment of a master curve using the time-temperature equivalence principle; this model is based on the Doolittle's free volume equation (**DFV**):

$$\textbf{DFV MODEL:}\ \mathrm{Ln}\,\zeta = \mathrm{Ln}\ \mathrm{A} + (1/\mathbf{f}) \tag{1}$$

where A is a constant that depends on the size and shape of the monomer as well as the particular SBS-asphalt structure and **f** is free volume of the compound material and ζ is the monomeric coefficient of friction.

Defining a temperature shift factor aT as:

$$\mathrm{aT} = \mathrm{Gc}(\mathrm{T}, \mathrm{Cc})/\mathrm{Gc}(\mathrm{T}^*, \mathrm{Cc}) \tag{2}$$

$$\textbf{WLF MODEL:}\ \mathrm{Log\,aT} = \frac{\mathrm{C}_1(\mathrm{T} - \mathrm{T}^*)}{\mathrm{C}_2 + (\mathrm{T} - \mathrm{T}^*)} \tag{3}$$

with Cc = Constant mass fraction of SBS

$C_1 = 1/(2.303\,\mathbf{f})$; $C_2 = \mathbf{f}/\alpha$ $\quad T^*$ = Reference Temperature.
Gc = Dynamic Shear Moduli of the compound material (composite).
f = free volume in the compound material asphalt-SBS and α is the expansion coefficient of free volume of the compound material at constant Concentration, Cc.

On the other hand, Fujita and Kishimoto [6] (**FK**) showed how to obtain an equivalent equation for the shift factor aC, which involves concentration instead of temperature; this model is also based on the Doolittle's equation (Eq. 1) where the concentration dependence of the free volume is introduced. Fujita and Kishimoto suppose that the relationship between monomeric coefficient of friction ζ and free volume **f** is similar to that proposed by Doolittle.

Defining a concentration shift factor aC as:

$$\mathrm{aC} = \mathrm{Gc}(\mathrm{C}, \mathrm{Tc})/\mathrm{Gc}(\mathrm{C}^*, \mathrm{Tc}) \tag{4}$$

$$\textbf{FK MODEL:}\ \mathrm{Log\,aC} = \frac{\mathrm{C}_1{}'(\mathrm{C} - \mathrm{C}^*)}{\mathrm{C}_2{}' + (\mathrm{C} - \mathrm{C}^*)} \tag{5}$$

with Tc = Constant Temperature

$C_1{}' = 1/(2.303\,\mathbf{f})$; $C_2{}' = \mathbf{f}/\beta$ $\quad C^*$ = Reference Concentration.
Gc = Dynamic Shear Moduli of the compound material (composite).
f = free volume into the compound material asphalt-SBS and β is the expansion coefficient of free volume of the compound material at constant Temperature, Tc.

Now, if it is possible to state a explicit free volume **f** relation as Temperature-Concentration function, it would be also possible to obtain the α, β expansion coefficients as functions of Temperature and Concentration and calculate the shift factors aT and aC by using Eqs. 3 and 5.

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Percolation Considerations

The percolation model (**PERC**) has been extensively used to explain the behavior of systems with connectivity at large extent. Particularly, this model has been used to explain the mechanical behavior of asphalt-SBS composites [2–3], where a phase segregation takes place. These kind of composites show a phase inversion when a particular value of the SBS concentration is reached.

At low values of the SBS concentration, the mechanical moduli increase linearly with the SBS content; when the phase inversion concentration is reached the elastic moduli grow faster with the SBS content; this dependence is well modeled with an exponential function. In this sense, an extension of the percolation expression can be used to fit, simultaneously, both regimes of concentration; this is shown in Eq. 6:

PERC MODEL: Gc =

$$\mathrm{Gi}\,\frac{[(1-\delta \mathrm{C}^{\gamma})+(\delta \mathrm{C}^{\gamma})\mathrm{C}]+[(\delta \mathrm{C}^{\gamma})(1-(\delta \mathrm{C}^{\gamma})-\mathrm{C})](\mathrm{Gi}/\mathrm{Gm})}{\mathrm{C}+[(1-(\delta \mathrm{C}^{\gamma})-\mathrm{C})](\mathrm{Gi}/\mathrm{Gm})} \tag{6}$$

Gc = Dynamic Shear Moduli of the compound material (composite),
Gm = Dynamic Shear Moduli of pure Asphalt,
Gi = Dynamic Shear Moduli of pure SBS,
C = mass fraction of SBS,
δ, γ = Adjustment parameters of percolation model.

EXPERIMENTAL

Different composites of asphalt-SBS were prepared at: 0, 4, 14, 20, 25, 30, and 40% by mass of SBS. The asphalt was an AC-20 supplied by Pemex, México and the SBS was a Solprene 411 from Dynasol, México. The samples were prepared by mixing the asphalt at 180°C with the rubber with a high shear mixer. The rheological measurements were carried out using a Bholin rheometer to determine G', G'' and Gc at different temperatures from 40 to 80°C in a frequency intervals of 0.001 at 10 Hz. The dynamic shear moduli of the composite Gc were obtained from G' and G''. Gc is usually called complex modulus and the nomenclature used is G^*.

RESULTS AND DISCUSSION

The rheological behavior of the asphalt-SBS composites at three representative concentrations is shown in Figure 1 (0%), Figure 2

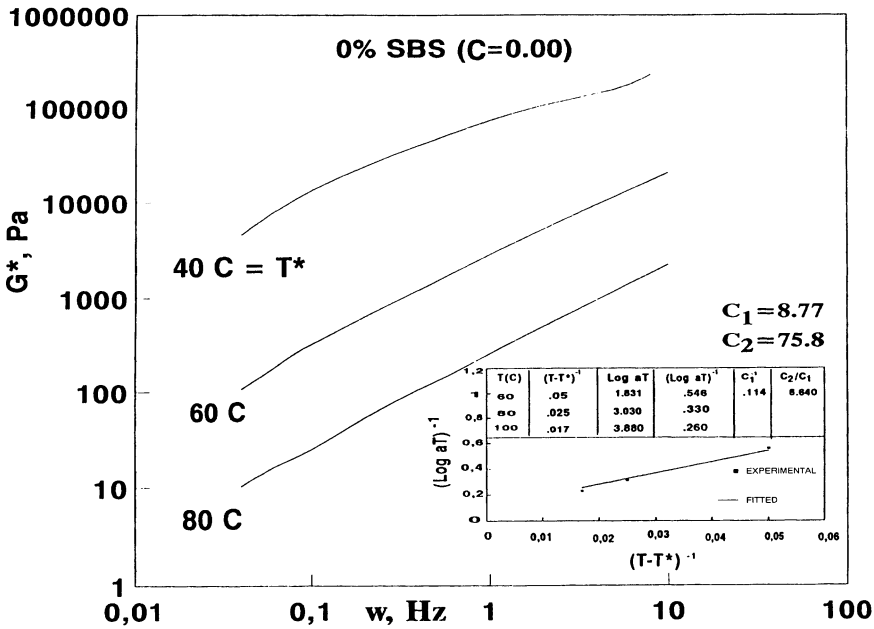

FIGURE 1 Dynamical Response G^* of the asphalt-SBS composite with 0% mass of SBS at three temperatures (40, 60, and 80° C).

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(4%), and Figure 3 (14%). The Complex Modulus G* or Dynamic Shear Moduli Gc of the compound material (composite) as a function of the frequency is shown at these concentrations varying the temperature in three levels (40, 60, and 80° C). The insert in each figure shows the Log $(aT)^{-1}$ as a function of $(T - T^*)^{-1}$, T^* being the reference temperature chosen as $T^* = 40°$ C. From each plot the values for C_1 and C_2 can be calculated and are shown in each figure. The same procedure was used for the remaining concentrations.

With this information it is possible to generate master curves as is shown in Figure 4, where there is a set of master curves for different concentrations. These master curves were obtained by shifting each curve from Figures 1–3 and the remaining concentrations. This set of master curves can be used to generate a super-master curve by a second shifting procedure. The insert in Figure 4 shows the Log $(aC)^{-1}$ as a function of $(C - C^*)^{-1}$, C^* being the reference concentration chosen as $C^* = 0.4$ (40% mass of SBS in the asphalt). In addition it is possible to observe the value of the two constants, $C_1' = -5.31$ and $C_2' = 0.786$; the super-master curve is shown in Figure 5 representing with circle symbols.

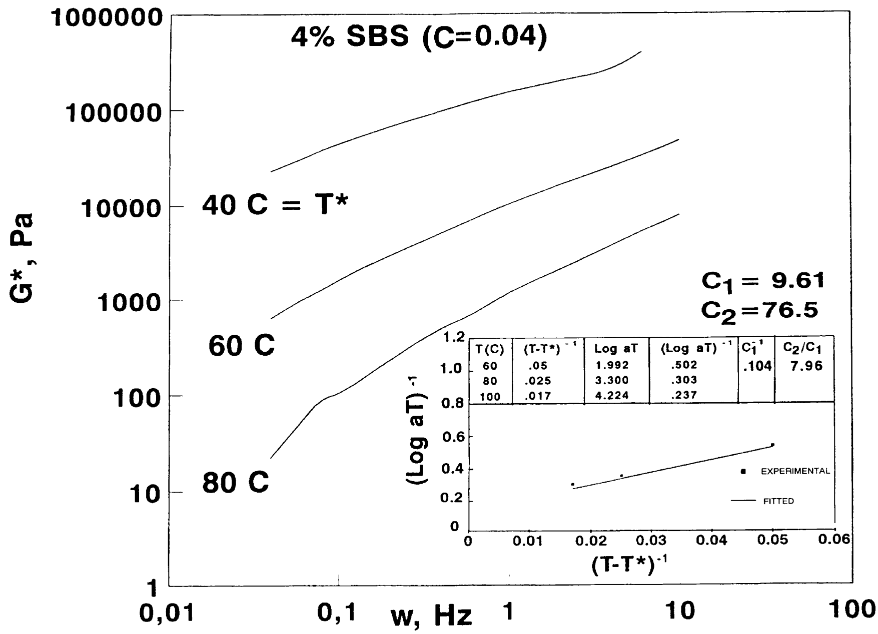

FIGURE 2 Dynamical Response G^* of the asphalt-SBS composite with 4% mass of SBS at three temperatures (40, 60, and 80° C).

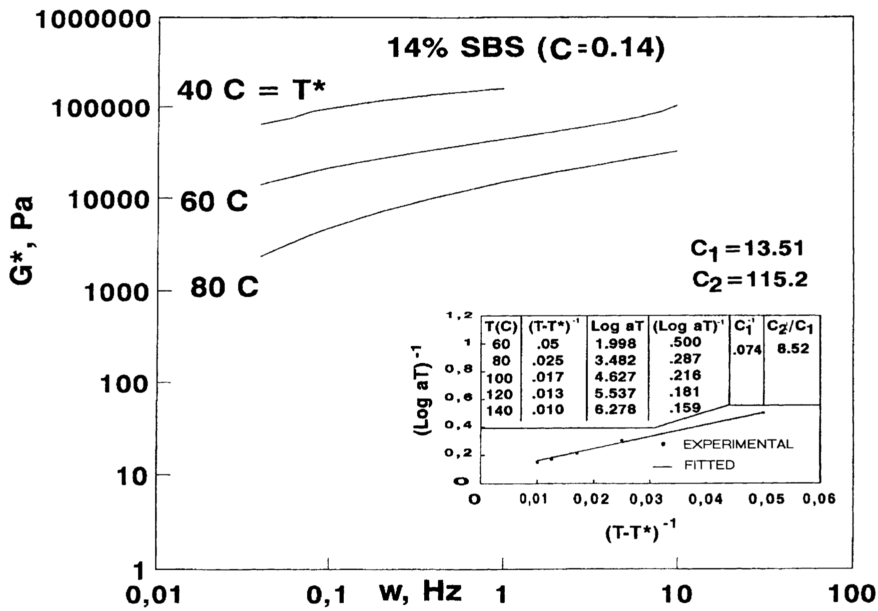

FIGURE 3 Dynamical Response G^* of the asphalt-SBS composite with 14% mass of SBS at three temperatures (40, 60, and 80° C).

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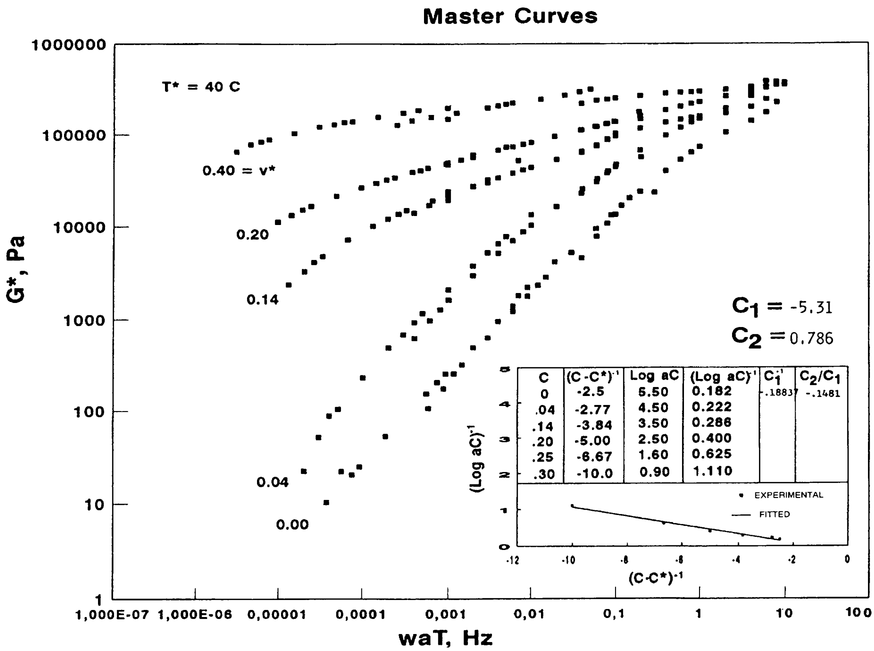

FIGURE 4 Set of master curves at different SBS concentrations.

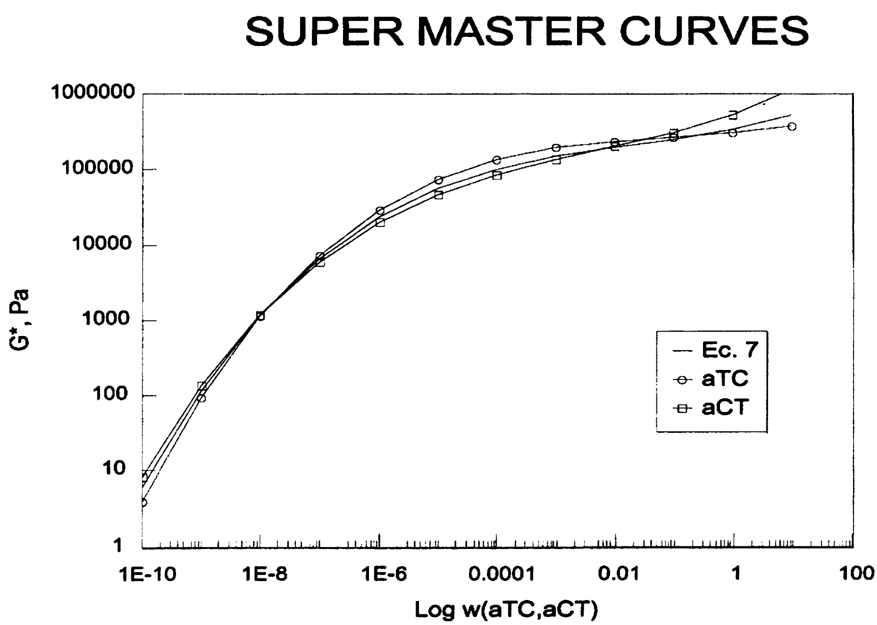

FIGURE 5 Super-master curves obtained by the way Log aTC and by the way Log aCT.

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So, this supermaster curve was obtained by shifting first along the temperature (Log aT) and second shifting along the concentration (Log aC). Therefore, the combined displacements are denoted by Log(aTC).

This is not the only way to obtain a super-master curve. Now the information is shown in other form. In Figures 6, 7, and 8 the complex modulus G^* is shown as a function of the frequency at the three temperatures under study, varying the concentration from 0.0 to 0.4. Each of these plots has an insert showing the correlation between Log $(aC)^{-1}$ and $(C - C^*)^{-1}$, where the reference concentration was chosen as $C^* = 0.4$ (40% mass of SBS in the asphalt). From each plots the values for C_1' and C_2' can be calculated and are shown in each figure.

With this information it is possible to generate master curves as is shown in Figure 9, where there is a set of master curves for different temperatures. These master curves were obtained by shifting each curve from Figures 6–8. This set of master curves can be used to generate a super-master curve by a second shifting procedure. The insert in Figure 9 shows the Log $(aT)^{-1}$ as a function of $(T - T^*)^{-1}$, T^* being the reference temperature chosen as $T^* = 40°$ C; in addition, it is possible to observe the value of the two constants, $C_1 = 11.1$ and

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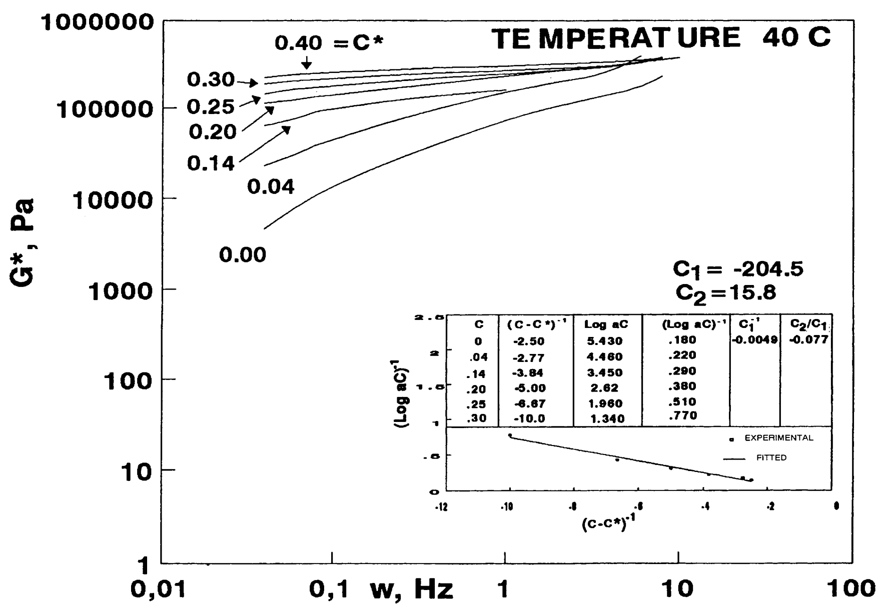

FIGURE 6 Dynamical Response G^* of asphalt-SBS composite at 40° C at different concentrations.

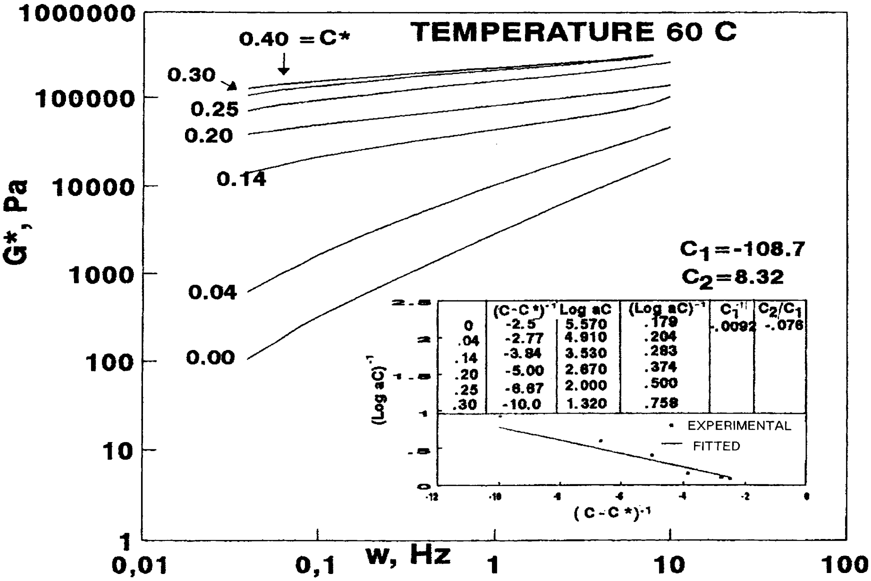

FIGURE 7 Dynamical Response G^* of asphalt-SBS composite at 60°C at different concentrations.

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$C_2 = 102.1$; the super-master curve is shown in Figure 10 represented by square symbols.

So, this super-master curve was obtained by shifting first along the concentration (Log aC) and second, shifting along the temperature (Log aT). The combined displacements are thus denoted by Log(aCT).

Figure 10 shows both super-master curves super-imposed one on top of the other. It is possible to observe a good agreement between them, showing that an extended correspondence principle can be stated: the equivalence is not only between time and temperature, but between time, temperature, and concentration. This extended correspondence principle is physically well understood because, using the Doolittle's equation, both the temperature and concentration modifies the viscosity and other rheological properties such as G^*. An analytical expression can be obtained to fit both super-master curves. This curve is also shown in Figure 10 as a continuous line.

$$\text{Log}\, G^* = 5.5347 + 0.1558(\text{Log}\, w) + 0.0322(\text{Log}\, w)^2 + 0.0064(\text{Log}\, w)^3 \quad (7)$$

In Figure 11a complete set of constants C_1' and C_2' and C_1' and C_2' is reported.

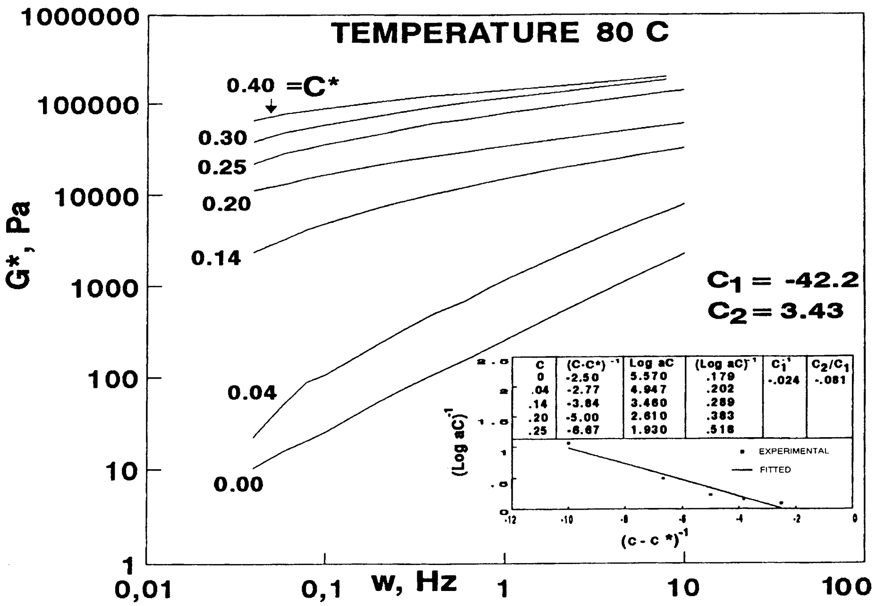

FIGURE 8 Dynamical Response G^* of asphalt-SBS composite at 80°C at different concentrations.

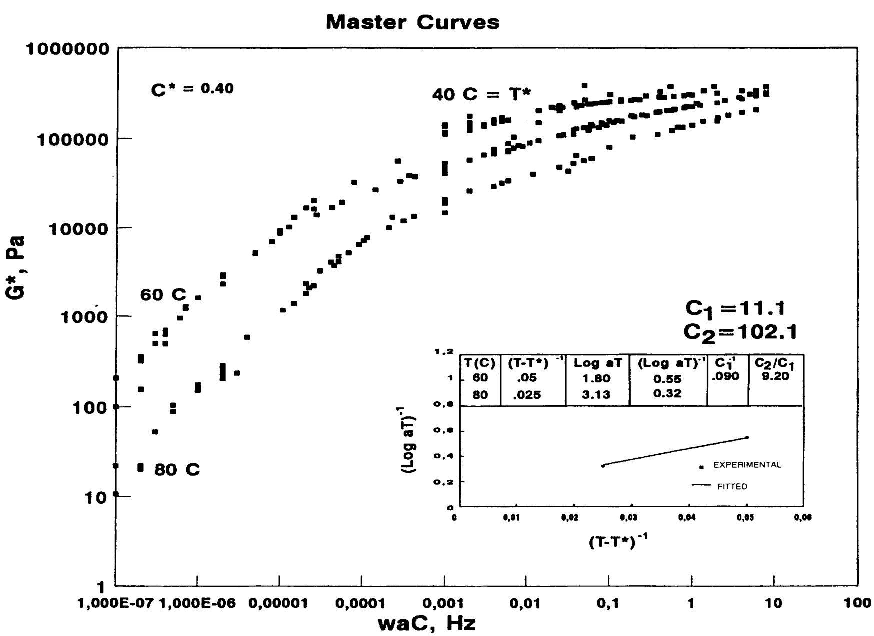

FIGURE 9 Set of master curves at different temperatures.

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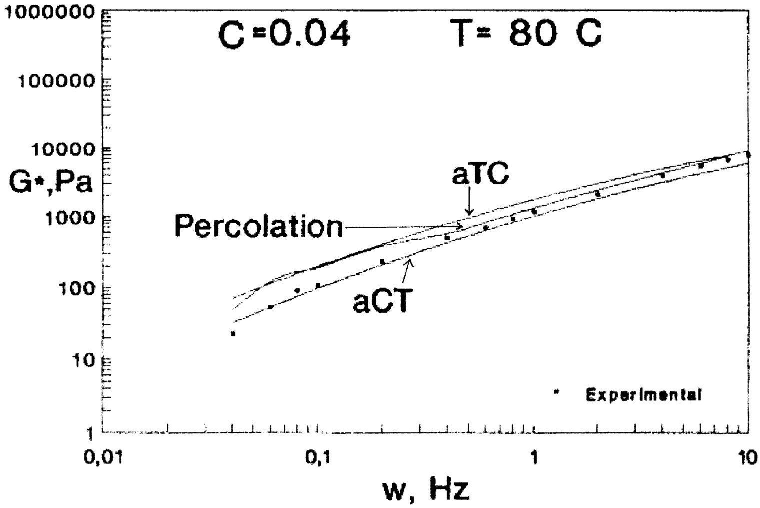

FIGURE 10 Prediction of Dynamical Response G^* of the asphalt-SBS composite with 4% mass of SBS using both models supported by Doolittle Equation and Perc Model at 80°C.

Shift Factors Data to Obtain Super Master Curve Temp-Conc.

Log aT

C	C_1	C_2	f	alpha
0	8.77	75.8	0.049	0.00064
0.04	9.61	76.5	0.045	0.00058
0.14	13.51	115.2	0.032	0.00028
0.2	17.86	157.3	0.024	0.00015
0.25	22.4	191.9	0.019	0.00009
0.3	24.55	211.5	0.017	0.00008
0.4	33.87	288.5	0.013	0.00005

$f = 1 / (2.303\ C_1)$ alpha $= f / C_2$

Log aTC

C_1	C_2
-5.31	0.786

Shift Factors Data to Obtain Super Master Curve Conc-Temp.

Log aC

T	C_1	C_2	f	beta
40	-204.5	15.8	0.0021	0.00013
60	-108.7	8.32	0.0039	0.00047
80	-42.2	3.43	0.01	0.00291

$f = / (2.303\ C_1)$ $\beta = f / C_2$

Log aCT

C_1	C_2
11.1	102.1

FIGURE 11 Shift Factors C_1, C_2, C_1', C_2', Log aTC, and Log aCT obtained from Figures 1–4 and 6–9.

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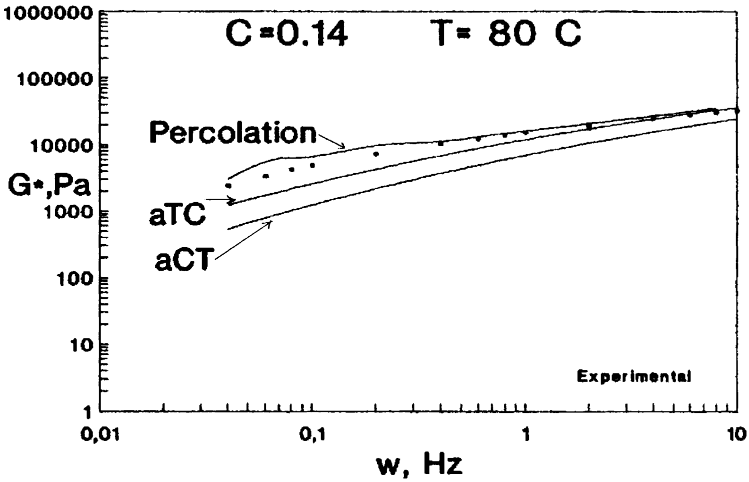

FIGURE 12 Prediction of Dynamical Response G^* of the asphalt-SBS composite with 14% mass of SBS using both models supported by Doolittle Equation and Perc Model at 80° C.

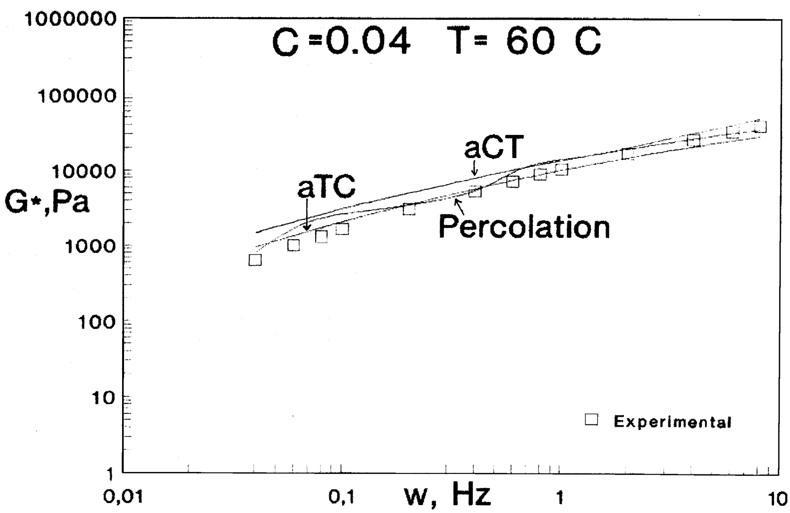

FIGURE 13 Prediction of Dynamical Response G^* of the asphalt-SBS composite with 4% mass of SBS using both models supported by Doolittle Equation and Perc Model at 60° C.

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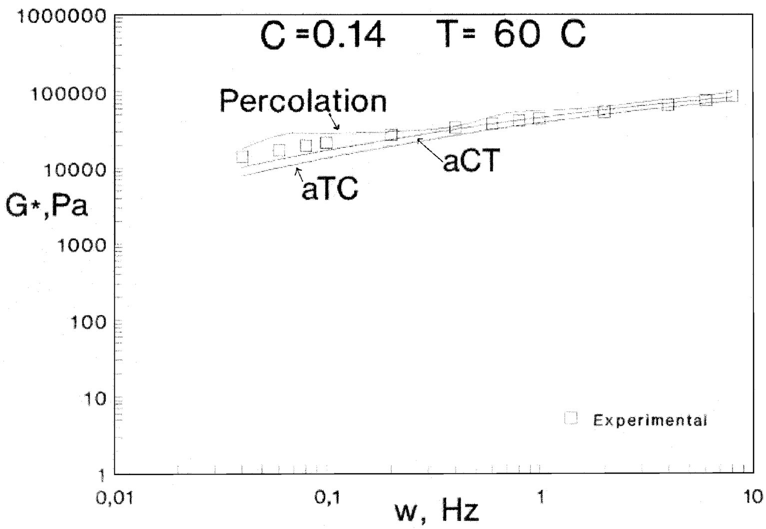

FIGURE 14 Prediction of Dynamical Response G^* of the asphalt-SBS composite with 14% mass of SBS using both models supported by Doolittle Equation and Perc Model at 60° C.

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The utility of the master and super-master curves is based on the capacity to predict, in this particular case, the dynamical behavior of an asphalt-SBS system once the temperature and the concentration are stated. In order to probe this utility, starting from both of the super-master curves, the dynamical behavior G* as a function of the frequency for specific values of temperature and concentration was obtained. Some of the results are shown in Figures 12 through 14. In addition, in these figures a fit using the percolation model also is showed (Eq. 6). As can be noticed the best agreement is obtained for the percolation model, but the prediction obtained from the super-master curves aTC and aCT is quite reasonable.

CONCLUSION

In this article the possibility to extend the time-temperature correspondence principle was analyzed. SBS modified asphalt at different concentrations and different temperatures were studied obtaining dynamical response G* or Gc. By using the WLF and FK models for time-temperature and time-concentration correspondence principles, it was possible to obtain the shift factors to generate the master curves and from them, two super-master curves: Log aCT and Log aTC. From these it was possible to predict the behavior of this kind of system once the temperature and concentration was specified. These results can be used as a basis to generate an extended correspondence principle for time, temperature, and concentration. Both dynamical models are supported by the Doolittle's equation where the concentration can be empirically introduced. In addition, it was possible to computer and predict the dynamical response by PERC model.

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