

**CHARACTERIZATION
OF RHEOLOGICAL AND THERMAL BEHAVIOR
OF ASPHALT CEMENTS MODIFIED BY ETHYLENE COPOLYMERS**

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1. INTRODUCTION

The rheological properties of bituminous binders govern the subsequent performance of special hot mixtures in pavements. In the case of road pavements, the constraints engendered by moving vehicles are of dynamic origin, and dynamic rheology can be used to analyze the visco-elastic behaviour of the materials subject to loadings whose frequencies are close to those to which the road is subjected.

Differential scanning calorimetry (DSC) can be used to analyze the thermal behaviour of ethylene-copolymer-modified bitumens, and reveals there to be a good match between the melting range of the copolymer and the zone of transition between visco-elastic behaviour and purely viscous behaviour of the material [1].

As a result of SHRP work, dynamic rheology can be used to determine an isomodulus temperature that can be proposed for monitoring performance at high temperatures.

The results given in this paper concern ethylene copolymer/bitumen blends whose melting (and crystallization) ranges and visco-elastic behaviour depend on the type of ethylene copolymer, among other things.

2. ETHYLENE-COPOLYMER-MODIFIED BITUMENS STUDIED

Binders made with a pure straight run bitumen (70/100) and different ethylene copolymers were studied.

The ethylene copolymers used have the following characteristics:

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|---------------------|--|
| Copolymer A: | ethylene and methyl acrylate copolymer (EMA) with high crystallinity and molecular weight. |
| Copolymer B: | ethylene and vinyl acetate copolymer (EVA) with moderate crystallinity and molecular weight. |
| Copolymer C: | ethylene and vinyl acetate copolymer (EVA) with low crystallinity and molecular weight. |

These bitumens modified with 10% ethylene copolymers have a continuous polymer matrix within which are dispersed bitumen globules of different sizes (see Figure 1).

3. DIFFERENTIAL SCANNING CALORIMETRY

Ethylene copolymers are semi-crystalline copolymers. They are made of polyethylene crystallites separated from each other by amorphous regions caused by the co-monomer. The peak of ethylene copolymer melting is at lower temperatures than that of the polyethylene, for the co-monomer results in a reduction in the length of crystallizable sequences. The amorphous region is characterized by a glass transition temperature. All these characteristics can be determined by differential scanning calorimetry (DSC).

3.1. Test method

The thermal behaviour of ethylene-copolymer-modified bitumens is characterized by differential scanning calorimetry (DSC) using a Mettler DSC 30 analyzer.

This technique can determine the enthalpy of changes in the physical state of the copolymer such as:

- | | |
|------------------|--|
| melting: | first-order transition characterized by an endothermic signal, |
| crystallization: | first-order transition characterized by an exothermic signal. |

The glass transition temperature (T_g), which is an important characteristic of amorphous materials, is a second-order transition. The glass transition temperature of ethylene copolymers is between -20 and -40°C , depending on the ethylene copolymer. This paper will deal only with first-order transitions.

In the experiments the ethylene-copolymer-modified bitumens are softened by heating them, and are placed in a sealed aluminum crucible. They have to be left to stand 24 hours before the sample can be analyzed (time for the structure to stabilize).

All the tests are carried out with a cooling rate of $5^\circ\text{C}\cdot\text{min}^{-1}$ to -80°C . The sample is then heated to 120°C at a rate of $5^\circ\text{C}\cdot\text{min}^{-1}$, then cooled to -20°C at a cooling rate of $5^\circ\text{C}\cdot\text{min}^{-1}$.

3.2 Thermograms of ethylene-copolymer-modified bitumens

The thermograms in Figure 2 show the melting ranges of the three ethylene copolymers solvated with a maltenic fraction of the bitumen.

From the thermograms of Figure 2 it would appear that the temperature range defining the melting ranges varies appreciably, depending on the type of ethylene copolymer:

Melting range of ethylene copolymer A: $63-99^\circ$ \rightarrow Melting peak : 86°C

Melting range of ethylene copolymer B: $35-81^\circ$ \rightarrow Melting peak : 53°C

Melting range of ethylene copolymer C: $27-62^\circ$ \rightarrow Melting peak : 48°C

Like the melting ranges, the crystallization ranges depend on the type of ethylene copolymer, as can be seen from the thermograms in Figure 3.

The kinetics of ethylene copolymer crystallization are slow because of copolymer dispersion in the bitumen, which explains the shift between the melting ranges and crystallization.

4. DYNAMIC RHEOLOGICAL TESTS

Pure bitumens and polymers are visco-elastic materials, i.e. their behaviour is between that of an elastic solid and that of a viscous liquid.

Dynamic rheology is an oscillation technique that can be used to study the structure of materials in accordance with frequency (isotherms) and/or temperature (isochrones). It involves submitting the sample to a sinusoidal stress or deformation and measuring the material's response to this loading.

4.1. Test method

Measurements are taken with a Bohlin rheometer which uses plane-plane geometry. The temperature of the sample (immersed in water) is controlled by a thermoregulator. The sinusoidal deformation is chosen after a stress scan in order to locate it within the range of linear visco-elasticity. The results are given in the form of a modulus, G^* , for which the imaginary part is the loss modulus, G'' (viscous component of the modulus), and the real part is the storage modulus, G' (elastic component of the modulus). The delta phase angle, δ , represents the lag between the stress and deformation.

4.2. Interpretation of results

Examination of the isochrones of the modulus (G^*) at 1.5 Hz, under the conditions proposed by the SHRP [2], and by means of analysis of the gradient of variation of modulus G^* with temperature, provides an assessment of the temperature susceptibility of bituminous binders [3].

Examination of the isochrones of the delta phase angle, δ determines the temperature range between the visco-elastic region and the flow region of the ethylene-copolymer-modified bitumen.

In addition, examination of G^* and δ isochrones allows for assessment of a temperature at which $G^*/\sin\delta = 1$ kPa, the figure the SHRP specifications propose for the verification of binder performance at high temperatures [2].

5. DSC/DYNAMIC RHEOLOGY RELATIONSHIP

The isochrones of the modulus and of the phase angle of bitumen mixes with ethylene copolymers A, B, and C are shown in Figures 4 and 5.

Visco-elastic range

The temperature at which the test begins (15°C) is within the visco-elastic range of the materials.

The rheological behaviour of the pure bitumen is different to that of the highly modified bitumens: its modulus decreases rapidly with the temperature, and it proves to be highly temperature-susceptible. The isochrone of the phase angle does not have a rubbery plateau, contrary to ethylene-copolymer-modified bitumens: its structure collapses gradually as the temperature rises. Its phase angle increases parabolically up to the asymptotic value of 90°. At as little as 18°C, more than 90% of the modulus of the pure bitumen is accounted for by the viscous component (phase angle greater than 65°).

From the isochrones of the modulus, G^* , of highly modified bitumens (Figure 4), it can be seen that the reduction of the modulus in accordance with temperature is much lower than that seen with pure bitumens, which is a reflection of the improvement in thermal susceptibility brought about by addition of ethylene copolymer. Additionally, the degree of this variation depends on the type of ethylene copolymer A.

Thus, examination of the isochrones of the modulus allows for classification of binders in decreasing order of temperature susceptibility [4]: pure 70/100 bitumen, bitumen with copolymer C, bitumen with copolymer B, bitumen with copolymer A.

The isochrones of the phase angle in the modified binders (Figure 5) show that these binders are substantially more elastic than pure bitumen (lower phase angles across the whole range of temperatures studied). However, the contribution of the elastic component of the modulus is specific to each ethylene copolymer. It becomes negligible when the phase angle exceeds 65°.

Thus, the bitumen blend with copolymer A is the most elastic of the three modified bitumens studied. This is true for the entire temperature range. The bitumen mix with copolymer B is more elastic than that with copolymer C.

The significant increase in the phase angle of the modified bitumen is observed above 53°C for copolymer B, and above 43°C for copolymer C. This increase is linked to the melting of the ethylene copolymer, as detected by DSC analysis.

Flow region

The flow region corresponds to melting of the ethylene copolymer.

From the thermograms of Figure 2 and the phase-angle isochrones of Figure 5, it can be seen that the increase in the phase angle of the bitumens with copolymers B and C is close to the melting peak (Pf) determined by DSC analysis (53°C and 43°C respectively). The increase in the phase angle induces a decrease in elastic effects and a rise in viscous phenomena. This is because more than 90% of the modulus is attributable to its viscous C component when the phase angle is higher than 65°C [4].

The temperature corresponding to a phase angle of 65° is close to 68°C for bitumen modified with copolymer B and 53°C for bitumen modified with copolymer C.

As for the bitumen modified with copolymer A, its melting range is at higher temperatures (melting peak at 86°C). This is why the phase angle is low (major elastic effects) in the temperature range studied (10-70°C), for the copolymer does not melt.

Copolymer melting therefore results in a major modification in the rheological behaviour of the binders. It shows the temperature range between the visco-elastic field and the flow field. The less temperature-susceptible the ethylene copolymer is, the later flow will start.

It thus appears to be possible to guide the choice of the ethylene copolymer in accordance with the climatic conditions of the site (maximum temperature of the pavement).

6. PROCEDURE FOR DYNAMIC RHEOLOGICAL TESTING

Knowledge of the melting and crystallization ranges of ethylene-copolymer-modified bitumens allows for informed discussion of the effect the procedure for dynamic rheological testing (Bohlin) has on results. This comment particularly concerns modified binders with high copolymer contents, i.e. with a continuous polymer matrix, for binders with a continuous bitumen matrix behave in much the same way as the bitumen itself.

If a sample is placed on the rheometer at a temperature either in the melting range or in the crystallization range, the modulus measured will depend on the temperature history of the material (overmelting phenomenon).

The usual procedure for studying rheological behaviour involves placing the sample at a temperature of around 30°C.

To study the effect of the temperature history on rheological behaviour, isochrones were determined for 15 to 95°C for the bitumen modified with copolymer A, and for 15 to 70°C for the bitumen modified with copolymer C. The sample was then cooled to 15°C and a second isochrone was determined.

Ethylene copolymer A had a melting peak at around 86°C, and its crystallization range is from around 73 to 53°C (Figure 3).

The two isochrones of the modulus were identical, as can be seen in Figure 6.

Ethylene copolymer B has a melting peak around 53°C, and its crystallization range is from around 81 to 35°C (Figure 3). The two isochrones of the modulus are identical, just as for copolymer A.

As for copolymer C, its melting peak is around 43°C, and it starts to crystallize at around 12°C, as is shown in Figures 2 and 3. When the second isochrone starts at 15°C, the crystallization of copolymer C has not yet started. The copolymer overmelts, resulting in a significant reduction of the modulus (Figure 7). The moduli become identical as they enter the flow region.

Knowledge of the thermal behaviour of the ethylene copolymers is therefore very important for proper interpretation of their rheological behaviours (thermal and rheological) depending on the characteristics of the copolymer.

7. SHRP HIGH SERVICE TEMPERATURES

The new SHRP specifications [2] propose that at the mean maximum weekly temperature of the pavement, the value of $G^*/\sin \delta$ of the binder as is should be 1 kPa at a frequency of 1.6 Hz. This value ($G^*/\sin \delta = 1$ kPa) expresses a minimum rigidity, as shown by the following expressions [5]:

$$G^* = 1/J^*$$
$$G^*/\sin \delta = 1/J^*\sin$$

where J^* is the complex compliance (1/Pa).

Associated with an SHRP performance criteria, this temperature can replace the ring and ball (R & B) softening point test in the case of polymer-modified bitumens for which it has been largely demonstrated that the test was not appropriate.

Through interpretation of their isochrones, the rheological behaviour characterization tests presented above allow for easy evaluation of the temperature for which $G^*/\sin \delta = 1$ kPa, and for identification of δ and G^* for that temperature (Table 1).

From Table 1 it can be seen that at temperatures where $G^*/\sin \delta = 1$ kPa, the difference between $G^*/\sin \delta$ and G^* is negligible. The phase angles are sufficiently great to allow the following simplification:

$$\sin \delta \rightarrow 1$$
$$G^*/\sin \delta \rightarrow G^*$$
$$G^*/\sin \delta \rightarrow 1/J^*$$

The isomodulus temperatures are considerably higher than the ring and ball softening points [4]. It is clear that the ring and ball temperatures for ethylene-copolymer-modified bitumens are not isomodulus temperatures.

8. CONCLUSION

Differential scanning calorimetry (DSC) is seen to be a promising technique for characterizing and understanding the behaviour of ethylene-copolymer-modified bitumens.

Dynamic rheology provides an appreciation of the temperature susceptibility of bituminous binders, on the basis of modulus isochrones.

In the case of highly modified ethylene-copolymer-modified bitumens (continuous polymer matrix), the melting ranges of the copolymers and the isochrones of the phase angle are used to determine the temperature range between the visco-elastic region and the flow region. Melting of the copolymer engenders an increase in the phase angle, which is reflected by a gradual decrease in elastic effects and an increase in viscous phenomena. The greater the

crystallinity and the molecular weight of the copolymer, the higher the temperature of the flow area will be.

In addition, knowledge of the thermal behaviour of ethylene copolymers in bitumen makes it possible to discuss the effect of the test procedure on the rheological behaviour analysis of modified binders and the interpretation of results.

The temperature for which $G^*/\sin \delta = 1$ kPa, which is the value proposed in SHRP specifications for checking high-temperature performance, also depends on the characteristics of the copolymer.

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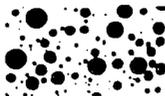
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	R&B (°C)	G^* at R&B temp. (Pa)	Phase angle at R&B temp.	$T(G^*/\sin \delta) = 1$ kPa (°C)	G^* (Pa) at isomodulus temp.	Phase angle at isomodulus temp.
Bitumen	45	9.65E + 03	83	62	998	83
Bitumen with copolymer A	86	1.85E + 03	63	96	974	75
Bitumen with copolymer B	68	3.63E + 03	69	79	996	79
Bitumen with copolymer C	56	2.67E + 03	70	70	998	80

Table 1: Conventional and SHRP characteristics at high service temperatures



Ethylene copolymer A-bitumen



Ethylene copolymer B-bitumen



Ethylene copolymer C-bitumen

Figure 1: Microstructure of ethylene-copolymer-modified bitumens (10% blends)

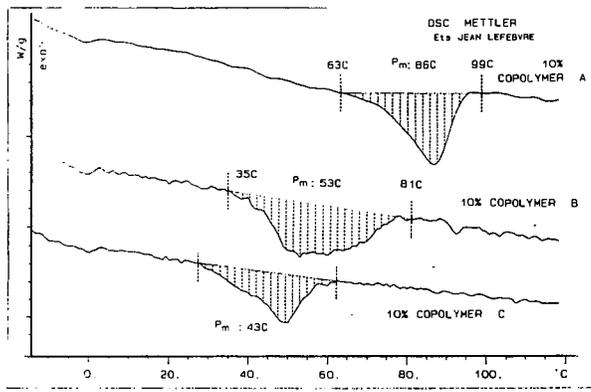


Figure 2: Thermograms of bitumen blends with ethylene copolymer A, B, and C
Melting ranges

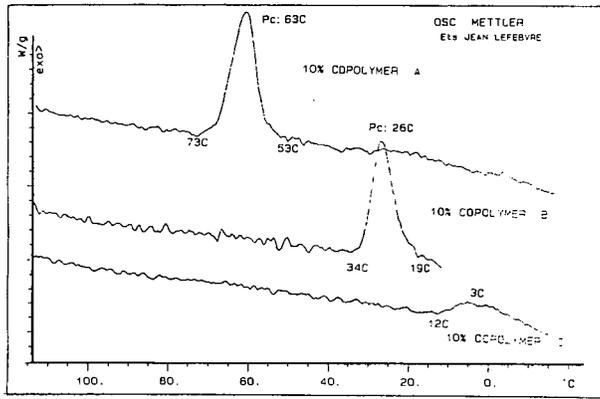


Figure 3: Thermograms of bitumen blends with ethylene copolymer A, B, and C
Crystallization ranges

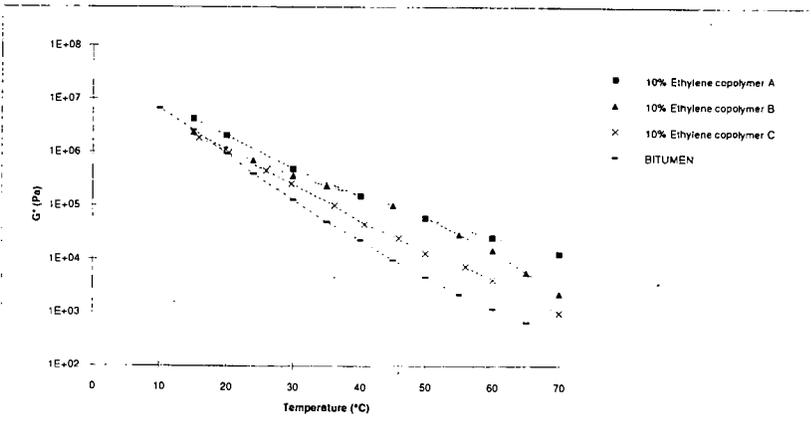


Figure 4: G^* isochrones (1.5 Hz) for bitumen blends with ethylene copolymers A, B, and C

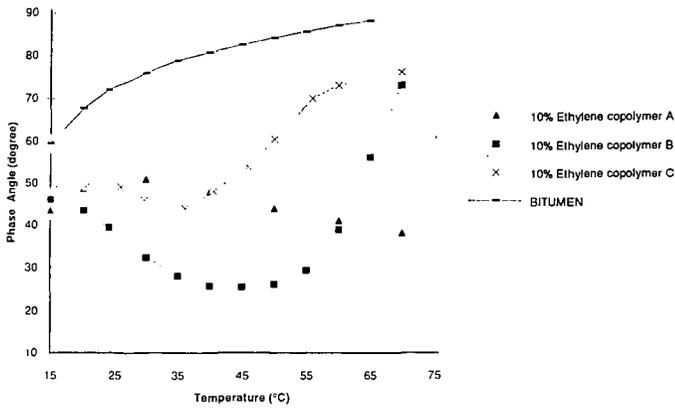


Figure 5: δ isochrones (1.5 Hz) for bitumen blends with ethylene copolymers A, B, and C

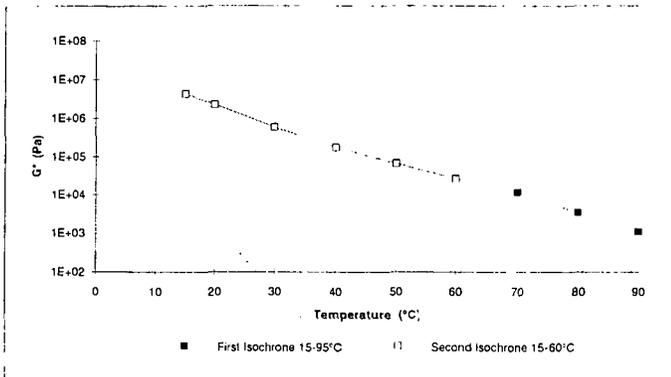


Figure 6: G^* isochrones for bitumen modified with 10% of copolymer A

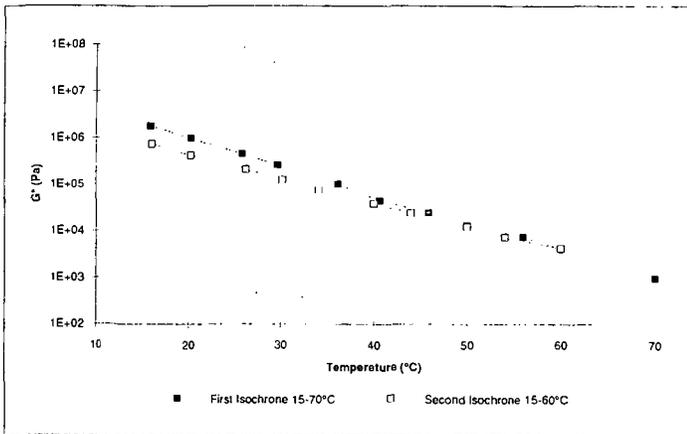


Figure 7: G^* isochrones for bitumen modified with 10% of copolymer C