THERMOMECHANICAL PROPERTIES OF SEVERAL POLYMER MODIFIED ASPHALTS

Ludo Zanzotto, Jiri Stastna* and Otakar Vacin

Bituminous Materials Chair, Faculty of Engineering, University of Calgary Calgary, Alberta T2N 1N4 Canada *e-mail: stastna@ucalgary.ca Fax: x1.403.220.7026

Received: 10.7.2000, Final version: 26.7.2000

Abstract

Costly deterioration of many roads and highways paved with asphalt generates a growing interest in polymer modified asphalts (PMA). Although asphalt represents only a fraction of asphalt paving mix, it is believed that it has a significant effect on the thermomechanical properties of asphalt pavements. Currently there is no consensus on the type of tests and specifications for polymer modified asphalts; however, it is clear that such specifications should be based on rheological testing of these systems. As a viscoelastic material asphalt is usually characterized by its dynamic material functions. An advantage of the use of modified loss tangent function in PMA systems is discussed in this contribution. Three polymer modifiers (SBS, EVA and EGA) commonly used in the asphalt paving industry were blended with base asphalt and various relaxations in the base, and its blends are studied here.

ZUSAMMENFASSUNG

Der kostspielige Verschleiss vieler asphaltierter Strassen und Autobahnen erzeugt ein wachsendes Interesse an Polymer modifizierten Asphalten (PMA). Obgleich Asphalt nur einen Bruchteil des Asphaltgemisches ausmacht, glaubt man, dass er eine wesentliche Anteil auf die thermo-mechanischen Eigenschaften von Asphaltbelägen hat. Gegenwärtig fehlt es an Konsens über die Art von Tests und Spezifikationen für Polymer modifizierte Asphalte. Klar ist jedoch, dass solche Spezifikationen auf rheologischen Tests dieser Systeme basieren sollten. Als ein viskoelastisches Material ist Asphalt gewöhnlich durch seine dynamischen Materialkennwerte charakterisiert. Dieser Beitrag diskutiert, welchen Vorteil die Anwendung eines modifizierter Verlustwinkels in PMA-Systemen hat. Drei Polymer-Modifikatoren (SBS, EVA und EGA), die allgemein in der Asphaltindustrie benutzt werden, wurden mit regulärem Asphalt gebunden und die verschiedene Relaxationen im Asphalt und seinen Mischungen untersucht.

Résumé

Les détériorations dispendieuses des routes et autoroutes pavées d'asphalte est d'un intérêt croissant dans le domaine des bitumes modifiés par polymères (BMP). Bien que l'asphalte ne représente qu'une fraction des mélanges de pavements d'asphalte, il est reconnu pour avoir un effet significatif sur les propriétés thermodynamiques de pavements d'asphalte. Présentement, il n'ya pas de consensus sur le type d'essais et spécifications pour les bitumes modifiés par polymères, bien qu'il soit clair que de telles spécifications devraient être basées sur des tests rhéologiques de ces systèmes. Etant un matériel viscoélastique, l'asphalte est habituellement caractérisé par ses fonctions dynamiques due matériel. Un avantage de l'utilisation de la fonction modifiée de déphasage dans les systèmes BMP est discuté dans cet article. Trois polymères modifiés (SBS, EVA et EGA) utilisés fréquemment dans l'industrie du pavage d'asphalte ont été mélangées avec de l'asphalte de base et plusieurs relâchements dans la base et ses mélanges sont ici étudiés.

KEY WORDS: Polymer modified asphalt, relaxation, dynamic material functions, characterization

1 ASPHALT – BASIC PROPERTIES

Conventional asphalt behaves similarly as a low molecular weight linear viscoelastic material [1-4] when tested at small strains and rates of strain. Even if there are some doubts about the thermorheological simplicity of asphalt it is believed that conventional and also PMA can be represented reasonably well by the master curves of their linear viscoelastic material functions [4-6]. It is quite common to characterize asphalt by its dynamic material functions [4, 6, 7]. A relatively strong viscous deformation contribution to these functions can be observed (especially at higher temperatures). The high temperature sensitivity of asphalt is one of its main characteristics. The Williams-Landel-Ferry (WLF) [8] form of the shift factor seems to describe well the thermal properties of conventional asphalt as well as PMA (see Discussion). At high temperatures (usually above 60 °C) asphalt behaves as a Newtonian fluid and at temperatures less than -20 °C asphalt systems are approaching their glassy state. In conventional asphalt, one can observe two main transitions. The first one is the transition to the glassy state (α -transition) and the second one (a'-transition) is the transition from a viscoelastic to the Newtonian fluid. In the dynamic mechanical testing, the domain of the α -transition.

© Appl. Rheol. 10, 3, 134-144 (2000)

This is an extract of the complete reprint-pdf, available at the Applied Rheology website http://www.appliedrheology.org

This is an extract of the complete reprint-pdf, available at the Applied Rheology of http://www.appliedrheology.org

Figure 10 (left): Isochrones, 10 rad/s; relative modified loss compliance and loss tangent, relative loss modulus (• Base, + 4% EVA, △ 4% SBS I, ◊ 4% SBSr).

Figure 11:

Isochrones, 10 rad/s; relative modified loss compliance and loss tangent, relative loss modulus (● 2% SBSr, △ 4% SBSr, ◊ 2% EGA).



lowed by a local maximum where the transition to a Newtonian fluid begins. The picture is changed for higher concentrations of polymer. This can be seen from tan δ_{e} for 8% SBSr. Roughly at the frequency where 4% blends exhibit absolute maximum the 8% blend has a local minimum, which is accompanied by two maxima, positioned left and right from this point. Both maxima are clearly separated and they are much lower than the maxima for 4% blends thus indicating smaller difference between the "nonviscous" dissipation energy and the stored energy. In the domains of maxima J"_e > J', and in the domains of minima J"_e < J'. A complete picture of all transitions in asphalt is obtained from the composition plots of relative functions J"er, G"r and tan δ_e (or tan δ_{er}). An example of such a plot is given in Fig. 10. Here the isochrones (based on the transformation (5) with ω = 10 rad/s) of the above mentioned functions are plotted for the base asphalt and its 4% blends with EVA, SBS I and SBSr. A large shift of α '-transition towards the higher temperatures is observed for SBS blends. Similar comparison of blends: 2% SBSr, 4% SBSr and 2% EGA, is shown in Fig. 11. It is clear from this figure that 2% EGA blend has a behavior resembling the one of 2% SBSr blend. However, the α '-transition of EGA blend is very close to the α '-transition for the 4% SBSr blend. There seems to be also a slight shift of the α -transition, for 2% EGA blend, towards the higher temperature when compared with 2% and 4% blends of SBSr. The next figure (Fig. 12) portrays a detail of the glass transition (α) region for some of the studied blends. It follows from Fig. 12 that in the base asphalt the domain of this transition is relatively wide (~ 6 °C). The transition is shifted to lower temperatures with increasing concentration of SBS. The α -transition domain is narrower for EVA and EGA blends and more interestingly their glass transition domain is slightly shifted towards the higher temperatures. Note again that all isochrones are calculated for the "testing" frequency of 10 rad/s, and that the positions of extrema, on the discussed isochronal plots, will be shifted for different "testing" frequencies.



It was shown in [6] that the complex dynamic compliance function, $J^*(\varpi)$, can be modeled by the following fractional rational function:

$$J^{*}(\varpi) = -\frac{i}{\eta_{o}\varpi} \left[\frac{-\prod_{1}^{n} (1+i\varpi\lambda_{k})}{\prod_{1}^{m} (1+i\varpi\mu_{k})} \right]^{\beta}$$

$$6$$

By subtracting the low frequency asymptote $i/\eta_0 \varpi$ from (6) and using $\beta = 1/(n-m)$, one can successfully model the modified complex dynamic compliance ($J^* = J^* - i/\eta_0 \varpi$) of the conventional asphalts and their blends with polymer modifiers. An example of the modeled modified loss tangent for 8% SBSr blend is presented in Fig. 13. In this case n = 7, and m = 2. More details about the model can be found in [6, 7].

6 CONCLUSION

In conclusion, one can see that the modification of the base asphalt by the studied polymers influences more the high temperature behavior of blends than the low temperature behavior. Only for blends of SBS with concentrations of polymer higher than 4% a shift of the α -transition (glass transition) towards the lower temperatures was observed. It seems to be true that the lower concentration of EGA polymer can produce transitions similar to the ones observed in higher concentrations of SBS and EVA, however, only at higher temperatures. The glass temperature transition for 2% EGA blend is actually higher than the one for the base asphalt, i.e. this polymer exhibits a slight antiplasticization behavior. Interestingly enough, the higher concentration SBSr blend behaves as plasticizer (T_g is shifted to lower temperatures); however, various high temperature mechanical transitions (observed on the graph of the modified loss tangent) decrease in intensity with increasing polymer content (this being a characteristic of antiplasticizers) [15, 16]. Generally by adding a polymer to the base asphalt the main transition (observed as the maximum of the modified loss tangent and lying between the α and α ' transi-

This is an extract of the complete reprint-pdf, available at the Applied Rheology website http://www.appliedrheology.org

Applied Rheology plete reprint-pdf, available at the Applied Rheology website July/August 2000 http://www.appliedrheology.org



tions) will split at least into two with increasing separation of these maxima and decreasing intensity, when the concentration of polymer is increassed. These effects (for the tested materials) are relatively weak for concentrations of polymer less than, or equal to 4%. Thus, it seems that various attempts to improve the thermomechanical properties of asphalt by blending it with different polymers can have only a limited success when low concentration blends are used. Lower concentration (< 4%) blends of the tested base asphalt with SBS and EVA polymers exhibit the shift of α '-transition towards the higher temperatures (w.r.t. the base asphalt), i.e. the temperature sensitivity is lowered. However, the thermomechanical properties of these blends are not much different from the ones of the base asphalt. In that sense the EGA polymer seems to be a strong asphalt modifier. It has to be stressed that these observations apply to higher and intermediate temperatures, only. At low temperatures the effect of the tested polymer modifiers is a "weak" one. The increased concentration of polymer can have an important effect in a wide temperature interval. Then the domains of transitions are relatively wide, and the difference between the energy stored and dissipated, in "nonviscous" manner is relatively small. In such a case the PMA will suppress the vibrations generated by traffic in a wide frequency window (much wider than in the base asphalt, see Fig. 9) at a given temperature, or in a wide temperature window at a given characteristic frequency of the traffic. For the studied blends this situation seems to be achieved by 8% blend of the radial SBS polymer with the base asphalt (200/300 Pen grade).

ACKNOWLEDGEMENT

The authors would like to express their gratitude to the Natural Sciences and Engineering Research Council of Canada and Husky Oil Ltd. for the financial support of this work.

REFERENCES

 JG Brodnyan, FH Gaskins, W Philippoff and EG Lendart: The rheology of asphalt I, Trans. Soc. Rheol. 2 (1958) 285-306.



- FH Gaskins, JG Brodnyan, W Philippoff and E Thelen: The rheology of asphalt II, III, Trans. Soc. Rheol. 4 (1960) 265-296.
- [3] JM Dealy: Rheological properties of oil sand bitumens, Canad. J. Chem. Eng. 57 (1979) 677-683.
- [4] DA Anderson, DW Christensen, HU Bahia, R Dongre, MG Sharma, CE Antle and J Batton: Binder Characterization and Evaluation – Physical Characterization, Strategic Highway Research Program, National Research Council, Washington, DC, Vol. 3 (1994).
- [5] D Lesueur, JF Gerard, P Claudy, JM Letoffe, JP Planche and D Martin: A structure-related model to describe asphalt linear viscoelasticity, J. Rheol. 40 (1996) 813-836.
- [6] J Stastna and L Zanzotto: Linear response of regular asphalts to external harmonic fields, J. Rheol. 43 (1999) 719-734.
- [7] J Stastna, L Zanzotto and K Ho: Fractional relaxation modulus manifested in asphalts, Rheol. Acta 33 (1999) 344-354.
- [8] JD Ferry: Viscoelastic Properties of Polymers, Wiley, New York (1980).
- [9] DJ Plazek: What's wrong with the moduli Charlie Brown? or get the H out and go to L, J. Rheol. 36 (1992) 1671-1690.
- [10] TF Yen and JP Dicke: Microstructure of the asphaltic fraction by various instrumental methods, Anal. Chem. 39 (1967) 1847-1852.
- [11] Modified binders, binders with additives and special bitumens – collection of papers, Roads-Routes, 303, (March 1999).
- [12] F. Bonemazzi, V. Braga, R. Corrieri, C. Giarariui and F. Sartori: Characteristics of Polymers and Polymer-modified Binders, Transp. Res. Record 1535 (1996) 36-47.
- [13] H. Watanabe, S. Kuwahara and T. Kotaka: Rheology of styrene-butadiene-styrene triblock copolymer in n-tetradecane systems, J. Rheol. 28 (1984) 393-409.
- [14] M. Baumgartel, P.R. Soskey and H.H. Winter: IRIS Manual, IRIS Development.
- [15] P. Hedvig: Dielectric Spectroscopy of Polymers, Wiley, New York (1977).
- [16] P. Simon and HJ Ploehn: Modeling the effect of plasticizer on the viscoelastic response of cross linked polymers using the tube-junction model, J. Rheol. 44 (2000) 169-183.



This is an extract of the complete reprint-pdf, available at the Applied Rheology website http://www.appliedrheology.org

This is an extract of the complete reprint-pdf, available at the Applied Rheology of the http://www.appliedrheology.org July/August 2000

Figure 12 (left): Isochrones, 10 rad/s; relative Ioss modulus (• Base, •+• 6% SBSr, △ 4% EVA, ◊ 2% SBSr, + 2% EGA).

Figure 13:

Modified loss tangent $(T_r = 0^\circ C: \triangle Base, \diamond 8\% SBSr, - experimental,$ • fractional model, Eq. 6).