

# Influence of de-icing agents on the viscoelastic properties of asphalt mastics

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Received: 23 December 2004 / Accepted: 14 October 2005 / Published online: 28 October 2006  
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**Abstract** A study using dynamic mechanical analysis (DMA) and stress rheometry was done on the viscoelastic properties of different bitumen-filler blends disposed to de-icing agents. The blends were mixtures of the same bitumen, B200 (B), and four different filler grades, limestone (L) filler, Oulu (O) stone (mica-gneiss with high biotite amount), Rovaniemi (R) stone (diabase) and Hietavaara (H) stone (diabase). The de-icing agents tested were water, formic acid, potassium acetate (KAc) and potassium formate (KFo). From the DMA measurements, the elastic modulus (stiffness) at  $-25\text{ }^{\circ}\text{C}$ , the glass transition temperature ( $T_g$ ) of the bitumen phase, and the softening temperature were measured. The stiffness data at  $-25\text{ }^{\circ}\text{C}$  proposed that all agents seem to decrease the stiffness levels of the B-O blend with biotite to a larger extent. Formic acid and 50% potassium formates significantly decreased the stiffness level of the B-L blend. The stiffness of B-H blends was not affected by the chemical treatment. A plasticizing effect of water, formic acid, and 5% potassium acetate, was found for the B-L blend. From the changes in the softening temperatures in the temperature range  $15\text{--}28\text{ }^{\circ}\text{C}$ , it was concluded that chemical treatment may have an increasing effect on the softening temperatures of all blends, although the effect of hardening could not be omitted. Oscillatory flow measurements with a shear stress rheometer demonstrated that the viscosities of the blends increased significantly after the immersion in de-icing agents.

## Introduction

Today a very large majority of roads and airfields are constructed using asphalt pavements consisting of mixtures of bitumen and mineral aggregates, often called mastics. Pavements tend to have several problems such as high temperature permanent deformation, rutting, low-temperature thermal cracking, and chemical aging or hardening [1]. Additionally, the need and use of de-icing agents to clean the surfaces of the runways has recently possibly caused a new type of asphalt surfacing problems in Sweden, Norway, Finland and Canada [2]. Due to environmental requirements, the de-icers urea, glycol, and chlorides, have now been replaced mainly by acetates and formates. After changing to these new chemicals, degradation of the asphalt pavement has been observed [3, 4]. Recently, bitumen spread and stripping, loose stones, degradation and softening of bitumens, were also observed at some airfields in northern Finland after the winter 2001 [2]. Although the possible influence of the new de-icing agents on these problems has not been confirmed to present date there exists a strong interest to secure if, and under which circumstances, these de-icers may affect the properties of the airfield pavements. This is of extreme importance when replacing the surfaces of the pavements on a periodical basis in order to guarantee high flight safety.

The factors which influence bitumen/aggregate adhesion are numerous and complex. Important are aggregate properties such as porosity and mineralogy, bitumen properties such as rheology, mix properties such as filler type, bitumen content and void content and finally many external influences such as temperature, temperature cycling, pH and presence of salts, just to mention a few [5]. Stripping due to lack of chemical interaction between asphalt and aggregate causes pavements to fail. Mostly

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stripping is defined as the breaking of the bond between aggregate and asphalt by the action of water [6]. Studies by scanning electron microscopy [7] showed that stripping of the asphalt from the aggregate was related to the number of freeze-thaw cycles performed. This increase in the separation with the increase in the number of freeze-thaw cycles was thought to be due to water that seeped into the cracks and expanded when frozen, thus displacing the asphalt from the aggregate. Other studies [8] connected the occurrence of localized damage at low temperatures as a result of differential thermal contraction of the binders and the mineral aggregates.

Results on the influence of de-icing agents on the properties of asphalt concrete pavement for airfields, is rarely reported. A recent report by Edwards and Aurstad [3] discuss results from a Norwegian/Swedish joint project on the detrimental effect the runway de-icing agents may have on the asphalt pavements. Surface tensile strength measurements and weather simulator tests on binders and asphalt concrete, showed that a degrading effect occurred under the influence of some runway de-icing agents. More recent results [9–11] suggest that high pH-values and the surface tension properties of the de-icing agent solution have an influence on the degradation of the bitumen. Soft binders are also more prone to attack [9, 11] by the de-icers, but soft binders do not degrade chemically by the effect of de-icers or the corresponding pure chemicals [12].

Although the bitumen content in asphalt concretes is low (mostly below 10 w%), the performance of the pavement depends to a large extent on the properties of bitumen itself, since it represents the only deformable component [13]. At the same time it is largely recognized that the characteristics of bitumen are affected by the mineral aggregate with which they come in contact [14]. The viscosity of mastic (bitumen-filler mixture) is a function of filler concentration, filler type and viscosity of the bitumen. [15]. A direct relationship between the viscosity of the mastic and the particle size is found; as the concentration of filler increases, the more rapid would be the increase in the viscosity of the mastic made by that filler [16]. The increased stiffness of mixes, due to addition of filler, is particularly critical at low temperatures where bituminous mixes become brittle [16] and the filler can promote oxidation and hardening of the binders [15, 17]. The rheology of asphalt concrete is predominantly influenced by the presence of the binder, with some aggregate interaction below  $-10\text{ }^{\circ}\text{C}$  but between  $10\text{ }^{\circ}\text{C}$  and  $50\text{ }^{\circ}\text{C}$  the asphalt concrete rheology is influenced by both the binder and the aggregate [18]. Andersson et al. [19, 20] employed rheological measurements to compare the properties of the mastic with the asphalt binder properties to describe the changes resulting from adding the fillers. The relative stiffening effects were observed to be asphalt specific and

oxidative aging was shown to change the rheological type of the mastic, to be asphalt specific, and to be independent of filler type. Scholz et al. [14] pointed out, by using a modified rheological method, that mineral aggregates can affect the rheological characteristics of bitumens.

In order to evaluate the different aspects of the stripping problems at some airports, a research project [21] on the effects of de-icers on asphalt surfaces was initiated in 2003, funded by administrative organizations, bitumen deliverers, constructors, stone and additive suppliers, and the National Technological Agency of Finland, TEKES. This work presents one subpart of the project with a target to evaluate how the different de-icing chemicals may affect the viscoelastic behaviour of the mastic pieces. The objective was to use dynamic mechanical analysis (DMA) for the studies of the solid state mechanical relaxations at sub-ambient temperatures and oscillatory flow measurements with a stress rheometer for studies above the main mechanical relaxation.

## Experimental

### De-icing agents

The chemicals consisted of commercially available de-icing agents, which have been used at airports in Finland. Analytical grades of these agents and water were included for purpose of comparison. The solutions used were as follows: Distilled water (abbreviation water), Formic acid, analytical grade, 5 w% potassium acetate, analytical grade (KAc5), 50 w% potassium acetate, analytical grade (KAc50), 5 w% potassium formate, analytical grade (KFo A5), 50 w% potassium formate, analytical grade (KFoA50), 5 w% potassium formate, technical grade (KFo T5), and 50 w% potassium formate, technical grade (KFoT50).

### Samples and sample preparation

The conventional bitumen, supplied by Fortum, was a soft grade, B200 (B), normally used for pavement applications in cold temperature areas in Finland. The aggregates were limestone filler (supplier Nordkalk) and stone materials from different regions, Oulu (mica gneiss containing higher amount of biotite, grade Hakoselkä), Rovaniemi (diabase-grade, Sukkularakka), and Hietavaara (diabase-grade, Rovaniemi 2), respectively. As stone material only the particles, which passed the 0.063 mm sieve were considered. 100% of the limestone filler passed the 0.25 mm sieve, 95% passed the 0.125 mm sieve, and 80% of the filler passed the 0.063 mm sieve. The mastics blends contained 60–70 weight percent filler: (a) B-L: B200-limestone

(30:70), (b) B-O: B200-Oulu stone (40:60), (c) B-R: B200-Rovaniemi stone (40:60), and (d) B-H: B200-Hietavaara stone (40:60).

The blends were made at the Laboratory of Highway Engineering Laboratory at Helsinki University of Technology by mixing at 145 °C about 10 min. Sample specimens (bars and discs) were made by pouring the hot mix into a metallic mould and allowed to cool. The specimens were removed from the mould, wiped clean, and attached to a polyester substrate before transmitted to a freezer (−18 °C), in order to avoid phase separation. Samples remained in the freezer until they were subjected to the chemical treatment for 1 week and 1 month, respectively.

For the chemical treatments the specimens were transferred to small glass bowls and soaked in a specific chemical. On the bottom a small polyester foil was placed in order to prevent the tacking of the specimen to the glass surface. The liquid surface remained about 3–4 mm above the upper part of the specimen and the bowl was covered with a lid. The storage at 22 °C lasted 1 week and 1 month, in some cases also only 1 day. The treated specimens, as well as, the untreated reference samples were kept in the freezer before the analysis procedure. Immediately after removal of the specimen from the freezer the small polyester sheet was peeled off easily from the asphalt specimen. As the bitumen used was very soft, and adhere strongly to most materials, the procedure described above was established in order to prevent any damage to the specimens before the measurements. However, for each blend series the thermal history of the specimens disposed to different chemicals was roughly the same.

## Measurements

The DMA-measurements were made on bars (average dimensions 18 mm × 4.5 mm × 2.2 mm) using a Perkin-Elmer DMA7 apparatus with a 3-point bending geometry. Temperature scans were made from −60 °C to 30 °C or up to the temperature when the sample became too soft to permit any further measurement. The time elapsed between cooling to testing temperature and running the test was closely the same in all determinations. The frequency was 1 Hz and the amplitude 2 μm.

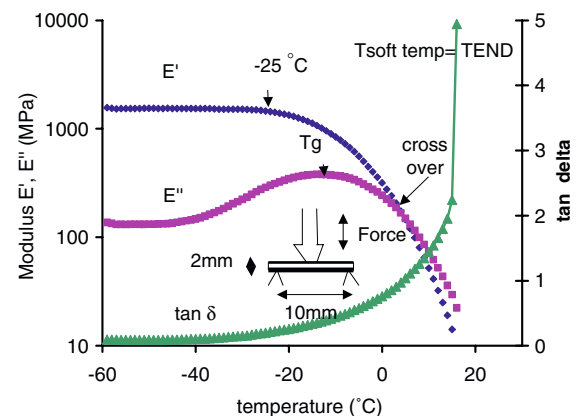
The oscillatory measurements of selected samples were made at 40 °C on discs (average dimensions 25 mm × 1.2 mm) with a Rheometrics shear stress rheometer SR500, equipped with a parallel plate system (plates with a 25 mm diameter used). The discs were conditioned for 40 min at 40 °C before the measurements in order to allow an equal relaxation time. Stress sweeps were carried out to establish linear viscoelasticity range of all samples and frequency sweeps were run from 0.02 rad/s to 100 rad/s. The gap was 1.0 mm.

## Results and discussion

### DMA-measurements

Typical DMA curves of a mastic sample are given in Fig. 1. Below the glass transition temperature ( $T_g$ ), seen as a maximum in the loss modulus ( $E''$ ) curve, only a minimal decrease in the storage modulus ( $E'$ ) curve is observed. Stiffness is equivalent to elastic modulus for a linear material, but is a function of time and temperature. For the materials in this study, the stiffness is a combined effect of elastic behaviour of the aggregate skeleton and viscoelastic behaviour of the asphalt binder. The  $E'$  value at −25 °C was chosen to represent the low temperature stiffness of the mastics samples. The binder rheological parameters associated with the limiting stiffness temperature has been associated with both the peak- $E''$  temperature and with the temperature at which the loss tangent equals 0.4 [18]. This is the temperature, where the contribution of the elastic nature,  $E'$ , of the binder is 2.5 times the contribution from the viscous nature,  $E''$ . With increasing temperature, the loss tangent,  $\tan \delta$ , may show a peak at higher temperatures or show a smoothly increasing function of temperature (depending on the nature of the base resin). The soft binder used in our mixtures cause the continuous increase in the loss tangent curve. Finally,  $T_{END}$  represents the softening temperature, where the specimen has lost its final rigidity. This temperature is noticed as a drastic increase in the  $\tan \delta$  curve.

The low temperature stiffness values (the  $E'$  values at −25 °C) and the softening temperatures ( $T_{END}$ ) from duplicate runs of the treated and untreated samples are presented in Tables 1 and 2, respectively. The standard deviations of the  $E'$  (−25 °C) values varied from  $\pm 0.2 \times 10^2$  MPa to  $\pm 0.5 \times 10^3$  MPa. Generally, all chemicals seemed to decrease the stiffness values of the blends. The most significant changes were observed for the



**Fig. 1** DMA curves of mastics sample.  $E'$  = storage modulus,  $E''$  = loss modulus and  $\tan \delta$  = loss tangent =  $E''/E'$

blend containing lime-stone (B-L); both formic acid and KAc50 significantly decreased the stiffness after a longer disposal to chemicals. The strong influence of formic acid on the B-L mastics can be seen in Fig. 2. After one-day disposal the stiffness at  $-25\text{ }^{\circ}\text{C}$  decreases from about 1770 MPa to about 830 MPa and after a disposal of 1 month the stiffness is at a level of 360 MPa. The level of the modulus curve of the sample disposed to formic acid exhibited a stepwise decrease already at about  $-45\text{ }^{\circ}\text{C}$ . A degrading effect was also visually observed after treatment with formic acid as these specimens were corroded and swollen.

A slight shift of the glass transition, measured from the maximum of the loss modulus curve, is evident. (To make the figure more clear the  $E''$ -curves after 1-day and 1-week exposure are not shown). The softening temperature shifts about six degrees from  $-8\text{ }^{\circ}\text{C}$  to  $-14\text{ }^{\circ}\text{C}$  as a result of a month exposure to formic acid, and this shift of the  $E''$  peak of the binder to lower temperatures may improve its resistance to thermally induced cracking [17].

In the temperature range above the  $T_g$  region, a continuous softening of the specimen takes place. Typically, the  $E'$  values of the chemically treated samples were higher at temperatures above about  $10\text{ }^{\circ}\text{C}$  than corresponding values of untreated specimen of the same composition.

These differences in the residual stiffness were also seen as differences in the corresponding softening temperatures, ( $T_{\text{END}}$ ), in the figures, and the decrease in  $\tan \delta$  values at increasing temperature, indicates a slight stiffening of the binder, but also an increase in the relative magnitude of the elastic component of the response [22].

An immersion of the mastic B-L in 50 w% analytical grade potassium acetate (KAc50) (Fig. 3) also exhibits a significant decrease in stiffness values (1770–1670–1170–600 MPa) due to longer soaking time. To our surprise the disposal to the lower concentration of potassium acetate, KAc5, exhibits only slight change in the stiffness levels and no changes are seen in the glass transitions. These results are opposite to those recently presented by Hassan et al. [4] on effects of de-icing chemicals on airfield asphalt concrete pavements, subjected to freeze-thaw cycles. The results in that study showed, that for all studied de-icers, potassium acetate included, the one that caused the greatest damage to the aggregates, was in the 1–2% range. In the same study it was found that conditioning asphalt samples using freeze-thaw cycles in the presence of a de-icer solution caused a decrease in the modulus of elasticity, in accordance with our results.

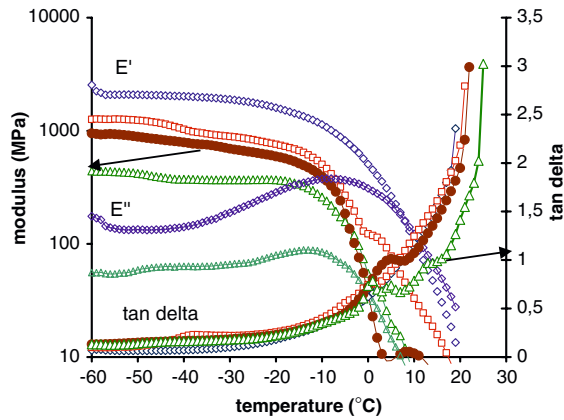
Figure 4 shows the DMA curves of the bitumen-lime-stone blend after disposal to water for different time periods.

**Table 1** Storage modulus ( $-25\text{ }^{\circ}\text{C}$ ) of mastics blends after immersion in de-icing agents

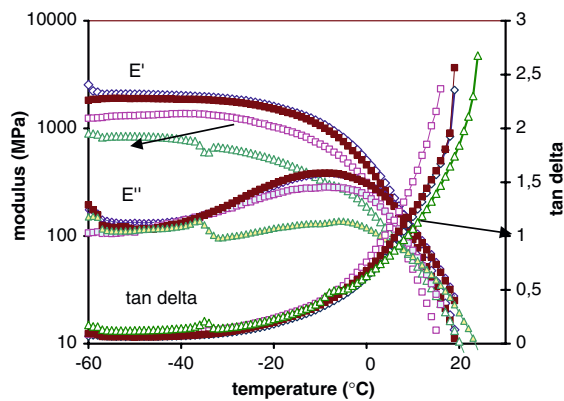
|             | B-O mastics       |                    | B-L mastics       |                    | B-H mastics       |                    | B-R mastics       |                    |
|-------------|-------------------|--------------------|-------------------|--------------------|-------------------|--------------------|-------------------|--------------------|
|             | 1 week $E'$ (MPa) | 1 month $E'$ (MPa) | 1 week $E'$ (MPa) | 1 month $E'$ (MPa) | 1 week $E'$ (MPa) | 1 month $E'$ (MPa) | 1 week $E'$ (MPa) | 1 month $E'$ (MPa) |
| Ref         | 1810              |                    | 1770              |                    | 1450              |                    | 1460              |                    |
| Water       | n.d               | 660                | 1430              | 1580               | 1130              | 1070               | 1120              | 1270               |
| Formic acid | 900               | 1140               | 640               | 360                | 1400              | 1770               | 1160              | n.d                |
| KAc50       | 780               | 650                | 1600              | 590                | n.d               | 1270               | 1330              | 900                |
| KAc5        | 970               | 860                | 1500              | 1600               | 1520              | 1490               | 700               | 940                |
| KFoA50      | 1320              | 910                | 1560              | 1400               | 1570              | 1040               | 770               | 900                |
| KFoA5       | 770               | n.d                | 1450              | 1150               | 1650              | 1020               | 1200              | n.d                |
| KFoT50      | 840               | 1010               | 1340              | 1480               | 1340              | 1160               | 920               | 1260               |
| KFoT5       | 970               | 1030               | 1210              | 1440               | 1340              | 1140               | 800               | 1280               |

**Table 2** Softening temperature ( $T_{\text{END}}$ ) of mastics blends after immersion in de-icing agents

|             | B-O mastics                   |                                | B-L mastics                   |                                | B-H mastics                   |                                | B-R mastics                   |                                |
|-------------|-------------------------------|--------------------------------|-------------------------------|--------------------------------|-------------------------------|--------------------------------|-------------------------------|--------------------------------|
|             | 1 week ( $^{\circ}\text{C}$ ) | 1 month ( $^{\circ}\text{C}$ ) | 1 week ( $^{\circ}\text{C}$ ) | 1 month ( $^{\circ}\text{C}$ ) | 1 week ( $^{\circ}\text{C}$ ) | 1 month ( $^{\circ}\text{C}$ ) | 1 week ( $^{\circ}\text{C}$ ) | 1 month ( $^{\circ}\text{C}$ ) |
| Ref         | 16.3                          |                                | 19.6                          |                                | 18.7                          |                                | 16.6                          |                                |
| Water       | n.d.                          | 24.1                           | 24.7                          | 23.2                           | 20.0                          | 21.5                           | 20.4                          | 23.0                           |
| Formic acid | 15.6                          | 23.4                           | 21.8                          | 24.3                           | 20.7                          | 21.8                           | 20.2                          | 20.2                           |
| KAc50       | 13.6                          | 20.6                           | 20.0                          | 24.3                           | n.d.                          | 20.6                           | 18.8                          | 21.0                           |
| KAc5        | 15.7                          | 23.0                           | 23.8                          | 24.0                           | 20.8                          | 22.3                           | 17.5                          | 21.5                           |
| KFoA50      | 16.8                          | 20.7                           | 21.4                          | 27.5                           | 20.3                          | 20.7                           | 18.3                          | 24.2                           |
| KFoA5       | 19.7                          | n.d                            | 22.6                          | 24.2                           | 20.8                          | 22.0                           | 19.5                          | n.d.                           |
| KFoT50      | 17.0                          | 22.3                           | 20.8                          | 22.8                           | 19.0                          | 22.3                           | 21.0                          | 21.2                           |
| KFoT5       | 19.0                          | 23.5                           | 22.6                          | 25.0                           | 20.7                          | 22.2                           | 18.6                          | 24.2                           |



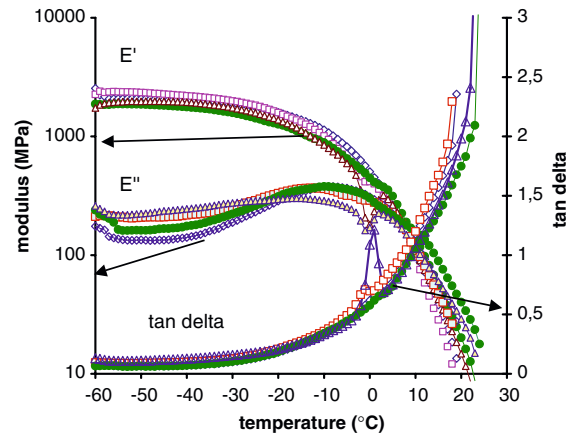
**Fig. 2** DMA curves of the bitumen-limestone blend (B-L), stored in formic acid for different time periods: Reference ( $\diamond$ ), 1 day ( $\square$ ), 1 week ( $\bullet$ ), 1 month ( $\Delta$ )



**Fig. 3** DMA curves of the bitumen-limestone blend (B-L), stored in 50 w% potassium acetate (Kac50) for different time periods: Reference ( $\diamond$ ), 1 day ( $\square$ ), 1 week ( $\bullet$ ), 1 month ( $\Delta$ )

Now we do not see any bigger differences in the stiffness values due to the exposure. However, the peaks appearing at about zero degree in all curves of Fig. 4 may suggest a release of frozen water molecules, which have penetrated into the interface between bitumen and aggregate. Therefore, some stripping action of water is not excluded. It is known that carbonate rocks, such as limestone, produce hydrophobic aggregates. Such aggregates have generally a higher resistance to stripping of asphalt films than do hydrophilic aggregates [23]. This may be due to the fact that these aggregates have larger pores on their exposed surfaces and therefore exhibit stronger bonds with asphalt than do aggregates that have fewer or smaller surface pores such as quartz. A slight shift of the glass transition towards lower temperatures takes place during a longer influence of water.

Compared to formic acid and 50 w% potassium acetate the effect of the other de-icers on the bitumen-limestone blends was rather modest. De-icing agents such as acetate and formate in concentrated form have high pH values (in the range of 9–12) and this factor is generally considered to



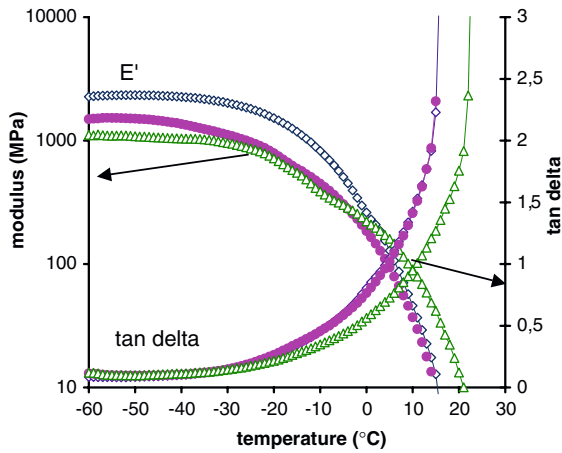
**Fig. 4** DMA curves of the bitumen-limestone blend (B-L), stored in water for different time periods: Reference ( $\diamond$ ), 1 day ( $\square$ ), 1 week ( $\bullet$ ), 1 month ( $\Delta$ )

be a disadvantage for adhesion between aggregate and bitumen [3]. The high pH value may also cause dissolving of minerals in the surface layer of the aggregate and a reduction of the surface tension of water, leading to higher penetration, has also been suggested to result in adhesion problems [3]. Although hydrophobic aggregates, such as limestone, generally are considered good adherents [23, 24], they are friable and may evidently undergo strong acid–base and electrostatic interactions with bitumen under influence of acetates and formates. For instance, some limestones contain high amounts of calcite, which looks up the calcium carbonate so it is not available for bonding to the asphalt [25].

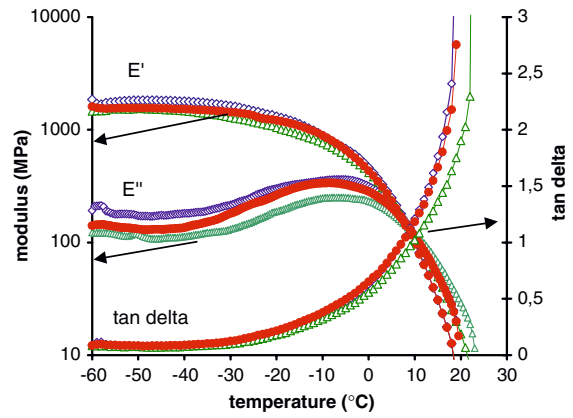
Potassium acetate, both in concentrations of 5 w% (Fig. 5) and 50 w%, strongly affected the low temperature stiffness of the bitumen-filler grade (B-O), containing mica-gneiss with higher amounts of biotite. For this blend also the disposal to water and to potassium formates (Fig. 6) exhibited a strong influence on the decrease in the low temperature stiffness. Biotite is known to give soluble potassium salts [23], which may have an effect on the stripping process. This may explain why the de-icers, with exception of formic acid 50 w% potassium acetate, affected the low temperature stiffness of the B-O-blend to a higher extent than the bitumen-limestone blend.

The two blends containing diabase filler aggregates, B-H and B-R respectively, were not quite so prone to stiffness changes after disposal to formic acid or 50 w% potassium acetate as the earlier discussed mastics. A very modest loss of elasticity is typical for the B-H mastics (Fig. 7) after a week disposal, compared to the B-R mastics samples, which exhibit faster damage, especially after immersion in 5 w% potassium acetate or the potassium formate de-icers (Fig. 8). The effect of water disposal is, however, more significant for the B-H mastic (Fig. 9) than for the B-R blend, which may be due to some unrecognized differences in the aggregates.

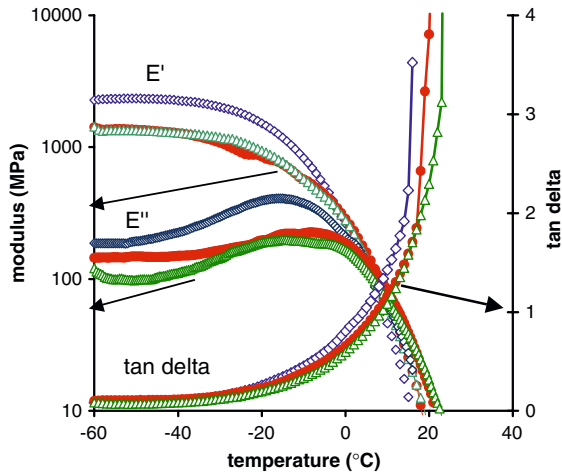




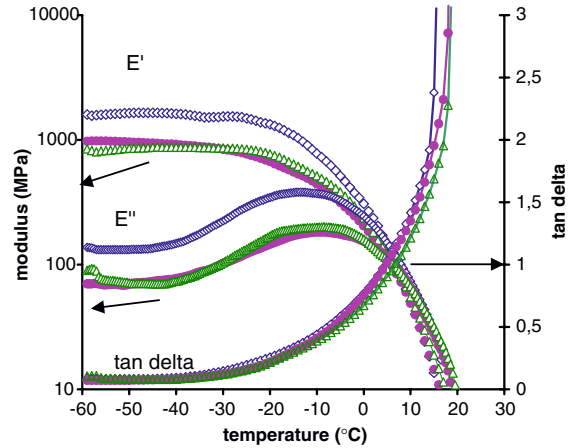
**Fig. 5** DMA curves of bitumen-Oulu stone, stored in 5 w% potassium acetate, analytical grade (KAc5), for different time periods: Reference ( $\diamond$ ), 1 week ( $\bullet$ ), 1 month ( $\Delta$ )



**Fig. 7** DMA curves of the bitumen-Hietavaara stone blend (B-H), stored in 50 w% potassium formate, technical grade (KFoT50), for different time periods: Reference ( $\diamond$ ), 1 week ( $\bullet$ ), 1 month ( $\Delta$ )



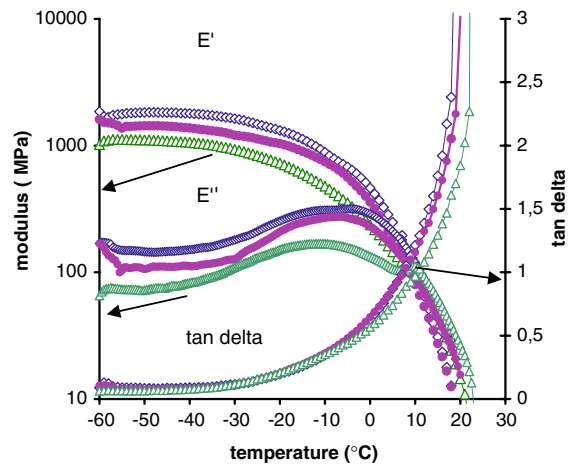
**Fig. 6** DMA curves of bitumen-Oulu stone blends stored in 50 w% potassium formate, technical grade (KFoT50), for different time periods: Reference ( $\diamond$ ), 1 week ( $\bullet$ ), 1 month ( $\Delta$ )



**Fig. 8** DMA curves of bitumen-Rovaniemi stone (B-R) stored in 50 w% potassium formate, analytical grade (KfoA50) for different time periods: Reference ( $\diamond$ ), 1 week ( $\bullet$ ), 1 month ( $\Delta$ )

Another difference in the behaviour of mastic blends containing diabase is in the influence of the exposure time on the stiffness levels. A clear loss of elasticity is seen for the B-H mastics as function of disposal time in contrast to the B-R blend, where no conclusions can be done on the effect of immersion time.

The  $E''$ -maximum peak from measurements of the untreated soft bitumen, B200, supported on a polyester foil, gave a  $T_g$  of  $-17$  °C. Corresponding peak maxima from loss modulus curves of the samples not immersed in de-icers were somewhat higher and exhibited slightly different glass transition temperatures depending on which aggregate was used:  $-15$  °C (blend B-O),  $-14.3$  °C (B-R),  $-9.4$  °C (B-L), and  $-6$  °C (B-H) with standard deviations better than  $1.1$  °C. These differences in  $T_g$ -values are probably a result of the aggregate influence. Glass transition is related to flow characteristics of asphalt at low



**Fig. 9** DMA curves of the bitumen-Hietavaara stone (B-H) blend, stored in water for different time periods: Reference ( $\diamond$ ), 1 week ( $\bullet$ ), 1 month ( $\Delta$ )

temperatures, but earlier reports [22] on binders and asphalt-aggregate mixtures explained that the  $E''$  peak of the binder is strongly affected by the aggregate and dramatic changes can occur when large aggregates are included. It has been pointed out that the glass transition temperature for asphalt is rather difficult to define [26]. When asphalts go through the glass transition zone, a delay of the molecules movements to achieve the minimum energy level is occurring, and continuous time dependent volume shrinkage takes place. This behaviour deteriorated some determinations of  $T_g$ . For the limestone filler blend the treatment with water, formic acid, and KAc5 slightly decreased the  $T_g$  after a longer disposal to chemicals; that is the bitumen phase of these blends became softer and the chemicals mentioned showed a plasticizing effect. The chemical treatment did not have any noticeable influence at all on the  $T_g$  of the B-H blend containing diabase, but slight anti-plasticizing effects (increase in  $T_g$ ) were observed for the mica-gneiss blend (B-O) and the mastic B-R (diabase), when immersed in potassium format solutions.

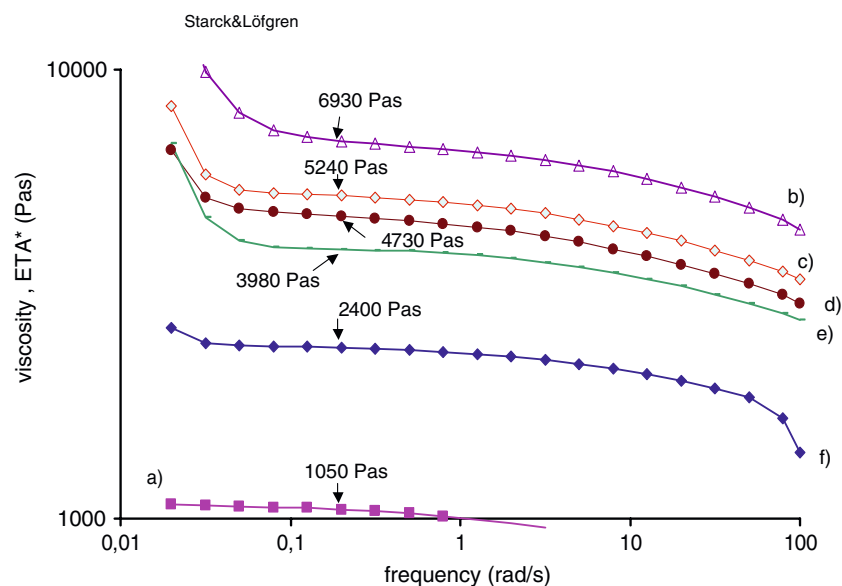
The exposure of the samples to different de-icers for a period of 1 week or 1 month increased the  $T_{END}$  temperatures to some extent. The longer the immersion time, the higher the  $T_{END}$ . That is the specimens at about ambient temperature contained some more residual stiffness after the chemical treatment, but an hardening effect cannot either be excluded. This influence is supported by the  $T_{END}$  values obtained after immersion in water, which in many cases are even higher than those shown after disposal to de-icers. As earlier mentioned, above 10 °C, the rheology of the mastics is influenced both by the bitumen and the aggregate. 50 w% potassium acetate shows some higher effect on the softening temperatures of the chemically treated B-L blends and B-R blends, respectively. Also an

immersion in 5 w% potassium formate for 1 month seems to harden the samples to some extent with exception of the B-H mastics. Indeed, the differences in the  $T_{END}$  values of the B-H blends were not significant in any case. Typical standard deviations for the  $T_{END}$  determinations were  $\pm 0.2$  to  $\pm 0.9$  °C.

#### Measurements with shear stress rheometer

Frequency sweep tests with the oscillatory stress rheometer at 40 °C gave the storage modulus  $G'$ , the loss modulus,  $G''$  and the complex viscosity,  $\eta^*$ , as function of frequency. At low frequency values a possible influence of aggregates was noticed, which appeared as unexpected high modulus and viscosity values. This effect increased with higher filler content and was not noticed at all in the run of the pure bitumen B200 specimen. At a fixed frequency higher modulus values corresponded to higher viscosities, and vice versa. Figure 10 shows the effect of filler type and amount on the viscosity of the blends. The curves represent the mean values of duplicate runs of the original blends. The viscosities at the frequency 0.2 rad/s are given for comparison in the figure. We notice that among the main blends the mastic with limestone filler has the highest viscosity and the mastic with Oulu mica-gneiss stone the lowest one. At the same concentration level differences are seen in the viscosity levels between B-O, B-R, and B-H, respectively. An earlier report [20] on effects of aggregates on fracture behaviour of hot-mix asphalt demonstrated that the increase in viscosity of mastics was mainly dependent on the volume concentration of mineral filler and to a less extent independent of source of filler. However, the physical or chemical properties of the binder are, besides the concentration of filler in the mix, also depending on the

**Fig. 10** Complex viscosities by stress rheometry (40 °C) of undisposed bitumen B200 (a) and mastics blends: (b) B-L = 30–70, (c) B-H = 40:60, (d) B-R = 40:60, (e) B-O: 40:60, (f) B-L = 50:50



type of filler and on the nature of filler (e.g. its physico-chemical activity) [16]. The percent of free asphalt may afford a slightly better correlation with viscosity than the volume concentration as this parameter also accounts for the packing characteristics of the fillers [20]. Minor differences in the mineralogical compositions may thus explain the slight differences in viscosity between the different mastics.

The viscosity data at the frequency 0.2 rad/s of the specimens subjected to de-icing agents for different exposure times are given in Table 3. The standard deviations from duplicate, similarly treated, runs varied from  $\pm 60$  Pa s to  $\pm 300$  Pa s. For all measurements the general trend of increasing viscosities due to immersion of the samples in the chemical persisted. Moreover, the longer the treatment time, the higher the viscosity. Figure 11 demonstrates this effect of water and treatment time on the B-H blend.

According to the results of Table 3 it can again be concluded that the effect of water immersion in most cases is as big as the effect of the most aggressive de-icers. Therefore, the viscosity increase may be, at least partly, an aging or hardening effect and only to a minor extent a result of the chemical treatment. Figure 12 shows another typical feature. For most specimens analyzed, the agent KFoT5 had a stronger influence on the viscosity than the more concentrated versions KFoT50 and KFoA50. This trend existed for the B-R, B-L, as well as for the B-O-blends. Interestingly, recent results from stripping tests [10] on similar blends suggested that low concentrations (5 w%) were more harmful than higher (50 w%) concentrations in causing stripping and similar results were also presented by Hassan et al [4].

The effect of remaining crystallites in the sample, strain hardening due to development of internal steric stresses, or insufficient thermal equilibrium time, may be some of the causes to the unexpected high viscosity results of the disposed samples, as well as to the higher softening temperatures seen in the DMA measurements. When testing at low temperatures care with the thermal history has been

emphasized [26] and one has to be very careful about the time the sample is stored before testing. Moreover, it has to be pointed out that as asphalt is cooled it reaches a state where the structure of the material is frozen in. Because of the non-equilibrium energy condition of the material, it will try to achieve its minimum energy and thus continues to shrink [22]. At low temperatures, crystallized fractions are greatly responsible for physical hardening occurring with time and Planche et al. [27] pointed out the influence of the time of conditioning on the low-temperature stiffness of asphalt cements. Therefore, in order to minimize these error sources, the sample preparation and loading procedure in this work was very similar for all samples in each series (blend/chemical type/treatment time). These precautions were expected to make it possible to confirm the differences in the qualitative influence of the chemicals on the viscoelastic properties.

## Conclusions

This study was done on viscoelastic properties of different bitumen-filler blends disposed to de-icing agents for different periods of time. DMA at sub-ambient temperatures demonstrated that all agents to some extent decrease the low temperature stiffness at  $-25$  °C of the immersed specimens. Formic acid and 50% potassium formates significantly decreased the stiffness level of the bitumen-limestone (B-L) blend and these de-icing agents also exhibited a plasticizing effect as the glass transition temperatures of the binders decreased as a result of the chemical treatment. At visual inspection deterioration of these specimens was also noticed. The effect of water, however, was insignificant on this mastic blend.

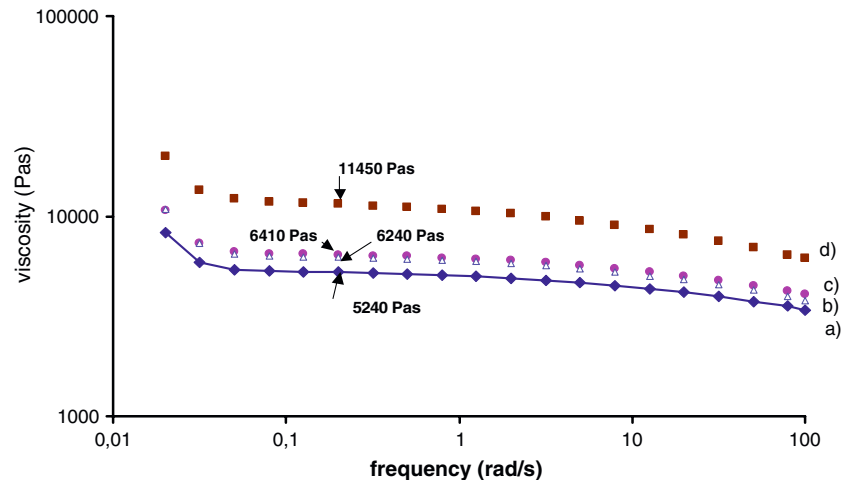
Potassium acetate, both in lower and higher concentrations, as well as water and potassium format, strongly decreased the low temperature stiffness of the mastic blend containing mica-gneiss aggregate with higher amount of biotite. This strong effect might be related to the property of biotite to produce soluble potassium salts.

**Table 3** Viscosities at 40 °C of mastic blends disposed to de-icing agents

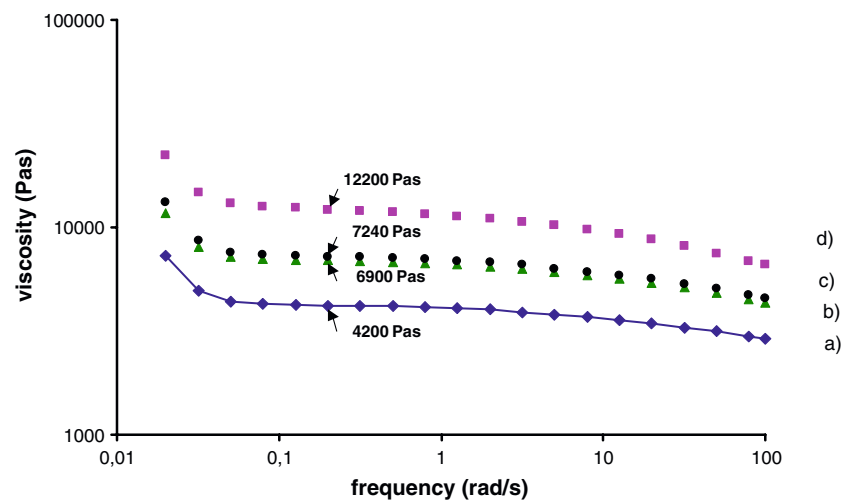
|             | B-H mastics                |                             | B-R mastics                |                             | B-O mastics                 | B-L mastics                |                             |
|-------------|----------------------------|-----------------------------|----------------------------|-----------------------------|-----------------------------|----------------------------|-----------------------------|
|             | 1 week<br>viscosity (Pa s) | 1 month<br>viscosity (Pa s) | 1 week<br>viscosity (Pa s) | 1 month<br>viscosity (Pa s) | 1 month<br>viscosity (Pa s) | 1 week<br>viscosity (Pa s) | 1 month<br>viscosity (Pa s) |
| Ref         | 5240                       |                             | 4730                       |                             | 3980                        | 6930                       |                             |
| Water       | 6420                       | 11,450                      | 6240                       | n.d.                        | 9550                        | 6410                       | 11,400                      |
| Formic acid | 6600                       | 11,270                      | 6250                       | n.d.                        | 10,200                      | n.d.                       | 11,300                      |
| KAc50       | n.d.                       | 7890                        | 4840                       | 7880                        | n.d.                        | 9540                       | 7890                        |
| KAc5        | 6790                       | 11,450                      | 6230                       | n.d.                        | n.d.                        | n.d.                       | 11,500                      |
| KFoA50      | 5840                       | 7240                        | 7870                       | n.d.                        | 7240                        | n.d.                       | 14,000                      |
| KFoA5       | 6590                       | 11,400                      | 6940                       | n.d.                        | n.d.                        | n.d.                       | 14,900                      |
| KFoT50      | 5870                       | 7260                        | n.d.                       | 8300                        | 6900                        | 8720                       | 11,300                      |
| KFoT5       | 6790                       | 11,270                      | n.d.                       | 12,000                      | 12,200                      | n.d.                       | 17,000                      |



**Fig. 11** Effect of water on the viscosity (40 °C) of the mastic blend B-H. (a) B-H, (b) B-H, water 1 week, (c) B-H, water 1 week, (d) B-H, water 1 month



**Fig. 12** Effect of potassium formate on the viscosity (40 °C) of mastic blend B-O. (a) B-O, (b) B-O, KFoT50 1 month, (c) B-O, KFoA50 1 month, (d) B-O, KFoT5 1 month



The mastics B-H and B-R, both containing higher diabase as component, showed dissimilar behavior after chemical treatment. The stiffness levels of the B-H blends were rather unaffected after a week disposal time, but the B-R blend was significantly influenced by the acetate and formates. Different glass transition temperatures of the reference specimens indicate that some differences in the mineralogical composition exist, which affect the relative affinity for water and bitumen

From the changes in the softening temperatures by DMA in the temperature range 15–28 °C, it is concluded that chemical treatment affects the softening temperatures of all blends; a longer disposal time to the agents increases the temperatures. Then the samples contained more “residual rigidity”. Among the B-L blends, the 50 w% potassium formate has the strongest effect on the increase of the softening temperature. The chemical treatment of the B-H blends had again only a slight increasing effect on the softening temperature.

The viscosity measurements at 40 °C with the stress rheometer suggested that the immersion of the mastics into

de-icing agents for specific times has an increasing effect on the viscosity values, but an aging or hardening of the specimens could be responsible for this change as well. In most cases lower concentrations of potassium formate and potassium acetate have a stronger increasing effect on the viscosities than corresponding higher concentrations. This may be in accordance with recent results showing that rather low concentrations of de-icers cause the greatest damage, although we were not able to determine any critical deicer concentration, corresponding to a maximum damaging effect.

Insufficient and different thermal equilibrium times may cause some of the differences in viscoelastic behaviour between disposed and reference samples. The difficulties to establish laboratory experiments corresponding to the real conditions at the asphalt pavements of the airfields, are of concern. Further rheological research on the effect of de-icing agent, using very controlled sample conditioning, different bituminous binders and polymer modified bitumen blends, may give some more information. However, the main problem with loss of adhesion and stripping of the

asphalt at the aggregate interface cannot be explained solely from viscoelastic measurements. For that purpose studies especially on surface tension and pH-effects also have to be included.

**Acknowledgements** The authors would like to thank Pekka Jauhiainen for making the specimens, Simo Toikkanen and Marek Zavinsky for the major part of the DMA and rheology measurements and TEKES for financial support.

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