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Time Scales in Polymer Modified Asphalts

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Summary: Historically, Maxwell was probably the first one who recognized the importance of time scales for understanding the mechanical response of asphalt. In instantaneous response asphalt behaves as an elastic, solid-like material, on the other hand its long time response is that of a viscous, fluid-like material. In the linear viscoelastic region asphalt behaves as a low molecular weight polymer. However, in the nonlinear region of high strains or rates of strain the behavior of some asphaltic systems can be rather complicated. In asphalts, asphaltenes, resins and alkanes compose a complex colloidal system, in which alkanes act as a solvent, asphaltenes as micelles and the polar resins as stabilizers. In order to enhance the mechanical properties of asphalts they are frequently modified by blending them with appropriate polymers. Changes in the impermanent network that can be formed in some of these blends can lead to an unexpected behavior of the steady shear viscosity function. Several different time scales emerge from this behavior. A possible relation of these "nonlinear" time scales to the linear viscoelastic time scales is discussed and examples of anomalous behavior of polymer-modified asphalts are given.

Keywords: asphalts; modelling; rheology; temporary networks; viscosity function

Introduction

Asphalt, a material with complex chemical structure that varies with its origin and method of preparation, is not a simple material for the study of various time scales appearing in its mechanical response to various strain fields. To improve its engineering properties, asphalt is frequently modified by various polymeric materials (thus forming polymer modified asphalts, henceforth PMA) usually added in percentages ranging from 3% to 8%, by weight.

When conventional asphalt is blended with polymers, its rheological behavior can be on one hand more complicated but on the other hand the manifestation of the internal structure can be observed in such blends. Because of the complicated structure, various time scales can be observed in different material functions of PMAs.

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From the late 1930s asphalt has been considered to be a colloid containing asphaltene micelles surrounded by a layer of low molecular weight hydrocarbons and dispersing oils. Not withstanding its structure, the conventional asphalt is rheologically similar to a low molecular weight polymeric system.[1,2] As such, asphalt can be characterized by its discrete relaxation spectrum, which relatively successfully generates all its linear viscoelastic material functions.[3] In industrial research, the temperature interval of interest is usually between -30 °C and +90 °C. In such an interval, the asphalt behavior changes from glass-like to Newtonian fluid-like behavior. The extension of this interval is desirable in PMAs and may bring some interesting results even in conventional asphalts. Almost all available studies cover the linear viscoelastic region of small deformations or rates of deformation. It is sometimes difficult to distinguish or to characterize different PMAs in the linear viscoelastic region, however a new picture emerges when this region is extended to large deformations. In this respect, the shear viscosity is probably the simplest non-linear function that can reveal the anomalous behavior of blends of conventional asphalts with polymers.

Even if very different in composition and structural characteristics, all polymers used in this work are copolymers able to strongly affect the physical and mechanical properties of asphalts thanks to their common ability to form networks which swell and include the whole asphaltic material. The two main categories of polymers used for asphalt modification are thermoplastic elastomers and plastomers. Styrene-butadiene-styrene block copolymer (SBS) is probably the most frequently used polymer belonging to the first category, while Ethylene-vinylacetate random copolymer (EVA) is a plastomer.

Studying the properties of asphalts modified with SBS or EVA, some similarities can be found between PMAs and amphiphilic or associating polymer networks when the shear viscosity function is studied well into the non-Newtonian region of shear rates.[4,5] The initial attempts to describe the linear viscoelastic behavior of such polymeric systems by one Maxwell mode[6] was found unjustified.[4] Similarly, the whole set of Maxwell modes is needed for the linear viscoelastic characterization of PMAs. On the other hand, for the description of the non-monotonous viscosity function of PMAs a smaller number of Maxwell modes is needed. Problems related to these observations in PMAs, are discussed in this note.

Experimental

Conventional asphalts of two different origins and penetration grades (a "soft" asphalt, Pen 200-300 dmm and a "hard" asphalt, Pen 70-100 dmm) were blended with radial SBS (MW=150,000, styrene content = 30 % by weight) or EVA (MI = 350, vinyl acetate = 25 %) at various concentrations. Rheological properties of the materials are described in detail elsewhere.[7] Dynamic and steady viscosity measurements were conducted in a Rheometric Scientific ARES A-33A rheometer. The geometries used were the cone and plate (25 and 50 mm diameters, cones of 0.01 rad. and 0.04 rad. respectively) for viscometry, and the parallel plate (25 and 50 mm diameters) and torsion bar (with linear dimensions of 35*12*2.7 mm, used at low temperatures) for dynamic measurements. From frequency sweep tests the master curves of the dynamic moduli were constructed and the linear viscoelastic characterization of the tested PMAs was obtained with the help of the rheological software IRIS.

Theoretical - constitutive equations

As mentioned above, some characteristic phenomena of PMAs are observed in the response of these materials to large deformations. A suitable nonlinear constitutive equation for the description of the observed behavior is the generalization of Lodge's rubberlike-liquid model.[8,9] This constitutive equation defines the material via the following expression for the extra stress tensor $\underset{\sim}{\tau}$,

$$\underset{\sim}{\tau} = \int_{-\infty}^{t} M(t-\tau, I, II)\, \underset{\sim}{C}_t^{-1}(\tau)\, d\tau \qquad (1)$$

where M is the memory function, $\underset{\sim}{C}_t$ is the relative Finger tensor and I and II are the first two principal invariants of $\underset{\sim}{C}_t$.

Assuming that the nonlinear memory function is separable as

$$M\left(t-\tau, \left|\gamma(t-\tau)\right|\right) = m(t-\tau)\, h\left(\left|\gamma(t,\tau)\right|\right) \qquad (2)$$

where m is the linear viscoelastic memory and h is the damping function, and assuming that the damping function $h\left(\left|\dot{\gamma} \cdot s\right|\right)$ is given as[10]

$$h\left(\left|\dot{\gamma}\cdot s\right|\right) = K\exp(-\alpha\left|\dot{\gamma}\right|s) + (1-K)\exp(-\beta\left|\dot{\gamma}\right|s) \qquad (3)$$

where s = t - τ, $\dot{\gamma}$ is the constant shear rate, K, α and β are constants, the following expression can be obtained for the viscosity function:

$$\eta(\dot{\gamma}) = K\sum_i \frac{g_i\lambda_i}{\left(1+\alpha\left|\dot{\gamma}\right|\lambda_i\right)^2} + \left(1-K\right)\sum_i \frac{g_i\lambda_i}{\left(1+\beta\left|\dot{\gamma}\right|\lambda_i\right)^2} \qquad (4)$$

If the sums in equation (4) are limited to the first three terms, the relation has a total of 9 parameters, which can be used to fit the experimental data.

Results and discussion

From a qualitative point of view, the viscosity curves for all unmodified asphalts are similar to those reported in Figure 1 for the soft asphalt.

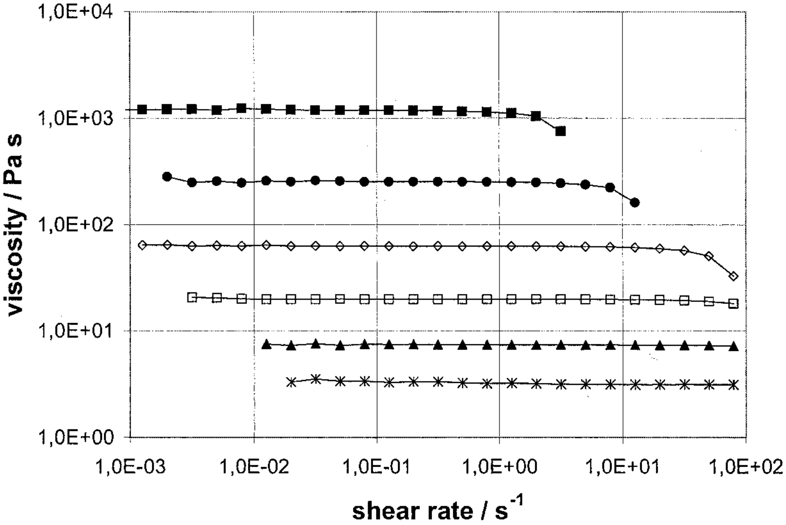

Figure 1. Viscosity functions, at different temperatures for the soft base asphalt: ■ = 40; ● = 50; ◊ = 60; □ = 70; ▲ = 80; * = 90 °C.

Starting from low shear rates, there is a long plateau where the asphalt behaves as a Newtonian fluid, then a "critical" shear rate value is reached and a sharp shear thinning starts. Due to their complex nature, it is always hard to identify transitions that occur in asphaltic materials. We can suppose that the shear stress alters the colloidal equilibrium and can either orient or disaggregate asphaltenic micelles or aggregates of micelles.

For PMAs, curves similar to those of base asphalts are sometimes obtained; however for some polymer concentrations and test temperatures, a different behavior may be found. As an example, two typical non-monotonous viscosity functions observed in PMAs are reported in Figures 2 and 3. The steady shear viscosity, at T = 80 °C, of the blend of the soft asphalt with 4 wt% of EVA is shown in Figure 2. The curve has two distinct shear thinning regions and this behavior was observed in many cases, both for EVA and SBS modified asphalts. A similar shape of the viscosity curve has been observed in other systems, e.g. low molar mass liquid crystals[11], mesomorphic carbon pitches[12] and, especially, liquid crystal polymers. [13-16] Onogi and Asada[11] defined the first decreasing part as "Region I", the intermediate plateau as "Region II", and the final shear thinning part as "Region III". Later, Sigillo and Grizzuti[16] called the Newtonian plateau at zero shear rate "Region 0".

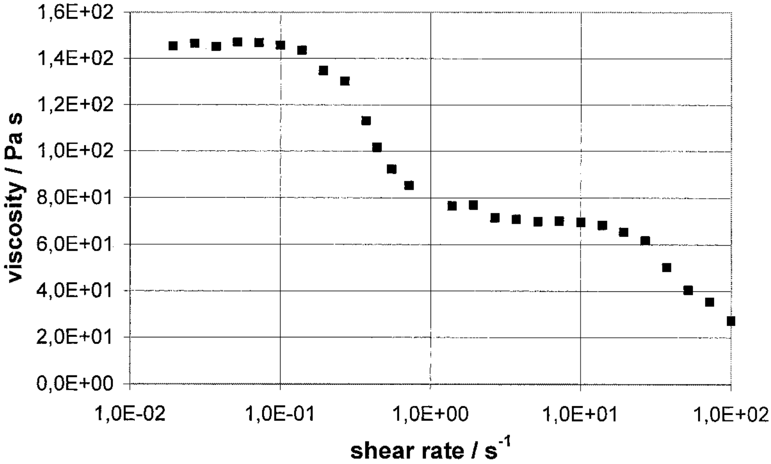

Figure 2. Viscosity function at 80 °C for PMA from soft asphalt modified with 4.0 % EVA.

In analyzing this viscosity curve, we can start from Region 0. EVA and SBS copolymers have some similarities in their structure. It is well known that SBS has a two-phase morphology consisting of glassy micro-domains made of polystyrene connected by the soft polybutadiene segments, thus exhibiting a physically cross-linked structure. When mixed with asphalt, the lightest components of asphalt swell the soft butadienic phase, but SBS is assumed to maintain its microstructure. This is why SBS confers elastomeric properties to the whole material. Similarly, the EVA modified asphalt contains a physical network where the cross-linking units are the crystallites formed by the ethylene sequences. Usually, block copolymers like SBS show Newtonian, rather than elastic, behavior for very low shear rates as was observed for both bulk polymers and concentrated solutions.[17-19] In this case, the zero shear rate plateau is possibly due to rigid "movement" of PS polydomains together with diffusion of the individual polymer chains. In other words, this mechanism can be seen as a result of the long-time scale impermanent nature of the physical network and is probably the same as that observed in the PMAs, obtained by adding either SBS or EVA. With regard to the double step shear thinning, the simplest explanation is that the second shear thinning (which has the lower characteristic time) is the same as observed in unmodified asphalts, while the first one (which has a higher characteristic time) is strictly related to the polymer, e.g. due to the orientation of crystalline or glassy (in case of SBS) domains.

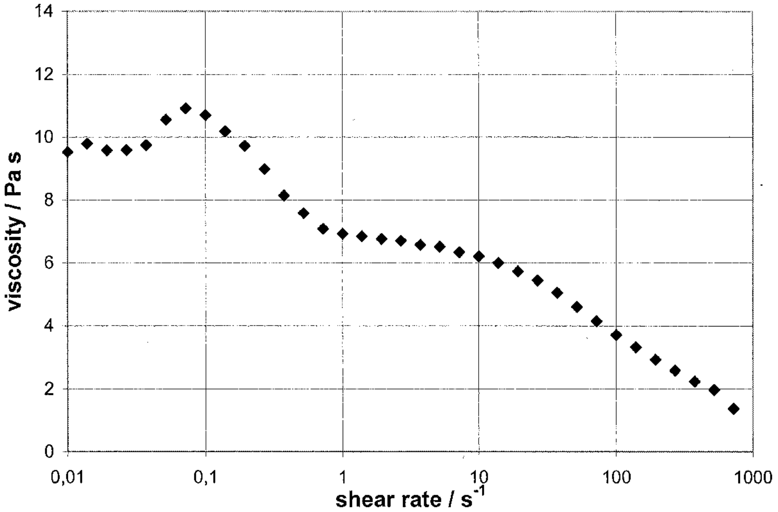

Figure 3. Viscosity function at 130 °C for PMA from hard asphalt modified with 7.2 % SBS.

Figure 3 shows the viscosity function at 130 °C of a 7.2 wt% SBS blend with the hard base asphalt. Here the zero shear viscosity domain is barely visible and is followed by a weak shear thickening after which a strong shear thinning is observed. Subsequently, a plateau extends over about one decade of shear rates and then the final shear thinning follows.

The most common examples of shear thickening are found in solutions of amphiphilic or associating polymers.[4-6,20] Asphalt is a complex organic material with a spectrum of components starting with low molecular weight oils followed by components with polycyclic and polyaromatic asphaltenes. According to Yen[21], the molecules of asphaltenes are in associated state either in the form of micelles or in the form of clusters of micelles. By blending asphalt with various polymers its linear viscoelastic properties are "strengthened" and more complicated behavior is observed. However, the structural understanding of this behavior is still lacking.

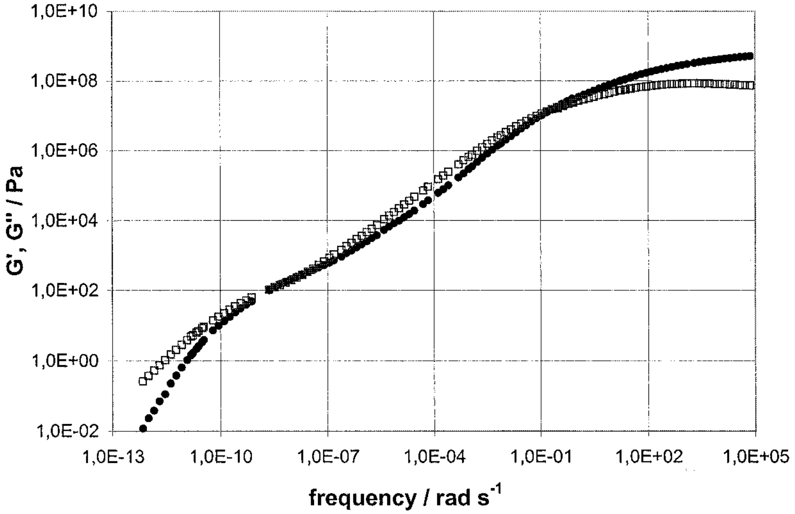

Figure 4. Master curves of storage (G') and loss (G") moduli for PMA from hard asphalt modified with 7.2 % SBS: reference temperature 0 °C; • = G'; □ = G".

In order to model the viscosity functions, the first attempt was made starting from the dynamic master curves (Figure 4), obtained in the linear region by applying the Time Temperature Superposition principle.[22] From the dynamic master curves, a discrete spectrum (Maxwell modes) can be calculated. The shear relaxation modulus is then given as

$$G(s)=\sum_i g_i \exp(-s/\lambda_i) \tag{5}$$

The spectrum then can be used either to calculate the stress growth coefficient or obtain the shear viscosity trough the Gleissle mirror rule[23]

$$\eta(\dot{\gamma})=\eta^{+}(t,\dot{\gamma})\Big|_{t=1/\dot{\gamma}} \tag{6}$$

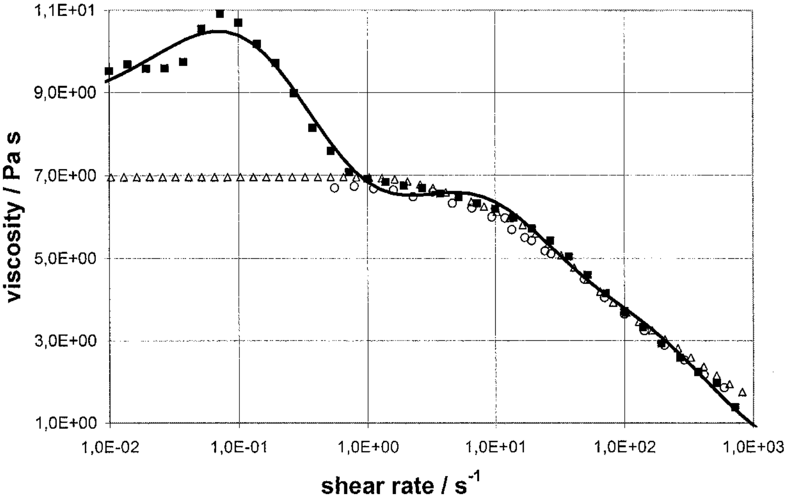

Figure 5. Experimental and calculated data: ■ = experimental; ○ = Cox-Merz; Δ = Gleissle; solid line = fit from equation (4) with the following values for the parameters: g_1 = 136.0 Pa, λ_1 = 0.02004, g_2 = 2.6344, λ_2 = 1.5060, g_3 = 1779.40, λ_3 = 0.0012, K = 2.4142, α = 1.1028 and β = 7.8962. Temperature: 130 °C.

or to calculate the complex viscosity and then to obtain the shear viscosity trough the Cox-Merz relation[24]

$$\eta(\dot{\gamma})=\left|\eta^{*}(\omega)\right|_{\omega=\dot{\gamma}} \tag{7}$$

Both empirical rules proved unable to describe the anomalous behavior reported in Figures 2 and 3; therefore, for a better description of these curves one has to turn to the non-linear constitutive equation (4). The obtained fit for the viscosity curve shown in Figure 3 is reported in Figure 5, together with the Cox-Merz and Gleissle relations. It can be seen that equation (4) is able to describe reasonably well both the shear thickening and the shear thinning regions while the two empirical rules fail to account for the shear thickening behavior. With regard to the fitting parameters, it should be underlined that the values reported in the figure caption are those produced by a commercial software; however, for a good fit it is not necessary to have five or more digits for the parameters (the fitting is quite robust and not highly sensitive to the number of digits). Finally, Figure 6 compares the complete linear viscoelastic spectrum, obtained from the dynamic master curves with the "short" spectrum given by the g_i, λ_i values calculated from the fit of the viscosity function. In order to properly compare the values, the frequency shift factors are used to obtain the linear spectrum at 130 °C as reference temperature. It is interesting to observe that the spectrum from the fit of $\eta(\dot{\gamma})$ covers the "tail", which corresponds to the largest relaxation times, of the "complete" linear viscoelastic spectrum (discrete).

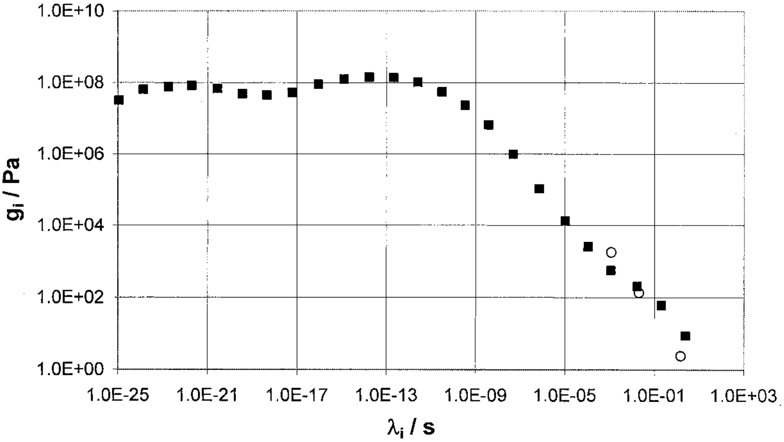

Figure 6. Comparison between the linear viscoelastic spectrum (■) and the spectrum from the fitting (○). Reference temperature: 130 °C.

Conclusions

The rheological behavior of two asphalts modified by radial SBS and EVA copolymers was tested at different temperatures and polymer concentrations. In same cases, the obtained results revealed, in the viscosity-shear rate curves, a two step shear thinning or a maximum, positioned at the end of the zero shear viscosity range. Similar behavior is known to exist in liquid crystalline materials, mesomorphic carbon pitches, associating polymers and solutions of rod-like polymers. Such behavior can be interpreted as a result of the temporary nature of the polymeric network present in PMAs. Two empirical rules and a phenomenological constitutive equation were tested to fit the anomalous viscosity data. The empirical rules were not able to describe the viscosity functions in the low shear rate range. The phenomenological equation, derived from the Wagner model, provided a good qualitative and quantitative fit of the experimental data. The relaxation spectrum resulting from the fit of shear viscosity is positioned at the tail of long relaxation times of a "complete" linear viscoelastic spectrum.

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