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Modeling the linear viscoelastic behavior of asphaltite-modified bitumens

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Abstract A modeling approach which allows predicting the linear viscoelastic behavior of bitumen blends from the linear viscoelastic properties of individual constituents is presented in this paper. This approach consists in a combination of the Tsengoglou rule for miscible viscoelastic materials with the Palierne model for viscoelastic emulsions. Based on some simple assumptions, this combination predicts satisfactorily the rheological behavior of asphaltite-modified bitumens and, consequently, it can be used for dosage purposes. Beyond asphaltite-modified bitumens, the modeling approach developed here can be applied on reclaimed asphalt-modified bitumens, polymer-modified bitumens, and on blends of partially miscible polymers presenting a suspended droplet morphology.

Keywords Bitumen blends · Modified bitumen · Asphaltite · Linear viscoelasticity · Partially miscible blends

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Introduction

The study of bitumen blends is of a real interest nowadays. The increasing use of recycled asphalts (Al-Qadi et al. 2007), natural asphalts, and different polymer modifiers (Bardesi et al. 1999) in combination with pure petroleum bitumens demands new calculation methods for predicting the rheological behavior of blends and enabling the formulation of new materials with requested properties.

Depending on constituents, the blends can be miscible, as it is the case of blends of petroleum bitumens of similar consistencies (Soleymani et al. 1999, Whiteoak 1990) or immiscible, as it is the case of polymer-modified bitumens which present distinct phases (Lesueur 2009). If the blending conditions of bitumens are favorable (low blending temperature, short blending time), partial miscibility (a certain quantity of component A is combined with component B and vice-versa) can be suspected, especially if the difference in viscosity between the two blended bitumens is important.

A large variety of rheological modeling approaches can be found in the literature for blends of miscible materials (Des Cloizeaux 1990, Doi & Edwards 1986, Groves et al. 1996, Haley & Lodge 2004, Soleymani et al. 1999, Tsengoglou 1987, Tsengoglou 1988a,b, Tsengoglou 1991) and blends of immiscible materials (Bousmina 1999, Choi & Schowalter 1975, Frohlich & Sack 1946, Kerner 1956, Oldroyd 1953, 1955, Palierne 1990, 1991, Taylor 1932).

In the case of miscible components, the microstructure can be considered as homogeneous at the molecular level. Instead, immiscible components, depending on interfacial properties, mixing protocols, and volume fraction of phases, may generate different structural organizations as co-continuous morphologies or suspended droplet-type systems (Ton-That et al. 2001). For immiscible systems, the morphological information (structural organization type, phase

quantities, droplet form, droplet size distribution, etc.) is input to the rheological models when the prediction of rheological properties is required (Bousmina & Muller 1993, Brahimi et al. 1991, Graebbling et al. 1994, Graebbling et al. 1993, Palierne 1990). In this case, the morphological properties should be established preliminarily by means of any microscopy techniques. For the study of bitumens and petroleum products, different techniques like atomic force microscopy (Loeber et al. 1996), small angle X-ray scattering and neutron scattering (Dwiggins 1965, Henaut et al. 2001, Overfield et al. 1989, Ravey et al. 1988), scanning electron microscopy (Loeber et al. 1996), confocal laser scanning microscopy (Bearsley et al. 2004, Florian et al. 2014, Lu et al. 2005), and microscopy under UV light (Lesueur et al. 1998, Soenen et al. 2008) are employed. Inversely, rheological measurements are often used to deduce the morphological features of the system (Friedrich et al. 1995, Roths et al. 2002, Vinckier et al. 1997, Vinckier et al. 1996), especially when it is difficult or impossible to establish them by other techniques.

In the framework of a wide research project, the potential of asphaltites as modifiers of petroleum bitumens was studied (Themeli 2015, Themeli et al. 2016). The asphaltites used in this study are very hard natural bitumens (zero penetration and softening point >120 °C), with a high content of polar constituents (resins + asphaltenes ≈ 75 %). In the case of our asphaltite-modified bitumens, the visualization of the blended components by microscopy techniques is impossible due to lack of contrast between the two materials. For this reason, we are not able to define the degree of miscibility between the asphaltite and the pure petroleum bitumen (miscible, partially miscible, or immiscible) and no morphological features can be established. In this context, for the purposes of our modeling, we assume an initial emulsion-type system of asphaltite droplets dispersed in the petroleum bitumen matrix. In addition, we assume that during the modifying process, the asphaltite gradually solubilizes into the petroleum bitumen and the system gradually evolves from an emulsion type into a miscible system. This kinetics seems to be logical and in order to model it at least two rheological approaches, one for immiscible systems and one for miscible ones, are necessary. We have chosen the Dickie variant (Dickie 1973) of the Palierne model for viscoelastic emulsions (Palierne 1990) and the Tsenoglou combination rule for miscible systems (Tsenoglou 1991). The Tsenoglou combination rule was chosen because, as it is shown later on in this paper, classic mixing rules traditionally used for bitumen blends were unable to model correctly our experimental data.

In this paper, the classic blending law, traditionally used in the bitumen science, is presented in a first time.

The Palierne model and the Tsenoglou combination rule are presented afterwards. Then, these models are applied to experimental results collected on asphaltite/petroleum-bitumen blends. Finally, in order to model the modification kinetics and allow the prediction of blends' linear viscoelastic behavior, a combination of both models is proposed.

Review of some rheological modeling approaches

In the following paragraphs, different approaches for modeling the linear viscoelastic behavior of blends based on the behavior of pure components are presented. The domain of rheological modeling of blended materials is large but we have limited our discussion to models which seem more appropriate to bitumens. First, the classic blending law, traditionally used for bitumen blends, is presented. Then, other rheological models, largely employed in polymer science; the Tsenoglou combination rule for blends of miscible materials; and the Palierne model for viscoelastic emulsions are detailed. We have also considered, but not detailed here, two other modeling approaches: a self-consistent approach (Hadrzynski & Such, 1998) and a second approach based on analogical elements (Mangiafico et al. 2014) which, for our asphaltite-modified bitumens, have not given satisfactory results.

Classic blending laws

The consistency of bitumens is characterized by two empirical tests: the penetration test and the softening point test carried out according to norms EN-1427 and EN-1426, respectively. Classic blending laws are used often for the prediction of the penetration, and the softening point of bitumen blends form the respective properties of pure components A and B (Whiteoak 1990, Widyatmoko & Elliott 2008):

$$\log(P_b) = x \cdot \log(P_A) + (1-x) \cdot \log(P_B) \quad (1)$$

$$SP_b = x \cdot SP_A + (1-x) \cdot SP_B \quad (2)$$

with:

P_b, P_A, P_B	Penetrations of blend, component A and component B, respectively
SP_b, SP_A, SP_B	Softening points of blend, component A and component B, respectively
x	Mass rate of component A in the blend

Soleymani et al. making the assumption that a linear relationship exists between the linear viscoelastic

properties of bitumen blends and the ratios of components in the blend, extended the use of the classic blending laws in the prediction of the linear viscoelastic properties (Soleymani et al. 1999):

$$\log|E_b^*(\omega, T)| = x \cdot \log|E_A^*(\omega, T)| + (1-x) \cdot \log|E_B^*(\omega, T)| \quad (3)$$

$$\delta_b(\omega, T) = x \cdot \delta_A(\omega, T) + (1-x) \cdot \delta_B(\omega, T) \quad (4)$$

with:

$ E_b^* , E_A^* , E_B^* $	Complex modulus norms of blend, component A and component B, respectively
$\delta_b, \delta_A, \delta_B$	Phase angle of blend, component A and component B, respectively
x	The mass rate of component A in the blend

The authors applied Eqs. 3 and 4 to rheological measurements performed on blends of reclaimed bitumens with pure petroleum bitumen, and they found that the predictions were accurate for components of similar consistency. However, they have reported important deviations from the classic blending law if the two components present very different viscoelastic properties (Soleymani et al. 1999).

Tsenoglou combination rule for miscible blends

Tsenoglou developed a rheological model in order to explain the linear viscoelastic behavior of miscible heteropolymer blends and that of homopolymer blends of dissimilar molecular weights (Tsenoglou 1987, Tsenoglou 1988a, b, Tsenoglou 1991). This model or variants of it are often used to interpret linear viscoelastic data issued from miscible polymer melts (Gell et al. 1997, Groves et al. 1996, Haley et al. 2003). The model is based on the assumption that the coupling probability between any two components along a single chain is proportional to the fractional participation of each component in the blend which yields to the following relaxation modulus for the blend:

$$G_b(t) = \left[\sum_{i=1}^n \phi_i \cdot G_i(t)^{1/2} \right]^2 \quad (5)$$

where ϕ_i and $G_i(t)$ are the volume fraction and the relaxation modulus of the i^{th} component and n the number of components in the blend.

Approximating the relaxation function of each component in the blend with a single exponential term, and introducing these approximations to Eq. 5, the storage and loss moduli of the blend were calculated and

expressed in terms of components' properties and fractions as follows (Tsenoglou 1991):

$$G_b'(\omega) \cong \sum_i^n \sum_j^n (G_{Ni})^{\frac{1}{2}} (G_{Nj})^{\frac{1}{2}} \phi_i \phi_j \left[1 + \frac{1}{4} \left(\left(\frac{G_{Ni}}{G_i'(\omega)} - 1 \right)^{\frac{1}{2}} + \left(\frac{G_{Nj}}{G_j'(\omega)} - 1 \right)^{\frac{1}{2}} \right)^2 \right]^{\frac{1}{2}} \quad (6)$$

$$G_b''(\omega) \cong \sum_{i=1}^n \sum_{j=1}^n (G_{Ni})^{\frac{1}{2}} (G_{Nj})^{\frac{1}{2}} \phi_i \phi_j \left(G_{ij} + \frac{1}{G_{ij}} \right)^{-1} \quad (7)$$

$$\text{with : } G_{ij} = \frac{G_{Ni} - G_i'(\omega)}{2G_i''(\omega)} + \frac{G_{Nj} - G_j'(\omega)}{2G_j''(\omega)}$$

where G_N denotes the plateau modulus. For binary blends where both components have equal plateau moduli and where $G_N \gg G'$ and G'' , Eqs. 6 and 7 are reduced to:

$$G_b'(\omega) \cong \phi_1^2 \cdot G_1'(\omega) + \phi_2^2 \cdot G_2'(\omega) + \frac{8 \cdot \phi_1 \cdot \phi_2 \cdot G_1'(\omega) \cdot G_2'(\omega)}{G_1'(\omega) + 2 \cdot G_1'(\omega)^{\frac{1}{2}} \cdot G_2'(\omega)^{\frac{1}{2}} + G_2'(\omega)} \quad (8)$$

$$G_b''(\omega) \cong \phi_1^2 \cdot G_1''(\omega) + \phi_2^2 \cdot G_2''(\omega) + \frac{4 \cdot \phi_1 \cdot \phi_2 \cdot G_1''(\omega) \cdot G_2''(\omega)}{G_1''(\omega) + G_2''(\omega)} \quad (9)$$

The assumption of an exponential relaxation function, which is correct for monodisperse systems, remains critical for bitumens. However, the model has given satisfactory prediction results on mixtures of highly polydisperse components (Lee & Denn 2000). In addition, as we will see in the discussion section hereafter, the Tsenoglou combination rule gives satisfactory modeling of the bitumen blends for a wide range of temperatures.

The Tsenoglou model assumes that the components have similar glass transitions. When the glass transition temperatures of the components are very different, the monomeric frictions of the components in the mixed state are different from those in the pure state at the same temperature. This difference comes from the change of the effective glass transition temperatures of the components in the mix. This difference is commonly compensated by introducing into the calculations the dynamic moduli of each component measured at the same temperature from the effective glass transition temperature (Gell et al. 1997).

The Tsenoglou model is conceived by considering the network architecture of entangled polymers in the blend. However, the treatment is also valid when some of the blend components are oligomers or regular solvents (Tsenoglou 1988a). In this study, we have applied the Tsenoglou model, for the first time to our knowledge, to bitumens which show viscoelastic behavior (Brodnyan et al. 1960) and can be

considered as low molecular weight natural polymers with a degree of polymerization, deduced from differential scanning calorimetry, around 10 (Masson & Polomark 2001).

Palierne model for immiscible blend

Palierne developed a model for the calculation of the linear viscoelastic behavior of emulsions of viscoelastic incompressible fluids (Palierne 1990). This model is the generalization of previous works of Einstein on the viscosity of dilute suspensions of rigid spheres in a Newtonian matrix, Frohlich and Sack on the viscoelasticity of dilute suspension of elastic deformable spheres in a Newtonian matrix (Frohlich & Sack 1946), Taylor and Oldroyd on the viscoelasticity of dilute emulsions of Newtonian drops in a Newtonian matrix (Oldroyd 1953, 1955, Taylor 1932), Choi and Schowalter for semi-dilute emulsions of Newtonian drops in a Newtonian matrix (Choi & Schowalter 1975), and of Kerner on the elastic behavior of a composite of Hookean spheres dispersed in a Hookean matrix (Kerner 1956), which are particular cases of the Palierne model.

The model considers viscoelastic spherical inclusions, with arbitrary size distribution, dispersed in a viscoelastic matrix in dilute and semi-dilute regimes. The mechanical contribution of the interfacial tension between the phases is taken into account. The interactions between particles are considered by averaging the complex shear modulus of the medium by a self-consistent treatment. In its general form, the Palierne model for the dilute regime ($\sum_i \phi_i < 10\%$) is:

$$G_b^* = G_M^* \left(1 + 2.5 \sum_i \frac{E_i^*}{D_i^*} \phi_i \right) \quad (10)$$

and for the semi-dilute regime is:

$$G_b^* = G_M^* \frac{1 + 1.5 \sum_i \frac{E_i^*}{D_i^*} \phi_i}{1 - \sum_i \frac{E_i^*}{D_i^*} \phi_i} \quad (11)$$

where:

$$\begin{aligned} E_i^* = & 2(G_I^* - G_M^*)(19G_I^* + 16G_M^*) + 48 \frac{\beta' \alpha}{R^2} \\ & + 32\beta'' \frac{(\alpha + \beta')}{R^2} + 8 \frac{\alpha}{R} (5G_I^* + 2G_M^*) \\ & + 2 \frac{\beta'}{R} (23G_I^* - 16G_M^*) + 4 \frac{\beta''}{R} (13G_I^* + 8G_M^*) \end{aligned} \quad (12)$$

and

$$\begin{aligned} D_i^* = & (2G_I^* + 3G_M^*)(19G_I^* + 16G_M^*) + 48 \frac{\beta' \alpha}{R^2} \\ & + 32\beta'' \frac{(\alpha + \beta')}{R^2} + 40 \frac{\alpha}{R} (G_I^* + G_M^*) \\ & + 2 \frac{\beta'}{R} (23G_I^* + 32G_M^*) + 4 \frac{\beta''}{R} (13G_I^* + 12G_M^*) \end{aligned} \quad (13)$$

with:

G_b^*, G_M^*, G_I^*	Complex moduli of blend, of matrix, and of dispersed inclusions, respectively
ϕ_i	Volume fraction of the dispersed particles of radius R_i
α	Static, isotropic part of the interfacial tension
$\beta'(\omega)$	Harmonic, isotropic part of the interfacial tension related to the variation of the interface area (elongation modulus of the interface)
$\beta''(\omega)$	Harmonic, non-isotropic part of the interfacial tension related to the shear of the interface without area variation (shear modulus of the interface)

The model is extensively used in the literature for the prediction of the linear viscoelastic behavior of polymer blends (Bousmina & Muller 1993, Brahimi et al. 1991, Friedrich et al. 1995, Graebing et al. 1993), for the determination of their interfacial tension or morphological features (Graebing et al. 1993, Graebing & Muller 1990, Graebing & Muller 1990, Kim et al. 1993, Lacroix et al. 1996, Riemann et al. 1996, 1997, Van Hemelrijck et al. 2004), or for the study of the mechanical contribution of additions of interfacial agents (Jacobs et al. 1999, Riemann et al. 1997). Applied to polymer-modified bitumens, it gives an interfacial tension $\alpha \approx 10 \mu\text{N/m}$ (Lesueur et al. 1998). It was never used, however, to study bitumen blends.

The harmonic parts of the interfacial tension are generally neglected in the literature. Considering a biphasic monodisperse system with null $\beta'(\omega)$ and $\beta''(\omega)$, the Palierne model for the semi-dilute regime reduces to:

$$G_b^* = G_M^* \frac{1 + 3\phi H(\omega)}{1 - 2\phi H(\omega)} \quad (14)$$

where:

$$H(\omega) = \frac{4 \frac{\alpha}{R} [2G_M^* + 5G_I^*] + [G_I^* - G_M^*] [16G_M^* + 19G_I^*]}{40 \frac{\alpha}{R} [G_M^* + G_I^*] + [2G_I^* + 3G_M^*] [16G_M^* + 19G_I^*]} \quad (15)$$

Table 1 Materials

Reference	Description
P50/70	50/70 grade <i>paraffinic</i> petroleum bitumen
NP50/70	50/70 grade <i>non-paraffinic</i> petroleum bitumen
P35/50	35/50 grade <i>paraffinic</i> petroleum bitumen
TAD	Organic phase of treated <i>asphaltite</i> mined in deep layers of the mine
95 % P50/70 + 5 % TAD	50/70 grade <i>paraffinic</i> bitumen modified with 5 % of asphaltite
90 % P50/70 + 10 % TAD	50/70 grade <i>paraffinic</i> bitumen modified with 10 % of asphaltite
85 % P50/70 + 15 % TAD	50/70 grade <i>paraffinic</i> bitumen modified with 15 % of asphaltite
95 % NP50/70 + 5 % TAD	50/70 grade <i>non-paraffinic</i> bitumen modified with 5 % of asphaltite
90 % NP50/70 + 10 % TAD	50/70 grade <i>non-paraffinic</i> bitumen modified with 10 % of asphaltite
85 % NP50/70 + 15 % TAD	50/70 grade <i>non-paraffinic</i> bitumen modified with 15 % of asphaltite
95 % P35/50 + 5 % TAD	35/50 grade <i>paraffinic</i> bitumen modified with 5 % of asphaltite
90 % P35/50 + 10 % TAD	35/50 grade <i>paraffinic</i> bitumen modified with 10 % of asphaltite

If, further, the static isotropic component of the interfacial tension, α , is set to 0, then the generalization of the Kerner model, for elastic composites, to viscoelasticity is obtained, which corresponds to the Dickie's result (Dickie 1973):

$$G_b^* = G_M^* \frac{[2G_I^* + 3G_M^*] + 3\phi[G_I^* - G_M^*]}{[2G_I^* + 3G_M^*] - 2\phi[G_I^* - G_M^*]} \quad (16)$$

Materials and experiments

Materials

All the materials considered in this study are presented in Table 1.

Three petroleum bitumens are considered. Two of them belong to the same penetration grade (50/70) but have different chemical natures. The third one has the same chemical nature as the first one but belongs to a harder grade (35/50).

The asphaltite used in this study is mined in Albania in the region of Selenizza. In its natural state, this asphaltite contains 15–20 % of mineral matter. Its organic phase, which is used in the present study to modify the petroleum bitumens, is isolated by dissolution in tetrachloroethylene and filter centri fagation.

The modifying process consists in adding the grinded organic phase of asphaltite ($\varnothing < 1$ mm) in the preheated (180 °C) petroleum-bitumen base and mixing with a high shear mixer for 1 h at 180 °C. Modification rates of 5, 10, and 15 % were chosen in order to obtain 35/50, 20/30, and 10/20 grade bitumens, respectively. Eight modified bitumens were prepared (Table 1).

Experiments and results

Complex modulus

Rheological properties in terms of complex modulus in the linear domain are determined by oscillatory rheological tests carried out on a viscoanalyser METRAVIB. Annular shearing (on rings of $h = 5$ mm, $D = 10$ mm, $d = 8$ mm) and traction-compression (on cylinders of $D = 9$ mm, $h = 18$ mm for pure and modified bitumens and on cylinders of $D = 7$ mm, $h = 21$ mm for asphaltites) modes were adopted for the high (20–70 °C for pure and modified bitumens and 90–140 °C for asphaltites) and the low (−10–20 °C for pure and modified bitumens and −10–90 °C for asphaltites) temperature domains, respectively. Sinusoidal loading with frequencies from 1 to 80 Hz for pure and modified bitumens and from 1 to 55 Hz for asphaltites were applied. In order to be in the linear domain, a displacement of 5 μ m was chosen in all the experiments except traction-compression tests on asphaltites where a displacement of 3 μ m was applied.

The complex shear modulus, obtained by annular shearing, is converted to complex traction-compression modulus by applying a Poisson's ratio of 0.5, thus considering the bitumen as an incompressible material above 20 °C. Master curves, constructed by means of the LCPC method (Chailleux et al. 2006) are presented in Fig. 1. The shift factors, presented in the [supplementary information](#) of this paper, follow the WLF rule.

The asphaltite is much harder and behaves much more elastically than the P50/70 petroleum bitumen. For example, at $T = 140$ °C and $f = 25$ Hz, the $|E^*|$ and the δ for the asphaltite vs. petroleum bitumen are respectively 149,144 vs. 6.67 Pa and 62.2 vs. 90°. Modified bitumens present intermediate behaviors (Fig. 1).

Fig. 1 Master curves of **a** complex modulus norm and complex modulus phase angle, **b** storage modulus, and **c** loss modulus of petroleum, modified, and natural bitumens. $T_{\text{ref}} = 30^\circ\text{C}$

Differential calorimetry

Thermic behavior of our bitumens was determined by modulated differential scanning calorimetry. The tests were carried out on a TA Instrument of type DSC Q100. Sealed pans were used to encapsulate around 10 mg of sample. After stabilization at 25°C , the sample is heated to 180°C at $10^\circ\text{C}/\text{min}$.

Next, it is cooled down to 40°C at $10^\circ\text{C}/\text{min}$, then down to -40°C at $1^\circ\text{C}/\text{min}$, and finally down to -80°C at $5^\circ\text{C}/\text{min}$. Next, applying a modulated ramp of $5^\circ\text{C}/\text{min}$ with an oscillation period of 60 s and amplitude $\pm 0.80^\circ\text{C}$, the heat flows were measured up to 160°C .

All the bitumens considered here present wide glass transitions which superpose (Fig. 2). The range between the onset

Fig. 2 Reversible heat flow curves of petroleum, modified, and natural bitumens

and the completion of the glass transition is $\Delta T_g \approx 30^\circ \text{C}$ for all samples. The glass transition temperatures of the asphaltite and of P50/70 bitumen, measured at the inflection point of the reversible heat flow curve, are respectively 8 and -12°C . The T_g s of components are not distinguishable in the heat flow curves of bitumen blends (Fig. 2). Considering the above, we assume that both materials have similar glass transitions. Consequently, we do not apply any temperature shift due to the differences of T_g values of pure components of our blends.

Discussion

Classic blending laws

Equations 3 and 4 are applied to our measurements in order to predict the linear viscoelastic properties of our blends from the respective properties of pure constituents. As shown in Fig. 3, the prediction is not accurate. Deviations from the classic blending rule confirm the results of (Soleymani et al. 1999) for blends of bitumens of very different consistencies. The observation of the results shows that both storage and loss

Fig. 3 Blend of 50/70 petroleum paraffinic bitumen with 15 % of asphaltite (85 % P50/70 + 15 % TAD). Prediction of classic blending law (Eqs. 3 and 4) vs. measurements. $T_{\text{ref}} = 30^\circ \text{C}$

Fig. 4 Blend of 50/70 petroleum paraffinic bitumen with 15 % of asphaltite (85 % P50/70 + 15 % TAD). Prediction of corrected classic blending law (Eqs. 17 and 18) vs. measurements. $T_{\text{ref}} = 30^\circ \text{C}$

moduli present a similar order of prediction error. This would suggest that the same correction factor applied to both storage and loss moduli would allow to obtain an accurate prediction.

A correction factor k is applied to Eqs. 3 and 4 which yields:

$$\log|E_b^*(\omega, T)| = \log|E_b^*(\omega, T)| + k \cdot x \cdot (\log|E_A^*(\omega, T)| - \log|E_B^*(\omega, T)|) \quad (17)$$

$$\delta_b(\omega, T) = \delta_B(\omega, T) + k \cdot x \cdot (\delta_A(\omega, T) - \delta_B(\omega, T)) \quad (18)$$

The notations are the same as them of Eqs. 3 and 4.

Applying Eqs. 17 and 18 to the experimental measurements, we have adjusted the correction factor. The adjustment is carried out by an error minimization procedure applied simultaneously on the complex modulus norm and the complex modulus phase angle data. The modeling is very satisfactory (Fig. 4). The adjusted correction factors of all blends are resumed in Table 2 with the sum of relative errors (SRE) before and after correction.

It is interesting to remark that the correction factor is unique for all viscoelastic properties, i.e., the same correction factor serves to correct the complex modulus norm, the phase angle, the storage, and loss moduli. This means that the correction factor describes a unique physical phenomenon reflected in all linear viscoelastic properties.

Application of the Tsenoglou model to asphaltite-modified bitumens

Making the hypothesis that the petroleum bitumens and the natural bitumens are miscible and obey the Tsenoglou assumptions, we have applied the Tsenoglou model to our measurements in order to predict the linear viscoelastic properties

Table 2 Correction factors and modeling improvement

Blend	Without correction factor		With correction factor		
	SRE $ E_b^* $	SRE δ_b	k	SRE $ E_b^* $	SRE δ_b
95 % P50/70 + 5 % TAD	4.1054	1.5448	1.702	1.1221	0.7366
90 % P50/70 + 10 % TAD	5.4870	2.7521	1.469	2.0752	1.7059
85 % P50/70 + 15 % TAD	12.177	5.2770	1.845	3.3333	1.8388
95 % NP50/70 + 5 % TAD	6.9325	2.5923	2.117	1.6727	0.6978
90 % NP50/70 + 10 % TAD	10.716	3.3590	1.893	2.3718	0.7287
85 % NP50/70 + 15 % TAD	11.591	4.2257	1.645	2.3464	1.0044
95 % P35/50 + 5 % TAD	8.4549	1.3412	2.382	4.3221	1.3108
90 % P35/50 + 10 % TAD	9.0228	1.6406	1.656	4.3594	1.6565

$$*SRE = \sum_{i=1}^n \left(\left| y_i^{\text{experimental}} - y_i^{\text{model}} \right| / y_i^{\text{experimental}} \right)$$

of our blends from the respective properties of pure constituents.

Measurements performed in the same temperature-frequency couples, according to Eqs. 19 and 20, were input to the model and the results were compared to the model output in Fig. 5.

$$G_b'(\omega, T) \cong \phi_1^2 \cdot G_1'(\omega, T) + \phi_2^2 \cdot G_2'(\omega, T) + \frac{8 \cdot \phi_1 \cdot \phi_2 \cdot G_1'(\omega, T) \cdot G_2'(\omega, T)}{G_1'(\omega, T) + 2 \cdot G_1'(\omega, T)^{\frac{1}{2}} \cdot G_2'(\omega, T)^{\frac{1}{2}} + G_2'(\omega, T)} \quad (19)$$

$$G_b''(\omega, T) \cong \phi_1^2 \cdot G_1''(\omega, T) + \phi_2^2 \cdot G_2''(\omega, T) + \frac{4 \cdot \phi_1 \cdot \phi_2 \cdot G_1''(\omega, T) \cdot G_2''(\omega, T)}{G_1''(\omega, T) + G_2''(\omega, T)} \quad (20)$$

The prediction appears to be very accurate in the low temperature domain (lower than 20 °C) and it declines with increasing the temperature (decreasing the frequency). The accuracy decline is particularly visible on the storage modulus.

Application of the Palierne model to asphaltite-modified bitumens

In a first time, we have applied the Palierne model in order to study the mechanical behavior of the interface. For this, each interfacial tension component was calculated considering the other components as equal to zero. This way of proceeding does not take into account an eventual simultaneous contribution of different components but allows a first approximation of the interface behavior.

The results presented in Fig. 6a show that α/R is not a real constant as it is reported for emulsions but a complex function of temperature and frequency. A complex isotropic interfacial tension is an incorrect back-calculation, yielding from the

suppression of the harmonic components of the interfacial tension. $\beta'(\omega)$ and $\beta''(\omega)$, presented in Fig. 6b and Fig. 6c, respectively, are continuous complex functions of temperature and frequency, indicating that the interface presents a viscoelastic behavior. These results seem to show that materials are not immiscible and an interphase is created between the asphaltite droplets and the petroleum bitumen matrix. This interphase would be responsible of the interfacial mechanical behavior observed in Fig. 6.

For polymer-modified bitumen, the isotropic interfacial tension is of order $\approx 10 \mu\text{N/m}$ (Lesueur et al. 1998). For an interfacial tension equal to $10 \mu\text{N/m}$, the particle size would be of order 0.1 nm in order to obtain a Laplace pressure (α/R) similar in intensity with the lowest observed values for the modulus, i.e., 100 kPa (Fig. 1). So, it is very probable that given the low interfacial tension of the system, no interfacial relaxation would occur in the considered experimental

Fig. 5 Blend of 50/70 petroleum paraffinic bitumen with 10 % of asphaltite (90 % P50/70 + 10 % TAD). Prediction of the Tsenoglou model (Eqs. 19 and 20) vs. measurements. $T_{\text{ref}} = 30 \text{ }^{\circ}\text{C}$

Fig. 6 Cole-Cole curve of **a** α/R , **b** β'/R , and **c** β''/R parameters of a blend of 50/70 petroleum paraffinic bitumen with 10 % of asphaltite (90 % P50/70 + 10 % TAD)

measurement range. The interfacial relaxation due to α would manifest for much lower measurement

Fig. 7 Blend of 50/70 petroleum paraffinic bitumen with 10 % of asphaltite (90 % P50/70 + 10 % TAD). Prediction of the Dickie model (Eq. 16) vs. measurements. $T_{\text{ref}} = 30^\circ\text{C}$

frequencies. The relaxations due to β' and β'' would be detectable for even lower frequencies (Riemann et al. 1997). Therefore, it looks like that the interfacial tension equal to zero ($\alpha=0$, $\beta'=0$, and $\beta''=0$), would be a correct assumption for applying the Palierne model to our system.

With interfacial contributions equal to zero, the Palierne model reduces to the Dickie's result for viscoelastic systems (Eq. 16). The prediction of the Dickie model, presented in Fig. 7, underestimates the experimental observations which may indicate that additional mechanisms participate to the mechanical response of the system.

Combination of the Tsenoglou and Dickie models for asphaltite-modified bitumens

Tsenoglou points out that his model may be employed for the study of partially miscible blends (Tsenoglou 1988a). He suggests to use his molecular approach for the description of each of the homogenous phases in which both components are in miscible state, and then to combine these individual results

Fig. 8 Evolution of inclusions during the modifying process, schematization

Table 3 Inter-diffusion parameter adjusted from the proposed combination of the Tsenoglou and Dickie models

Reference	ϕ_1
95 % P50/70 + 5 % TAD	0.203
90 % P50/70 + 10 % TAD	0.250
85 % P50/70 + 15 % TAD	0.209
95 % NP50/70 + 5 % TAD	0.158
90 % NP50/70 + 10 % TAD	0.192
85 % NP50/70 + 15 % TAD	0.235
95 % P35/50 + 5 % TAD	0.155
90 % P35/50 + 10 % TAD	0.230

with a suitable continuum model in order to allow the description of the multiphase blend as a whole. Following these ideas, Lee et.al proposed a hybrid approach coupling the Tsenoglou combination rule with the Palierne model in order to estimate the interfacial tension in partially miscible polymer mixtures (Lee & Denn 2000, Lee & Kim 2005). They deduced the phases' inter-diffusions from differential scanning calorimetry and based on these results they calculated the fractions of dispersed and matrix phases and the fractions of each component in each of the phases. However, in our case, such a calculation is impossible because, as stated before, the glass transitions or other thermic events of the components are not distinguishable in the heat flow curves of bitumen blends.

Because of the lack of contrast between the materials, we were not able to define the morphological features of our asphaltite/petroleum-bitumen blends. As a consequence, we could not establish the miscibility degree between the components (miscible, partially miscible, or immiscible?). However, it seems logical to hypothesize that, once the grinded asphaltite is introduced into the petroleum-bitumen matrix, an emulsion-type system of asphaltite inclusions dispersed in the petroleum-bitumen matrix is obtained. The fact that the two materials have very accentuated differences of viscoelastic behavior supports this scenario. During the mixing, the asphaltite is gradually solubilized into the petroleum bitumen,

dispersed inclusions absorbing matrix material and increasing their size. The system would gradually evolve from an emulsion-type to a miscible one, the asphaltite/petroleum-bitumen interface expanding and after some time disappearing (schematization in Fig. 8). Making the additional assumptions that:

- The system remains a dispersion of modified inclusions in a petroleum-bitumen matrix
- Inside the inclusions, the asphaltite and the petroleum bitumen are miscible
- The inclusions have the same asphaltite/petroleum-bitumen constitution
- During the modification process, the matrix properties do not alter
- The system is monodisperse

and combining the Dickies and Tsenoglou models as detailed below, we can calculate a miscibility factor which would allow an estimation of the miscibility degree between the phases.

Considering the materials inside the inclusions as miscible, their complex modulus can be calculated by the Tsenoglou rule (Eqs. 19 and 20) in which ϕ_1 denotes the fraction of asphaltite in inclusions and $\phi_2 = 1 - \phi_1$ denotes the fraction of the petroleum bitumen in inclusions. In the context of our hypotheses, ϕ_1 expresses the inter-diffusion of phases or, in other words, the miscibility degree between them. The fraction of modified inclusions in the system is:

$$\phi' = \frac{\phi}{\phi_1} \quad (21)$$

where ϕ is the fraction of asphaltite in the system.

Based on the discussion of the previous paragraph, null interfacial contributions can be justified and the Dickie model (Eq. 16) can be used to model the system as a whole. Mathematically, the problem is formalized as follows:

$$\left\{ \begin{array}{l} G_b^*(\omega, T) = G_B^*(\omega, T) \frac{[2G_I^*(\omega, T) + 3G_B^*(\omega, T)] + 3\frac{\phi}{\phi_1} [G_I^*(\omega, T) - G_B^*(\omega, T)]}{[2G_I^*(\omega, T) + 3G_B^*(\omega, T)] - 2\frac{\phi}{\phi_1} [G_I^*(\omega, T) - G_B^*(\omega, T)]} \\ G_I^*(\omega, T) = \phi_1^2 \cdot G_A'(\omega, T) + (1 - \phi_1)^2 \cdot G_B'(\omega, T) + \frac{8 \cdot \phi_1 \cdot (1 - \phi_1) \cdot G_A'(\omega, T) \cdot G_B'(\omega, T)}{G_A'(\omega, T) + 2 \cdot G_A'(\omega, T)^{\frac{1}{2}} \cdot G_B'(\omega, T)^{\frac{1}{2}} + G_B'(\omega, T)} + \\ + i \left(\phi_1^2 \cdot G_A''(\omega, T) + (1 - \phi_1)^2 \cdot G_B''(\omega, T) + \frac{4 \cdot \phi_1 \cdot (1 - \phi_1) \cdot G_A''(\omega, T) \cdot G_B''(\omega, T)}{G_A''(\omega, T) + G_B''(\omega, T)} \right) \end{array} \right. \quad (22)$$

where:

G_b^*	Complex modulus of the blend
G_I^*	Complex modulus of modified inclusions
$G_B^* = G'_B + i \cdot G''_B$	Complex modulus of petroleum
G'_B, G''_B	Storage and loss moduli of petroleum
G'_A, G''_A	Storage and loss moduli of asphaltite
ϕ_1	The fraction of asphaltite in inclusions
ϕ	The fraction of asphaltite in the blend

We have adjusted the inter-diffusion parameter ϕ_1 (which is the only unknown of our problem), and the results for all the studied blends are summarized in Table 3. The adjustment of ϕ_1 is carried out by an error minimization procedure simultaneously applied on the complex modulus norm and on the complex modulus phase angle data. The modeling quality is very satisfactory (Fig. 9). Modeling vs. experimental measurements of other blends are presented in the [supplementary information](#) of this paper.

We note that the values of ϕ_1 in Table 3 is comprised between 0 and 1 as expected. The values are of similar order of magnitude, and this may be related to the mixing conditions which are identical for all considered blends. However, in most of the cases, the fraction of asphaltite in the inclusions (ϕ_1) increases with the asphaltite content in the blend.

The results obtained by the proposed approach do not contradict the calculation hypotheses. These results suggest a partial miscibility between the phases. The values of ϕ_1 can be used to characterize the miscibility of the blend. However, it is unlikely that these values have fundamental physical meaning, i.e., corresponding to the real fraction of asphaltite in the inclusions.

The dotted lines in Fig. 9 give the response of the proposed combination of models for $\pm 20\%$ deviation from the adjusted value of ϕ_1 . Twenty percent is the maximum relative standard deviation of values of ϕ_1 observed in a group of three blends of the same petroleum bitumen with 5, 10, and 15 % of asphaltite. The $\pm 20\%$ deviations show that the approach can be used for prediction purposes with an acceptable level of error. So, the assumption of an average value for the ϕ_1 would give satisfactory results for the prediction of linear viscoelastic properties of blends based on the initial properties of pure constituents and their fractions in the blend. In practical terms, this means that the approach can be used for dosage purposes after a preliminary calibration of ϕ_1 .

Fig. 9 Blends of 30/50 petroleum paraffinic bitumen with 10 % of asphaltite. Prediction of the proposed combination of models vs. measurements. $T_{ref} = 30\text{ }^{\circ}\text{C}$

Conclusions

The work presented in this paper constitutes a basis for further discussion on bitumen blends, asphaltite-modified bitumens, and polymer-modified bitumens.

The proposed approach allows an accurate prediction of the linear viscoelastic behavior of asphaltite-modified bitumens based on the linear viscoelastic properties of pure constituents and as a consequence, it can be used for dosage purposes in order to obtain asphaltite-modified bitumens with predefined viscoelastic properties.

The interpretation of the results suggests a partial miscibility between the asphaltite and petroleum bitumens which is probable considering the fact that both components are chemically similar and they present an accentuated difference of linear viscoelastic properties. However, any experimental prove would be necessary to validate this conclusion. Future experimental work may focus on the incidence of different factors (like the asphaltite grain size, the mixing temperature and duration, the curing time) in the inter-diffusion parameter.

The proposed approach seems adequate for the study of polymer-modified bitumens, of reclaimed asphalt-modified bitumens as well as of partially miscible polymer blends presenting suspended droplet morphology.

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