Rheological Characterization of Polymer Modified Bitumens

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ABSTRACT

Various polymer modified bitumens (PmBs) were prepared and characterized using a dynamic shear rheometer and a bending beam rheometer. PmBs differ considerably in viscoelastic properties depending on base bitumen, and polymer type and content. The rheology of PmBs is strongly related to the morphology, and is also affected by sample preparation.

INTRODUCTION

Bitumen is a semi-solid hydrocarbon material produced from certain crude oils. The majority of bitumen has been used as a binder in asphalt road pavements. During the time of service, and due to high traffic density and increases in axle loading and tyre pressure, plus insufficient maintenance, asphalt pavements can deteriorate and the distress signs often take the form of rutting, cracking and stone loss. In practice, the performance of an asphalt pavement is significantly affected by the rheological properties of the bitumen. To minimize the deterioration and thereby to increase the life-time of asphalt roads, polymer modified bitumens (or polymer modified binders, PmBs) may be used[1].

PmBs are produced through the incorporation of a polymer in hot liquid bitumen using mechanical mixing or chemical reaction. Unlike conventional bitumens, PmBs are normally two-phase systems, and their rheological properties are greatly dependent on the nature of the base bitumen, polymer characteristics, polymer content, as well as the process of manufacturing[2-5].

In this paper, various PmBs are prepared and characterized using a dynamic shear rheometer (DSR) and a bending beam rheometer (BBR) over a wide range of temperatures and frequencies or loading times. By these fundamental tests, improved rheological properties are demonstrated for PmBs. The paper will address the morphology-dependence of PmB rheology, as well as the importance of sample preparation.

MATERIALS

Seven bitumens of different sources, denoted as B1, B2, etc., were used in the preparation of PmBs. Typical parameters of the base bitumens are shown in Table 1.

Table 1. Base bitumens.

Bitumen samples	Penetration, mm^{-1}	Softening point, ˚C
B1	183	38.8
B2	180	41.0
B3	188	44.3
B4	99	43.0
B5	93	43.2
B6	86	43.4
B7	93	45.5

The polymers investigated are styrene-butadiene-styrene (SBS, linear), styrene-ethylene-butylene-styrene (SEBS), and ethylene vinyl acetate (EVA) copolymers. The SBS and SEBS polymers contain 31 and 29% styrene, respectively. The EVA contains 18% vinyl acetate and has a melt index of 158.

The modified binders were prepared at 180°C using a low shear mixer. Polymer contents were 3 to 6% by weight of the modified binders.

DSR CHARACTERIZATION

As a viscoelastic material, bitumen exhibits either elastic or viscous behaviour, or a combination of these, depending on the temperature and time over which the material is observed. At sufficiently low temperatures and/or high rates of strain (frequencies), bitumen behaves essentially as an elastic solid. As temperature increases and/or loading rate decreases, the viscous property of bitumen becomes more obvious. At sufficiently high temperatures and/or long loading time, bitumen is essentially a *Newtonian* liquid, and can be described by a shear rate independent viscosity value. An important aspect in this connection is that the response gradually changes from mainly elastic to mainly viscous as temperature increases or strain rate decreases. Within the linear viscoelastic region, the interrelation of stress and strain is linear, and is affected by temperature and frequency or time.

The viscoelastic behaviour of bitumen may change significantly if a modifier like polymer is added to the bitumen. This is investigated by means of DSR. Using DSR (Physica MCR 501, Anton Paar, and RDA II, Rheometrics), frequency sweeps and temperature sweeps were carried out with parallel plates of diameter 8 or 25 mm. Sample specimens were prepared in silicon moulds or directly on the bottom plate. The DSR tests involve the application of a sinusoidally varying shear strain or stress to the binder specimen (Fig. 1). The complex modulus (G*) is given by Eq.1.

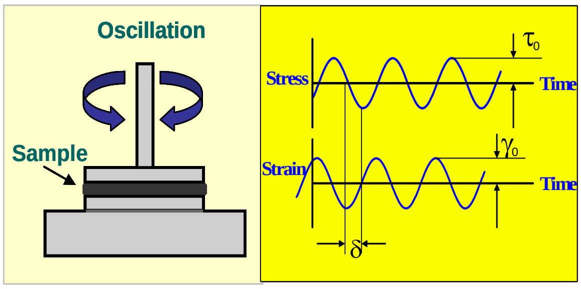

Figure 1. DSR testing of asphalt binders.

$$G^* = G' + iG'' = (\tau_0/\gamma_0)(\cos\delta + i\sin\delta) \qquad (1)$$

For bitumens and PmBs, complex modulus G* is a measure of the overall resistance to deformation, while phase angle δ reflects the viscoelastic character. These binder parameters are critical for asphalt performance in the field, e.g. resistance to rutting and cracking. Examples of complex modulus *versus* phase angle obtained by temperature sweeps at 1 rad/s are shown in Fig. 2. In bitumen area, this type of plot is called Black Diagram, by which the rheological changes as related to pavement performance, e.g. resistance to permanent deformation, can be easily characterized when modified and unmodified bitumens are compared.

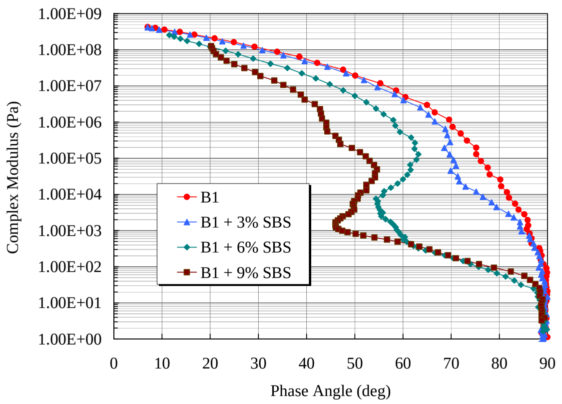

Figure 2. Complex modulus *versus* phase angle – Effect of polymer content.

Fig. 2 shows that, at a given stiffness level, e.g. 1 MPa, the SBS polymer increases the elasticity of the bitumen, as indicated by the decreased phase angles. Evidently, such improvement is highly dependent on content of the polymer used in the modified binder. For the modified binder containing 3% SBS, the rheological changes are relatively small.

In Fig. 3, storage modulus (G′) and phase angle as a function of temperature are exemplified for different bitumens modified by different polymers. Again the polymer modified bitumens show improved elasticity, particularly at the temperatures exceeding about 20°C. The reason is that above this temperature, the viscosity of the bitumen is low enough to allow the elastic network of the polymer to affect the mechanical properties of the modified binders. With increasing temperature, phase angle may pass through a maximum followed by a minimum, or show a smoothly increasing function of temperature, depending on the base bitumen and polymer type.

The phase angle minimum corresponds to a plateau region of storage modulus where the modulus changes little with temperature. The plateau region and the phase angle minimum are indicative of polymer networks or continuous polymer phase in the modified binders. The formation of polymer networks is determined by several factors, including the chemical nature of the base bitumen, polymer characteristics and content, as well as the thermal history of the binder that will be discussed later.

As shown in Fig. 3, for the modified binder with B3, the plateau region is not so evident and no apparent phase angle minimum observed. This implies that there is no or only a very weak polymer network in the binder, which has been confirmed by fluorescence microscopy. In addition, SBS and SEBS result in a more pronounced plateau region as compared with EVA. It should be noticed that for EVA, the plateau region is also affected by the degree of crystallinity.

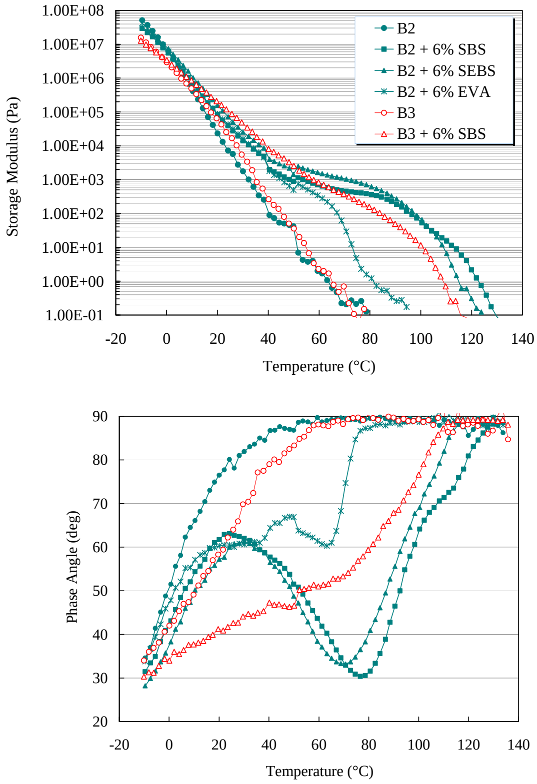

Figure 3. Storage modulus and phase angle *versus* temperature.

Because of their viscoelastic nature, bitumens, particularly if modified by polymers, show complex responses in viscosity under different conditions. It was found that polymer modification generally increases the degree of the *non-Newtonian* behaviour of bitumen. As shown in Fig. 4, for the base bitumen (B1) and the modified binder containing a low polymer content (3% SBS in this case), the dynamic viscosity $(\eta' = G''/\omega)$ measured by DSR at a low stress level is relatively independent of the shear frequency, indicating these binders are in principle purely *Newtonian* fluids at 60˚C. In contrast, for the binder with 6% SBS, the dynamic viscosity decreases with increasing shear frequency, i.e. displays shear-thinning behaviour.

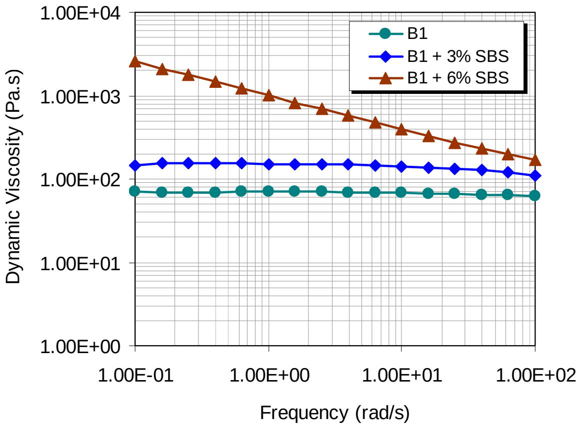

Figure 4. Viscosity measurements at 60°C.

The shear-thinning behaviour of PmBs may be observed at very low frequencies, making the determination of zero-shear viscosity (ZSV) very difficult. In road paving application, zero-shear viscosity is a binder parameter often used to evaluate permanent deformation resistance[6]. Because of the difficulty just mentioned, for PmBs, low-shear viscosity is recommended.

RELATION TO MORPHOLOGY

As already described, the rheological properties of PmBs are affected by the phase structure or polymer morphology in the binders. A fine dispersion of polymers and a continuous polymer phase in the modified binders are normally desired to achieve an optimal rheological improvement[7-9].

In Fig. 5, the black diagrams obtained by plotting the results of frequency sweeps at different temperatures are shown for a number of PmBs made of 5% SBS. The DSR tests were performed on the samples taken from 180˚C and after fast cooling. The morphologies of the same PmBs taken after 1 hour annealing at this temperature of 180˚C are shown in Fig. 6. The microscope used is a Carl Zeiss Axioskop 40F1, equipped with a digital camera, deltapix DP200.

As can be seen, the modified binders B5+5%SBS and B6+5%SBS display a homogeneous morphology (and polymer networks), thus showing a rubbery-like behaviour at phase angle of 30 - 60° and stiffness level around 1000 Pa. However, for the other two modified binders, the polymer is observed as a separated phase (the white parts in Fig. 6), consequently, the rubbery-like behaviour is much weaker.

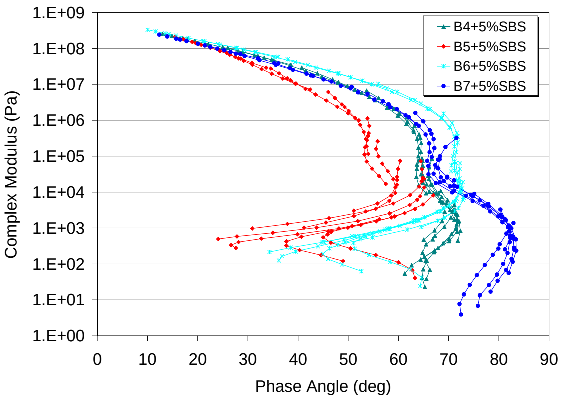

Figure 5. Black diagrams of different PmBs.

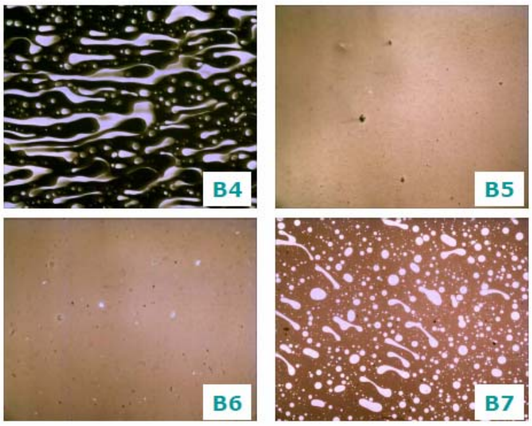

Figure 6. Morphologies of the bitumens modified by 5% SBS (magnification = 50x).

EFFECT OF SAMPLE PREPARATION

For a given PmB, the rheological behaviour may be largely affected by the thermal history and the procedure of sample preparation. Examples showing the effect of sample preparation are given in Fig. 7 for B4+5%SBS. For this modified binder, two specimens were first prepared by taking the sample from two different temperatures, 160 and 200˚C, respectively. A third sample was also taken from 200°C and then conditioned at 120°C for 30 minutes before cooling to room temperature. Finally, a sample was again taken from 200°C, but was slowly cooled to room temperature.

Obviously, these sample specimens behave differently in the rheological tests. The shape differences in the black diagrams seen from Fig. 7 are closely linked to the morphological differences in the samples, as illustrated in Fig. 8. As soon as the polymers are more phase-separated as unconnected domains, the rubbery-like behaviour becomes weaker at temperatures around 50˚C.

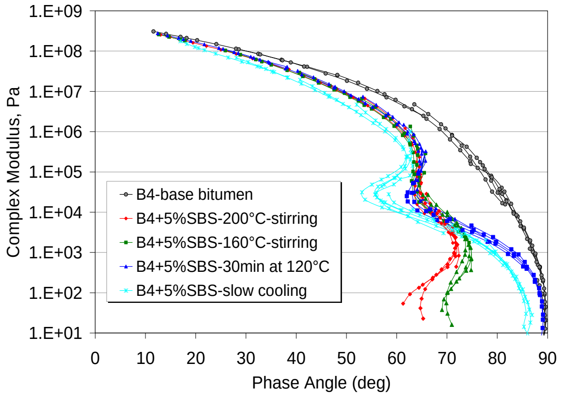

Figure 7. Effect of sample preparation on binder rheology (B4+5%SBS).

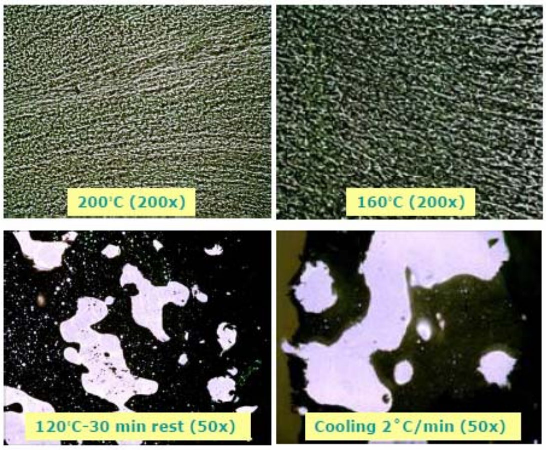

Figure 8. Effect of sample preparation on binder morphology (B4+5%SBS).

The effect of sample preparation is further shown in Fig. 9 and Fig. 10 for the modified binders B1+5%SBS and B5+5%SBS, respectively.

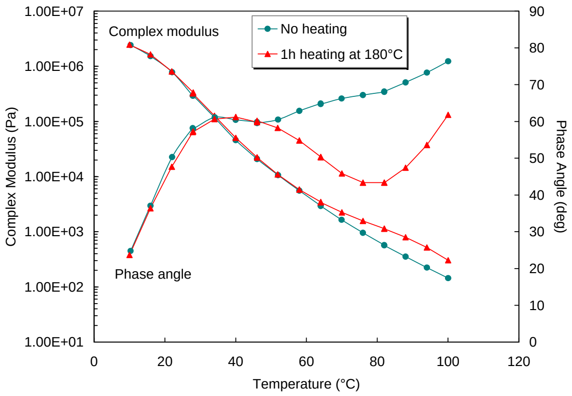

Figure. 9. Temperature sweeps for B1+5%SBS.

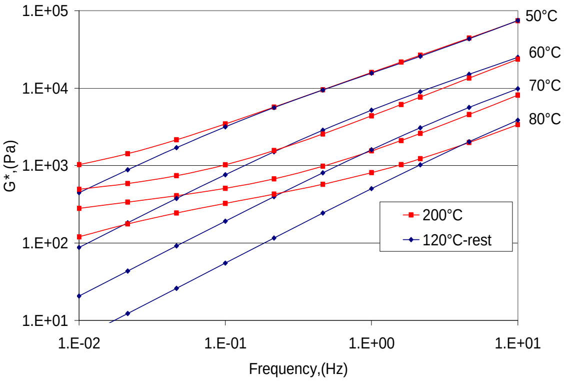

Figure 10. Frequency sweeps for B5+5%SBS.

In Fig. 9, temperature sweeps are conducted at 1.59 Hz (10 rad/s) for two specimens prepared directly on the bottom plate of DSR but in two different ways: one from the binder sample at ambient temperature, and another one from the sample which has been heated in oven at 180˚C for 1 hour. In Fig. 10, frequency sweeps are carried out at different temperatures for two sample specimens prepared in silicon moulds; one is taken at 200°C and quickly cooled, and another one is left at 120°C for 30 minutes. Again, these samples differ significantly in the DSR tests, and the rheological differences are attributed to different morphologies created in the binder samples.

LOW TEMPERATURE PROPERTIES

In cold areas like the Nordic countries, low-temperature cracking can be a serious failure mode in the asphalt road pavement. This type of failure occurs when the thermal stress induced at low temperatures exceeds the tensile strength of the asphalt mixture. To reduce the risk of low temperature cracking, bituminous binder should have good flexibility, as reflected by low stiffness and high ability of stress relaxation, at the lowest pavement temperature. In this paper, the low temperature properties are studied by creep tests using BBR (Cannon Instrument).

In the BBR test (Fig. 11), sample beam was prepared by pouring hot binder (heated ant stirred at 180˚C) to a mould of 125 mm long, 12.5 mm wide and 6.25 mm thick. After about 1.5 hours at room temperature, de-moulding was made at approximately 0°C. The rectangular beam was conditioned in a liquid bath at test temperature for 1 hour. Then a constant load of 100 g was applied to the beam. The deflection of center point was measured continuously for 240 s, and stiffness (*S*) and creep rate (*m-value*) were determined at different loading times. The m-value is the slope of the curve of log (stiffness) *versus* log (loading time), which measures binder's ability of stress relaxation.

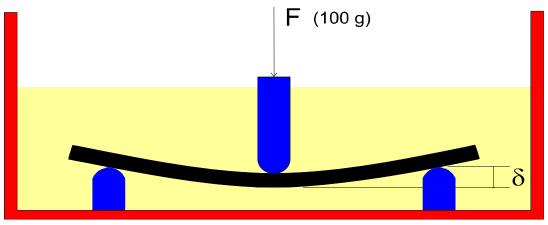

Figure 11. Schematic illustration of BBR.

Examples of the BBR results are shown in Fig. 12 for B1, before and after polymer modification. As indicated, at -25˚C, the addition of 6% SBS to the bitumen reduces the stiffness of the bitumen, at the same time also decreases the m-value of the bitumen. The same observation can be made when the stiffness and m-value are examined at different temperatures (see Fig. 13).

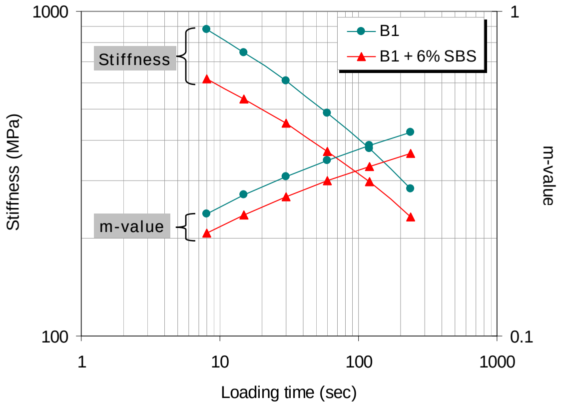

Figure 12. BBR results obtained at -25˚C.

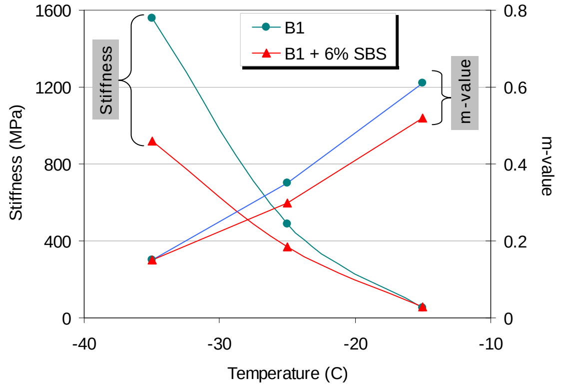

Figure 13. Stiffness and m-value at a loading time of 60 s *versus* temperature.

From the plots of stiffness and m-value at a loading time of 60s *versus* temperature, the limiting temperatures at 300 MPa stiffness (LST) and at m-value of 0.300 (LmT) are used to assess binders' low temperature properties[10]. In most cases, the limiting temperatures are found to depend mainly on the base bitumen, while the polymers show comparatively only a small effect, as exemplified in Fig.14.

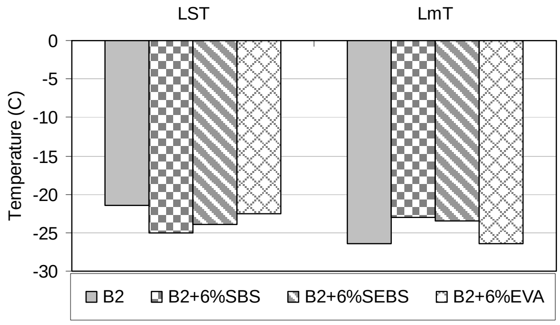

Figure 14. Effect of polymers on the limiting temperatures.

A limited number of experiments were also made on two modified binders (B4+5%SBS, and B+5%SBS) to see if sample preparation affects the low temperature properties of the PmBs. For this purpose, sample beams were prepared after the binders being heated for 1 hour at 160˚C and 200˚C, and homogenized at the respective temperature. For each binder and at each preparation temperature, three beams were prepared. The BBR tests were performed at -10˚C. The results of averaged measurement on three beams are shown in Table 2. As can be seen, the differences caused by sample preparation temperature are in this test not so significant.

Table 2. Stiffness (MPa) and m-value measured at -10˚C and 60s loading time.

Prep. temp.	B4+5%SBS		B5+5%SBS	
	S	m	S	m
160˚C	45.9	0.525	70.8	0.440
200˚C	47.5	0.506	65.0	0.431
Diff., %	+3.5	-3.6	-8.2	-2.0

CONCLUSIONS

The DSR and BBR tests for characterizing PmBs are demonstrated. As expected, the rheological properties of PmBs are largely dependent on base bitumen, polymer type and polymer content.

The rheological behaviour of PmBs is strongly related to the morphology or the phase structure of the polymer as visualized by fluorescence microscopy. Normally, a fine dispersion of polymers and a continuous polymer phase in the modified binders are desired to achieve an optimal rheological improvement.

Sample preparation (temperature, cooling rate, isothermal annealing, etc.) has a significant effect on the morphology, thus considerably affecting the viscoelastic properties of PmBs.

The low temperature properties of PmBs as measured by BBR tests are mainly determined by the base bitumen, and are only slightly affected by polymer modification.

REFERENCES

1. Isacsson, U., and Lu, X. (1995), "Testing and Appraisal of Polymer Modified Road Bitumens – State of the Art", *Materials and Structures*, **28**, 139-159.

2. Lu, X., and Isacsson, U. (1997), “Rheological Characterization of Styrene-Butadiene-Styrene Copolymer Modified Bitumens”, *Construction and Building Materials*, **11**, 23-32.

3. Wilson, A., Fuchs, G., Scramoncin, C., Martin D., and Planche, J.P. (2000), “Localization of the Polymer Phase in Bitumen/Polymer Blends by Field Emission Cryo-Scanning Electron Microscopy”, *Energy & Fuels*, **14**, 575-584.

4. Masson, J.F., Collins, P., Robertson, G., Woods, J.R., and Margeson, J. (2003), “Thermodynamics, Phase Diagrams, and Stability of Bitumen-Polymer Blends”, *Energy & Fuels*, **17**, 714-724.

5. Pérez-Lepe, A., Martinez-Boza, F.J., and Gallegos, C. (2007), “High Temperature Stability of Different Polymer-Modified Bitumens: A Rheological Evaluation”,

Journal of Applied Polymer Science, **103**, 1166-1171.

6. BiTVal (2006), "Analysis of Available Data for Validation of Bitumen Tests", FEHRL Report.

7. Soenen, H., Lu, X., and Redelius, P. (2008), "The Morphology of Bitumen-SBS Blends by UV Microscopy: An Evaluation of Preparation Methods", *Road Materials and Pavement Design*, **9**, 97-110.

8. Soenen, H., Lu, X., and Redelius, P. (2009), "The Morphology of SBS Modified Bitumen in Binders and in Asphalt Mix", *The 7th RILEM Symposium on Advanced Testing and Characterization of Bituminous Materials*, ATCBM09, 27-29 May, Rhodes. Greece.

9. Lu, X., Soenen, H., and Redelius, P. (2010), "SBS Modified Bitumens: Does Their Morphology and Storage Stability Influence Asphalt Mix Performance", *The 11th ISAP International Conference on Asphalt Pavements*, 1-6 August, Nagoya, Japan.

10. Anderson, D. A., and Kennedy, T. W. (1993), "Development of SHRP Binder Specification", *AAPT*, **62**, 481-507.