

New approach for modeling polymer modified bitumens as polymer solutions: power-law scaling of rheological constants

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ABSTRACT

A new framework is developed to predict rheological properties of polymer modified bitumens (PMBs) as a function of polymer concentration. Specifically, bitumen modified with associating styrene-butadiene-styrene (SBS) block copolymers is considered. Experimental results are compared with the theoretical predictions and literature data for polymer solutions.

INTRODUCTION

Bitumen is often modified with polymers or other additives to improve its performance in various engineering applications, such as asphalt paving and roofing^{1,2}. In terms of rheological properties, polymer modification of bitumen typically results in enhanced elastic properties and reduced temperature susceptibility³. However, despite the widespread use of polymer modified bitumens (PMBs), there is no robust, quantitative method to predict the rheological properties of PMBs as a function of polymer concentration (we emphasize that the Palierne emulsion model⁴ employed by Lesueur et al.⁵ is only applicable to a very limited number of PMBs in which the polymer does not form a continuous elastic network).

At elevated temperatures (above ~60 °C), bitumen can be considered as a

Newtonian fluid that does not exhibit significant elasticity⁶. Therefore, in this temperature range, bitumen can be regarded as a solvent for polymers and, consequently, PMBs can be treated as polymer solutions. This observation opens up new perspectives for the rheological modeling of PMBs as will be demonstrated in this paper.

In particular, thermoplastic block copolymers, such as styrene-butadiene-styrene (SBS), are frequently used in bitumen modification^{1,2,7}. These types of polymers are known to form a three-dimensional network structure within bitumen already at relatively low concentrations, with associating copolymer endblocks acting as reversible physical crosslinks^{1,8}. In addition, it is important to note that bitumen is a good solvent for many polymers, including SBS (or the PB midblock of SBS, to be more exact), resulting in polymer swelling⁸.

The scope of this paper is to introduce a new framework for analyzing and predicting rheological properties of PMBs as a function of polymer concentration. Specifically, bitumen modified with associating block copolymers is considered. Theories of polymer solution rheology are used as the basis of the analysis. In addition, comparisons with relevant literature data are made.

THEORY

In this section, selected theories of polymer solution rheology are briefly reviewed. The predictions of these theories are compared with our experimental results later in this paper.

Polymer solutions are usually divided into three concentration regimes: dilute, semidilute, and concentrated. Further, semidilute and concentrated polymer solutions can be either unentangled or entangled. As the PMBs studied in this paper have polymer concentrations in the semidilute regime and are entangled, we limit the discussion in the following to the theory of semidilute entangled polymer solutions.

Homopolymer solutions

The concentration dependences of some rheological properties of semidilute entangled homopolymer solutions can be derived from the reptation theory^{9,10}. As shown in Table 1, the reptation theory predicts power-law concentration dependencies both for the elastic properties (the plateau modulus G_N^0 and the steady-state recoverable compliance J_e^0) and viscous properties (the viscosity η) of this type of polymer solution. These theoretical predictions are in good agreement with experimental results from the literature¹¹.

Solutions of block copolymers in selective solvents

It is well known that block copolymers tend to associate into micelles in selective solvents¹². Further, at high enough polymer concentrations, these micelles may form a gel-like network structure that contributes to the elastic properties of the block copolymer solution¹³. However, even in this case the elasticity is often dominated by entanglements, and consequently the predictions for the concentration dependence of the elastic properties G_N^0 and J_e^0 are identical, or at least very similar, to

the ones for homopolymer solutions in the semidilute concentration regime (see Table 1).

On the contrary, the viscous properties of block copolymer solutions are significantly impacted by the intermolecular associations. As shown in Table 1, η has much stronger concentration dependence in associating block copolymer solutions than in homopolymer solutions. Note that the predicted value of the power-law exponent for the viscosity varies depending on the model assumptions and polymer concentration range. For brevity, details and assumptions of the models listed in Table 1 are not discussed here; the reader is referred to the original publications for the complete model descriptions.

Table 1. Theoretical predictions of the power-law concentration dependences of rheological constants for semidilute entangled polymer solutions in a good solvent ($\nu = 0.588$). Please refer to the original publications for complete details.

Model	Elastic prop. $G_N^0 \sim c^\alpha$ $J_e^0 \sim c^{-\alpha}$	Viscous prop. $\eta \sim c^\beta$
<i>Homopolymer solutions</i>		
Reptation ^{9,10}	$\alpha \approx 2.31$	$\beta \approx 3.93$ (for $\eta \sim M^3$) $\beta \approx 4.45$ (for $\eta \sim M^{3.4}$)
<i>Associating block copolymer solutions</i>		
Semenov et al. ¹³ ($f=2$)	$\alpha \approx 2.31$ (for $\phi > \phi_e$)	no power-law concentration dependence
Sticky reptation ¹⁴ ($f \gg 1$)	$\alpha \approx 2.31$	$\beta \approx 4.13$
Sticky reptation ¹⁵ ($f \gg 1$, very low ϕ_{open})	$\alpha \approx 2.31$ (for $\phi < \phi_s$) $\alpha \approx 2.60$ (for $\phi > \phi_s$)	$\beta \approx 6.8$ (for $\phi_e < \phi < \phi_{ren}$) $\beta \approx 8.5$ (for $\phi_{ren} < \phi < \phi_s$) $\beta \approx 3.75$ (for $\phi_s < \phi < \phi_{le}$)

EXPERIMENTAL

Materials

A paving grade bitumen 160/220 was melt blended with one of two commercial SBS triblock copolymers, having either a linear or star-shaped structure. The concentration of SBS in bitumen was varied in the range of 3-10 wt%, representing volume fractions of $\phi \approx 0.03$ -0.11 and corresponding to the semidilute concentration regime. The basic properties of the bitumen and SBS block copolymers are summarized in Tables 2 and 3, respectively.

Table 2. Basic properties of the bitumen.

Property	Method	Value
Penetration	EN 1426	177 dmm
Ring-and-Ball softening point	EN 1427	38.4 °C
S/A/R/A fractions	Iatroscan (TLC-FID)	5/54/23/18 wt%

Table 3. Basic properties of the SBS triblock copolymers.

	Star SBS	Linear SBS
Commercial name	Calprene 411	Kraton D1101
Architecture	3-arm star	linear chain
S:B ratio	30:70 wt%	31:69 wt%
SB diblock content	8 wt%	16 wt%
M_n	311 kg/mol	193 kg/mol
M_w	343 kg/mol	219 kg/mol
M_w/M_n	1.11	1.13

Rheological characterization

Rheological properties of the SBS modified bitumens were measured using a stress-controlled Anton Paar Physica MCR 301 rheometer, equipped with 25-mm diameter parallel plates set at a gap of 1 mm. A Peltier plate and active hood were used to provide accurate and gradient-free temperature control. Frequency sweep measurements ($f = 0.01 \dots 10$ Hz) were

performed at various temperatures ranging from 30 to 90 °C with 10 K intervals. The strain amplitude was kept constant at 1%, which ensured that the rheological behavior was measured within the linear viscoelastic regime. Moreover, creep experiments were performed at increasing creep stress levels (from 25 to 25,600 Pa) at 50 °C.

In addition, rheological properties of the pure SBS block copolymers were measured using two different experimental setups. At high temperatures (90 ... 180 °C), a stress-controlled Malvern Kinexus Pro rheometer was used with 8-mm diameter parallel plates set at a gap of approximately 1 mm. In the lower temperature range (-120 ... 90 °C), the MCR 301 rheometer was used, equipped with a solid rectangular fixture (SRF 12) and a CTD 450 convection oven. The SRF 12 experiments were performed in torsion on a rectangular specimen with dimensions of approximately $32 \times 10 \times 0.65$ mm³. Frequency sweep measurements (0.01 ... 10 Hz in the case of 8-mm parallel plates; 0.01 ... 1 Hz in the case of SRF 12) were performed at various temperatures in the linear viscoelastic regime.

Determination of rheological constants

The equations used to calculate rheological constants are given in Table 4. The discrete relaxation time spectra used in the calculation of J_e^0 , η_0 and $\psi_{1,0}$ were determined using the method of Baumgaertel and Winter^{16,17}.

Polymer solution data from the literature

G_N^0 and J_e^0 data for various semidilute entangled polymer solutions were compiled from the literature and compared with the corresponding measured data for the SBS modified bitumens. A summary of the literature data used in this study is presented in Table 5. It is noted that this table includes polymer solutions in both good and theta solvents.

Table 4. Equations for the calculation of rheological constants.

Rheological constant	Equation
Plateau modulus G_N^0	$G_N^0 = G'(\omega)_{\delta_{min}}$ (see Ref. 18)
Steady-state recoverable compliance J_e^0	$J_e^0 = \frac{\sum_{i=1}^N g_i \tau_i^2}{(\sum_{i=1}^N g_i \tau_i)^2}$
Zero-shear viscosity η_0	$\eta_0 = \sum_{i=1}^N g_i \tau_i$
Zero-shear first normal stress coefficient $\psi_{1,0}$ (from dynamic data)	$\psi_{1,0} = 2 \sum_{i=1}^N g_i \tau_i^2$
Zero-shear first normal stress coefficient $\psi_{1,0}$ (from creep data)	$\psi_{1,0} = \lim_{\dot{\gamma} \rightarrow 0} \frac{N_1}{\dot{\gamma}^2}$

Table 5. Summary of the literature data analyzed in this study.

Source of data	Solvent(s)	Type of data
<i>PB homopolymer solutions</i>		
Raju et al. 19	hydrocarbon oils, tetradecane, low- M_w PB, isobutyl acetate	G_N^0 and J_e^0
Colby et al. 20	phenyloctane, dioctyl phthalate	G_N^0 and J_e^0
<i>PS homopolymer solutions</i>		
Adam and Delsanti ²¹	benzene	G_N^0
Adam and Delsanti ²²	cyclohexane	G_N^0
Takahashi et al. 23	α -chloronaphthalene	J_e^0
Plazek et al. 24	tricresyl phosphate	J_e^0
<i>SBS block copolymer solutions</i>		
Watanabe et al. 25	<i>n</i> -tetradecane	G_N^0

RESULTS AND DISCUSSION

A rubbery plateau region is observed in the master curves of all the investigated SBS polymer modified bitumens, thus evidencing the formation of entanglements in these

materials. Consequently, the previous assumption that these materials can be treated as semidilute *entangled* polymer solutions is confirmed.

As expected, the plateau modulus G_N^0 follows a power-law concentration dependence in the SBS modified bitumens. The exponent of this power law is 2.26, in excellent agreement with the theoretical predictions for associating block copolymer solutions (Table 1). Similarly, the steady-state recoverable compliance J_e^0 exhibits a power-law concentration dependence with an exponent of -2.32, again in excellent agreement with the theoretical predictions.

The concentration-dependent G_N^0 and J_e^0 data of the SBS modified bitumens are found to overlap with those of SBS/*n*-tetradecane solutions²⁵. Furthermore, when plotted as a function of the PB phase concentration and corrected for the filler reinforcement effect caused by glassy PS particles²⁵, these data perfectly overlap with the G_N^0 and J_e^0 data of the PB homopolymer solutions. This observation can be explained by the fact that both the elasticity of the PB homopolymer solutions and of the SBS block copolymer solutions are due to the entanglement of PB chains.

The polymer contribution to viscosity is given by the specific viscosity η_{sp} :

$$\eta_{sp} = \frac{\eta - \eta_s}{\eta_s} \quad (1)$$

where η is the (zero-shear) viscosity of the solution and η_s is the (zero-shear) viscosity of the solvent. The predictions for the concentration dependence of η_{sp} are the same as for η (Table 1) when $\eta \gg \eta_s$. In SBS modified bitumens, η_{sp} is found to follow a power-law concentration dependence with an exponent of about 4.2 at polymer volume fractions above 0.05. This is in excellent agreement with the prediction of the sticky reptation model as derived by Leibler et al.¹⁴; in this case, the number of

free stickers (unassociated PS blocks) is assumed to be relatively high. At low polymer volume fractions ($\phi < 0.05$), evidence of a weaker concentration dependence of η_{sp} is found. The above observations are consistent with the findings for other associating polymer solutions²⁶⁻²⁸.

In addition, the zero-shear first normal stress coefficient $\psi_{1,0}$ is found to exhibit a power-law concentration dependence with an exponent of about 3.8. As far as the authors know, this type of concentration dependence has not been reported previously for $\psi_{1,0}$. Furthermore, there is no model or theory available to explain this result. Further studies need to be conducted to test the universality of this finding in different types of polymer solutions.

Finally, it is noted that the bitumen and SBS polymers used in this study are compatible with each other, resulting in the thermorheologically simple behavior of SBS modified bitumens. However, not all PMBs are thermorheologically simple²⁹, in which case the determination of the analyzed rheological constants may not be always possible. This can be considered as a limitation of the presented methodology.

CONCLUSION

In this paper, a new approach for analyzing and predicting the rheological properties of PMBs is described. The presented framework is based on the theories of polymer solution rheology, resulting in the power-law scaling of rheological constants as a function of polymer concentration. The elastic properties of PMBs, i.e. G_N^0 and J_e^0 , are determined solely by the elastic properties and concentration of the polymer, and in the case of SBS modified bitumens these elastic characteristics coincide with those of PB homopolymer solutions. Similarly, the viscosity of PMBs scales with a power law of the polymer concentration as predicted by

the theory and as previously observed for other associating polymer solutions. The proposed framework can be used to optimize the engineering properties of PMBs in their various applications.

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