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Effect of SBS on Rheological Properties of Different Base Asphalts

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Summary: In this note rheological properties of two different polymer modified asphalts (PMA) are compared. PMAs were prepared from two different base asphalts, a soft one (200/300 Pen grade) and a hard one (70/100 Pen grade), by addition of 4% by weight of radial SBS as modifier. Dynamic mechanical properties were determined in a wide temperature range for bases and modified asphalts both before and after artificial aging. As expected, the moduli of the soft base are more sensitive to polymer addition and the two PMAs attain similar maximum values after aging. However a significant difference in the frequency at which the maxima of the loss modulus are reached is maintained within the two materials irrespectively of aging or polymer addition.

Keywords: asphalt; modification; rheology; styrene-butadiene-styrene; time-temperature-superposition

Introduction

The most frequent use of asphalt, in technological applications, can be found in paving industry. Even though asphalt constitutes only a small fraction of the complex construction composite (hot-mix asphalt concrete) it has a significant impact on the performance of pavements. The interest in improving asphalt engineering properties is considerable. To achieve this goal the conventional asphalt is often blended with various polymers. Such a blending produces new materials, called polymer modified asphalts (PMA). With the right combination of polymer, its concentration and the base (conventional) asphalt, the PMA may have improved mechanical properties which are also reflected in the improved performance of paving mixes.[1] The blends of the base

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(conventional) asphalt with a polymer are multiphase systems. At low concentrations of polymer, a continuous asphalt phase with dispersed polymer is observed. At higher concentrations, phase inversion occurs and a continuous polymer phase with dispersed asphalt phase can be observed. The properties of asphalt-polymer blends usually start to change at a polymer concentration ranging from 4 to 6% by weight. These concentrations are considered as economically viable for the modification of paving asphalts and are thus frequently studied.[2,3]

One of the most successful polymers, used as a modifier in paving asphalts, is the styrene-butadiene-styrene block copolymer (SBS) either with linear or star structure.[1-4] Polystyrene (PS) aromatic end blocks are not thermodynamically compatible with polybutadiene (PB) olefinic blocks and thus polystyrene forms uniformly distributed micro-domains which are dispersed in a PB phase. At usual operating temperatures the PS domains are below their glass transition temperature (about 100 °C) while the PB phase (glass transition temperature at about -80 °C) is in the rubbery state. Therefore, the material exhibits a two-phase morphology consisting of glassy micro-domains made of PS connected by flexible PB segments. It results in a physical cross-linking responsible for the thermoplastic and elastomeric properties of the polymer.[5]

When mixed with asphalt the PB phase is swollen especially by the lightest asphalt components but the PS domains maintain their structure and therefore SBS is able to confer elastomeric properties to the whole mass without loosing melt processability at temperatures above the PS glass transition. Since the SBS structure is due to physical, rather than chemical bonds, the cross-linking is reversible even if repeated heating and cooling cycles are applied, hence making SBS a good asphalt modifier. Conventional asphalt (not modified) is a complex multidisperse micellar system with composition varying with the source of crude oil and the method of manufacturing.[3,4] Rheologically, the conventional asphalts behave as low molecular weight polymers.[6-8] As such, conventional asphalts are most frequently studied in small amplitude shear oscillations. It is quite common to construct master curves of dynamic material functions from these measurements.[9] Under the same experimental conditions it is possible to construct also the master curves of dynamic material functions of polymer modified asphalts.[3] The rheological properties of two commercially available PMAs, obtained by blending different base asphalts with radial SBS are compared in this note.

Materials and Methods

Both PMAs contain 4% (by weight) of radial SBS (molecular weight of about 200,000; styrene content = 30 % w). There are more than three polystyrene blocks in the molecule, but no information on the number of polybutadiene arms are available from the manufacturers. The first of the studied asphalts (denoted as PMA1) is obtained from an asphalt 200/300 Pen grade (denoted as A1), while the second one (PMA2) is obtained from a 70/100 Pen grade base asphalt (A2). Both PMAs are produced by blending asphalt and polymer at about 170-180°C in a colloidal mill (high-shear process). Materials were studied before and after blending with SBS and in both cases before and after artificial aging. Artificial ageing is conducted according to Rolling Thin Film Oven (RTFO) procedure (AASHTO T240, or ASTM D 2872).

Rheological testing at low and mid temperatures was performed in the strain control rheometer ARES of Rheometric Scientific. The testing geometries were parallel-plate (mid temperatures) and torsion bar (low temperatures). For testing at high temperatures the stress control rheometer CVO 200 of Bohlin Instruments was used. This rheometer is equipped with the bob and cup geometry which allows also the dynamic testing of liquid samples with better reliability than the plate-plate geometry.[10] Both samples (PMA1 and PMA2) were tested in the temperature range (-30, +90 °C) with the step 10 °C. By applying the time–temperature superposition principle, the master curves of the storage (G') and the loss (G") moduli were constructed.[11]

Results and discussion

In the following, master curves for both base and modified asphalts are discussed. Closed symbols in figures refer either to asphalt A1 or modified asphalt PMA1, while empty symbols refer either to asphalt A2 or modified asphalt PMA2. Reference temperature (T_r) is 0 °C for all master curves and the reader can distinguish G" from G' because the former shows a maximum at high frequencies.

The base asphalts are compared in Figures 1 and 2. The harder asphalt A2 attains higher values of G' and G", in comparison with the asphalt A1, see Figure 1. The glass transition, characterized by the position of the absolute maximum of G", is better shown in a linear scale, Figure 2, and appears at $\log \varpi$ ~5, for the base A1 and at $\log \varpi$ ~3 for the base A2 (here ϖ represents the reduced frequency). The rate (in mathematical sense of analyzing the graphs) of reaching this transition is higher in A2 than in A1 (almost twice).

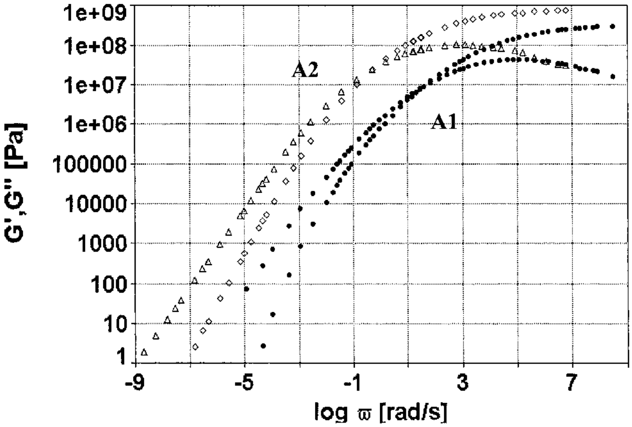

Figure 1. G' (Pa) and G" (Pa) for base asphalts. Tr = 0 °C.

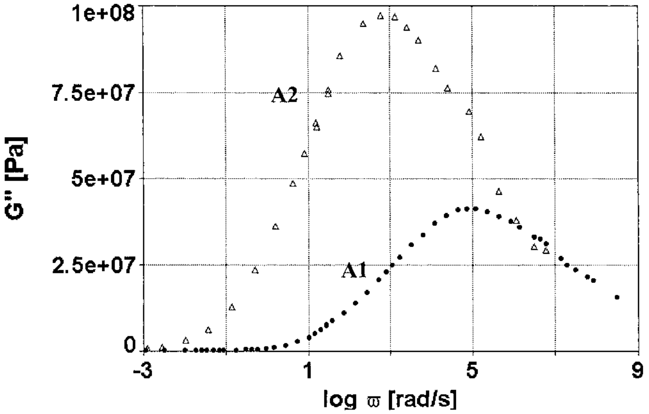

Figure 2. G" (Pa) for base asphalts. Tr = 0 °C.

The picture is very much changed when the bases are compared after the artificial aging in the rolling thin film oven, Figures 3 and 4. Both asphalts undergo some change, but A1 is the most affected by the thermal treatment, Figure 3. This was expected due to the softer nature of A1 with respect to A2, which means higher content of low molecular weight volatile components. The maximum values of G" are now much closer than before aging. The rates of change of G" are also "closer" than in the non-aged base asphalts.

After modification, the low temperature behaviour of both asphalts is quite similar, fig.5. The glass transition in both samples appears roughly at the same reduced frequency as in the bases. The maximum value of G" is almost same for both polymer modified asphalts, and is much higher than in aged (not modified) asphalts, fig.6. In fact, the maximum value of G" increases of about one order of magnitude for the harder asphalt and two orders of magnitude for the softer one.

The rates of approaching the glass transition in PMA1 and PMA2 are again comparable. Looking at the shapes of the master curves, it seems that at mid temperatures artificial aging have a stronger impact on sample PMA1, (Figs. 7 and 8) than on sample PMA2. The maximum of G" is again at $\log\varpi$ ~5, for PMA1. In PMA2, the position of the maximum of G" is shifted to $\log\varpi$ ~2.5. The rate with which PMA1 is approaching the glass transition is almost twice of that for PMA2.

The comparison of asphalts A1 and A2 at high temperatures is given in Figs. 9 and 10. In these figures the function ($1/\varpi$ J") is portrayed for all the studied asphalts (bases, bases after RTFOT, PMAs and PMAs after RTFOT). Considering that the reference temperature is 0°C, quite close to asphalt glass transition, we prefer the plot of $1/\varpi$ J" instead of the plot of the real part of complex viscosity (which might be more common for the case of melts).

Since the loss compliance is given as,

$$J''(\varpi) = \int_{-\infty}^{\infty} \frac{L(\Lambda)\varpi\Lambda d\ln\Lambda}{(1+(\varpi\Lambda)^2)} + \frac{1}{\varpi\eta_0} \qquad (1)$$

where L is the retardation spectrum and η_o the zero shear viscosity.

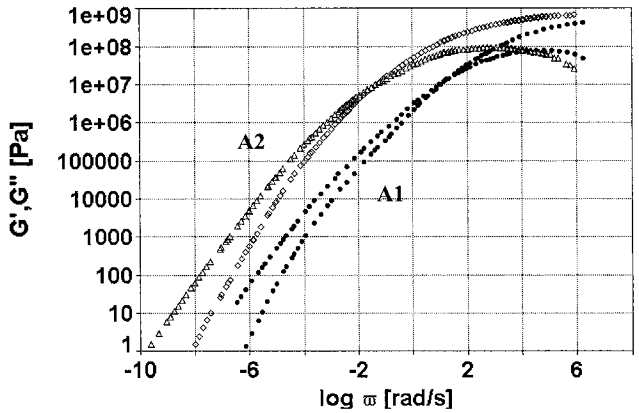

Figure 3. G' (Pa) and G" (Pa) for base asphalts after artificial aging. Tr = 0 °C.

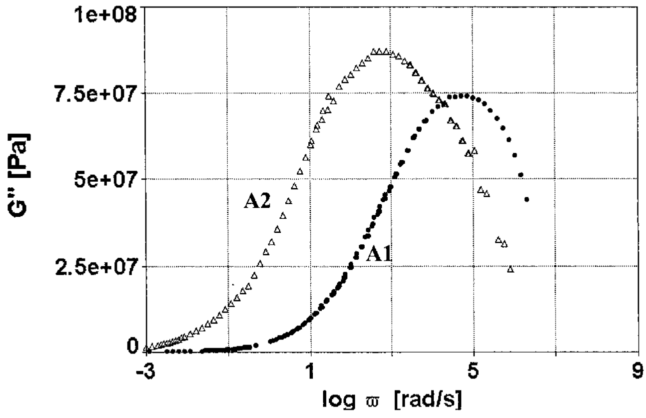

Figure 4. G" (Pa) for base asphalts after artificial aging. Tr = 0 °C.

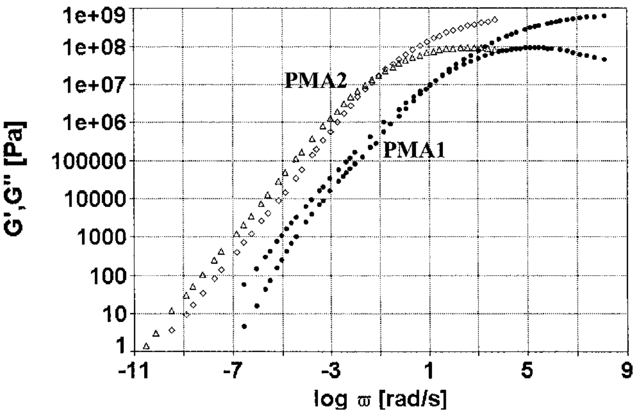

Figure 5. G' (Pa) and G" (Pa) for 4% SBS modified asphalts. Tr = 0 °C.

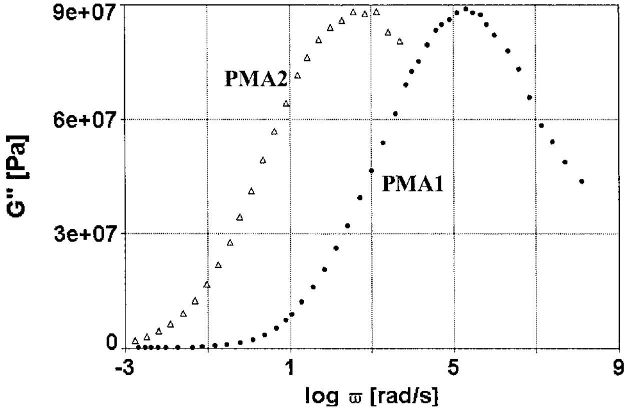

Figure 6. G" (Pa) for 4% SBS modified asphalts. Tr = 0 °C.

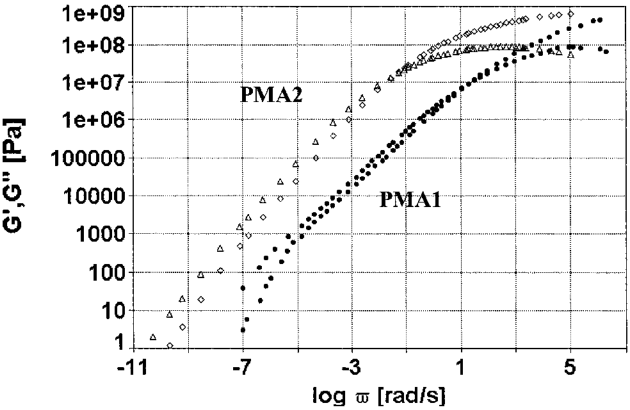

Figure 7. G' (Pa) and G" (Pa) for 4% SBS modified asphalts. Tr = 0 °C.

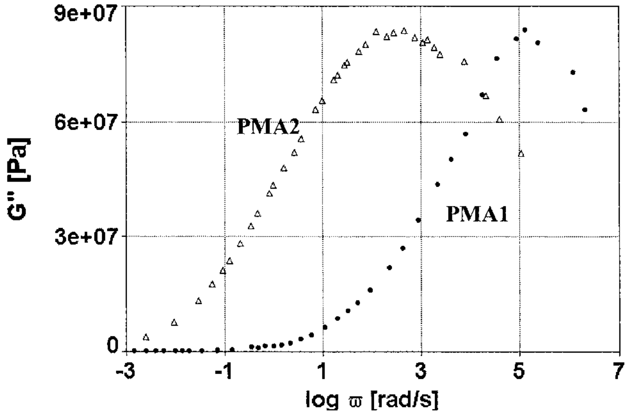

Figure 8. G" (Pa) for 4% SBS modified asphalts after artificial ageing. Tr = 0 °C.

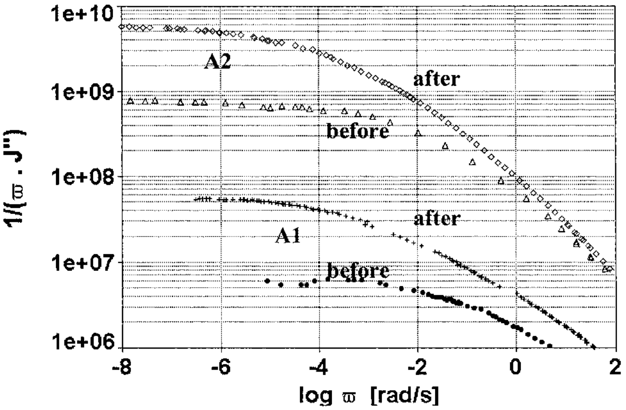

Figure 9. (1/ϖ J") (Pa s) for base asphalts before and after artificial aging. Tr = 0 °C.

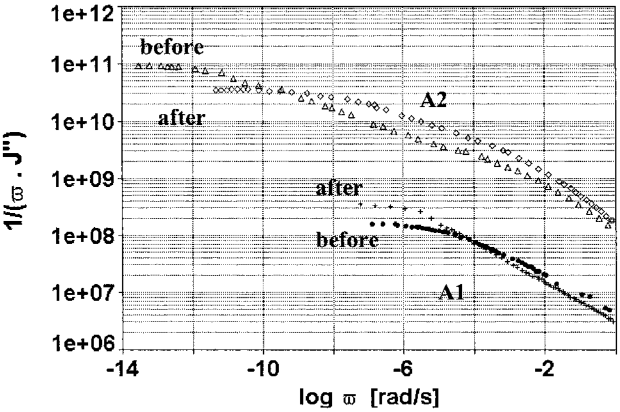

Figure 10. (1/ϖ J") (Pa s) for 4% SBS PMAs before and after artificial aging. Tr = 0 °C.

The function ($1/\varpi J''$) thus yields the estimate of η_o, when ϖ is close to 0. Figure 9 shows that in both base asphalts the zero shear viscosity after aging is much higher than before aging, and that aging has a similar effect on both asphalts. The modification hardens both base asphalts. In sample PMA1 the zero shear viscosity of aged asphalt is higher than the zero shear viscosity of non aged PMA1. Surprisingly the zero shear viscosity of aged PMA2 is lower than the zero shear viscosity of non aged PMA2, Figure 10. If this "softening" is reflected also in the paving mix it might lead to more rutting problems in the aged paving.

Conclusions

Generally the modification "slows down" the rate with which both asphalts approach the glass transition. For asphalt A1, the proportion of this slowing in aged and in not aged asphalt is almost same in modified and not modified samples. Asphalt A2 approaches the glass transition faster in all but the aged PMA samples. Aging seems to have a larger impact on asphalts A2 (base and modified) than on asphalts A1, as far as the rates of approach to glass transition are concerned. With respect to absolute values of the dynamic functions, it can be observed that after aging the master curves of modified asphalts seem to be different only by a horizontal shifting. This seems to indicate that starting from a harder base instead of a soft one, gives a material with similar mechanical properties, simply shifted on a temperature scale.

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