

# Relationships between Rheological Properties, Morphological Characteristics, and Composition of Bitumen–Styrene Butadiene Styrene Copolymers Mixes.

## II. A Thermodynamical Interpretation

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**ABSTRACT:** The variations of the dynamic mechanical properties (at 5 Hz) of bitumen–SBS mixes in the function of their composition (polymer content, bitumen composition) have been established. The relationships between the viscoelastic measurements and the morphological characteristics, previously determined, have been used to interpret these variations in terms of change of morphological characteristics (phase composition, phase content in the blends). Finally, a theoretical approach based on the thermodynamics of mixing is proposed to explain the relationships between the composition and the morphological characteristics. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 1609–1618, 1997

**Key words:** bitumen–SBS mixes; dynamic mechanical properties; viscoelastic measurements

### INTRODUCTION

This article attempts to rationalize the present knowledge on the mechanism that is effective during the mixing of bitumen and polymer. Bitumen is a complex chemical mixture that can be separated<sup>1</sup> in four broad chemical constituents: “saturates,” “aromatics,” “resins,” and “asphaltenes.” It is a colloidal system<sup>2</sup> in which the asphaltenes (the insoluble constituents with high molecular weight and polarity) form the dispersed phase, while the mixture of saturates and aromatics represents the continuous phase. The resins act as dispersing agents, stabilizing the system. Bitumen has been used for many decades as a waterproofing agent. However, it is viscoelastic in nature and suffers from some important limitations,

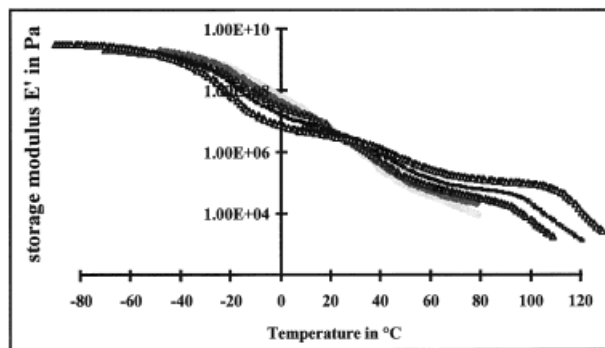
due to the high temperature susceptibility of its mechanical properties. With the development of macromolecules,<sup>3</sup> new bituminous materials have been proposed for such applications: bitumen–polymer blends. Indeed, by adding a polymer to a bitumen, the range of temperatures at which the roofing material is serviceable can be broadened. Nevertheless, one needs particular bitumens to manufacture such waterproofing materials showing a real improvement of their properties. These particular bitumens are called “compatible bitumens.” The compatibility of a bitumen with a polymer depends, not only on the generic composition (in terms of saturates, aromatics, resins, asphaltenes), but also on the polarity of the bitumen (chemical nature of these different generic groups, especially resins and asphaltenes). That is the reason why it is impossible to anticipate bitumen/polymer compatibility, knowing only its generic composition but having no information about its nature. Similarly, it is impossible to se-

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**Figure 1** Storage modulus vs. temperature of SBS/bitumen blends (frequency: 5 Hz). Influence of the polymer content:  $\blacklozenge$  100/130PX + 7% D1101;  $\blacklozenge$  100/130PX + 9% D1101;  $\blacktriangle$  100/130PX + 11% D1101;  $\blacksquare$  100/130PX + 15% D1101;  $\triangle$  100/130PX + 20% D1101.

lect bitumens considering only their mechanical “technological” properties (ring and ball test, penetration test at 25°C, penetration index) because two bitumens may have the same mechanical properties, but not the same generic composition and, hence, not the same solubility properties. Presently, the definition of the compatibility is based on different characteristics of the final bituminous product<sup>4,5</sup> such as mechanical properties, stability during storage at higher temperature, micromorphology, and stability during aging. Nevertheless, bitumens may be “compatible” but may not exhibit satisfactory properties. Thereby, the choice of bitumen for the preparation of efficient bitumen–polymer mixes is rather difficult. In this study, we propose a theoretical approach to explain the phenomena that are occurring when bitumen and polymer are mixed together.

## EXPERIMENTAL

### Materials

A styrene–butadiene–styrene (SBS) block copolymer was used—the Kraton (D1101) from Shell. The characteristics of this copolymer were reported previously.<sup>12</sup> Several petroleum derivatives were employed: two bitumens, the 100/130PX from Shell, and a short residue RC400 from Shell and two bituminous oils, an “aromatic extract” and a “deasphalted product” from Shell. The compositions of these four petroleum derivatives in terms of “saturates,” “aromatics,” “resins,” and “asphaltenes” were reported previously.<sup>12</sup>

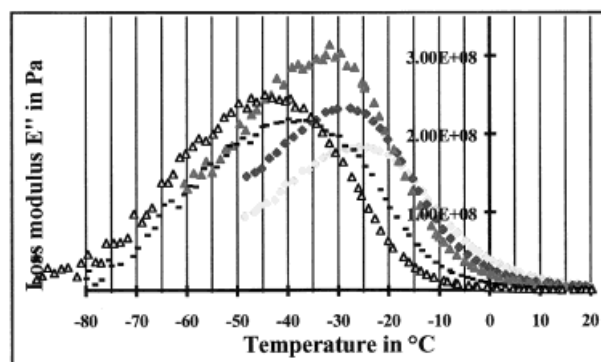
The short residue comes from a paraffinic crude oil from the Middle East. The bitumen 100/130PX is obtained by mixing: one of its components being the short residue 400. This bitumen has been chosen because of its particular “compatibility” with SBS at a mass content of about 12%. The “deasphalted product” comes from the deasphalting, using propane, of the short residue 400. The “aromatic extract” is obtained by extraction with furfural of a short residue. This is the only product in this study that does not come from the short residue 400. However, the crude oil, from which it stems, is also a paraffinic crude oil.

### Preparation of Blends

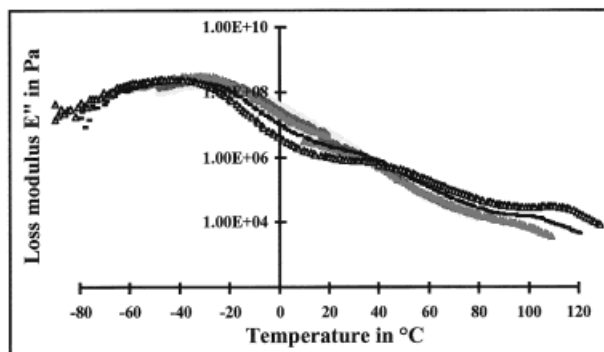
Petroleum derivatives and thermoplastic polymer were mixed by first heating the petroleum derivatives up to 180°C, in a round flask under constant stirring at 400 rpm, and then adding the polymer (in powder form), keeping the temperature at 180°C. The mixing time is about 50 min after the addition of the polymer. The blend was finally poured into small metal containers and cooled down to the ambient temperature.

### Dynamic Mechanical Thermal Analysis

Dynamic mechanical thermal analysis was performed with a Metravig viscoanalyzer (Metravig, Ecully, France). The results of these measurements are the isochrones of the storage modulus,  $E' = f(T)$ , the loss modulus,  $E'' = f(T)$ , and the loss angle,  $\delta = f(T)$ . All the curves presented in



**Figure 2** Loss modulus vs. temperature of SBS/bitumen blends (frequency: 5 Hz). Influence of the polymer content:  $\blacklozenge$  100/130PX + 7% D1101;  $\blacklozenge$  100/130PX + 9% D1101;  $\blacktriangle$  100/130PX + 11% D1101;  $\blacksquare$  100/130PX + 15% D1101;  $\triangle$  100/130PX + 20% D1101.



**Figure 3** Loss modulus vs. temperature of SBS/bitumen blends (frequency: 5 Hz). Influence of the polymer content:  $\blacklozenge$  100/130PX + 7% D1101;  $\blacklozenge$  100/130PX + 9% D1101;  $\blacktriangle$  100/130PX + 11% D1101;  $\blacksquare$  100/130PX + 15% D1101;  $\triangle$  100/130PX + 20% D1101.

this article were obtained with a temperature rate increase of 1°C/min.

## RESULTS AND DISCUSSION

The most common model for the description of the asphaltenes/resins interaction is the colloidal model.<sup>2</sup> However, recent studies<sup>6,7</sup> of asphaltenes' structure show that the basic molecule has a molecular weight that is of the same order of magnitude as are those of the other constituents of the bitumen. Furthermore, some authors<sup>8-11</sup> managed to determine the solubility parameters for all the bitumen constituents. This is the reason why this article proposes a theoretical approach based on the thermodynamics of mixing to understand the mechanisms that operate when bitumens and polymers are mixed together.

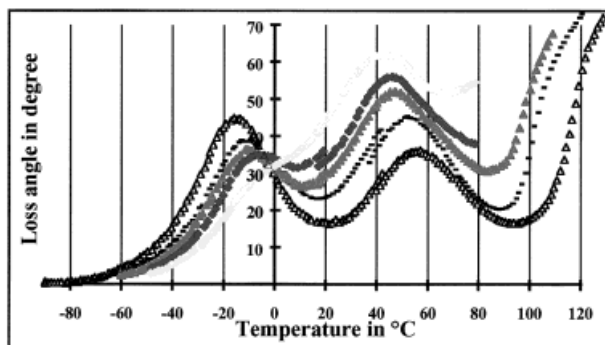
In the previous article,<sup>12</sup> we proposed an interpretation, in terms of the micromorphological characteristics (phases number, phases compositions, phase contents in the blend), of the results of the dynamic mechanical thermal analysis of bitumen/polymer mixes. Therefore, we first shortly recall the relationships that have been established to correlate the results of the dynamic mechanical thermal analysis with the micromorphological characteristics.

Because bitumen-SBS mixes are three-phase systems, it is possible to detect three transition phenomena by dynamic mechanical measurements and to select particular points, on the storage modulus  $E' = f(T)$ , loss modulus  $E'' = f(T)$ , and loss angle  $\delta = f(T)$  curves, to characterize

each of these three transitions. Consequently, the first transition is completely characterized by both the abscissa of the first peak of the loss modulus  $T_{E''_{\max}}$  and by the value of the first maximum of the loss angle  $\delta_{\max_1}$ . This first transition can be attributed to the swollen polybutadiene phase and its position and its amplitude depend on its composition and its content in the blend.  $T_{E''_{\max}}$  is an increasing function, on the one hand of the swelling ratio, and on the other hand of the transition temperature of the bituminous oil that swells this phase.  $\delta_{\max_1}$  is an increasing function of the content of this swollen polybutadiene phase in the blend. The second transition, which can be entirely defined by the coordinates of the second peak of the loss angle,  $T_{\delta_{\max_2}}$  and  $\delta_{\max_2}$ , is associated with the bitumen phase. Furthermore,  $T_{\delta_{\max_2}}$  and  $\delta_{\max_2}$  are increasing functions, respectively, of the asphaltenes content of this bitumen phase and of the content of the bitumen phase in the blend. The third transition can be attributed to the swollen polystyrene phase, but it is more complicated to exactly determine its amplitude and its position. Finally, we have also shown that the value of the second minimum of the loss angle  $\delta_{\min_2}$  is an increasing function of the bitumen phase/polymer phase ratio.

### Change in Viscoelastic and Morphological Characteristics of Bitumen-Polymer Mixes: Influence of the Polymer Content

An increase of the polymer content induces considerable changes in the bitumen-polymer blends. We shall first describe the changes of the



**Figure 4** Loss angle vs. temperature of SBS/bitumen blends (frequency: 5 Hz). Influence of the polymer content:  $\blacklozenge$  100/130PX + 7% D1101;  $\blacklozenge$  100/130PX + 9% D1101;  $\blacktriangle$  100/130PX + 11% D1101;  $\blacksquare$  100/130PX + 15% D1101;  $\triangle$  100/130PX + 20% D1101.

**Table I** Generic Compositions (Weight %) of Bitumens

Bitumen	Saturates	Aromatics	Resins	Asphaltenes
RC400	9.2	64.5	17.6	5.7
100/130PX	7.5	62	23	7.5
100/130PX + 10% aromatic extract	7	66	20.7	6.3
100/130PX + 20% deasphalted product	11.6	63.3	19.5	5.6

viscoelastic properties with such an evolution of the blend composition. Next, an interpretation of these changes in terms of morphological characteristics will be given on the basis of the results we recalled above.

When the polymer content increases, important changes of the storage modulus are observed. On the curve relating the storage modulus to the temperature, we notice, in Figure 1, a decrease of the abscissa of the first inflexion point and an increase of the abscissa of the inflexion point corresponding to the transition of the swollen polystyrene phase. It can also be seen that the three transitions become more and more apparent when increasing the polymer contents. Indeed, the blend with 20% of polymer shows three well-defined inflexion points and two plateau zones, whereas the blend with 9% exhibits only two inflexion points.

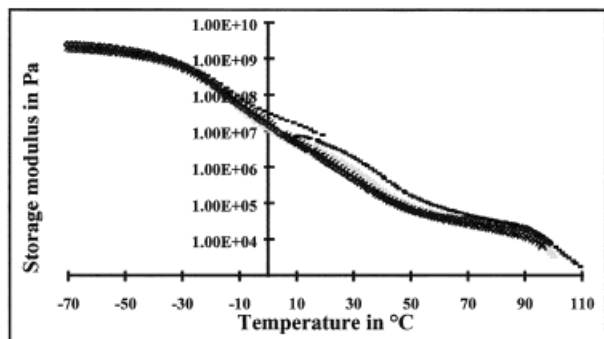
Concerning the loss modulus, the increase of the polymer contents induces a decrease of the temperature of the first maximum present on the curves below 0°C (Fig. 2). Furthermore, we also observe that the two maxima or pseudomaxima corresponding to the two other transitions become more and more visible with an augmentation of the polymer contents (Fig. 3). This last point can be correlated with the remark we just made concerning the inflexion points of the storage modulus.

So, the variation of the polymer content influences all three transitions. However, it is difficult to precisely quantify all of these evolutions without any additional information. That is the reason why it is interesting to note that precise points define the loss angle and may be used to characterize each transition allowing the comparison of the different blends. These particular points exhibit two coordinates: the abscissa, i.e., the temperature, which gives information about the phase composition; and the ordinate, i.e., the value of the loss angle, which gives information about the phase content in the blend. Figure 4,

where the three transition phenomena corresponding to the three phases are shown, indicates that the angle value at the first maximum increases when the polymer content increases and that the abscissa of this maximum decreases. Both from observations and from the results of our previous article, the polybutadiene content in the swollen polybutadiene phase appears to be an increasing function of the polymer content in the blend. In the same way, the asphaltenes content of the bitumen phase is an increasing function of the polymer content of the blend, because the abscissa of the second peak increases with an increase of the polymer content.

It is often difficult to determine the coordinates of the first minimum. Nevertheless, the decrease of the angle value at this minimum is real when the polymer content increases, and probably results from a better resolution of the two peaks corresponding to the first two transitions. Finally, the loss angle value at the second minimum decreases when the polymer content increases. This last fact and the evolution of the loss angle value in the whole temperature range, permit conclusion that an increase of the polymer content induces an increase of the (polymer phase/bitumen phase) ratio. These evolutions of the phase angle at high temperature when the polymer content increases are similar to those observed by Goodrich<sup>13</sup> on bitumen-polymer blends with another polymer (ethylene copolymer). In short, the increase of the polymer content in the bitumen-polymer mixes induces a decrease of the transition temperature of the swollen polybutadiene phase, an increase of the transition temperature of the bitumen phase, and an increase of the transition temperature of the swollen polystyrene phase.

From the point of view of the micromorphological characteristics, these changes indicate that an increase of the polymer content causes an increase of the (polymer phase/bitumen phase) ratio, an increase of the (polymer/bituminous constit-



**Figure 5** Storage modulus vs. temperature of SBS/bitumen blends (frequency: 5 Hz). Influence of the bitumen composition:  $\triangle$  100/130PX + 10% aromatic extract;  $\diamond$  100/130PX + 20% deasphalted product;  $\times$  RC 400;  $\blacksquare$  100/130PX.

uents) ratio in the polymer phases, and an increase of the asphaltenes content in the bitumen phase.

#### Change in Viscoelastic and Morphological Characteristics of Bitumen-Polymer Mixes: Influence of the Bitumen Composition

To evidence the influence of the generic composition of the bitumen on the rheological and morphological characteristics, we prepared several bitumen-SBS blends with 11% of linear SBS (D1101), and with bitumens of different compositions. The composition of these different bitumens are reported in Table I.

Comparing the blend prepared with 100/130PX to blends prepared with bitumens that are poorer in (resins + asphaltenes), one notices a significant evolution of the curves  $E' = f(T)$ . Indeed, for the blend prepared with 100/130PX, the curve exhibits two inflexion points, whereas for the other blends there is only one inflexion point (Fig. 5). Furthermore, for the blends prepared with these other bitumens, there is an important rubbery plateau between 50 and 90°C.

Looking at the curves  $E'' = f(T)$ , it is also possible to note a significant difference between the blend with 100/130PX and the other blends. Indeed, the pseudopeak, located near 30°C for the blend (100/130PX + 11% D1101) is no longer discernible for the three other blends (Fig. 6).

Moreover, for the blend prepared with (100/130PX + 20% deasphalted product), the first peak present on the curve  $E'' = f(T)$  is situated

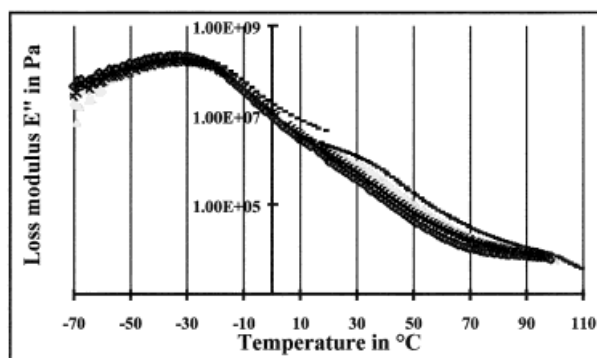
at a lower temperature than for the other blends (Fig. 7).

In Figure 8, the value of the first maximum of the loss angle is higher for the blend with lower (resins + asphaltenes) contents than for the blend with 100/130PX, and the abscissa of this peak is somewhat higher. It can also be observed that the abscissa of the second peak is lower, as well as is the value of the loss angle of the second minimum. Last, the value of the first minimum is higher for the three blends enriched in (saturates + aromatics) than for the blend with 100/130PX.

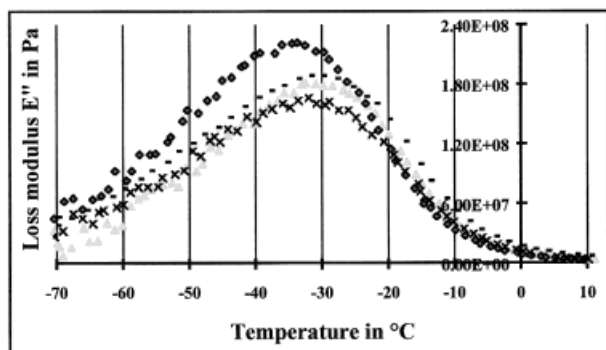
In short, the study of the influence of the bitumen composition on the viscoelastic characteristics shows that an addition of (saturates + aromatics) in a bitumen induces a broadening of the transition zone of the swollen polybutadiene phase because  $(T\delta_{\max_1} - T_{E''_{\max}})$  increases; a decrease of the mechanical transition temperature of the bitumen phase (Table II); and a decrease of the gap between the two first transitions, which is materialized by a lower resolution between the two peaks of the loss angle corresponding to these two transitions.

From the point of view of the micromorphological characteristics and taking into account the relationships between rheological and morphological characteristics, these observations show that an increase of (saturates + aromatics/resins + asphaltenes) ratio induces an increase of the swelling ratio of the polymer and a decrease of the asphaltenes content of the bitumen phase.

This increase of the swelling ratio of the polymer with an increase of the (saturates + aromatics/resins + asphaltenes) ratio is also proved by



**Figure 6** Loss modulus vs. temperature of SBS/bitumen blends (frequency: 5 Hz). Influence of the bitumen composition:  $\triangle$  100/130PX + 10% aromatic extract;  $\diamond$  100/130PX + 20% deasphalted product;  $\times$  RC 400;  $\blacksquare$  100/130PX.



**Figure 7** Loss modulus vs. temperature of SBS/bitumen blends (frequency: 5 Hz). Influence of the bitumen composition:  $\triangle$  100/130PX + 10% aromatic extract;  $\blacktriangle$  100/130PX + 20% deasphalted product;  $\times$  RC 400;  $\blacksquare$  100/130PX.

the evolution of the value of the second minimum of the loss angle, which had not been mentioned yet. Indeed, this value of the second minimum of the loss angle is clearly lower for the blend prepared with such bitumens than for the blend prepared only with 100/130PX.

Notice that the magnitude of the changes observed will depend not only on the magnitude of the modification of the (saturates + aromatics/resins + asphaltenes) ratio, but also on the nature of the generic fractions of the bitumen. This is the reason why it is not possible to compare the three blends that we compared to the (100/130PX + 11% D1101) blend. Indeed, the nature of the aromatic extract is not exactly the same than for the other petroleum derivatives used here.

### Thermodynamic Interpretation

When two homopolymers are mixed together, the variation in the free energy of mixing is given<sup>14</sup> by:

$$\Delta G^M = V^M(\delta_A - \delta_B)^2\Phi_A\Phi_B + RT\left(\frac{\Phi_A}{r_A} \ln \Phi_A + \frac{\Phi_B}{r_B} \ln \Phi_B\right)$$

where  $V^M$  is the molar volume of the mixture,  $\Phi_A$  and  $\Phi_B$  are the volume fractions,  $\delta_A$  and  $\delta_B$  are the solubility parameters, and  $r_A$  and  $r_B$  the polymer-

ization degrees of the two polymers. This free energy variation must be negative to observe the miscibility of the two polymers. Hence, the miscibility is promoted when  $\delta_A$  and  $\delta_B$  are close, and  $r_A$  and  $r_B$  are low. In the case of the polyphasic systems, the partial miscibility and the compatibility still depend on these factors, but the thermodynamic equilibrium can be described by the equality of the chemical potential of each constituent in each phase

$$\mu_i^{\phi_j} = \mu_i^{\phi_k}$$

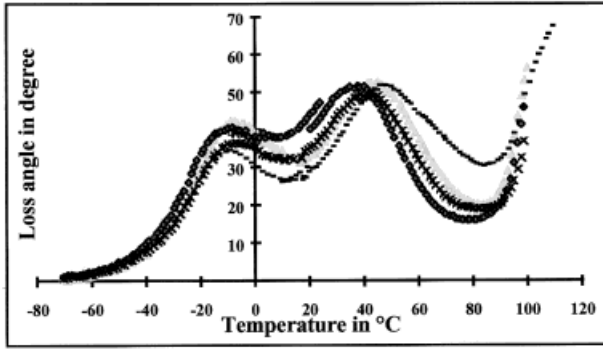
These concepts will now be used to explain what happens when a bitumen and a polymer are mixed together, keeping in mind that the use of this theory for bitumen–polymer blends presents some difficulties because quantities such as the polymerization degree, for instance, cannot be defined for bituminous constituents. Nevertheless, the polymerization degree can be replaced by the molecular weight because in the statistical thermodynamics it is only employed to describe the length of the macromolecules.<sup>15–17</sup> Furthermore, the theory supposes some assumptions that are not necessarily respected in this study. In spite of all these restrictions, the application of the theory will allow interpretation of the relationships between composition, morphology, and mechanical properties, as we will show.

### Polyphasic Bitumen–SBS Mixes

The “solubility parameters” of the constituents of the bitumen–polymer mixes are reported in Table III. Comparing the “solubility parameters” of the different constituents of the bitumen–SBS mixes, it is possible to qualitatively analyze the composition of each phase of the blend. Thus, the polystyrene phase can be composed of not only the polystyrene sequences but also of aromatics, resins,

**Table II** Transition Temperature of the Bitumen Phase

Bitumen	$T_\delta$ Bitumen Phase (°C)
100/130PX	47 $\pm$ 2
100/130PX + 10% aromatic extract	43 $\pm$ 2
100/130PX + 20% deasphalted product	37.5 $\pm$ 2
RC400	41.5 $\pm$ 2



**Figure 8** Loss angle vs. temperature of SBS/bitumen blends (frequency: 5 Hz). Influence of the bitumen composition:  $\triangle$  100/130PX + 10% aromatic extract;  $\blacktriangle$  100/130PX + 20% deasphalted product;  $\times$  RC 400;  $\blacksquare$  100/130PX.

and asphaltenes. If they are enough peptized ( $\delta$  close to 19.6), the polybutadiene phase can be swollen by saturates, aromatics, and resins, and the bitumen phase will be constituted of the four broad chemical constituents mentioned before. Further, the concentration of each constituent in each phase will be dictated by the thermodynamical equilibrium. Indeed:

$$\mu_i^{\varphi_{PS}} = \mu_i^{\varphi_{PB}} = \mu_i^{\varphi_B} \quad (1)$$

with  $\varphi_{PS}$ ,  $\varphi_{PB}$ ,  $\varphi_B$  representing, respectively, the polystyrene phase, the polybutadiene phase, and the bitumen phase.

For each constituent  $i$  in phase  $\varphi_j$ :

$$\mu_i^{\varphi_j} = \mu_i^{\varphi_j} + RT \ln x_i^{\varphi_j} \gamma_i^{\varphi_j}$$

with

$$x_i^{\varphi_j}$$

and

$$\gamma_i^{\varphi_j}$$

respectively, the molar fraction and the activity coefficient of the constituent  $i$  in phase  $\varphi_j$ .

$$\begin{aligned} \mu_i^{\varphi_{PS}} + RT \ln x_i^{\varphi_{PS}} \gamma_i^{\varphi_{PS}} &= \mu_i^{\varphi_{PB}} + RT \ln x_i^{\varphi_{PB}} \gamma_i^{\varphi_{PB}} \\ &= \mu_i^{\varphi_B} + RT \ln x_i^{\varphi_B} \gamma_i^{\varphi_B}. \end{aligned} \quad (2)$$

For an easier understanding, the system can be simplified by considering that it is a two-phase

system with a polymer phase and a bitumen phase. Furthermore, the bitumen will be considered like a two constituents system called, respectively, B and NA. B is the part of bitumen that is incompatible with the polymer P, and NA (nonasphaltene) is the part that is compatible with B and P. So, bitumen-SBS mixes can be modeled as systems with two phases, B and P, both swollen with the component NA.

The thermodynamic equilibrium is then given by:

$$\mu_{NA}^{\varphi_P} = \mu_{NA}^{\varphi_B} \quad (3)$$

or

$$\begin{aligned} \mu_{NA}^{0\varphi_P} + RT \ln x_{NA}^{\varphi_P} \gamma_{NA}^{\varphi_P} \\ = \mu_{NA}^{0\varphi_B} + RT \ln x_{NA}^{\varphi_B} \gamma_{NA}^{\varphi_B} \end{aligned} \quad (4)$$

with

$$x_{NA}^{\varphi_P} = \frac{n_{NA}^{\varphi_P}}{n_P + n_{NA}^{\varphi_P}} \quad (5)$$

and

$$x_{NA}^{\varphi_B} = \frac{n_{NA}^{\varphi_B}}{n_B + n_{NA}^{\varphi_B}} \quad (5')$$

where

$$-x_{NA}^{\varphi_P} \text{ and } x_{NA}^{\varphi_B}$$

are the molar fractions of NA, respectively, of the polymer phase and bitumen phase, and express, in other respects, the swelling ratio of each of those with the constituent NA— $n_P$  is the mol number of polymer in the mix,  $n_B$  is the mol num-

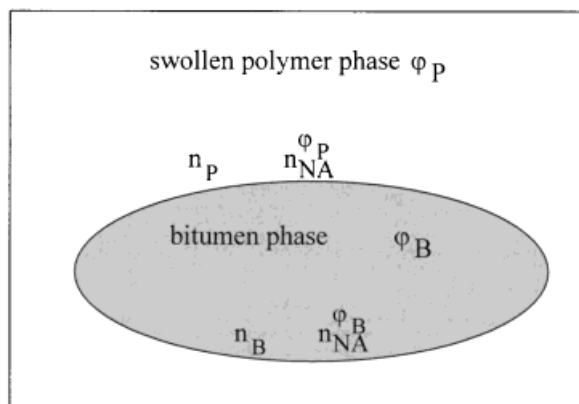
**Table III** “Solubility Parameters” of the Constituents of the Bitumen-SBS Mixes

Constituents	$\delta$ in (MPa) <sup>0.5</sup>		
Polybutadiene	16.7 <sup>a</sup>	16.6–17.6 <sup>b</sup>	16.6 <sup>c</sup>
Polystyrene	18.6 <sup>a</sup>	17.4–19 <sup>b</sup>	19.4 <sup>c</sup>
Saturates		$\approx 14.3^8$	
Aromatics		$\approx 17.8^8$	
Resins		$\approx 19.4$ to $20.1^8$	
Asphaltenes		$\approx 19.6$ to $26^{6,9,10}$	

<sup>a</sup> Information from Shell.

<sup>b</sup> Values obtained experimentally.<sup>18</sup>

<sup>c</sup> Values obtained by calculation.<sup>18</sup>



**Figure 9** Schematic representation of the modelization of the bitumen/SBS mixes by a system composed of three constituents and two phases.

ber of B in the mix,  $n_{NA}^{\phi_P}$  is the mol number of NA in the polymer phase,  $n_{NA}^{\phi_B}$  is the mol number of NA in the bitumen phase.

Figure 9 schematically represents our modelization of the bitumen/polymer system.

Notice here that the constituents B and NA, which are bituminous products, cannot readily be defined by mol numbers, due to the high molecular weight polydispersity. Nevertheless, one may, from their average molecular mass, define an apparent mol number. This justifies our theoretical approach.

Expression (4) is equivalent to expression (6), which expresses that the ratio of the molar fractions of NA (and so of the swelling ratio) in each bitumen and polymer phases is constant (depending only on temperature  $T$ ).

$$\frac{x_{NA}^{\phi_B}}{x_{NA}^{\phi_P}} = C(T). \quad (6)$$

Having besides, the expressions relating these swelling ratios to the blends' compositions (5 and 5'), a prediction both of the variations of the composition of each phase and phase content in the blend, in function of the blend composition, becomes possible. We shall now use this thermodynamic interpretation to explain the relationships between composition and viscoelastic characteristics of bitumen-polymer mixes.

#### Application of the Thermodynamic Interpretation to Explain the Variation of the Viscoelastic Characteristics of Bitumen-SBS Mixes with a Variation of the Polymer Content

As the polymer content increases,  $n_P$  increases ( $n_{NA}$  and  $n_B$  being constant). So, the two molar

fractions of NA decrease, inducing a decrease of the swelling ratios of the two phases with the constituents NA. This allows conclusion that the polymer phase/bitumen phase ratio is an increasing function of the polymer content. What is the influence of such an evolution on the viscoelastic characteristics of the mixes?

#### Polymer Phase

As the polymer content increases, the swelling ratio of the polymer phase decreases, so the mechanical characteristics of the two phases of this polymer (SBS) may change. Taking into account relationships between morphological characteristics and viscoelastic measurements, the decrease of bituminous constituents content in the polybutadiene phase should induce a decrease of the transition temperature of this phase. It is exactly the experimental result we observe when the polymer content increases (Fig. 2). Indeed,  $T_{E^{\max}}$ , which is the characteristic temperature of the polydiene transition, decreases with an increase of the polymer content. For the same reason, the transition temperature of the swollen polystyrene phase should increase with an increase of the polymer content. It is what we observe on the curves giving the viscoelastic characteristic vs. the temperature (Figs. 1, 3, and 4).

#### Bitumen Phase

As the polymer content increases, the B/NA ratio of the bitumen phase increases. The component B is rich in asphaltenes, due to its definition. So, this increase of the polymer content induces an increase of the asphaltenes content of the bitumen phase. Furthermore, taking into account the relationships between viscoelastic and morphological characteristics, such a variation of the bitumen phase composition should induce an increase of the abscissa of the peak of the loss angle corresponding to the transition of this bitumen phase. Again, this is the experimental result as seen on Figure 4.

#### Totally of the Mix

Still taking into account the relationships between viscoelastic and morphological characteristics, the increase of the (polymer phase/bitumen phase) ratio should be characterized by a decrease of the value of the second minimum of the loss angle. Our thermodynamic interpretation fore-



casts an increase of this ratio with an increase of the polymer content. So, experimentally, our modelization and the thermodynamic interpretation are in good agreement because the value of the second minimum of the loss angle decreases as the polymer content increases (Fig. 4).

#### Application of the Thermodynamic Interpretation to Explain the Variation of the Viscoelastic Characteristics of Bitumen-SBS Mixes with a Variation of the Bitumen Composition

By definition, B is primarily composed of resins and asphaltenes, whereas NA corresponds rather to the two other generic families of the bitumen, the saturates and the aromatics. When the (saturates + aromatics/resins + asphaltenes) ratios of the bitumen evolve, the NA/B ratios vary in the same way. But

$$\left(\frac{\partial x_{NA}^{\varphi_P}}{\partial n_{NA}^{\varphi_P}}\right)_{n_P} > 0.$$

So, when  $n_{NA}$  increase,  $n_{NA}^{\varphi_P}$  increases, too. Indeed, if  $n_{NA}^{\varphi_P}$  decreases, then  $n_{NA}^{\varphi_B}$  increases. This is impossible according to relation (6), because  $x_{NA}^{\varphi_P}$  would decrease, whereas  $x_{NA}^{\varphi_B}$  would increase. Thereby, when (saturates + aromatics/resins + asphaltenes) ratios increase, the swelling of each bitumen phase and polymer phase increases; that means that the (polymer phase/bitumen phase) ratio increases also.

#### Polymer Phase

As discussed previously, taking into account the solubility parameter of polybutadiene and of some bitumen constituents, the swollen polybutadiene phase should be composed, for the main part, of saturates, aromatics, and resins. So, when the (saturates + aromatics/resins + asphaltenes) ratios of the initial bitumen increase, the composition of the constituent NA that swells the polybutadiene will evolve in the same way. This evolution will inevitably have a consequence on the mechanical properties of this phase. For instance, a decrease of the resins (or asphaltenes) content in bitumen induces a decrease of the transition temperature (19). In the same way, at constant aromatics/resins ratio, an increase of the saturates content can lead to a decrease of this transition temperature. Last, when the saturates/res-

ins ratio is constant and when the only variation of the composition is an increase of the aromatics content, it becomes impossible to conclude. In fact, such an evolution induces a decrease of the resins content, and one may expect that the transition temperature will increase. However, at the same time, the saturates concentration decreases: a situation that can induce an opposite evolution of this transition temperature. In the cases we analyzed, the contribution of the variation of the swelling ratio, which can have a bad influence on the transition temperature of the polybutadiene phase (an increase), seems to be balanced by an evolution of the transition temperature of the constituent NA that swells the polymer. Going on with our reasoning, the great increase of the saturates content in the bitumen, compared with the asphaltenes content, like for the blend with (100/130PX + 20% deasphalted product), seems to induce a real decrease of the transition temperature of the constituent NA, which swells polybutadiene because, in spite of a most important swelling ratio, the transition temperature of this swollen polybutadiene phase is lower than the one of the blend prepared with 100/130PX.

#### Bitumen Phase

When the NA/B ratio of bitumen increases, the swelling ratio of B with the constituent NA increases. This induces a decrease of the (saturates + aromatics/resins + asphaltenes) ratio, which can result in a decrease of the mechanical transition temperature of this bitumen phase. It is exactly what the experiments show. Notice here, that taking into account the relationships between rheological and morphological characteristics, an increase of the (polymer phase/bitumen phase) ratio can have the same result. This is actually the case. So, this evolution of the abscissa of the second peak of the loss angle can be due to those phenomena, that is to say:

- an increase of the  $\frac{\text{saturates} + \text{aromatics}}{\text{resins} + \text{asphaltenes}}$  ratio,
- an increase of the  $\frac{\text{polymer phase}}{\text{bitumen phase}}$  ratio.

#### Totality of the Blend

An increase of the (saturates + aromatics/resins + asphaltenes) ratio induces, taking into account our thermodynamic interpretation, an increase of

the (polymer phase/bitumen phase) ratio. The change of the value of the second minimum of the loss angle we considered as a decreasing function of this ratio (relationships between rheological and morphological characteristics) is in good agreement with the experimental results. This is also the case for the values of the loss angle in the total studied temperature range.

We may recall that the changes of the viscoelastic characteristics of the bitumen–SBS mixes depend not only on the (saturates + aromatics/resins + asphaltenes) ratio but also on the nature of the different generic families of bitumen. This is the reason why the analysis we just presented is only correct when we start from a particular bitumen and modify its composition by adding bitumen constituents. So, it is possible to compare the blend prepared with 100/130PX to the three other blends, but it is impossible to compare between themselves these three last blends because of their slight differences in nature.

## CONCLUSION

The bitumen–SBS blends, which are three-phase systems, exhibit three transition phenomena evidenced by dynamic mechanical analysis, which can be attributed to each of these three phases. In a previous article, relationships between such viscoelastic measurements and morphological characteristics (number of phases, phase composition, phase content in the blend) were established. In this article, this result has been used to interpret the change of morphological characteristics with the variation of the composition of the blends. We then proposed a theoretical interpretation based on the thermodynamics of mixing to explain such changes of the morphological characteristics. This interpretation is open to criticism because of the nonpolymeric nature of bitumen constituents. Nevertheless, it gives an interesting insight in the bitumen–polymer mixes, which

allows us to understand the evolution of such blends with the variation of their composition.

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