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Rheological characterisation of bitumen diffusion

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Abstract Diffusion is considered important in the process of mixing old and new binders during asphalt recycling. The degree of mixing is presumed to greatly influence the final properties of recycled asphalt concrete. Previously, studies have been undertaken to investigate diffusion using FTIR-ATR (Fourier Transform Infrared Spectroscopy using Attenuated Total Reflectance). A need was identified to verify, if the rates of diffusion detected using FTIR-ATR were accompanied by changes in rheological properties. In this paper, a dynamic shear rheometer (DSR) with parallel plates is used for monitoring diffusion. Diffusion coefficients obtained at 60, 80 and 100 °C from tests of a soft bitumen (rejuvenator) diffusing into a stiff one are presented. The diffusion coefficients determined are compared with the corresponding diffusion coefficients obtained using FTIR-ATR. The comparison shows that the rates of diffusion detected by the DSR are of the same magnitude, but somewhat higher than the ones detected by FTIR-ATR.

Introduction

Being limited natural resources, bitumen and stone materials used in asphalt concrete need to be used in an optimum way. Today, road asphalt materials are recycled to a great extent, and the quality of the recycled asphalt concrete is generally high. In most cases, during asphalt concrete recycling, old and new bitumen are mixed to create a recycled asphalt binder with desired properties. Old bitumen usually becomes stiffer due to ageing. Consequently, softer binders, often referred to as rejuvenators, needs to be added to adjust the stiffness of the recycled binder to an acceptable level. Incomplete mixing of the binders will likely influence the properties of the recycled asphalt mixture. The success of the binder mixing process is assumed to be dependent on, among other things, proper mechanical mixing, diffusion, as well as compatibility between the binders. Results of studies on this subject have been reported earlier by Oliver [1], Karlsson and Isacsson [2], Karlsson and Isacsson [3]. In this paper, a method using a dynamic shear rheometer (DSR) for measuring rate of diffusion in bitumen is adopted and tentative results presented.

A method based on FTIR-ATR (Fourier Transform Infrared Spectroscopy using Attenuated Total Reflectance) was developed and described earlier by Karlsson and Isacsson [2], which measures diffusion in bituminous binders. Using this method, factors generally considered important to diffusion were investigated, such as influence of temperature, viscosity, molecular size, shape and polarity. Since viscosity is important to diffusion, the influence of ageing and subsequent increase in binder stiffness was given extra attention by Karlsson and Isacsson [3]. A positive outcome of this study was that ageing showed very little influence on diffusion and that diffusion seemed to take place in the un-associated fraction of bitumen, often referred to as the maltene phase, at a faster rate than expected from the high viscosity of bitumen as a whole. Since the maltene phase appears to govern the

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rate of diffusion, addition of soft rejuvenators having the same maltene phase viscosity will not substantially increase the rate of diffusion. A survey by Branthaver et al. [4] showed that the viscosity of maltenes from different bitumen sources varies less than one order.

Bitumen is a residue gained by vacuum distillation of heavy crude oils. It has a chemically extremely complex constitution, which generally make all kinds of chemical investigations difficult to interpret. Bitumen shows visco-elastic behaviour when subjected to loading. The visco-elastic behaviour is strongly influenced by temperature. Bitumen also shows thixotropic softening when subjected to shear. Bitumen chemistry and its influence on rheological properties is still subject to ongoing research. One example of current research that illustrates the complexity of the area is the controversy whether bitumen should be regarded as being constituted of micelles or being a solution. Another example is the issue of the true molecular weight distribution of bitumens. Studying a molecular process by monitoring rheological properties may hence be difficult, but the results will complement those obtained by FTIR-ATR, as is explained below. A specific problem when detecting diffusion by monitoring changes in chemical constitution is that the diffusion coefficients measured might be representative for some constituents of a specific binder but not reflect a mean diffusion coefficient representing the binder as a whole. In Ref. [4] it is described how molecules that are responsible for building viscosity more frequently are associated to other molecules. This will likely lead to these viscosity building molecules diffusing at a slower rate than other components of the bitumen. However, such molecules may probably show a proportionally large influence on rheological properties. Consequently, since the changes in rheology (recycled binder stiffness) was one of the reasons for studying diffusion, a need was expressed to correlate the experimental results obtained using FTIR-ATR with measurements of changes in rheological properties due to diffusion.

Method

Rheological tools have been applied to study diffusion at polymer/polymer interfaces as described by Bousmina et al. [5], Qui and Bousmina [6, 7] and to study diffusion of plasticizers in elastomers by Joubert et al. [8]. The principle for measuring diffusion by rheological measurements described in these papers is to combine changes in visco-elastic response from samples consisting of layered materials with changes in concentration governed by Fick's second law of diffusion. The research described in this paper is based on the same principle. Studies of bitumen diffusion are simpler compared to diffusion in polymers, because bitumen consists of mutually soluble molecules of lower molecular size, which are not kept in a rigid molecular network as suggested in the so called reptation model used for description of polymers in the papers referred to above. In the reptation model (referring to a snake-like motion) the polymer chains are imagined as confined within a curved tube where diffusion is governed by the tube and polymer geometry as well as the polymer chain dynamics. Furthermore, the elastic response (storage modulus) of bitumen is small compared to the viscous part (loss modulus) in the range of temperatures studied in this paper.

The shear viscosity of the binders was measured using a Dynamic Shear Rheometer (RDA II, Rheometrics). Parallel plates with a diameter of 25 mm were used. A sinusoidal strain was applied by an actuator at the bottom plate and the actual strain and torque were measured.

The samples were prepared by weighing given amounts of binder, corresponding to the required thickness of each binder when evenly distributed on the rheometer plates, assuming the density of each binder to be 1.0 g/cm^3. Thin layers were created by carefully heating the binders to allow it to float out on the two plates (cf. Fig. 1, step 1). The plates were conditioned at test temperature before being brought into contact (step 2). When brought into contact, the plates were parallel. Due to surface tension, the binder surfaces were of such a finish, that no air was trapped between the layers, when finally pushed into contact with each other (step 3). The measurements then started immediately.

Calculation of diffusion coefficients based on DSR measurements were done in two different manners:

- by assuming the response to be viscous and integrating the response from continuum layers
- by viscoelastic modeling and arbitrarily dividing the binder layers into 20 equally thick sub-layers (Fig. 1).

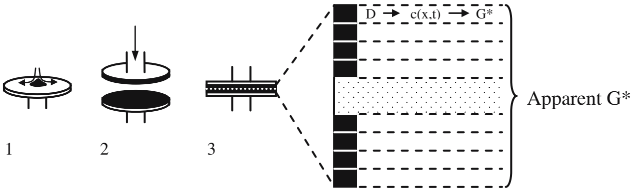
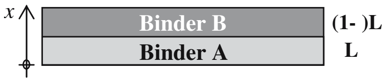


Fig. 1 Sample preparation and procedure for calculation of diffusion coefficients, *D*, by dividing into sub-layers, calculating sub-layer response, adding up and iteratively adjusting *D* to measured apparent *G**



$$c(x,0) = 0 \qquad 0 \le x \le \alpha L$$
$$c(x,0) = c_0 \qquad \alpha L < x \le L$$
$$\frac{\partial c(0,t)}{\partial x} = \frac{\partial c(L,t)}{\partial x} = 0$$

Fig. 2 Definition of initial and boundary conditions

A diffusion coefficient, D, equal in all layers, was assumed and the concentration of binders in each sub-layer was calculated in time steps. Given time and position, the concentration of each binder was calculated using Eq. 2, which is the analytical solution to Fick's law (Eq. 1) for the initial and boundary conditions given (cf. Fig. 2), where x is the cross sectional coordinate, t is time, c is concentration (in percent), c_0 initial concentration of binder B, L is the total layer thickness of binder A and B, and αL is the fractional thickness of binder A. The initial conditions simply state, that the concentration of binder B is zero in binder A and c_0 in binder B at the start of the diffusion process. The boundary condition means, that no transport of matter is allowed through the boundaries (at $x = 0$ and $x = L$) during the time of the process ($0 \le t \le \infty$). Fick's law, which is written

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \tag{1}$$

is based on the assumption that no matter is generated in the sample and that flux of matter is proportional to the concentration gradient ($\partial c/\partial x$), often called Fourier's law. This leads to the formulation of the boundary conditions given above (zero concentration gradient). When initial and boundary conditions given in Fig. 2 are applied to Fick's law, Eq. 2 is obtained as described in Ref. [2].

$$c(x,t) = (1-\alpha)c_0 - \frac{2c_0}{\pi}\sum_{n=1}^{\infty}\frac{\sin(\alpha n\pi)}{n} \cos\left[\frac{n\pi x}{L}\right]e^{-[n(\pi/L)]^2 Dt} \tag{2}$$

Given calculated concentrations, the viscosity of mixes of binder A and B was estimated using Eq. 3, which is a mixing rule originally presented by Arrhenius [9] and later found valid for mixtures of bituminous binders by Davison et al. [10].

$$\eta_{\mathrm{mix}} = e^{c_{\mathrm{A}}\ln(\eta_{\mathrm{A}})+c_{\mathrm{B}}\ln(\eta_{\mathrm{B}})} = \frac{\eta_{\mathrm{A}}^{\alpha}\eta_{\mathrm{B}}}{\eta_{\mathrm{B}}^{\alpha}} \tag{3}$$

where η is viscosity, indexes A and B indicate the type of binders and c and α the concentration and fraction of binder A, respectively ($\alpha = c_{\mathrm{A}}$). Rheological measurements were performed on pure binders, as well as, on 50% mixtures, in order to check the validity of Eq. 3 for the bitumens studied, cf. Fig. 3. The relationship was found to predict mixture viscosity at 50% fairly well, although slightly lower compared to a straight line as suggested by Eq. 3. Also the dynamic modulus, i.e. the amplitude of the complex modulus, $|G^*|$ (henceforth G^*), appeared to follow the same mixing rule. It was expected that the same mixing rules would apply to both viscosity and G^*, because of the linear Cox–Merz relationship between viscosity and G^*, described by Barnes et al. [11]. Phase angle showed an approximately linear relationship with concentration, but a more sophisticated relationship would have been desirable.

The response from loading was calculated based on the assumption, that the binder mixture was purely viscous in Section 2.1. In order to verify the viscous model, this approach was also extended by considering effects of phase angle in Section 2.2.

Viscous modeling

Modeling bitumen as a viscous (Newtonian fluid) is fairly accurate at higher temperatures and the calculations are greatly simplified if purely viscous behavior can be assumed. In this study, such an assumption seems to be reasonable, as the stiffest material (penetration grade 15 dmm) utilized showed a phase angle of 79° at 60 °C, the lowest temperature used. If inertia forces are negligible, shear forces are fairly equal in a

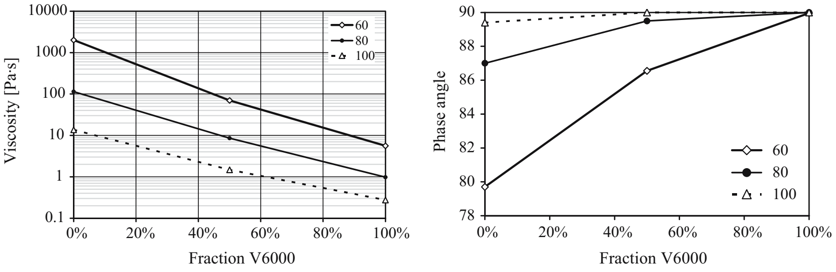


Fig. 3 Measured viscosities and phase angles of pen15 and V6000, as well as 50–50% blends at 60, 80 and 100 °C

cross section through the binder sample, given a specific distance from the rotational axis of the rheometer. This means that the shear stress, σ, is equal in all sub-layers. Shear strain, γ, is calculated as

$$\gamma = \frac{\sigma}{\eta} \tag{4}$$

The total shear displacement, $\gamma_{\text{tot}} L$, integrated for the total thickness, L, is:

$$\gamma_{\text{tot}} L = \int_0^L \gamma \mathrm{d}x = \int_0^L \frac{\sigma}{\frac{\eta_{\text{A}}^{c(x,t)} \eta_{\text{B}}}{\eta_{\text{B}}^{c(x,t)}}} \mathrm{d}x \tag{5}$$

Since the shear stress is equally distributed in all sub-layers, Eqs. 4 and 5 give

$$\eta_{\text{tot}} = \frac{L}{\int_0^L \frac{\eta_{\text{B}}^{c(x,t)}}{\eta_{\text{A}}^{c(x,t)} \eta_{\text{B}}} \mathrm{d}x} \tag{6}$$

where η_{tot} is the theoretical viscosity of all binder layers altogether, as measured by the DSR, referred to as the apparent viscosity. The apparent viscosity is calculated at time steps to obtain a theoretically simulated curve (Eq. 13). This curve is then compared to experimental data obtained at different times using the DSR. The theoretical curve is fitted to the experimental data by iterative changing of the diffusion coefficient in Eq. 2.

In order to increase the accuracy of the diffusion measurements, the measured change in apparent viscosity needs to be as large as possible, as instrumental errors will confuse the measurements performed during the long periods of time required for the diffusion tests. The theoretical change in apparent viscosity can be derived as described below.

Initially, most of the shear deformation will occur in the softest binder. If α is the fraction of soft binder (A in this case), the initial apparent viscosity, η_0, (at $t = 0$) becomes

$$\eta_0 = \eta_{\text{A}} / \alpha \tag{7}$$

When the diffusion process is complete (when $t \to \infty$), the binders are fully mixed and the apparent viscosity can be written as

$$\eta_\infty = \frac{\eta_{\text{A}}^{\alpha} \eta_{\text{B}}}{\eta_{\text{B}}^{\alpha}} \tag{8}$$

The theoretical difference in apparent viscosity during a test can be expressed as the ratio, R, between η_∞ and η_0.

$$R = \frac{\eta_\infty}{\eta_0} = \alpha \left(\frac{\eta_{\text{A}}}{\eta_{\text{B}}} \right)^{\alpha - 1} \tag{9}$$

It is of great interest to know at which α the ratio R is reaching a maximum, i.e. for which layer setup the change in apparent viscosity is at the largest. The maximum can be obtained by derivation of Eq. 9 with respect to α, which gives

$$\alpha_{\max} = \frac{1}{\ln(\eta_{\text{B}} / \eta_{\text{A}})} \tag{10}$$

If the difference in viscosity between the two binders is large, $\alpha_{\max}$ (Eq. 10) shows that R (Eq. 9) is reaching a maximum when the amount of the soft binder (rejuvenator) is relatively small. This in turn implies, that, in practice, it ought to be difficult to control recycled binder properties when adding small amounts of a comparably soft binder to a severely aged, stiff binder, since both degree of mixing and the accuracy of the amount of soft binder added is crucial to the apparent recycled binder viscosity. Figure 4 demonstrates the difference in R (the theoretical maximum of the relative increase in apparent viscosity during mixing) when adding different amounts of three soft binders (V115, V6000 and 160/220) to a stiff one (pen15). The soft binders show dynamic viscosities at 60 °C of 115, 6000 and 43000 mm^2/s, respectively. It should be noted that these binders previously have been commonly used in asphalt recycling operations. V115 is a commercial rejuvenator used in hot in-place asphalt recycling. V6000 has been used in cold and warm asphalt

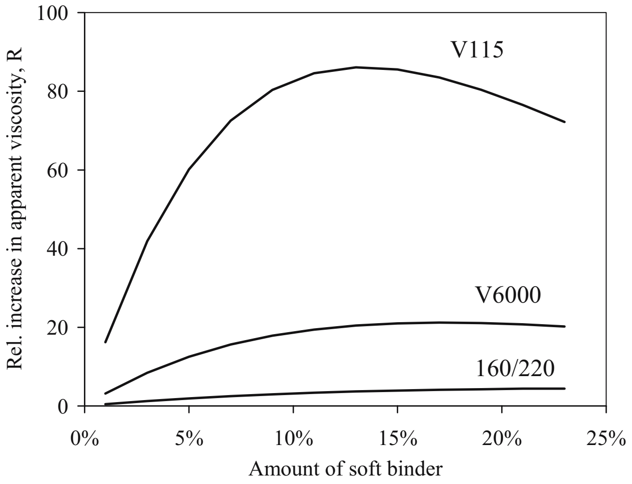


Fig. 4 Demonstration of the increase in R (maximum relative increase in apparent viscosity due to diffusion) when soft binders of various viscosities are used to rejuvenate an old binder (penetration 15 dmm at 25 °C) at 60 °C

recycling and 160/220 (a penetration grade bitumen) in hot in-plant asphalt recycling. Theoretically, as illustrated in Fig. 4, the apparent viscosity when mixing V115 and pen15 may increase over 80 times if 13% V115 (by weight of total binder) is added. This increase in apparent viscosity indicates the possible extent to which mixing of old and new binders may influence mechanical properties of recycled asphalt mixtures.

However, soft binders are more effective in reducing stiffness of aged binders and therefore desirable to use from that point of view. If the pen15 (dynamic viscosity at 60 °C approximately 2×10^6 mm^2/s) binder was to be recycled into a binder with a target penetration of pen85 (dynamic viscosity at 60 °C approximately 1.2×10^5 mm^2/s), Eq. 3 implies that about 38% of the recycled binder would have to consist of V115, while the amount of binder V6000 and 160/220 needed would have been 48 and 73% by weight, respectively. This means that the recycled asphalt mixture may consist of about twice as much old bitumen (pen15) if V6000 is used compared to 160/220, given the binder content of the recycled mixture and the old mixture is the same. The extra benefit of using the even softer V115 is fairly small compared to V6000 in this case. It should be noted that Equation 3 is approximate, and deviations from the equation occur due to the chemistry of the binders mixed, as described by Davison et al. [10], for example. Consequently, selection of a suitable binder (rejuvenator) for softening should preferably include testing viscosity of mixtures of recovered and new binders.

Visco-elastic modeling

In the same way as described above, the visco-elastic parameters G^* and δ (loss angle or phase angle), can be used to obtain diffusion coefficients. However, the total binder layer was divided into sub-layers where material properties were calculated one by one. The elastic contribution to deformation was small in the range of temperatures studied (cf. below), but visco-elastic modeling using G^* and δ provided a check of the results obtained using viscous modeling. G^* and δ of mixtures of the two binders pen15 and V6000 were estimated using Eqs. 11 and 12 (cf. Fig. 3).

$$\delta_{\mathrm{mix}} = \alpha\delta_{\mathrm{A}} + (1-\alpha)\delta_{\mathrm{B}} \tag{11}$$

$$G^*_{\mathrm{mix}} = \frac{\left(G^*_{\mathrm{A}}\right)^{\alpha} G^*_{\mathrm{B}}}{\left(G^*_{\mathrm{B}}\right)^{\alpha}} \tag{12}$$

The DSR used controlled displacement in the experiments, i.e. the plate rotational angle was sinusoidal over time, which was applied on the bottom plate. Equal shear stresses through all binder layers also apply to this case. This means that the shear strain, γ_l, in sub-layer i is related to the shear strain and phase angle of the bottom layer (sub-layer 1). A general expression for the shear strain in layer i is obtained as follows. First, the strain for sub-layer 1 is given, then the strain in layer 2 is calculated by assuming equal shear stresses in layer 1 and 2. Finally, the general relationship for the strain in sub-layer i is obtained in the same way.

$$\begin{aligned}
\gamma_1 &= \hat{\gamma}_1 \sin(\omega t) \\
\sigma_1 &= \hat{\gamma}_1 G_1^* \sin(\omega t + \delta_1) \\
\sigma_1 &= \tau_2 = \hat{\gamma}_2 G_2^* \sin(\omega t + \delta_1) \\
\gamma_2 &= \frac{\hat{\gamma}_1 G_1^*}{G_2^*} \sin(\omega t + \delta_1 - \delta_2)
\end{aligned}$$

and so forth for the other sub-layers, giving the general relationship

$$\Rightarrow \gamma_i = \frac{\hat{\gamma}_1 G_1^*}{G_i^*} \sin(\omega t + \delta_1 - \delta_i) \tag{13}$$

where $\hat{\gamma}$ is the shear strain amplitude and ω is the rotational frequency of the DSR. $\hat{\gamma}_1$ is unknown and has to be determined by iteration in such a way that the sum of all shear deformations (Eq. 5) is equal to the total shear deformation measured by the DSR. Finally, the apparent G^* was calculated by

$$G^* = \frac{\tau}{\sum\limits_{i=1}^{20} \gamma_i} \tag{14}$$

Estimating diffusion coefficients by curve fitting

Diffusion coefficients were determined by adjusting the theoretical curves of apparent viscosity or G^*, to experimental data. An example is shown in Fig. 5. The reason for using a logarithmic time scale for curve fitting (cf. Fig. 5) was that three distinct phases of development of the curve could be identified. The curves consist of two semi-infinite horizontal lines on both sides of a sloping line, where the location of the sloping line in the horizontal direction is determined by the diffusion coefficient D. However, emphasis was put on fitting the curve to the early recorded data since the instrument drifted slightly after a long period of time. The measured apparent viscosity and G^* and the ones predicted from Eqs. 6 and 14, showed fairly good agreement. Deviations could mainly be attributed to problems of filling the gap with binder at the periphery of the plates without disturbing the layers. In practice,

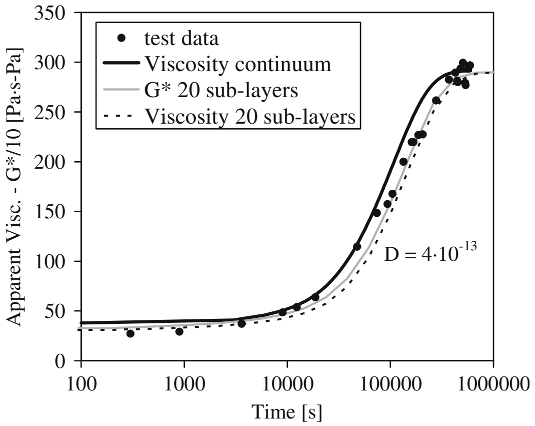


Fig. 5 Comparison of methods for determining diffusion coefficient by curve fitting

the actual sample diameter was slightly smaller than the nominal plate diameter. This problem was reduced by dividing the viscosities and *G** by the initial value.

Characterisation of diffusion using FTIR-ATR

To compare results obtained using the DSR approach, characterisation of diffusion using FTIR-ATR was also performed (cf. next section). ATR exploits the total internal reflectance of infrared light in a non-absorbing prism. Any absorbing substances in contact with the prism surface will attenuate the internally reflected light and, as a consequence, an infrared absorption spectra is obtained, corresponding to a spectra recorded if the light passed through the surface layer of the material studied.

To determine diffusion rates of a rejuvenator penetrating a bitumen, thin layers of the two compounds were applied on top of a zinc selenide (ZnSe) ATR prism (Fig. 6). The application was accomplished by gluing brass frames on the top of the prism. The thickness of the frames used in this study was 200 µm. Using two frames, with different slot widths on top of each other, two thin layers of binder were created by scraping. After application of the layers, the temperature was set and infrared absorption recorded.

Fig. 6 Schematic picture showing the application of the two-layer system using frames glued onto the ATR ZnSe prism and a scraper

To be able to monitor the diffusion process continuously over a time span of up to 72 h, computer programs were written for automating the data acquisition and processing. Diffusion coefficients were determined by curve fitting of Eq. 2 to experimental data.

The instrument used was a Mattson Infinity 60 AR spectrophotometer fitted with a Graseby Specac ATR heatable to 200 °C. The number of scans taken was 256 (up to 100 °C) with a resolution of 4 cm^{-1}. The absorbance at certain wavenumbers was calculated using the integrated peak area or peak height. Further details of the test method used are given by Karlsson and Isacsson [2].

Results

One soft bitumen, graded as having kinematic viscosity of 6000 mm^2/s at 60 °C and referred to as V6000, and one hard bitumen with a penetration grade of 15 dmm at 25 °C, referred to as pen15, was used in the diffusion tests. Rate of diffusion at 60, 80 and 100 °C was measured using both FTIR-ATR and DSR. The layer thickness used in the DSR tests was 250 µm V6000 and 500 µm pen15, and in the FTIR-ATR tests 200 µm for both. These thicknesses were chosen for practical reasons, but the variation in thickness is not believed to show a major influence on the rate of diffusion, which is discussed more in detail by Karlsson and Isacsson [2]. It should be noted that this type of testing is very time-consuming and it is necessary to keep the layer thickness down to save time. It took about two weeks to complete the test at 60 °C, during the time of which the DSR was not available for other analyses. The diffusion coefficients obtained are shown in Fig. 7. The diffusion coefficients obtained using the DSR are systematically higher compared to those obtained using the FTIR-ATR, even though of the same order of magnitude. By experience, most bitumens show close to log-linear relationships between diffusion coefficients and temperature for such a limited temperature range as the one used in this study (60–100 °C). This would indicate, that the results obtained using DSR are reasonable, as they are aligned on a straight line.

Equations 9 and 10 can be used to estimate the expected change in apparent viscosity and the optimum layer thicknesses, respectively. Viscosities on pure binders and mixtures were measured at 60, 80 and

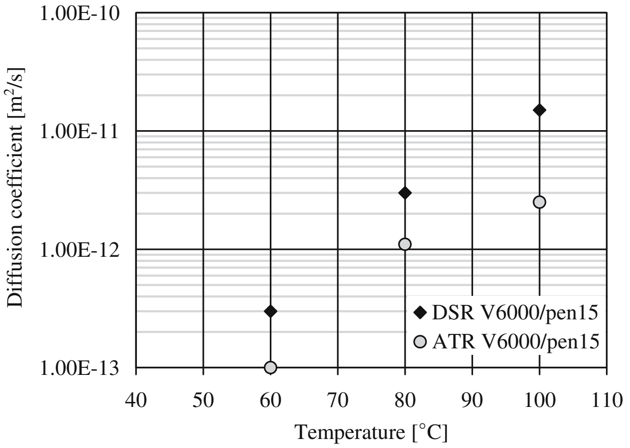


Fig. 7 Diffusion coefficients obtained from bitumens V6000 and pen15

100 °C, cf. Fig. 3. If the viscosities measured at 60 °C is taken as an example, the viscosities are 2010 Pa s for pen15 and 5.6 Pa s for V6000 at zero shear. The two layer setups used above, 500 + 250 and 200 + 200 μm, would give an expected increase in apparent viscosity, *R*, of 17 and 9.5 times, respectively. However, the measured viscosities at the end of the tests were lower than expected. Equation 10 suggests, that the fraction of soft binder should have been 17% of the total thickness, in order to observe the greatest change in apparent viscosity. However, this was not considered practical, since creating binder films thinner than 250 μm was difficult.

Discussion and conclusions

A concept of monitoring diffusion by rheological measurements, originally developed for studies of polymers, has been adopted and applied to studies of bitumen diffusion. The concept is based on rheology and diffusion theory to model the process in which two thin layers of bituminous binders mix. It is critical, that the layers created show the intended layer thicknesses, which is believed to be the case if the described procedure for application is used. Furthermore, air entrapped between the layers must be avoided and the layers need to adhere completely to each other and must not deform.

The surface tension of the binders appears to, at least partly, solve these problems, as visually, the layers looked equally thick and slightly curved at the edge. However, the curved surface at the edge meant, that the effective sample diameter was slightly less than the nominal plate diameter. The slightly smaller sample diameter in turn led to underestimations of the apparent viscosity. By dividing the apparent viscosities, both experimental and theoretical, with the initial apparent viscosity, the negative effect on accuracy when determining diffusion coefficients could be minimised.

By comparing diffusion coefficients obtained using a DSR with results obtained using FTIR-ATR, it was shown that diffusion detected chemically by FTIR-ATR is accompanied by a change in rheological properties. Throughout the work performed using FTIR-ATR for monitoring diffusion, softening of stiff binders by softer ones have been observed, but no quantification of the changes in rheological properties has been obtained until now. Even though the rates of diffusion differ, the results are still of the same order. The major outcome of this study is the indication, that the time scales for diffusion detected by FTIR-ATR and rheological changes due to diffusion are of the same order of magnitude; thus supporting the previous conclusions that the rate of diffusion in bitumen is sufficient to contribute to the creation of homogenous recycled binders during asphalt recycling.

Regarding the difference in the rate of diffusion measured using the two methods; there are a number of likely explanations. The rheological measurements may monitor diffusion of faster molecules, the small and un-associated molecules, which have a disproportionately large influence on the rheological properties. The rheological measurement may also locally increase the mobility of molecules by the large strains initially applied to the soft part of the samples. Heating should not be a problem since the measurements are not run continuously. The diffusion measurements are also fundamentally different. One is chemical, the other mechanical. One measures in the bulk, the other at the surface. Consequently, differences in measurement results are expected, considering both the difference between the methods and the extremely complex chemical constitution of bitumens.

However, recording diffusion using rheological measurements is not intended as a general tool for studying diffusion in bituminous binders, since a very large difference in viscosity of the binders studied is required. Another drawback of the rheological method is the fact that it is very time-consuming.

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