

Relationships between Rheological Properties, Morphological Characteristics, and Composition of Bitumen–Styrene Butadiene Styrene Copolymers Mixes. I. A Three-Phase System

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ABSTRACT: The variation, with temperature, of the dynamic mechanical properties (at 5 Hz) of bitumen–SBS mixes has been established. Typical features of the storage modulus, the loss modulus, and the loss angle variations with temperature could be attributed to the different phases that compose the mix. Finally, relationships between viscoelastic measurements and morphological characteristics (number of phases, phase composition, and phase content in the blend) have been proposed. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 1595–1607, 1997

Key words: bitumen; styrene–butadiene copolymers; phases; rheology; morphology

INTRODUCTION

Bitumen has been used for centuries as a waterproofing agent. It behaves like a viscoelastic material with limited stress-resistance properties, brittleness at low temperature, excessive fluidity at working temperatures, and finally aging, followed by hardening and viscosity increases. Nowadays, one often prefers new types of bituminous materials for waterproofing applications: these are bitumen–polymer blends. Indeed, the addition for such type of applications of various polymers and, in particular, some thermoplastic elastomers, in bitumen gives materials with better rheological properties than bitumen alone.^{1–3} In this study, we describe the rheological behavior of a particular type of bitumen–polymer blends: the bitumen block copolymer styrene–butadiene–styrene (SBS) system. This article proposes a modeliza-

tion that allows interpretation of the dynamic mechanical measurements in terms of morphological characteristics (number of phases of the system, compositions of the different phases, contents of the different phases in the blend).

Bitumen are complex chemical mixtures that can be separated, according to their solubility in organic media, into four broad chemical families of constituents⁴ called, “saturates,” “aromatics,” “resins,” and “asphaltenes.” These components are more or less compatible with the two sequences, polystyrene and polybutadiene, of SBS. So, bitumen–SBS blends may be considered as multiphase systems⁵ with: one bitumen phase, whose composition is different from that of the initial bitumen, and one SBS phase, swollen with the constituents of the asphalt, which are compatible with one of the two sequences of the copolymer. Within this SBS phase, there are two additional phases—swollen polybutadiene and swollen polystyrene. Therefore, such a system is a three-phase system. However, it is not the only one that we can obtain. Indeed, it is also possible to prepare blends without a bitumen phase or

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Table I Polymer Characteristics

	Kraton D 1101	Kraton D 1184
Styrene/butadiene ratio	29/71	30/70
Molecular weight	104,000	208,000
Polydispersity	≈ 1,1	≈ 1,3
Molecular structure	linear	branched
Solid state structure	lamellar	?

even without a polymer phase when the polymer is dissolved in bitumen. Blends that have the best properties for waterproofing applications are those exhibiting a three-phase morphology.

Furthermore, such three-phases systems present, when examined by dynamic mechanical thermal analysis, three transition phenomena. Hence, it may be interesting to find relationships between morphological characteristics (phase compositions, number of phases, importance of each phase) and viscoelastic characteristics, i.e., singular points that we are going to define in this article.

EXPERIMENTAL

Materials

Two styrene block copolymers were used: Kraton D1101 and D1184, which are both two styrene-butadiene-styrene copolymers (SBS). These two copolymers differ in molecular weight and in molecular structure, as shown in Table I. Furthermore, four petroleum products were used: two bitumens, the 100/130PX from Shell and “asphaltenes from propane,” and two bituminous oils, an “aromatic extract” and a “deasphalted product.” The compositions of these four petroleum derivatives, in terms of “saturates,” “aromatics,” “resins,” and “asphaltenes,” are reported in Table II.

Preparation of Blends

Petroleum products and thermoplastic polymers were mixed by first heating the petroleum prod-

ucts 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 Analyses and DSC

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

Differential scanning calorimetry measurements were performed with a Mettler Thermoanalyser TA 4000. The thermal data were taken from the DSC traces that were scanned at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Viscoelastic Characteristics of Bitumen-SBS Blends

Dynamic mechanical thermal analysis (at a frequency of 5 Hz and from -70 to 120°C) points to three transition phenomena for bitumen-SBS blends (Fig. 1): (1) a transition below 0°C, which is materialized by an inflexion point on the curve $E' = f(T)$, a maximum on the curve $E'' = f(T)$, and a peak on the curve $\delta = f(T)$; (2) a second transition, centered near 40°C, with an inflexion point on the curve $E' = f(T)$, a pseudopoint on the curve $E'' = f(T)$, and a maximum on the curve $\delta = f(T)$; and (3) a third transition near 100°C, which is evidenced by a drop of the storage modulus $E' = f(T)$, a peak or a pseudopoint on the loss modulus curve $E'' = f(T)$, and an increase of the loss angle (Fig. 1).

Consequently, we may define or choose several particular points from these different curves re-

Table II Petroleum Derivatives Compositions (wt %)

	Saturates	Aromatics	Resins	Asphaltenes
100/130PX	7.5	62	23	7.5
Asphaltenes from propane	3.6	64.1	22.6	9.7
Aromatic extract	10.3	78.9	10.8	—
Deasphalted product	25.9	68.4	5.7	—

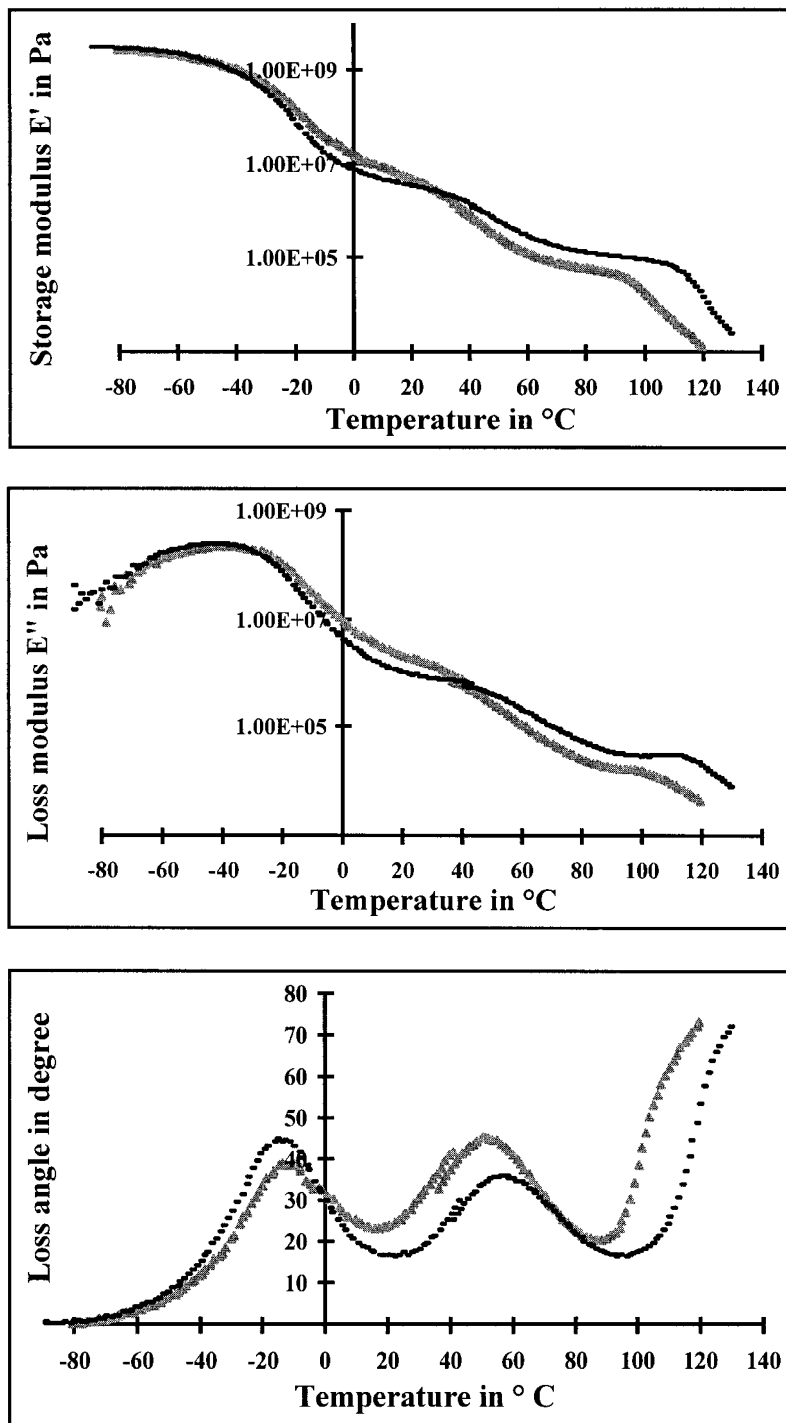


Figure 1 (a) Storage modulus vs. temperature of SBS/bitumen blends (frequency: 5 Hz): \blacktriangle 100/130PX + 15% D1101; \blacksquare 100/130PX + 20% D1101. (b) Loss modulus vs. temperature of SBS/bitumen blends (frequency: 5 Hz): \blacktriangle 100/130PX + 15% D1101; \blacksquare 100/130PX + 20% d1101. (c) Loss angle vs. temperature for SBS/bitumen blends (frequency: 5 Hz): \blacktriangle 100/130PX + 15% D1101; \blacksquare 100/130PX + 20% D1101.

lating storage modulus, loss modulus, and loss angle to the temperature variation for comparison of different bitumen-polymer blends.

Thus, the first transition is defined by both the temperature of the first maximum of the loss modulus, which is called $T_{E''_{max}}$, and the coordinates

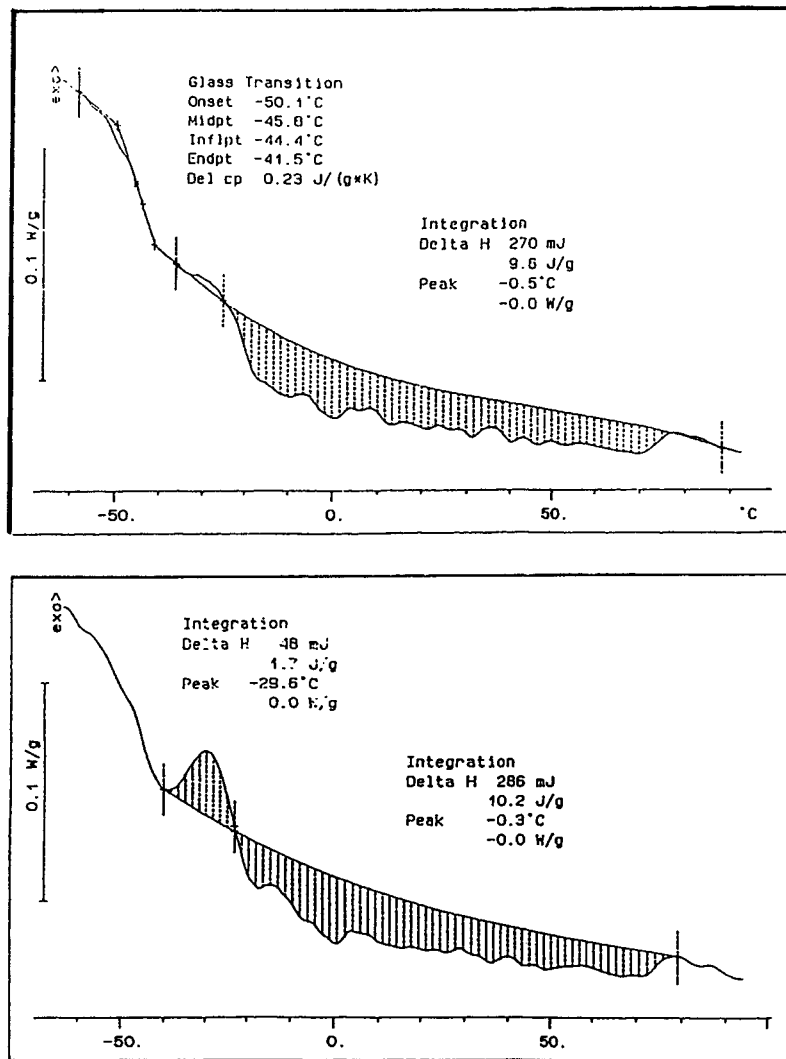


Figure 2 (a) Thermogram (DSC) of deasphalted product, obtained during the increase of temperature, after a decrease from 25 to -70°C at a rate of 10°C/min including an isothermal step of 10 min at the crystallization temperature. (b) Thermogram (DSC) of deasphalted product, obtained during the increase of temperature after a decrease from 25 to -70°C at a rate of 10°C/min without step at the crystallization temperature.

of the first peak of the loss angle, $T\delta_{max_1}$ and δ_{max_1} . The second transition can be entirely characterized by the coordinates of the second peak of the loss angle, $T\delta_{max_2}$ and δ_{max_2} . Finally, it is more difficult to define the third transition, but it is possible to approximately identify it by the coordinates of the second minimum of the loss angle, i.e., $T\delta_{min_2}$, δ_{min_2} , located between the second and the third transitions. The value of this loss angle, δ_{min_2} , will be also an indicator of the bitumen phase/polymer phase ratio. The accuracy of the values is:

$$T_{E''_{max}} = X \pm 2^\circ\text{C},$$

$$T_{\delta_{max_1}} = Y_1 \pm 2^\circ\text{C},$$

$$\delta_{max_1} = Y_2 \pm 2,$$

$$T\delta_{max_2} = Z_1 \pm 1^\circ\text{C},$$

$$\delta_{max_2} = Z_2 \pm 2,$$

$$T\delta_{min_2} = W_1 \pm 3^\circ\text{C},$$

$$\delta_{min_2} = W_2 \pm 3.$$

We may note that all these peculiar points are

Table III Glass Transition Temperatures of the Oils Determined by DSC

Oil	T_g (°C) Measured by DSC	Crystallisation Temperature (°C)
Deasphalted product	-45 ± 2	-28
Aromatic extract	-33 ± 2	-11

observed with the two types of blends (containing either 15 or 20% of Kraton D 1101) having different properties. Now, using simpler systems than the bitumen-SBS blends, we shall try to establish relationships between the three phases of bitumen-SBS blends (composition, content of each of those, etc.) and the three mechanical transitions, shown by dynamic mechanical thermal analysis and identified by the particular points we just defined.

Transition Phenomena of "Model" SBS-Bitumen Components Mixes

The SBS copolymer used in our study can be considered as a two phases system exhibiting two "glass" mechanical transitions, respectively, near -90°C (polybutadiene) and near 100°C (polystyrene). When SBS and a petroleum oil are mixed together, the copolymer is swollen and each of its two sequences exhibits a new rheological behavior that depends on⁶: the glass transition of the oil, the nature of the oil, the polymer/oil ratio, and the molecular structure of the SBS (molecular weight, linear or branched, two or three blocks). Based on studies of different SBS/oil blends, we now propose a modelization of the behavior of the two polymer phases in the bitumen-SBS blends.

The characteristics of the two petroleum oils and the two SBS copolymers used are given in Tables I and II. The glass transition temperatures of the two oils have been determined by differential scanning calorimetry. The determination of these temperatures is made on the thermograms, obtained during the increase of temperature from -70 to 100°C at a rate of $10^\circ\text{C}/\text{min}$. Beforehand, the samples are cooled from ambient temperature to -70°C with an isothermal of 10 min at the crystallization temperature of the crystallizable fractions, in order to make the determination of the glass transition more easily (Fig. 2). The results are reported in Table III.

The two petroleum oils used here do not have the same nature (not the same polarity, for in-

stance), and exhibit two quite different thermal behaviors. Therefore, they may have different influences on the viscoelastic properties of the swollen copolymer.

The Fox⁷ and Gordon-Taylor⁸ relationships can be used to predict the evolution of the glass transition temperature of a binary blend knowing the mass fractions and the glass transition temperature of each of the two components of this blend, in the case where only weak interactions (no polar interaction) intervene.

$$\frac{1}{T_g^M} = \frac{M_1}{T_{g1}} + \frac{M_2}{T_{g2}} \quad (\text{Fox})$$

$$T_g^M = M_1 T_{g1} + M_2 T_{g2} \quad (\text{Gordon and Taylor})$$

where T_g^M , T_{g1} , and T_{g2} are the glass transition temperatures of the blend and of the two components 1 and 2, and M_1 and M_2 the mass fractions of constituents 1 and 2 in the blend. These laws are often used for polymers⁹ and sometimes for bitumen.¹⁰⁻¹³ The increase of the swelling ratio, obtained by increasing the oil/SBS ratio in the blend, results in (Fig. 3): (1) an increase of the glass transition temperature of the swollen polybutadiene phase: the abscissas of the first inflexion point on the curve $E' = f(T)$ and of the peaks on the curves $E'' = f(T)$ and $\delta = f(T)$ seem to be increasing function of the swelling rate; (2) a decrease of the glass transition temperature of the swollen polystyrene phase: the abscissas of the second inflexion point of the curve $E'' = f(T)$ and of the second peaks on the curves $E'' = f(T)$ and $\delta = f(T)$ decrease when the swelling rate increases; (3) a decrease of the modulus; (4) an increase of the value of the loss angle before the mechanical transition of polystyrene (Fig. 3).

We may notice that the swelling of the polydiene phase is accompanied not only by a decrease of the glass transition of this phase, but also by a broadening of the glass transition temperature range [$(TE''_{\text{max}} - T\delta_{\text{max}})$ increase]. In short, the behaviors of the two phases, polybutadiene and polystyrene, towards the oils used are very different. At first sight, the variation of the "glass" transition temperature, with the swelling ratio, seems to follow the Fox or Gordon-Taylor laws, i.e., the transition temperature of the two constituents is located between the temperatures of the two components and is a decreasing function of the mass fraction of the lower transition temperature constituent. Moreover, if we compare the "glass" transition temperatures, determined by DSC, of the

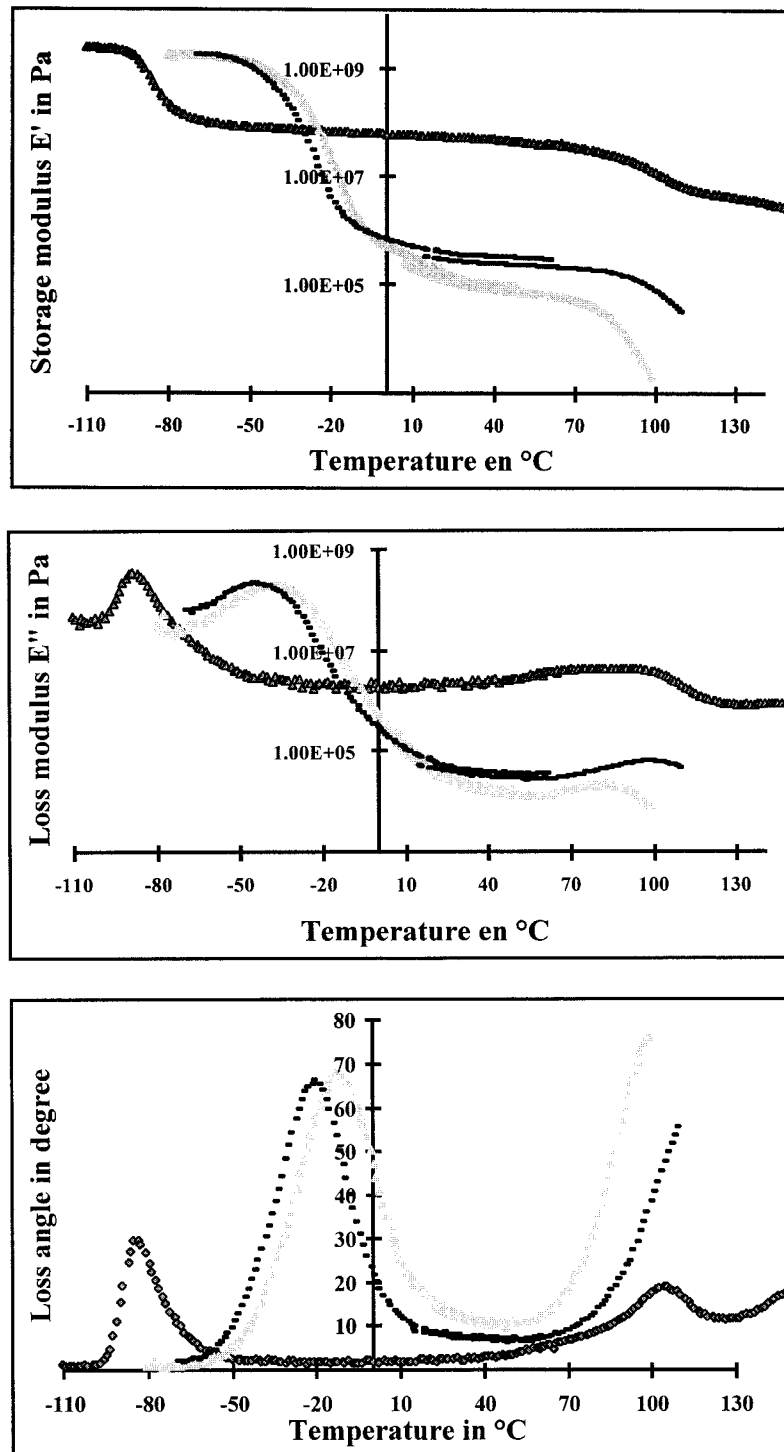


Figure 3 (a) Influence of swelling ratio on the storage modulus of SBS/oil blends (frequency: 5 Hz): ▲ D1101; △ 20% D1101 + 80% aromatic extract; ■ 30% D1101 + 70% aromatic extract. (b) Influence of swelling ratio on the loss modulus of SBS/oil blends (frequency: 5 Hz): ▲ D1101; △ 20% D1101 + 80% aromatic extract; ■ 30% D1101 + 70% aromatic extract.

Table IV Transition Temperatures Measured by DSC or Calculated with Fox' or Gordon-Taylor's Laws

Components	Transition Temperature (°C) Measured by DSC	Transition Temperature (°C) Calculated with Fox' Relation	Transition Temperature (°C) Calculated with Gordon-Taylor's Relation
Polybutadiene	−91		
Aromatic extract	−33		
20% SBS + 80% aromatic extract	−50	−48	−46
30% SBS + 70% aromatic extract	−58	−55	−51

polybutadiene phase of a pure SBS, of the aromatic extract and of the blends (20% SBS + 80% aromatic extract) and (30% SBS + 70% aromatic extract), and those calculated using Fox or Gordon-Taylor relations (Table IV), we notice that the Fox' law is perhaps the most appropriate to describe the behavior of such systems.

However, these relations predict, at constant swelling ratio, that the glass transition temperature of swollen polymers are increasing functions of the glass transition temperature of the oil. This holds for the swollen polybutadiene phase, but not for the swollen polystyrene phase. Indeed, the deasphalted product, which has a lower transition temperature than the aromatic extract, gives at the same swelling ratio a swollen polybutadiene phase with the lowest transition temperature (Fig. 4). However, this is different for the swollen polystyrene phase. With the deasphalted product, there is a very important “antiplastification effect.”

Such a behavior can be attributed to the presence, in the deasphalted product, of more polar constituents, which can interact strongly with polystyrene and produce an increase of the transition temperature of this polymer phase. In this case, the Fox' or Gordon-Taylor's relations can be employed, but it's necessary to add a term including the strong interactions. These relations can then be written in the following form:

$$\frac{1}{T_g^M} = \frac{M_1}{T_{g1}} + \frac{M_2}{T_{g2}} - K$$

$$T_g^M = M_1 T_{g1} + M_2 T_{g2} + K'$$

where K and K' are positive numbers, depending both on the mass fractions of 1 and 2,¹⁴ and on

the interaction parameter between 1 and 2.¹⁵ We can still notice, on the one hand, that the compositions of the petroleum products that swell the polybutadiene phase and the polystyrene phase are not identical, and on the other hand, that our reasoning is only qualitative, in order to show how and to understand why, the transition temperatures of SBS change when the copolymer is swollen with a bituminous product. The molecular structure of the copolymer may also influence the swollen polymer phase behavior. Figure 5(a)-(c) gives, respectively, the variation of the loss angle and the loss modulus vs. temperature for blends varying either in molecular structure of the terpolymer or in the chemical composition of the petroleum oil.

The polybutadiene phases of the two SBS, the Kraton D 1101 and D 1184, have the same behavior. Indeed, the curves $E'' = f(T)$ and $\delta = f(T)$ are superposed in the temperature range -80 to 30°C (temperature domain of the polybutadiene transition). On the opposite, the polystyrene phase has a behavior that varies considerably, depending on the linear or branched structure of the SBS. In fact, the curves in Figures 5 are no more superposable in the temperature range 50 to 150°C (transition domain of the swollen polystyrene phase). We may also notice that the “antiplastification effect,” observed with the deasphalted product, is much more important with the branched SBS than with the linear one. However, we have no real explanation for these phenomena.

In short, the swelling of SBS with a petroleum oil results in an important change of the transition temperature of the polybutadiene phase. This change can be qualitatively appreciated considering both the swelling ratio and the transition tem-

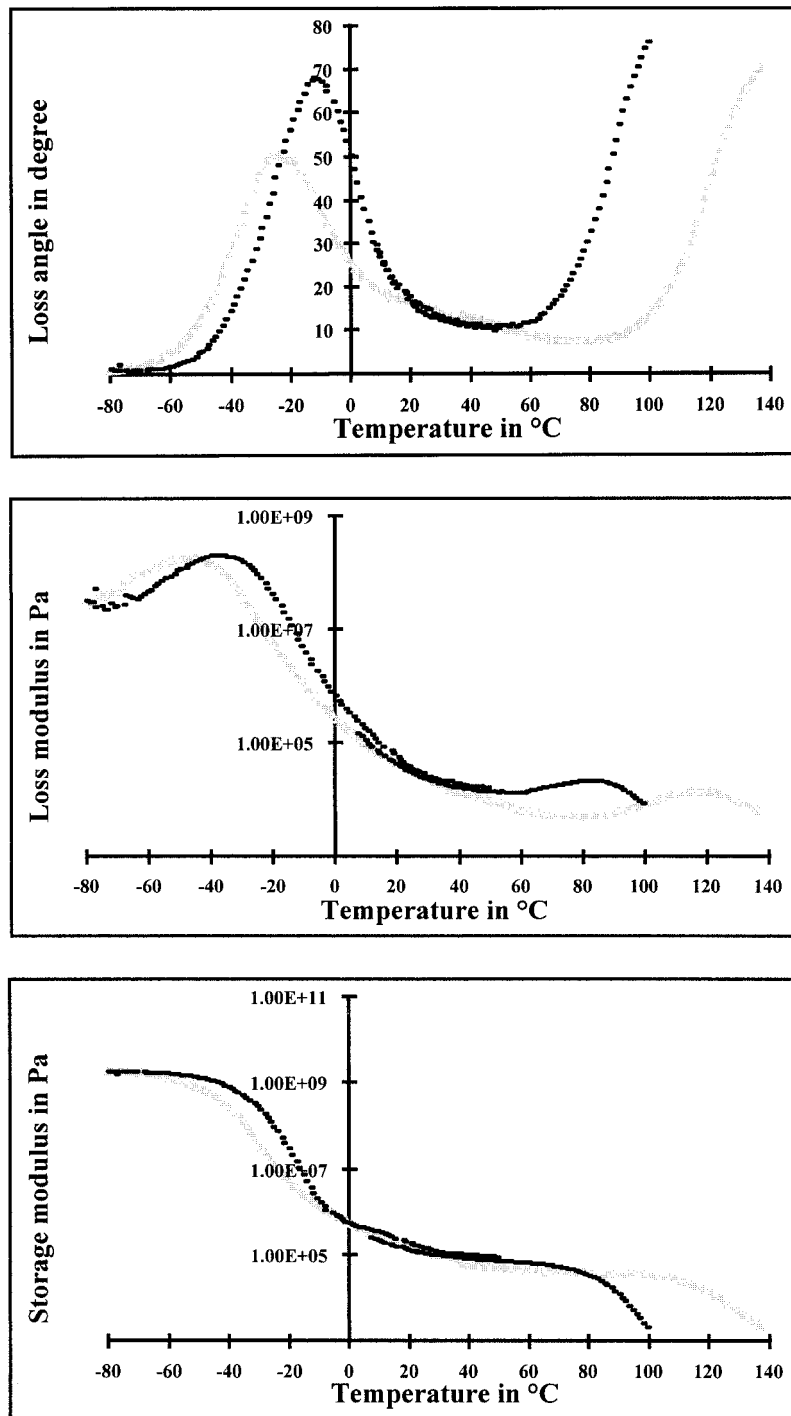


Figure 4 (a) Influence of the nature of the oil on the viscoelastic behavior of swollen polybutadiene and polystyrene phases. Loss angle vs. temperature (frequency: 5 Hz): ▲ 20% D1101 + 80% deasphalted product; ■ 20% D1101 + 80% aromatic extract. (b) Influence of the nature of the oil on the viscoelastic behavior of swollen polybutadiene and polystyrene phases. Loss modulus vs. temperature (frequency: 5 Hz): ▲ 20% D1101 + 80% deasphalted product; ■ 20% D1101 + 80% aromatic extract. (c) Influence of the nature of the oil on the viscoelastic behavior of swollen polybutadiene and polystyrene phases. Storage modulus vs. temperature (frequency: 5 Hz): ▲ 20% D1101 + 80% deasphalted product; ■ 20% D1101 + 80% aromatic extract.

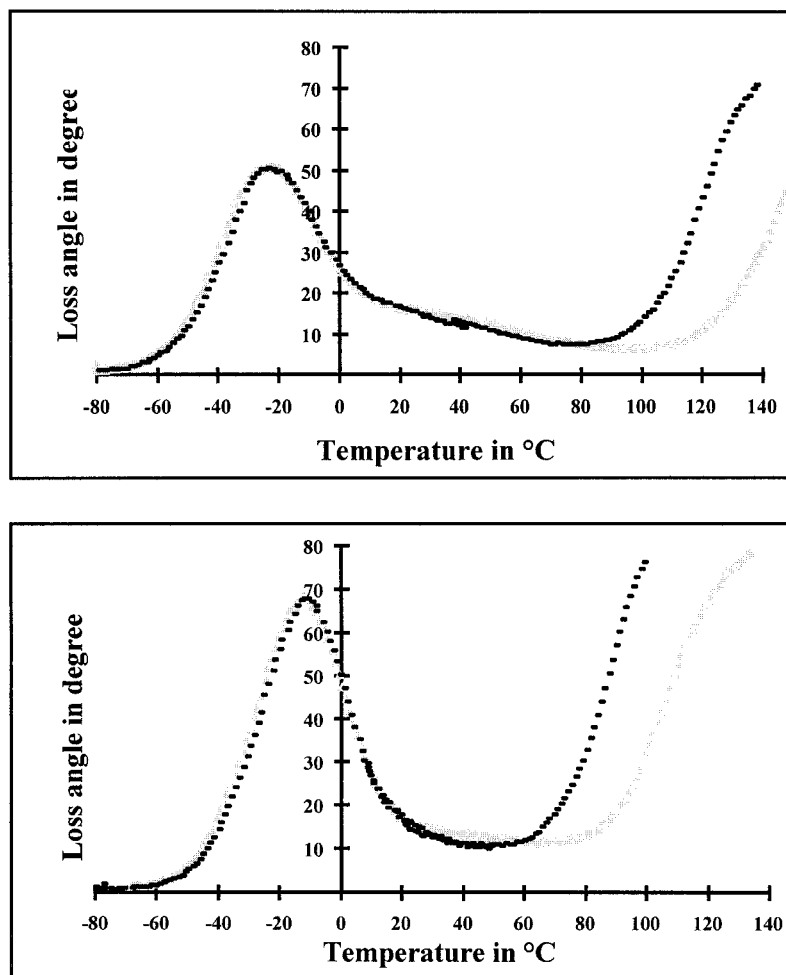


Figure 5 (a) Influence of the molecular structure on the viscoelastic behavior of swollen polybutadiene and polystyrene phases of SBS/deasphalted product blends. Loss angle vs. temperature (frequency: 5 Hz): \blacktriangle 20% D1184 + 80% deasphalted product; \blacksquare 20% D1101 + 80% aromatic extract. (b) Influence of the molecular structure on the viscoelastic behavior of swollen polybutadiene and polystyrene phases of SBS/aromatic extract blends. Loss angle vs. temperature (frequency: 5 Hz): \blacktriangle 20% D1184 + 80% aromatic extract; \blacksquare 20% D1101 + 80% aromatic extract. (c) Influence of the molecular structure on the viscoelastic behavior of swollen polybutadiene and polystyrene phases of SBS/deasphalted product blends. Loss modulus vs. temperature (frequency: 5 Hz): \blacktriangle 20% D1184 + 80% deasphalted Product; \blacksquare 20% D1101 + 80% deasphalted product. (d) Influence of the molecular structure on the viscoelastic behavior of swollen polybutadiene and polystyrene phases of SBS/aromatic extract blends. Loss modulus vs. temperature (frequency: 5 Hz): \blacktriangle 20% D1184 + 80% aromatic extract; \blacksquare 20% D1101 + 80% aromatic extract.

perature of the petroleum product using Fox' or Gordon-Taylor's relations. For the polystyrene swollen phase, the problem is much more complicated. Indeed, the swelling behavior of the polystyrene sequences can be described by Fox or Gordon-Taylor's relations only for the swelling ratio. Finally, the molecular structure of SBS has an important influence on the mechanical behavior of the swollen polystyrene phase. We must still

be aware that the compositions of the petroleum oil in each of the two polymer phases, polystyrene and polybutadiene, are not necessarily the same.

Transition Phenomena Associated with the Bitumen Phase

The rheological study of amorphous materials indicates, in general, two characteristic tempera-

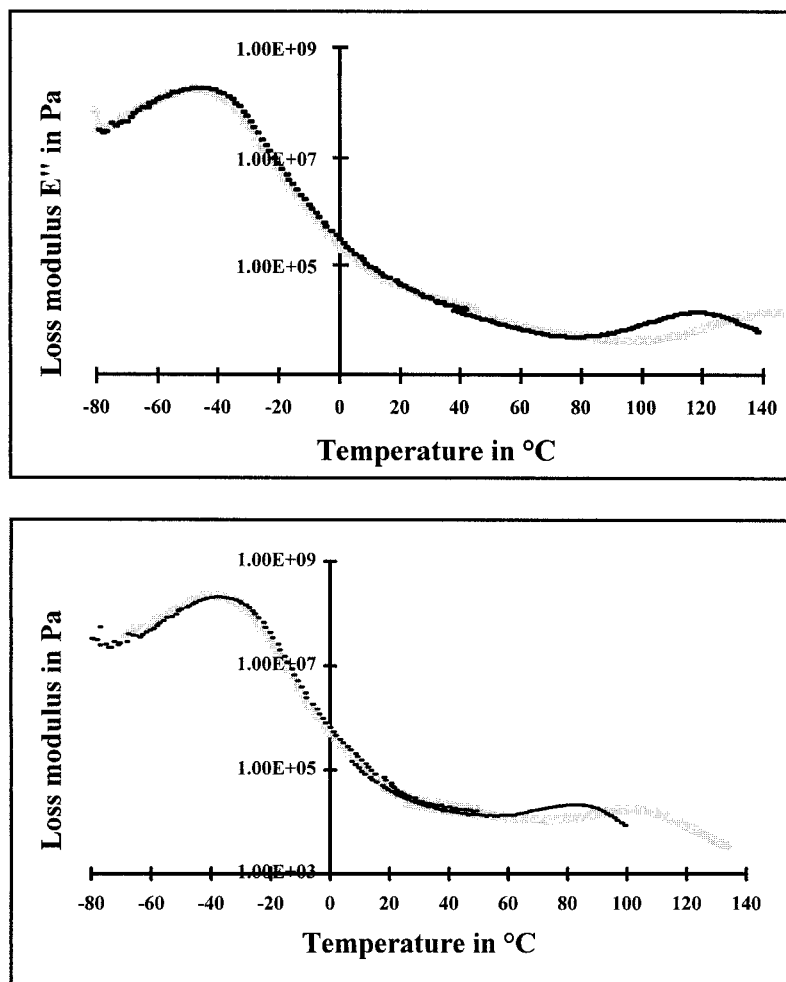


Figure 5 (Continued from previous page)

tures: a glass transition temperature and a softening temperature.^{16,17} Using dynamic mechanical measurement, these two temperatures are pointed out by: (1) an inflexion point on the curve $E' = f(T)$, a peak on the curve $E'' = f(T)$, and a peak on the curve $\delta = f(T)$, for the glass transition temperature; and (2) an abrupt change of the slope of the curve $E' = f(T)$ and an increase of the loss angle, for the softening temperature.

Bitumens behave like such materials. However, the molecular weights of the bitumen components are relatively low, and this may perhaps explains the disappearance of the rubbery plateau due to the closeness of the two characteristic temperatures. The two transitions are no more discernible on the curves $E' = f(T)$ and $\delta = f(T)$. The only points of comparison between the two bitumens are the abscissa of the peak of the loss modulus [Fig. 6(a)] and the slope of the curve giving the storage modulus vs. temperature. With

this slope, it is possible to compare the nature of the two bitumens, i.e., the quality of the four broad component groups that compose bitumen, whereas the position of the peak on the curve $E'' = f(T)$ allows appreciation of relative quantities of each of these four groups.

Therefore, two bitumens of the same nature, like 100/130PX and "asphaltenes from propane," show $E' = f(T)$, $E'' = f(T)$ and $\delta = f(T)$ curves, which are parallel. Nevertheless, the position of these curves, which can be quantified by the abscissa of the peak of the loss modulus, are very different for the two bitumens, due to a slight difference in their compositions. So, Figure 6(a) shows, taking the abscissa of the peak of the loss modulus, that a slight impoverishment in saturates (from 8 to 3.6%) in favor of asphaltenes (from 7.5 to 9.7), results in a strong increase of the transition temperature of the bitumen (from -10 to 13°C). This result is in good agreement with other studies,¹⁰ which conclude

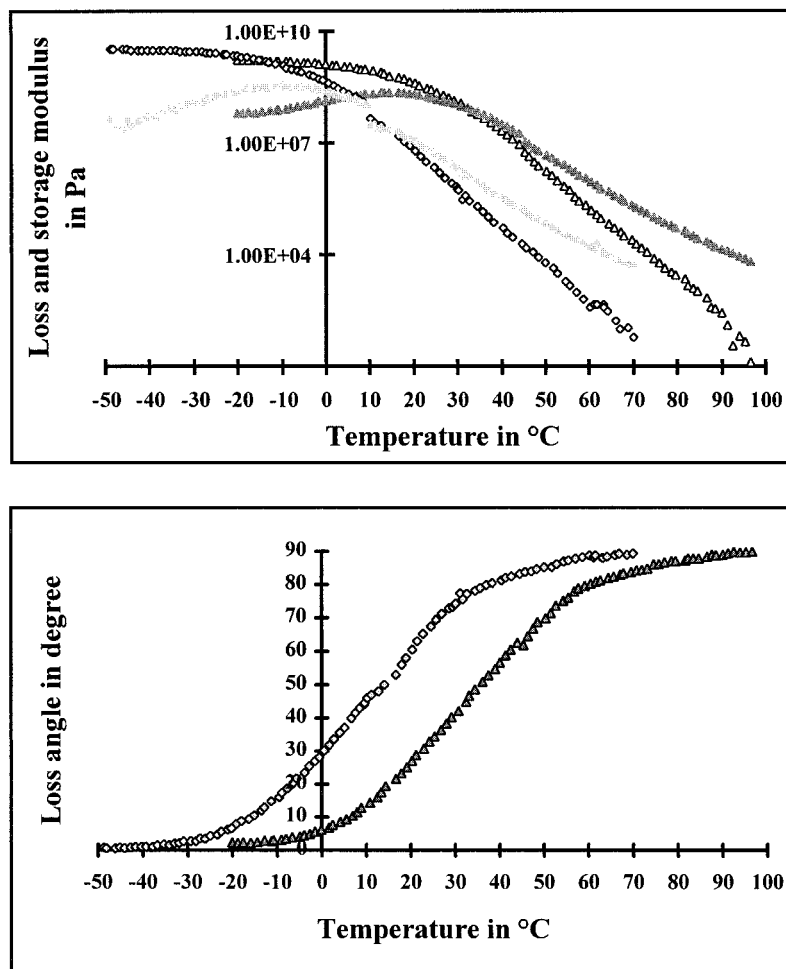


Figure 6 (a) Influence of the bitumen composition on the transition temperature. Variation with temperature of the loss (in gray) and storage (in white) moduli for two bitumens of the same nature, but with different compositions (frequency: 5 Hz): Δ Asphaltenes from propane; \triangle Asphaltenes from propane; \diamond 100/130PX; \blacklozenge 100/130PX. (b) Influence of the bitumen composition on the curve $\delta = f(T)$ (frequency 5 Hz): \triangle Asphaltenes from propane; \diamond 100/130 PX.

that an increase in asphaltenes content leads to an increase of the mechanical transition temperature of bitumen.

So, the bitumen transition, which can be estimated from the peak of the loss modulus, is not apparent on the curve of the loss angle $\delta = f(T)$ [Fig. 6(b)] because the storage modulus continues to decrease just after this transition.

But, we may then suppose that the coexistence in a blend of (1) one swollen polymer phase, which can still keep a high constant value of the storage modulus up to the transition of the swollen polystyrene phase; and (2) one bitumen phase, which exhibits, alone, a transition near 0, 10, or 20°C (abscissa of the loss modulus peak) could allow the bitumen phase transition in this blend to be

characterised by a peak on the curve $\delta = f(T)$ near 30, 40, or 50°C.

Therefore, we imagined a system that may represent such a situation, and we calculated the moduli and loss angle of fictitious bitumen/SBS blends. These fictitious blends are made of one polymer phase modeled by the blend (20% TR1101 + 80% deasphalted product) and one bitumen phase modeled by “asphaltenes from propane.”

Furthermore, calculating these moduli for four bitumen phase/polymer phase ratios, we show how the coordinates of the particular points coming from the curve $\delta = f(T)$ change with the relative importance of the two phases of the system.

We used the following expression for our calculations:

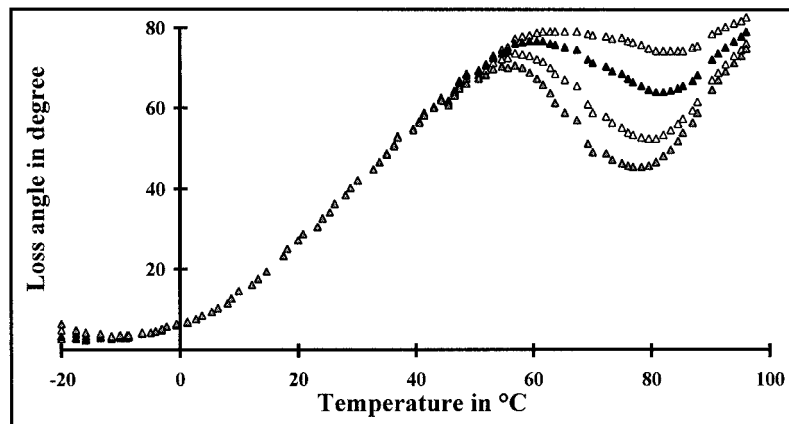


Figure 7 Modelization of the viscoelastic behavior of bitumen/SBS blends. Influence of polymer phase/bitumen phase ratio on the coordinates of the particular points presented by the loss angle curve vs. temperature (frequency: 5 Hz). Clear triangles, 30% Asp/70% swollen polymer; shaded triangles, 70% Asp/30% swollen polymer; solid triangles, 50% Asp/50% swollen polymer; shaded triangles, 20% Asp/80% swollen polymer.

$$E'_{\text{blend}} = xE'_{\varphi_P} + (1 - x)E'_{\varphi_B}$$

$$E''_{\text{blend}} = xE''_{\varphi_P} + (1 - x)E''_{\varphi_B}$$

and

$$\tan \delta_{\text{blend}} = \frac{E''_{\text{blend}}}{E'_{\text{blend}}}$$

where x and $(1 - x)$ are the volume fractions, respectively, of the polymer phase and of the bitumen phase. The results obtained are illustrated in Figure 7, showing the variation of the loss angle vs. the temperature for different bitumen phase/polymer phase ratios.

This modelization points to the following conclusions: (1) at constant compositions of bitumen and swollen polymer phases: the abscissa of the loss angle peak corresponding to the bitumen phase ($T\delta\text{max}_2$ near 50°C), the value of the loss angle at this maximum (δmax_2), the coordinates of the second minimum of the loss angle before the polystyrene transition, increase with an increase of the bitumen phase/polymer phase ratio. (2) At constant phases ratio: due to—on the one hand, that the bitumen phase transition appears in a temperature range where the polymer phase modulus stays constant, and—on the other hand, that the transition temperature of the bitumen is an increasing function of the asphaltenes content, the increase of asphaltenes content of the bitumen may show up by a decrease of the characteristic temperature of the bitumen phase ($T\delta\text{max}_2$).

To sum up: the first transition is completely

characterized by both the abscissa of the first peak of the loss modulus ($T_{E''\text{max}}$) and by the value of the first maximum of the loss angle (δmax_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. $T_{E''\text{max}}$ 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. δmax_1 is an increasing function of the content of this swollen polybutadiene phase in the blend. The second transition, which can be completely defined by the coordinates of the second peak of the loss angle, ($T\delta\text{max}_2$ and δmax_2), is associated with the bitumen phase. Furthermore, $T\delta\text{max}_2$ and δmax_2 are increasing functions, respectively, of the asphaltenes content of this bitumen phase and of the content of bitumen phase in the blend. The third transition can be attributed to the swollen polystyrene phase, but it is more complicated to precisely calculate its amplitude and its position. Finally, we have also shown that the value of the second minimum of the loss angle δmin_2 is an increasing function of the bitumen phase/polymer phase ratio.

CONCLUSION

Bitumen/SBS blends can be considered as three-phase systems. Studied by dynamic mechanical thermal analysis, such type of blends exhibit three transition phenomena that can be associ-

ated with each of the three phases. It has then been possible to choose some particular points, coming from the curves relating the storage modulus, the loss modulus, and the loss angle to temperature, in order to characterize in amplitude and in position each transition phenomena. The study of "model" systems makes it possible for the establishment of relationships between the morphological characteristics (phase number, phase compositions, phase content in the blend) and these different particular points. This study also allows one to show the particular behavior of the swollen polymer vs. both the nature of the swelling product and the molecular structure of the polymer. In the following article we shall use these conclusions to argue a theoretical approach of bitumen-polymer mixes based on the thermodynamics of mixing. The aim of this approach is to explain the relationships between morphological characteristics and global composition of the mixes.

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