Influence of M_w of LDPE and Vinyl Acetate Content of EVA on the Rheology of Polymer Modified Asphalt

Ibnelwaleed A. Hussein[1]*, Mohammad H. Iqbal[1], Hamad I. Al-Abdul Wahhab[2]

[1]Department of Chemical Engineering, [2]Department of Civil Engineering
King Fahd University of Petroleum & Minerals
Dhahran 31261, Saudi Arabia

ABSTRACT

Asphalt binder was modified by low density polyethylene (LDPE) and ethyl vinyl acetate (EVA) polymers to investigate the structure-property relationships of polymer modified asphalt (PMA). The PMA was prepared in a high shear blender at 160^{o}C. The optimum blending time (OBT) for each polymer was determined following a separate investigation. OBT was influenced by Mw, MWD, and polymer structure. The influence of Mw of LDPE and vinyl acetate (VA) content of EVA on PMAs was studied by rheological tools. Polymer modification improved the rheological properties of base asphalt. EVA PMAs were found to be less temperature sensitive than LDPE modified asphalts. LDPE modification increased flow activation energy (E_a) but EVA modification decreased E_a. Both VA content and Mw of LDPE have influenced the storage stability of PMAs. The low temperature properties of PMAs and short ageing tests were not influenced by polymer type. On the other hand, the high temperature properties of PMAs were strongly influenced by Mw of LDPE and VA content of EVA. Overall, EVA with low VA content showed the best temperature resistance to high temperature deformations, the highest upper service temperature as well as the best storage stability.

Key words: polymer modified asphalt, rheology, LDPE, EVA, storage stability

***Corresponding Author**

Email: ihussein@kfupm.edu.sa; Phone: +966 3 860 2235; Fax 860 2235.

Introduction

Asphalt is used as road carpeting material throughout the world. Because of the availability of relatively low cost binders, the roadway networks in the Gulf Countries have developed rapidly more than those of many other industrialized countries (Al-Dubabe et. al., 1998). The increase in road traffic during the last two decades in combination with an insufficient degree of maintenance has caused an accelerated deterioration of road structures in many countries (Isacsson and Lu, 1995; Lu and Isacsson, 1997). To minimize the deterioration and thereby to increase the long term durability of a flexible pavement, the asphalt layers should be improved with regard to performance related properties, such as resistance to permanent deformation, low temperature cracking, load-associated fatigue, wear, stripping and ageing. Moreover, for certain applications, such as bridges, runways and surfaces with high traffic loading, special binders are urgently required (Lu and Isacsson, 1997).

Asphalt modification with different materials was done in the past (Lu and Isacsson, 1997; Zanzotto et. al., 1996; Bouldin et. al., 1991; Muncy et. al., 1987; Goodrich 1988). Recently, a large number of investigations showed that asphalt properties (e.g., viscoelasticity and temperature susceptibility) can be improved by using an additives or a chemical modification for high temperature as well as low temperature applications (Isacsson and Zheng, 1998; Lu and Isacsson, 2001; Lu et. al., 1998; Fawcett et. al., 2000a, 2000b, Johansson and Isacsson, 1998; Nair et. al., 1998; Collins et. al., 1991; Bahia and Davis, 1994; Bonemazzi et. al., 1996; Blanko et. al., 1996; Adedeji et. al., 1996; Ali et. al., 1999; Wen et. al., 2002). Among the different types of additives, polymers are the most promising modifiers. Although there are many polymers, only few

are suitable for asphalt modification (Lu and Isacsson, 2001). These polymers should resist the degradation at asphalt mixing temperatures (about 160^{o}C) and maintain their premium properties during storage and application (Varma et. al., 2002; Sabbagh and Lesser, 1998; Rozeveld et. al., 1997). Also, the polymer should be compatible with asphalt; capable of being processed with conventional mixing/laying equipment, and cost effective (Garcia-Morales et. al., 2004; Gao et. al., 2002; Lu et. al., 1999). To achieve the goal of improving asphalt properties, the selected polymer should create a secondary network or a new balanced system within asphalt by molecular interaction. The formation of a functional modified binder system is based on the dissolution and/or fine dispersion of polymer in asphalt and on the compatibility of the polymer/asphalt system.

In addition to the influence of polymer molecular parameters, there is a significant effect of blending time and temperature on PMA. Long blending time causes structural damages of asphalt (Yousefi 2003; Al-Dubabe et. al., 1998). Further, high shear rates disintegrate polymers and reduce their sizes to micrometer and submicrometer scales in asphalt medium. This will inhibit polymer entanglement with asphalt phase. Blending time can be selected by measuring the softening point after a certain time interval at the time of blending (Al-Dubabe et. al., 1998).

In this study, the influence of Mw of low density polyethylene (LDPE), VA content of EVA as well as polymer type and polymer concentration on asphalt modification was investigated. Two polymers that are widely used in asphalt modification namely, polyethylene and EVA were selected. The influence of Mw (or Melt Flow Index, MFI) of the polymer was examined by using two LDPE samples of the same density but of different MFIs. The influence of VA content on asphalt modification

was investigated by selecting two EVA resins of similar MFI and of different VA content. Also, a comparison of LDPE and EVA (of almost similar MFI) would reveal the influence of polymer type. Here, the influences of these parameters, such as M_w (or MFI) and VA content or structural parameters (LDPE vs. EVA) were studied one parameter at a time. Also, most of the previous work was performed in cold climates (Canada and Sweden) where improvement of the low temperature performance of PMAs was of great concern. For Saudi Arabia (and other hot climates in the world), the high temperature performance of PMA is important for PMAs. Here, the high temperature performance of PMAs is emphasized. This study is part of a research plan aiming at selecting a proper type of polymer that could be used for polymer modification of local asphalt. The plan involves testing the PMA concrete mixes, too. In this paper, the PMAs of LDPE and EVA are studied.

Experimental

Materials

2 LDPEs and 2 EVAs were used in this study. All are commercial polymers and were supplied by ExxonMobil. Table 1 provides characterization data such as density, MFI at 190^{o}C/2.16 kg and melting point as provided by ExxonMobil. The number-average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (PDI) were obtained by a gel permeation chromatography (GPC). GPC data was obtained by using 1,2,4 trichlorobenzene as solvent at 150^{o}C in a WATER GPC2000 instrument. Polystyrene standards were used for calibration. Branch content was obtained for LDPE polymer by NMR and it was 18.8 and 18.2 CH_3/1000C for LDPE1 and LDPE2, respectively. On the other hand, the VA content of the EVA

samples was 19 wt% and 27.5 wt%, respectively. The VA content was provided by the supplier and the ratio was confirmed by NMR. The low M_w LDPE and the low VA content EVA were denoted by label 1, where the high M_w LDPE and the high VA content EVA were assigned the label 2.

Asphalt of 60/70 penetration grade was used in this study. This asphalt was obtained from Saudi Aramco Riyadh Refinery. The weight percentage of C, H, S and N content of asphalt was obtained by elemental analysis as 85.70%, 10.26, 3.90% and 0.4%, respectively. To determine the amount of the heavy fractions in asphalt (asphaltenes), asphalt was dissolved in toluene and 0.45-μm filter was used for filtration (El-Mubarak et. al., 1999). According to this gravimetric method, asphalt, used in this study, was found to contain 30% asphaltenes.

Determination of Optimum Blending Time (OBT)

To avoid long blending time, the OBT for the 8% concentration was obtained. Complex shear modulus ($|G^*|$) at 76°C was used to monitor the consistency of PMA during blending. The temperature of 76°C was selected since it represents the highest performance grading requirements in the Gulf countries (Al-Dubabe et. al., 1998). $|G^*|$ was measured for samples collected during the blending at 5, 10, 15, 20, 25, 30, 40 and 50 minutes of the start of the blending process. The OBT was determined as the time needed for $|G^*|$ (or torque) to reach steady state. The steady state was defined as the first plateau of torque-time curve. Prolonged heating is believed to be behind the increase in torque following the plateau as a result of x-linking (Yousefi, 2003). For all other parts of this study, all PMA samples were prepared at the OBT obtained for the 8% polymer concentration.

PMA Sample Preparation

800 g of asphalt were heated at 160^{o}C for 50 minutes. Oil bath was used to control the temperature. Pre-weighed polymer was poured in the asphalt. A special blender composed of high shear blade (Al-Dubabe et. al., 1998; Iqbal, 2004) was used to blend the polymer with the asphalt; the blending speed was controlled with a DC motor capable of producing up to 3000 rpm. Three different polymer concentrations (4%, 6% and 8 wt %) were used. After blending at the OBT, samples were collected in a rubber mould of 25 mm diameter and 2 mm thickness and tested within 24 hrs.

Polymer Specimen Preparation

Before rheological testing, as received polymers were given a controlled thermomechanical history (molding) in a Carver press. 25 mm diameter and 2 mm thick polymer flat discs were prepared. Molding was conducted according to the melting point of polymer. Polymer pellets were charged between the platens of the press under 3 metric tons of pressure for 1 min. Then, pressure was increased to 5 metric tons and held for 1 min. Thereafter, pellets were kept for 5 min at 7 metric tons pressure. Finally, water was used to cool the platens to room temperature and discs were collected for rheological testing.

Rheological Characterization

All rheological tests of pure asphalt as well as polymers and PMAs were carried out in a strain controlled ARES rheometer. Parallel plate geometry with a diameter of 25 mm and a gap of 1.5 mm was used in all of these studies. This is mainly due to the fact that cone-and-plate geometry was not used for temperature sweeps to avoid metal-metal

contact. Strain sweep tests were performed on PMAs and base asphalt to check for the linear viscoelastic range and 20% strain amplitude was selected. All tests were conducted under nitrogen environment to avoid any possible degradation. Reproducibility tests were performed on the 4% LDPE1 PMA to check for any possible degradation in PMA (Hussein et. al., 2000). The samples were obtained from two different batches. The results of reproducibility tests are given in Figure 1. The agreement of both viscous and elastic properties shows the excellent reproducibility of these measurements. The frequency sweep was carried out at 76^{o}C in the range 100 to 0.1 rad/s. Temperature sweep test was done over the temperature range 50^{o}-100^{o}C at 5^{o}C/min ramp rate (to avoid long exposure time at high temperature) and a frequency ω=10 rad/s. Also, frequency-temperature sweep tests were performed to construct time-temperature superposition (TTS) curve. In that case, the temperature range covered was 50-90^{o}C at a step of 10^{o}C. In all temperature sweep tests, 2.5 microns/^{o}C were used as tool thermal expansion coefficient following a separate calibration experiment.

Storage Stability Test

The tests aim at assessing the storage stability of PMA, which is related to the miscibility of asphalt-polymer blend. The storage stability of asphalt binders was performed as follows: after blending 800 g of asphalt sample at OBT, the container was placed in an oil bath at 160^{o}C for continuous agitation at 500 rpm. After 72 hours, the samples were collected from the top and the bottom of the container by a pipette. The storage stability of the modified asphalt binders was evaluated according to the Laboratory of Asphalt Stability Test (LAST) procedure (Bahia et. al., 2001). G* values at 76^{o}C and 10 rad/s were measured in ARES rheometer for the top and the bottom samples.

Then, the difference was calculated. This test helps in assessing the miscibility of polymer-asphalt blend, which is critical for storage and final use of PMA.

Rolling Thin Film Oven (RTFO) Test

RTFO was used to perform ageing of asphalt binders according to ASTM D 2872 procedure. This test simulates the ageing process that takes place during the production and up to the first year of the service life of the pavement. After blending, asphalt binder was poured into cylindrical bottles, placed horizontally in a convection oven and rotated at 163^{o}C for 85 minutes. Air was supplied into the bottle to accelerate ageing. A thin film was created on asphalt. After completing the run, samples were collected for rheological testing in ARES.

Performance Grading (PG)

PG of PMAs was done for all samples with a 4% polymer concentration. The steps of the PG are as follows: residue from RTFO was placed in a Pressure Aging Vessel (PAV) where temperature was held at 110^{o}C and oxygen was supplied continuously following Strategic Highway Research Program (SHRP) B-005 test procedure. After 20 hours, samples were collected from the PAV for measurement of $|G^*|$. According to SHRP, the upper limit of PG represents the temperature at which $|G^*|/\sin\delta$ is at least 1 kPa. Also, beams (12.4 cm$\times$1.2 cm$\times$0.6 cm) were prepared to find the lower temperature limit of PG using a Fisher's Bending Beam Rheometer (BBR).

Results and Discussion

Optimum Blending Time

The values of $|G^*|$ are shown in Figure 2 for all PMAs. Base asphalt was treated under the same conditions. The diamond, upper triangle, lower triangle, circle and square symbols represent base asphalt, LDPE1, LDPE2, EVA1 and EVA2 PMAs, respectively. $|G^*|$ value of asphalt was smaller than 1 kPa (SHRP minimum requirement) over the whole time range; however, polymer modification increased $|G^*|$. Initially, $|G^*|$ increased rapidly and then the rate of increase slowed down with time. The minimum time required by $|G^*|$ (torque) to attain at the steady state is taken as the OBT. It should be noted that after the first plateau increase in torque was observed, which is likely due to x-linking as a result of prolonged heating. OBTs of 8% LDPE1, 8% LDPE2, 8% EVA1 and 8% EVA2 PMAs were 30, 20, 15 and 20 minutes, respectively. EVA1 PMA showed rapid initial increase in $|G^*|$, while EVA2 PMA showed the least initial increase. The initial behavior of OBT curve of the LDPE modified asphalt was similar. However, LDPE2 (low MFI, high Mw) reached the steady state faster than LDPE1 (high MFI, low Mw), while the reverse was expected.

Although MFI characterizes the thermoplastic polymers, the rheological behavior of a polymer at high shear rate indicates the degree of mixing with asphalt. This can be clearly explained by power law model. Low power-law index polymer gives more shear thinning behavior at high shear rate and need less time for dispersion. So, knowledge of MFI of polymers is not sufficient since the shear thinning behavior is significant, too. Frequency sweep tests of pure polymers were performed and the value of power law indices (n) were 0.73, 0.63, 0.72 and 0.85 for LDPE1, LDPE2, EVA1 and EVA2

polymer, respectively. It can be seen that LDPE2 exhibits more shear thinning behavior and its power low index is less than LDPE1. So, it has a low viscosity at high shear rate and LDPE2 takes less time to attain steady state in the high shear blender. Also, GPC analysis (Table 1) showed higher PDI for LDPE2 (the high Mw polymer) in comparison with LDPE1 (the low Mw resin). This explains the shear thinning behavior of LDPE2 and the low OBT. In the case of EVA polymer, this explanation was quite clear. Both EVA polymers have the same MFI but their shear thinning behavior is different. For EVA2, n value is high so the PMA took more time to reach steady state in comparison to EVA1. It should be noted that PDI obtained from GPC is almost the same for EVA polymers. However, rheology is more sensitive than GPC in detecting these differences (Hussein et. al., 2000).

Moreover, polymer type has significant effect on the blending time. EVA polymers took less time to reach steady state although LDPE1, EVA1 and EVA2 have almost the same MFI (~150). It was observed that as-received LDPE1 and EVA1 showed similar rheological behavior (power law indices are almost identical) and almost similar MFI. So, these two polymers were later compared to study the effect of polymer type on asphalt modification.

Rheological Analysis

The comparison of asphalt and PMAs are presented in Figure 3, which reports the dynamic viscosity (η') at 76^{o}C as a function of ω. In this case, the 4% concentration of different polymers was taken. The base asphalt showed typical Newtonian behavior over almost the whole ω-range with a zero shear viscosity, η_o, of 95.485 Pa-s. Similar observations were reported in the literature (Zupancic and Zumer, 2002; Bahia and

Davies, 1994). Addition of 4% of a polymer has increased η′ of PMAs at low-ω. However, the results depend on the type of the polymer. EVA1 PMA showed the highest increase in viscosity at low frequency region. EVA2 modified asphalt showed a decrease in η′ at high-ω. LDPE2 modified asphalt displayed the same viscosity as EVA1 at high-ω. This effect is quite clear in Figure 4, where $|G^*|$ was plotted as a function of phase angle (δ). This diagram was generated with frequency sweep data. PMA showed substantial decrease in δ (increase in elastic response) with decreasing $|G^*|$ compared to base asphalt. Both EVA PMAs is found to decrease more in comparison to LDPE PMAs. The effect of polymer concentration on η′(ω) (filled symbol) and G′(ω) (open symbol) of LDPE1 is shown in Figure 5 for the three different polymer concentrations. It was observed that both rheological properties of modified asphalt increased with the increase of polymer content, which is expected.

The effect of polymer concentration on η′(T) was studied by performing temperature sweeps on LDPE1 PMA at three different polymer concentrations. The results are shown in Figure 6. At high temperatures (~90^{o}C), the 8% LDPE1 PMA showed a sudden decrease in η′ values. High polymer concentrations result in PMA with higher elasticity; however, the blend has the tendency to phase separate. Phase separation was suggested for PMA with more than 7 wt% polymer concentration (Brule, 1996). However, high temperature would weaken the interfacial tension between the dispersed LDPE1 phase and the asphalt continuous phase. This would result in improvement of the blend miscibility and hence reduce the viscosity of the blend (Hameed and Hussein, 2002). The observed drop of the 8% LDPE1 PMA viscosity at high temperature supports the existence of a multiphase system at lower temperatures since Arrhenius behavior was

not followed. In fact, at these low temperatures LDPE1 is below its melting point (see Table 1) and it is a semisolid in a matrix of asphalt melt which justifies the multiphase explanation.

Temperature sweep tests were also used to obtain flow activation energy from well known Arrehenius equation.

$$\eta^* = A\, e^{Ea/RT} \text{---------- (1)}$$

where A is the pre-exponential term, E_a is activation energy, T is temperature and R is universal constant. Table 2 shows the values of flow activation energy (E_a) and the pre-exponent (A) of modified asphalt for three different polymer concentrations of each polymer. E_a increased when LDPE was used. Flow activation energy increased with the increase of LDPE concentration. This behavior of LDPE modified asphalt is similar to previous observations of different researchers (Zupancic and Zumer, 2002; Carreau et. al., 2000; Ait-kadi et. al., 1996). On the other hand, EVA modified asphalt decreased the flow activation energy significantly and lower E_a values were obtained at higher polymer content. Low activation energies are preferred since they result in lowering the change of viscosity with the change of temperature.

Both EVA1 and EVA2 polymers showed similar behavior with regard to the influence of polymer content on E_a. This behavior is likely due to the rigid nature of the EVA molecule (double bond in the backbone). Here, we would like to offer tentative explanations. The high VA content EVA2 is likely to act as a rigid molecule that reinforces the flexible asphalt matrix, while EVA1 acts as a flexible polymer chain that entangles with asphalt molecules. Higher VA content is likely to reduce the degree of entanglement of polymer asphalt molecules. So, it seems like low VA content would

allow the polymer molecule to entangle with asphalt; hence increase the elasticity of PMA. However, high VA content would likely render the polymer molecule too stiff and reduce the entanglement density of polymer-asphalt micelles. Here, we are excluding any other explanations based on chemical reaction. This is mainly due to the fact that blending of EVA polymers with asphalt for long times (50 min) in the high shear blender did not produce significant increase in the elasticity of PMA. Still the polymers used in this part of the study were blended at much less time (see optimum blending time part). Also, $|G^*|$ for asphalt was stable over a long period of time (see the OBT curve). Hence, these polymer modifications are dominated by physical rather than chemical interactions.

The percent decrease in viscosity of PMA due to the increase in temperature from 50^{o}C to 60^{o}C was calculated by Arrhenius equation and results are shown in Table 2. These temperatures were selected because about this temperature range asphalt goes to Newtonian region (Polacco et. al., 2003). It was observed that the difference was high for LDPE polymers and the difference has increased with the increase of polymer concentration. But EVA polymers showed less decrease in viscosity when temperature was increased from 50^{o}C to 60^{o}C. This decrease in viscosity is even less at high EVA concentrations.

As PMA is a viscoelastic material, it exhibits non-Newtonian behavior over wide temperature range and cannot be defined only by zero-shear viscosity (Singh et. al., 2003; Zupancic and Zumer, 2002; Carreau et. al., 2000). Time-temperature superposition (TTS) is used to explain this behavior. For TTS, Williams-Landel-Ferry (WLF) equation is used.

$$\log a_T = \log \frac{\eta_0(T)}{\eta_0(T_R)} = \frac{-C_1(T - T_R)}{C_2 + (T - T_R)} \text{ ----------(2)}$$

where, C_1 and C_2 are constants and $T_R \geq T_g$+100^{o}C and T_g is the glass transition temperature. Figure 7 shows the elastic modulus (G′) as a function of reduced frequency (ωa_T) obtained from temperature-frequency sweeps. Data are presented for the 4 % polymer concentration systems. The reference temperature was 70^{o}C. The temperature dependence of the shift factor, a_T, is given in Figure 8**.** Similar behavior was reported in the literature (Zupancic and Zumer, 2002; Carreau et. al., 2000, Challa et. al., 1996, 1997; Chebil et. al., 1996). It is observed that time-temperature superposition (TTS) principle holds for LDPE and EVA polymers over the experimental range of temperatures and frequencies.

The fact that the four PMAs covered in this study follow TTS suggests that the polymer-asphalt blend is miscible. At low ω, EVA1 PMA showed the highest G′ among all polymers. LDPE modified asphalt displayed higher elasticity in comparison to base asphalt. In the high-ω range, the effect of polymer type was not pronounced. The low-ω (long time) range reflects the high temperature behavior of PMA. This suggests that EVA1 of low VA content would show higher modulus at high temperature, which is preferred for hot climates. These results are in agreement with the previous findings from Figure 3. The high VA content polymer (EVA2) displayed the lowest modulus among the four polymers. Hence, EVA1 of low VA content is expected to have the best high temperature resistance to permanent deformations (rutting).

At low-ω, the slopes of base asphalt, LDPE1 and EVA1 PMAs were found to be 1.2, 0.92 and 0.73, respectively. Since these slopes were obtained in the low-ω range (corresponds to high temperature according to TTS), the elastic properties of EVA1 are

expected to be less temperature sensitive compared to other polymers. Accordingly, EVA1 PMA is expected to show better performance in rutting resistance. Hence, the information extracted from the slopes of G′ vs. ω is consistent with the above findings obtained from the comparison of G′ data. To improve the rutting resistance of PMA, higher values of G′ are needed. In the high-ω region (corresponds to low temperature according to TTS), PMAs with high loss modulus (G″) are preferred to prevent crack initiation. However, the low temperature behavior of all of the above polymers approaches similar values at high ω. Therefore, the high temperature performance is the main factor in the selection of the polymer type. This is likely to be applied in hot climates only where temperature sensitivity is important.

According to SHRP method, the asphalt can be used up to that temperature when $|G^*|/\sin\delta$ value is at least 1 kPa. These values are 70°C, 80°C, 80°C, 82°C and 77°C for asphalt, 4% LDPE1, 4% LDPE2, 4% EVA1 and 4% EVA2 PMA, respectively. Polymer modification has improved the service temperature according to SHRP specification. Among all polymers, EVA1 gave the highest service temperature (82°C) at $|G^*|/\sin\delta=1$ kPa. Moreover, the 4% polymer concentration of all polymers satisfies the high service temperature requirement for the Gulf region (76°C). So, further analysis was performed on the PMA with only 4% polymer concentration.

Storage Stability Test

Structurally, asphalt is very complex (Stastna et. al., 2003; Gao et. al., 2002; Rassamdana et al 1996). It is composed of different phases. Addition of polymer enhances this complexity. Always there is a possibility of phase separation during storage at elevated temperature. 4% of all polymers were used and measured $|G^*|$ increased

after 72 hrs of continuous mixing at 160^{o}C. The high temperature and long mixing time would result in considerable oxidation that would eventually lead to the observed increase in $|G^*|$. The bottom sample showed higher values of $|G^*|$ than that of the top. The percent differences between top and bottom value of $|G^*|$ are 9, 3, 5 and 18 for LDPE1, LDPE2, EVA1 and EVA2 PMAs, respectively. EVA2 showed the highest degree of phase separation, while LDPE2 was the least for LDPE2. Also, EVA1 showed better storage stability than LDPE1, which is in line with the previous observations on the phase separation of the 8% LDPE. EVA1 (low VA content) showed better storage stability than EVA2 (high VA content). EVA2 is more rigid as it contains more VA than EVA1 and it is not compatible with asphalt. Isacsson and Lu (1999) concluded that high vinyl acetate (VA) content leads to poor storage stability. However, the ethyl vinyl acetate (EVA) polymers used in that study were of different molecular weights. So, it is difficult to conclude whether that observation was due to the influence of molecular weight (Mw) or VA content. Also, the fact that EVA2 showed more phase separation supports our tentative explanation that the rigid EVA2 has less entanglement with asphalt and is just reinforcing the asphalt matrix phase. This finding is in agreement with previous literature reports (Lu et al., 1999). So, EVA with low VA content has the best storage stability compared to other polymers covered in this study.

Rolling Thin Film Oven (RTFO) Test

Figures 9 and Figure 10 show $\eta^*(T)$ value of base asphalt and the 4% PMAs before and after treatment in the RTFO. Ageing has increased the complex viscosity without much influence on the flow activation energy (almost similar slope). The values of viscoelastic properties of aged specimens were generally higher than those of unaged

samples. It is quite similar to the physics of ageing processes that involve x-linking. Temperature ageing favors the volatilization of low molecular weight constituents of asphalt. But high molecular weight constituents remain in the asphalt. Both oxidation and volatilization of asphalt lead to the observed increase in η*. A look at Figures 9 and 10 suggests that both the Mw of LDPE and the VA content of EVA did not show a strong influence on the results of the RTFO test over this short ageing period (85 minutes).

Performance Grading

According to SHRP, the highest PG in the Kingdom is 76-10. PG for asphalt, 4% LDPE1, 4% LDPE2, 4% EVA1 and 4% EVA2 are 64-22, 76-16, 76-10, 82-10 and 76-16, respectively. EVA1 modified asphalt showed the highest service temperature. Other PMA systems have satisfied the required upper limit service temperature of 76^{o}C. Moreover, all PMAs with 4% polymer concentration satisfied the lower limit of -10^{o}C.

Conclusion

The influence of Mw of LDPE and the vinyl acetate content of EVA on modification of asphalt were investigated. Optimum blending time for EVA modified asphalt was found to be lower than that of LDPE modified asphalt due to the difference in Mw. For EVA polymers with similar Mw, higher MWD (or PDI) resulted in shorter blending times in the high shear blender. So, both Mw and MWD as well as polymer structure (LDPE1 vs EVA1) have influenced the OBT.

Polymer modification has significantly enhanced the rheological properties of asphalt. Viscous and elastic properties of modified asphalt increased with the increase of polymer content. Both EVA polymers decrease the flow activation energy. The reduction

of the flow activation energy reduces the degree of temperature sensitivity; hence, reduce the change of viscosity due to temperature change. The VA content of EVA had little or no influence on flow activation energy. The activation energy for LDPE PMAs increased with the increase of polymer concentration, while that of EVA PMAs decreased. This suggests that LDPE PMAs are more temperature sensitive than EVA polymers. Storage stability was found to be acceptable for LDPE and low VA content EVA modified asphalt. However, EVA with high VA content showed the highest degree of phase separation. Also, LDPE of low Mw displayed higher extent of immiscibility with the asphalt used in this study. Comparison of EVA1 (low VA content) and LDPE1 (low Mw) PMAs shows that the storage stability of EVA1 modified asphalts is better.

Both asphalt and PMAs were found to harden due to ageing with no strong influence for Mw or VA content. Both the Mw of LDPE and the VA content of EVA did not show a strong influence on the results of the RTFO test performed over the short ageing period (85 minutes) according to ASTM D 2872 test procedure. The performance grading of the 4% PMAs was carried out and all polymers satisfied the required PG. EVA with low VA content extended the upper service temperature of asphalt by 6^{o}C above the required temperature. On the other hand,

Overall, EVA1 of low VA content has the best high temperature resistance to permanent deformations (rutting) and the highest service temperature as well as the best storage stability (compatibility with asphalt). Both EVA1 and EVA2 polymers showed similar behavior with regard to the influence of polymer content on E_a. Whereas, LDPE of higher Mw showed better compatibility with asphalt and higher elasticity. Otherwise, the Mw of LDPE showed little or no influence on temperature sensitivity (flow activation

energy) or the upper service temperature. Finally, the Mw of LDPE and VA content of EVA have influenced the rheology, the storage stability and the ageing of PMAs differently. Overall, EVA with low VA content was the best asphalt modifier among the polymers covered in this investigation.

Acknowledgement

The authors would like to thank KFUPM for its support for this research. The authors are thankful to Mr. Willy Leyson of ExxonMobil, Belgium for providing the polymer samples and Prof. H. Persanowaski and Mr. Arab from the Chemistry Department for their help with the NMR analysis. We also thank to Dr. Naseem Akhtar of Research Institute, KFUPM for the GPC characterization of the polymers.

References

Adedeji A, Grunfelder T, Bates FS, Macosko C W, Gardiner S M, Newcomb DE (1996) Asphalt Modified by SBS Triblock Copolymer: Structures and Properties. Poly Eng Sci 36(12): 1707-1723.

Ait-Kadi A, Brahimi B, Bousmina M (1996) Polymer Blends for Enhanced Asphalt Binders Polym Eng Sci, 36(12): 1724-1733.

Al-Dubabe IA, Al-Abdul Wahhab HI, Asi IM, Ali MF (1998) Polymer Modification of Arab Asphalt. ASCE Material J 10(3): 161-167.

Ali M, Al-Abdul Wahhab HI, Asi I, Al-Dubabe I (1999) Characterization of Polymer Modified Gulf Asphalts. Petroleum Science and Technology 17(1, 2): 125-146.

Bahia HU, Hanson DI, Zeng M, Zhai H, Khatri MA, Anderson RM (2001) Characterization of Modified Asphalt Binders in Superpave Mix Design. NCHP Report 459, National Academy Press, Washington D.C.

Bahia HU, Davies R (1994) Effect of Crumb Rubber Modifiers on Performance Related Properties of Asphalt Binders. Proc. AAPT 63: 414-450.

Blanko R, Rodriguez R, Garcia-Garduno M, Castano VM (1996) Rheological Properties of Styrene-Butadiene Copolymer-reinforced Asphalt. J Appl Polym Sci 61: 1496-1501.

Bonemazzi F, Braga V, Corrieri R, Giavarini C, Sartori F (1996) Characteristics of Polymers And Polymer-Modified Binders. *TRB*.1535: 36-47.

Bouldin MG, Collins JH, Berker A (1991) Rheology and Microstructure of Polymer/Asphalt Blends. J Rubber Chem & Tech 67(4): 577-600.

Brule B (1996) Polymer Modified Asphalt Cements Used in the Road Construction Industry: Basic Principles. *TRB*1535: 48-53.

Carreau P J, Bousmina M, Bonniot F (2000) "The viscoelastic properties of Polymer-Modified Asphalt. The Canadian J Chemical Eng 78(3): 495-502.

Challa A, Ciochina OG, Roy C, Bousmina M (1997) Rheological Properties of Bitumen Modified with Used Tyre-Derived Pyrolytic Oil Residue. Polym Recycling 3(1):1-14.

Challa A, Roy C, Ait-kadi A (1996) Rheological Properties of Bitumen Modified with Pyrolytic Carbon Black. Fuel 75(13): 1575-1583.

Chebil S, Challa A, Roy C (1996) Modification of Bitumen with Scrape Tyre Pyrolytic Carbon Black. Comparison with Commercial Carbon Black Part I: Mechanical and Rheological Properties. Polym Recycling 2(4): 257-269.

Collins JH, Bouldin MG (1991) Stability of Straight and Polymer Modified Asphalts, *TRB*. 1342: 92-100.

El-Mubarak AH, Sheikheldin SY, Fayad NM, Khaja N (1999) Development of a Simple Monitoring Technique for Oil pollution in Sediment. J Environ Sci Health A34(2):391-404.

Fawcett AH, McNally TM (2000a) A Dynamic Mechanical and Thermal Study of Various Rubber-Bitumen Blends. J Appl Polym Sci 76:586-601.

Fawcett AH, McNally T (2000b) Blends of bitumen with various polyolefins. Polymer 41: 5315-5326.

Gao Gt, Zhang Y, Zhang YX, Sun K, Fan YZ (2002) Improved Storage Stability of LDPE/SBS Blends Modified Asphalt. Polym & Polym Comp, 10(3): 229-236.

García-Morales M, Partal P, Navarro F J, Martinez-Boza F, Mackley M R, Gallegos C (2004) The rheology of recycled EVA/LDPE modified bitumen. Rheol Acta in press.

Goodrich J L (1988) Asphalt and Polymer Modified Asphalt Properties Related to the Performance of Asphalt Concrete Mixes. Asphalt Paving Technology, 57: 116-175.

Hameed T, Hussein IA (2002) Rheological Study of the influence of Mw and Comonomer Type on the miscibility of m-LLDPE and LDPE. Polymer, 43: 6911-6929

Hussein IA, Ho K, Goyal SK, Karbashewski E, Williams MC (2000) Thermomechanical Degradation in the Preparation of Polyethylene Blends. Polymer Degradation & Stability 68(3):381-392.

Iqbal MH (2004) Influence of Polymer Type and Structure on the Modification of Saudi Asphalt. MS Thesis (KFUPM).

Isacsson U, Lu X (1999) Laboratory Investigation of Polymer Modified Bitumens. J Association of Asphalt Paving Technol (AAPT) 68: 35-63.

Isacsson U, Zeng H (1998) Cracking of Asphalt at Low Temperature as Related to Bitumen Rheology. J Materials and Structures 33(8):2165-2170.

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

Johansson L S, Isacsson U (1998) Effect of filler on Low Temperature Physical Hardening of Bitumen. Construction and Building Materials 12: 463-470.

Lu X, Isacsson U (2001) Effect of Binder Rheology on the Low-Temperature Cracking of Asphalt Mixtures. Road Materials and Pavement Design 2(1): 29-47.

Lu X, Isacsson U, Ekblad J (1999) Phase Separation of SBS Polymer Modified Bitumens. J Mat Civil Eng 11: 51-57.

Lu X, Isacsson U, Ekblad J (1998) Low Temperature Properties of Styrene-Butadiene-Styrene Polymer Modified Bitumens. Construction and Building Materials, 12: 405-414.

Lu X, Isacsson U (1997) Influence of Styrene-Butadiene-Styrene Polymer Modification on Bitumen Viscosity. Fuel 76(14/15): 1079-1180.

Muncy H W, King G N, Prudhomme B (1987) Improved Rheological Properties of Polymer-Modified Asphalts. ASTM Special Technical Publication, 941 (Asphalt Rheology): 147-165.

Nair N R, Mathew NM, Thomas S, Chatterjee P, Siddiqui MA (1998) Physical and Rheological Characteristics of Liquid Natural Rubber Modified Bitumen. J Appl Polym Sci 68: 53-61.

Polacco G, Vacin O J, Biondi D, Stastna J, Zanzotto L (2003) Dynamic Master Curve of Polymer Modified Asphalt from Three Different Geometries. Appl Rheol 13(3): 118-124.

Rassamdana H, Dabir B, Nematy M, Farhani M, Sahimi M (1996) Asphalt Flocculation and Deposition: I. The Onset of Precipitaiton. AIChE J 42(1): 10-22.

Rozeveld SJ, Shin EE, Bhurke A, France L, Drzal LT (1997) Network Morphology of Polymer Modified Asphalt Cements. Microscopy Research and Technique 38: 529-543.

Sabbagh A B, Lesser A J (1998) Effect of Particle Morphology on the Emulsion Stability and Mechanical Performance of Polyolefin Modified Asphalts. Poly Eng Sci 38(5): 707-715.

Singh B, Tarannum H, Gupta M (2003) Use of Isocyanate Production Waste in the Preparation of Improved Waterproofing Bitumen. J Appl Polym Sci 90: 1365-1377.

Singh B, Gupta M, Tarannum H (2003) Mastic of Polymer-Modified Bitumen and Poly(vinyl chloride) Wastes. J Appl Polym Sci 90: 1347-1356.

Stastna J, Zanzotto L, Vacin O J (2003) Viscosity Function in Polymer Modified Asphalt. J Colloid and Interface Sci 259(1): 200-207.

Varma R, Takeichi H, Hall JE, Ozawa YF, Kyu T (2002) Miscibility Studies on Blends of Kraton Block Copolymer and Asphalt. Polymer 43: 1-5.

Wen G, Zhang Y, Zhang YX (2002) Improved Properties of SBS-Modified Asphalt with Dynamic Vulcanization. Poly Eng Sci 42(5): 1070-1081.

Yousefi AA (2003) Polyethylene Dispersions in Bitumen: The effect of the Polymer Structural Parameters. J Appl Polym Sci 90: 3183-3190.

Zanzotto L, Stastna J, Ho K, (1996) Characterization of Regular and Modified Bitumens via Their Complex Modulus. . J Appl Polym Sci , 59: 1897-1905.

Zupancic A, Zumer M (2002) Rheological Examination of Temperature Dependence of Conventional and Polymer-Modified Road Bitumens. The Canadian J Chemical Eng 82(2): 253-263.

Table 1: Characterization of polymers

Polymer	**Density (g/cm^3)**	**MFI (g/10min)**	**Melting Point, ^oC**	**M_n (kg/mol)**	**M_w (kg/mol)**	**M_Z (kg/mol)**	**M_w/M_n**
LDPE1	0.914	155	100	7.376	71.920	425.852	9.7
LDPE2	0.914	70	100	8.304	102.929	448.224	12.4
EVA1	0.948	150	81	7.566	35.629	110.434	4.7
EVA2	0.95	150	68	5.757	30.486	97.120	5.3

Table 2: Comparison of Arrhenius parameters for modified asphalt

Material type	**Polymer wt%**	**A (Pa-s)**	**E_a (kJ/mol)**	**η* (Pa-s), @ 50°C**	**η*(Pa-s), @ 60°C**	**% Difference**
asphalt	0	5.00E-16	114	1.34E+03	3.75E+02	72.01
LDPE1	4%	3.00E-16	118.47	4.24E+03	1.13E+03	73.35
	6%	7.00E-17	124.86	1.07E+04	2.65E+03	75.23
	8%	6.00E-17	127.27	2.24E+04	5.41E+03	75.48
LDPE2	4%	3.00E-16	118.94	5.05E+03	1.34E+03	73.46
	6%	1.00E-16	122.96	7.52E+03	1.90E+03	74.73
	8%	1.00E-16	124.93	1.57E+04	3.88E+03	75.28
EVA1	4%	9.00E-14	101.97	2.74E+03	8.76E+02	68.03
	6%	3.00E-13	99.89	4.21E+03	1.38E+03	67.22
	8%	8.00E-12	91.78	5.48E+03	1.99E+03	63.68
EVA2	4%	1.00E-13	100.2	1.57E+03	5.14E+02	67.26
	6%	6.00E-12	90.04	2.15E+03	7.87E+02	63.40
	8%	4.00E-12	91.18	2.58E+03	9.93E+02	61.62

List of Figures

Figure 1: Batch reproducibility test, $\eta'(\omega)$ and $G'(\omega)$ for 4% LDPE1 and asphalt blend. ($T=76^oC$, $\gamma^o= 20\%$).

Figure 2: Blending time determination.

Figure 3: $\eta'(\omega)$ of the asphalt and polymer modified asphalts at 76^oC ($\gamma^o = 20\%$).

Figure 4: G* as a function of δ. ($T = 76^oC$).

Figure 5: Effect of polymer concentration on $\eta'(\omega)$ and $G'(\omega)$ at 76^oC ($\gamma^o = 20\%$).

Figure 6: Effect of polymer concentration on $\eta^*(T)$ ($\omega = 10$ rad/s, $\gamma^o = 20\%$)

Figure 7: $G'(\omega)$ master curve for all polymer modified asphalt at $T_{ref}=70^oC$.

Figure 8: a_T vs. T ($T_{ref} = 70^oC$).

Figure 9: Effect of LDPE on the asphalt binder ageing ($\omega = 10$ rad/s, $\gamma^o = 20\%$).

Figure 10: Effect of EVA on asphalt binder ageing ($\omega = 10$ rad/s, $\gamma^o = 20\%$).

Fig 1

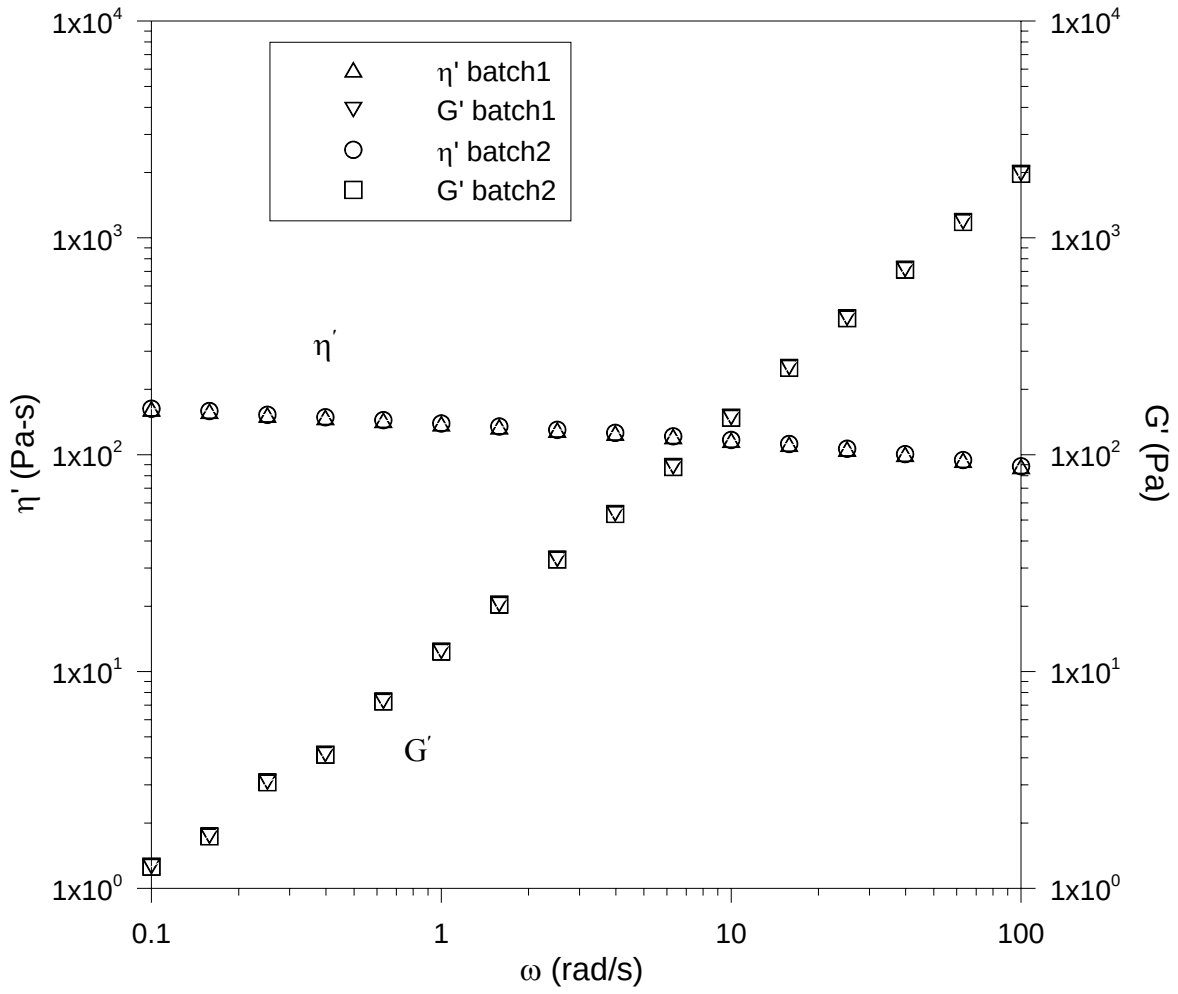
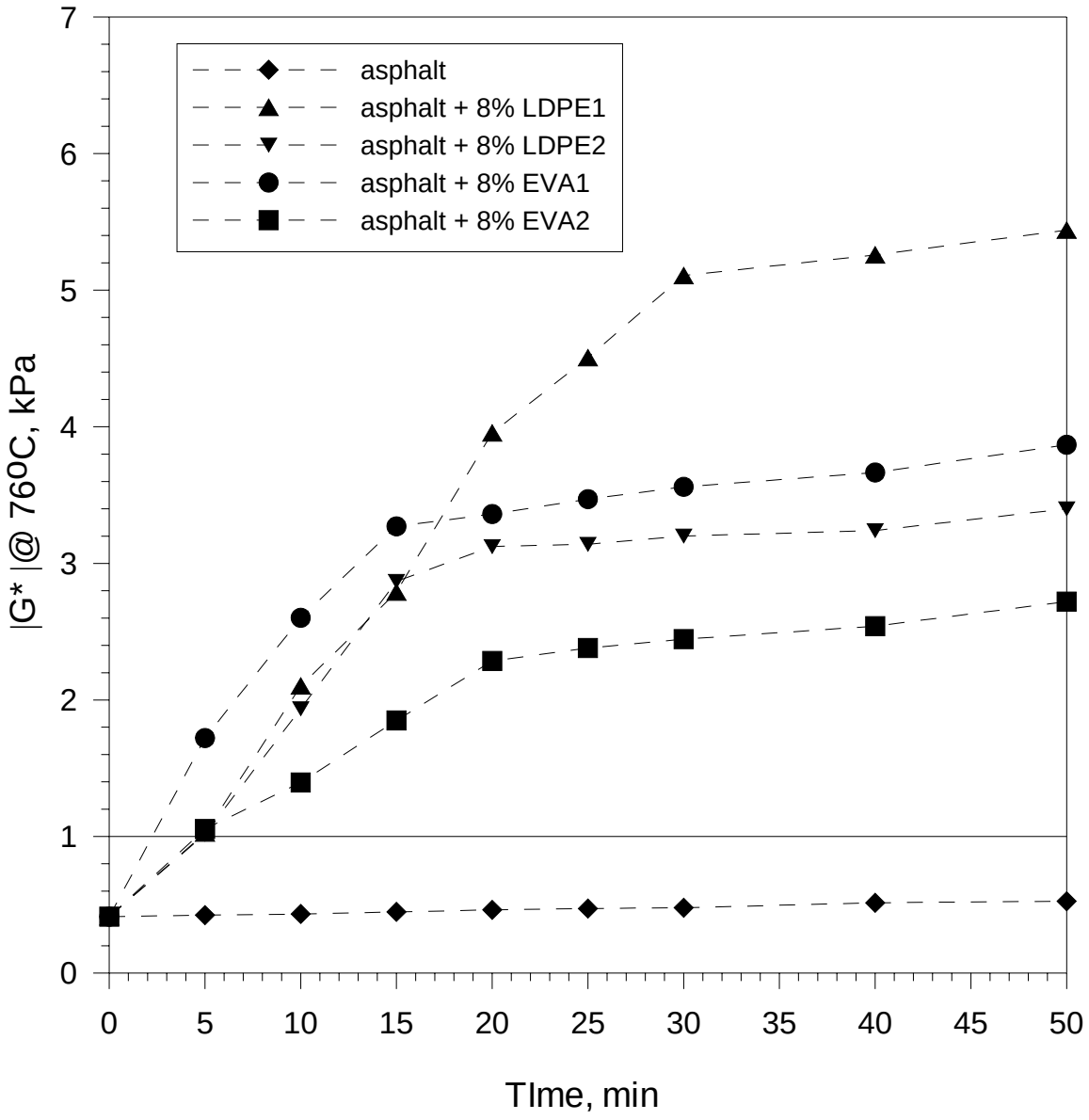

η' batch1
G' batch1
η' batch2
G' batch2
η′
G′
η' (Pa-s)
G' (Pa)
ω (rad/s)
1x10^4
1x10^3
1x10^2
1x10^1
1x10^0
0.1
1
10
100

Fig 2


asphalt
asphalt + 8% LDPE1
asphalt + 8% LDPE2
asphalt + 8% EVA1
asphalt + 8% EVA2
|G* |@ 76oC, kPa
TIme, min
0
1
2
3
4
5
6
7
0
5
10
15
20
25
30
35
40
45
50

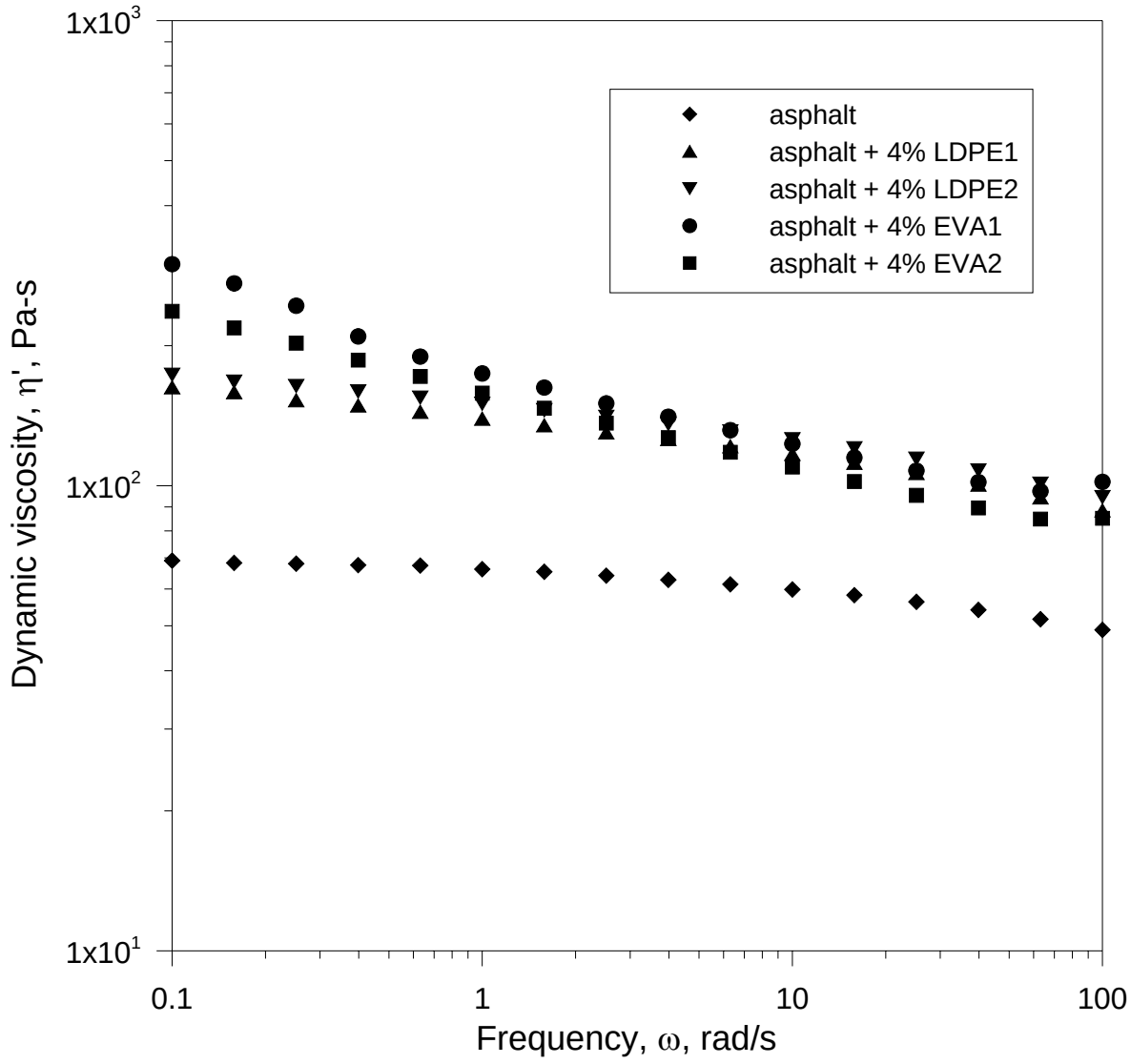

1x10^3
1x10^2
1x10^1
Dynamic viscosity, η', Pa-s
0.1
1
10
100
Frequency, ω, rad/s
asphalt
asphalt + 4% LDPE1
asphalt + 4% LDPE2
asphalt + 4% EVA1
asphalt + 4% EVA2

Fig 4

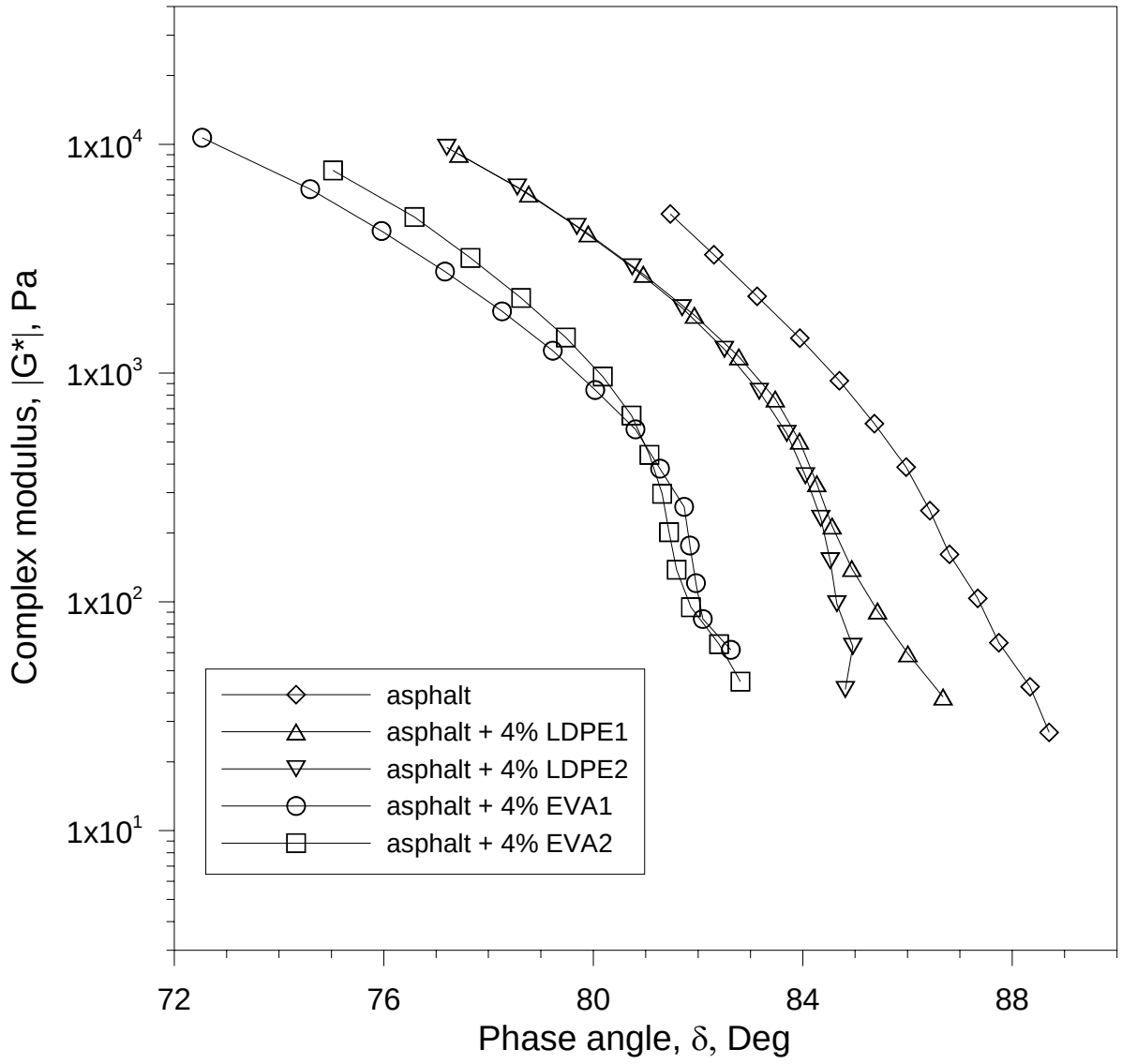

Complex modulus, |G*|, Pa
1x10^4
1x10^3
1x10^2
1x10^1
72
76
80
84
88
Phase angle, δ, Deg
asphalt
asphalt + 4% LDPE1
asphalt + 4% LDPE2
asphalt + 4% EVA1
asphalt + 4% EVA2

Fig 5

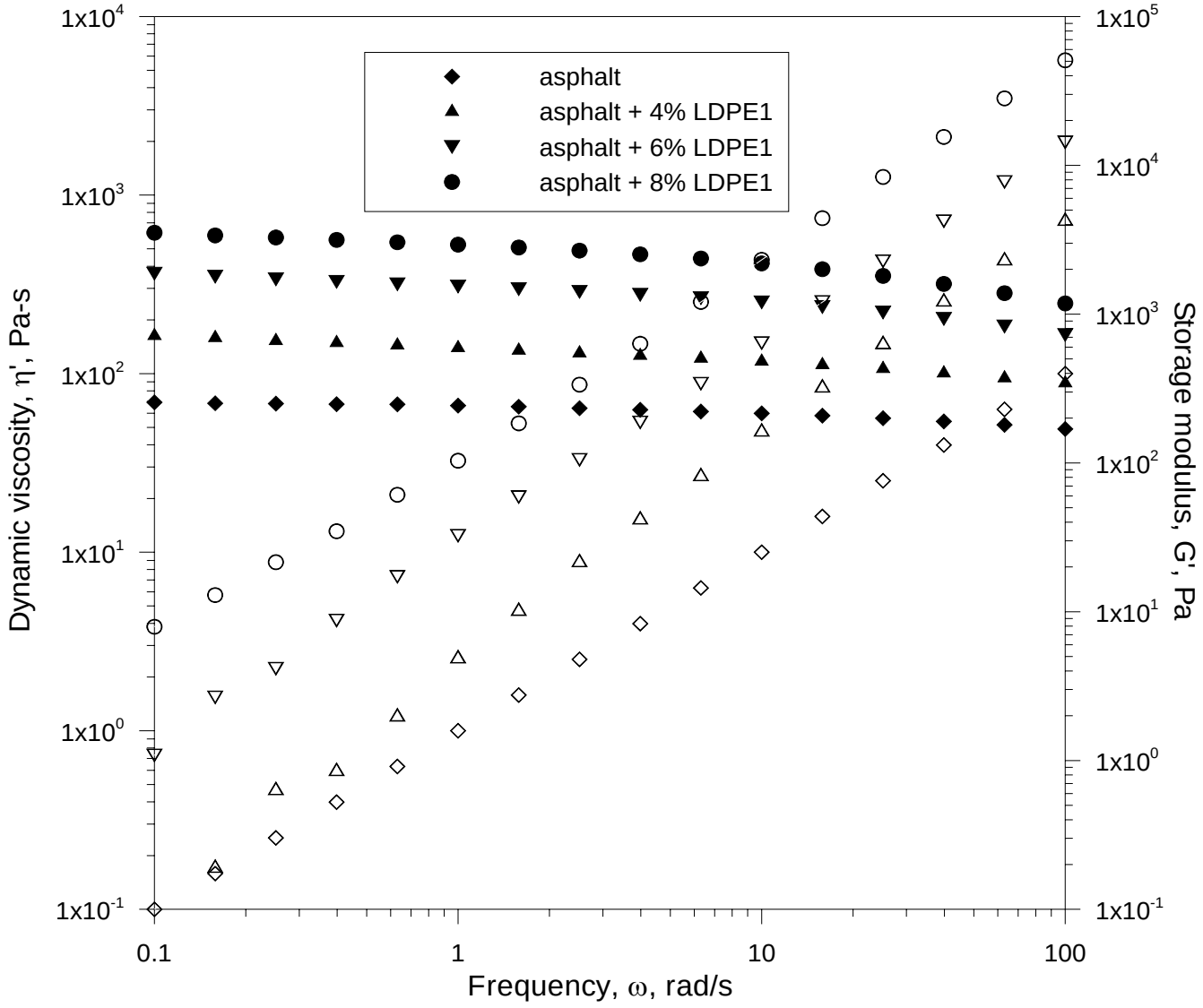

asphalt
asphalt + 4% LDPE1
asphalt + 6% LDPE1
asphalt + 8% LDPE1
Dynamic viscosity, η', Pa-s
Storage modulus, G', Pa
Frequency, ω, rad/s
1x10^4
1x10^3
1x10^2
1x10^1
1x10^0
1x10^-1
1x10^5
0.1
1
10
100

Fig 6

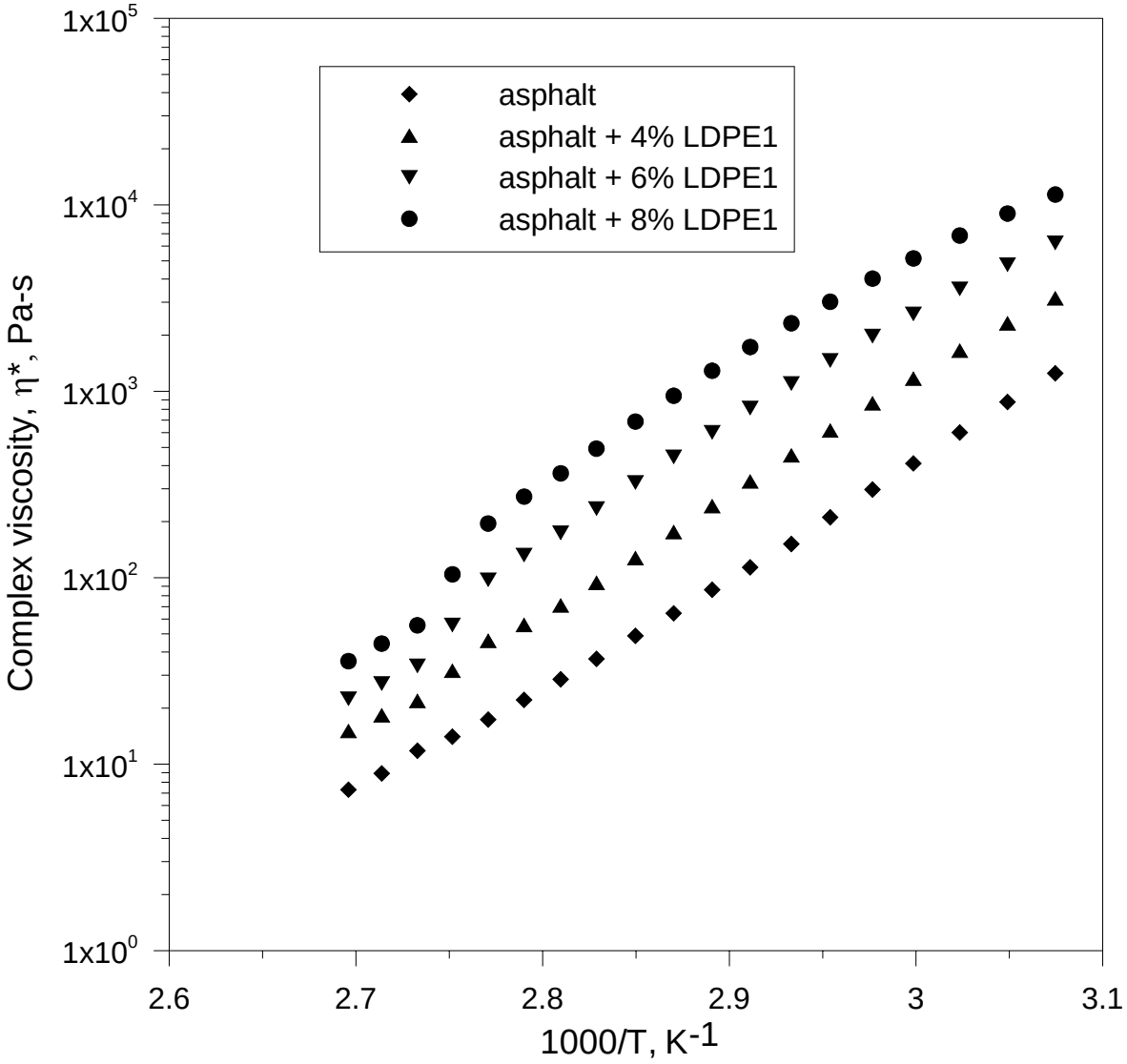

asphalt
asphalt + 4% LDPE1
asphalt + 6% LDPE1
asphalt + 8% LDPE1
Complex viscosity, η*, Pa-s
1x10^5
1x10^4
1x10^3
1x10^2
1x10^1
1x10^0
2.6
2.7
2.8
2.9
3
3.1
1000/T, K^-1

Fig 7

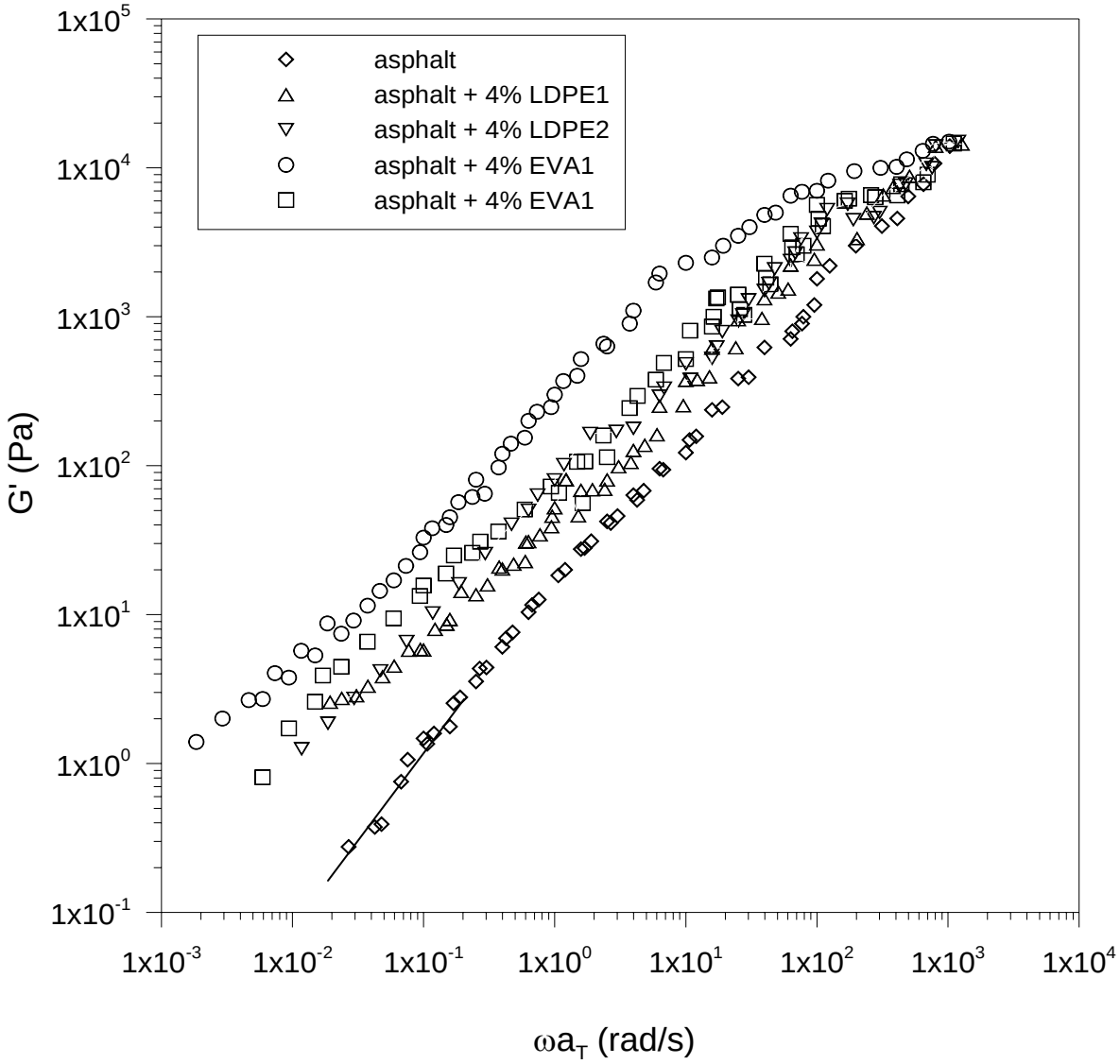

asphalt
asphalt + 4% LDPE1
asphalt + 4% LDPE2
asphalt + 4% EVA1
asphalt + 4% EVA1
G' (Pa)
1x10^5
1x10^4
1x10^3
1x10^2
1x10^1
1x10^0
1x10^-1
1x10^-3
1x10^-2
1x10^-1
1x10^0
1x10^1
1x10^2
1x10^3
1x10^4
ωa_T (rad/s)

Fig 8

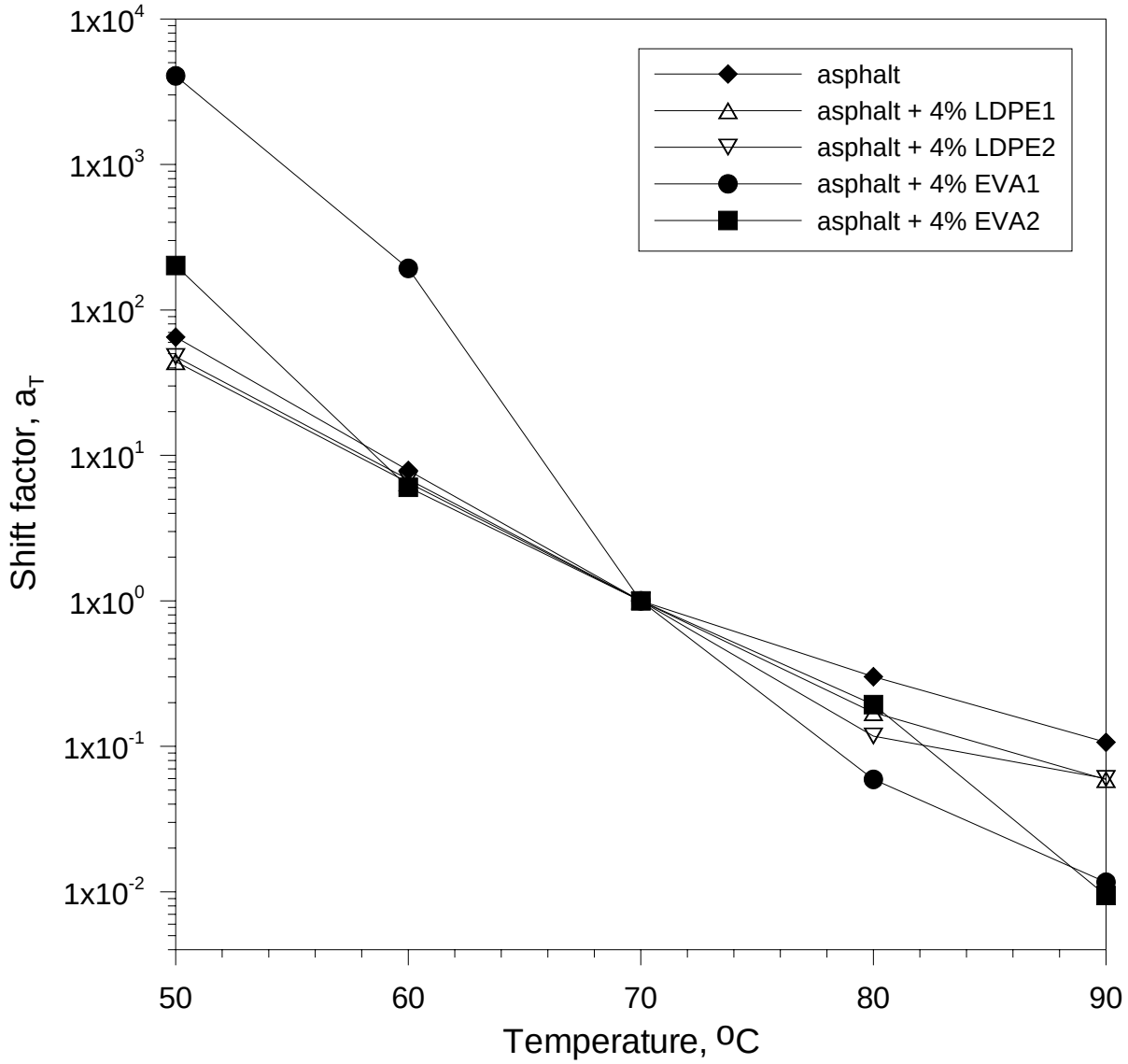

1x10^4
1x10^3
1x10^2
1x10^1
1x10^0
1x10^-1
1x10^-2
Shift factor, a_T
50
60
70
80
90
Temperature, °C
asphalt
asphalt + 4% LDPE1
asphalt + 4% LDPE2
asphalt + 4% EVA1
asphalt + 4% EVA2

Fig 9

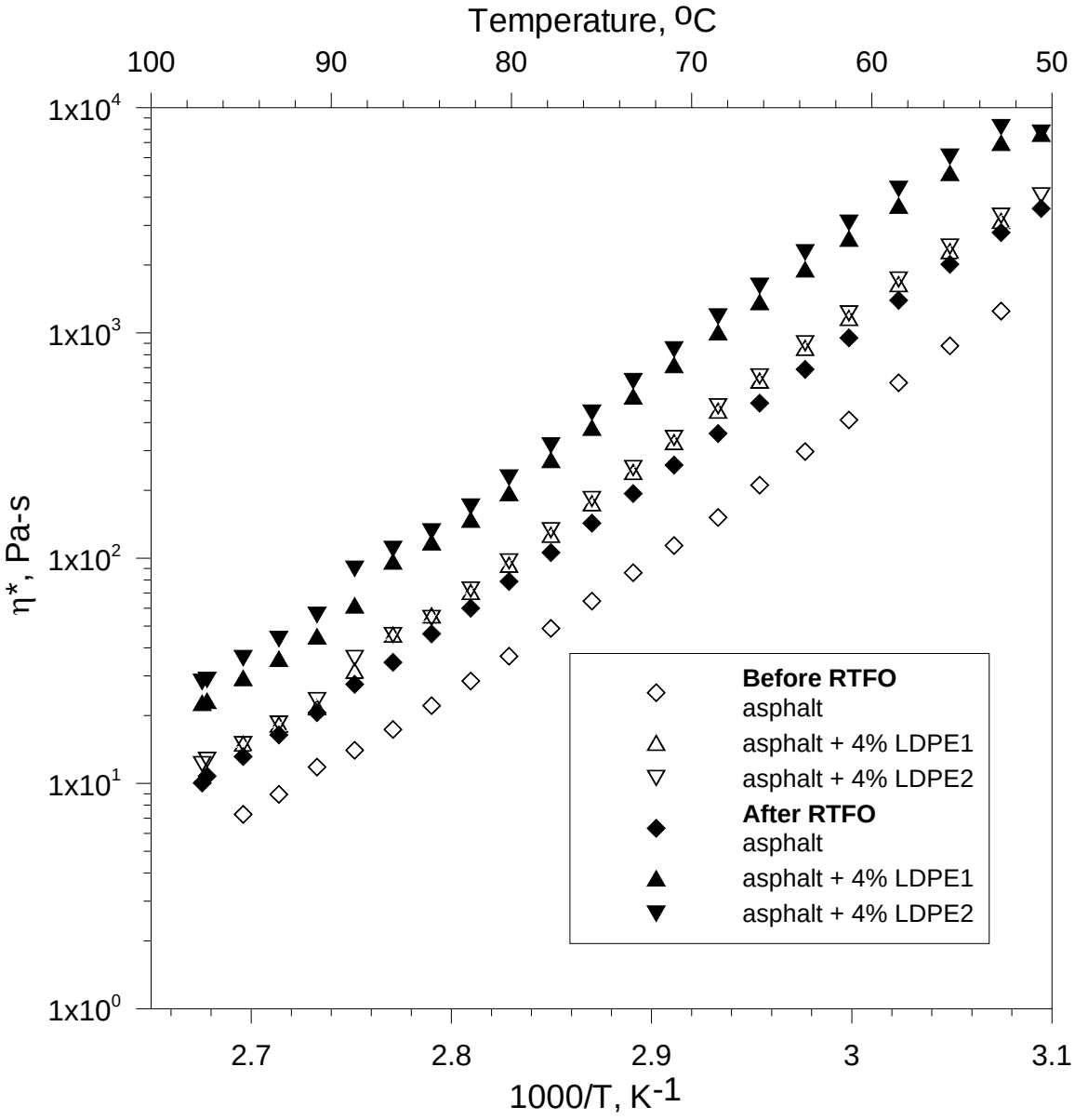
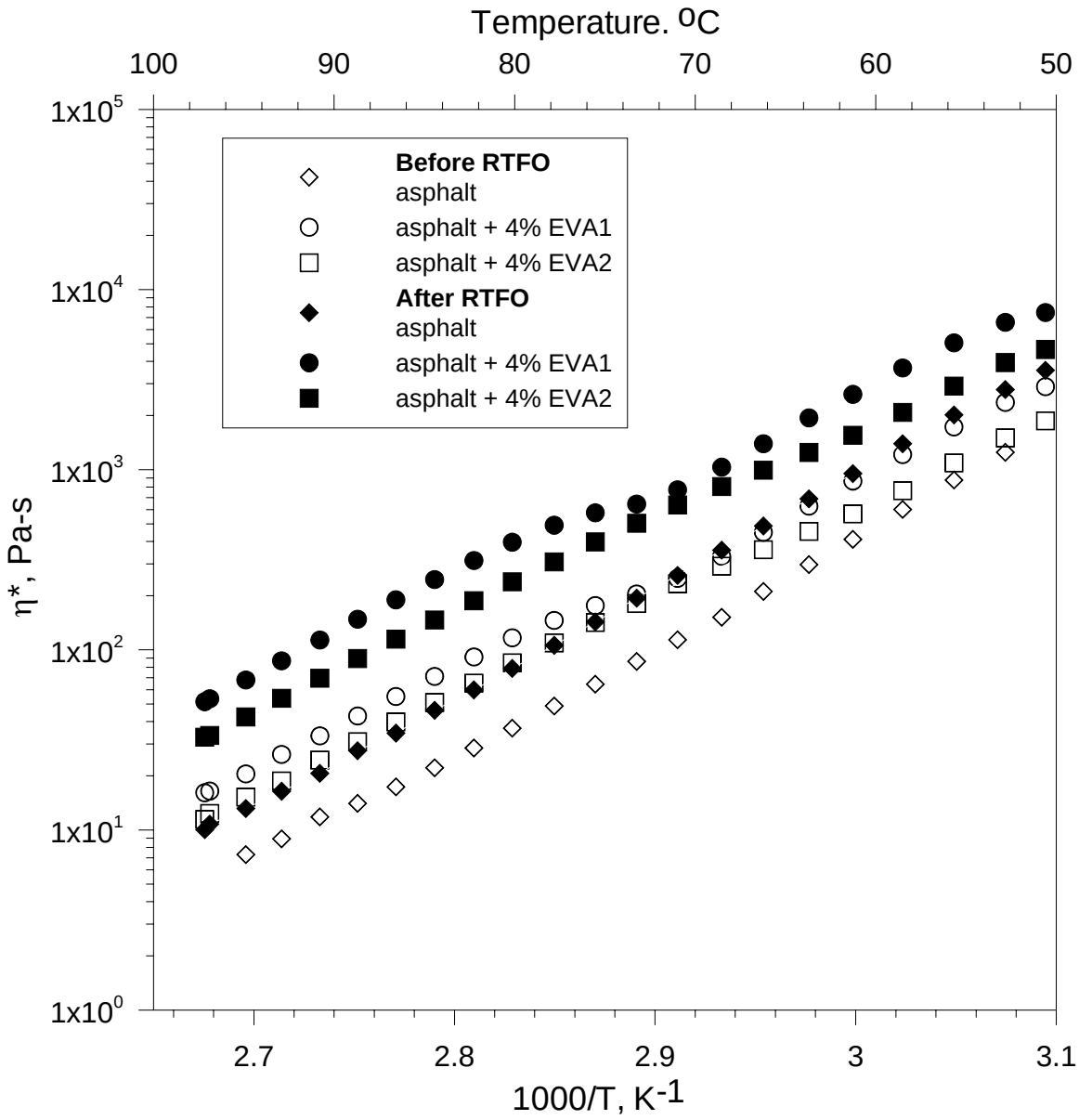

Temperature, °C
100
90
80
70
60
50
1x10^4
1x10^3
1x10^2
1x10^1
1x10^0
η*, Pa-s
2.7
2.8
2.9
3
3.1
1000/T, K^-1
Before RTFO
asphalt
asphalt + 4% LDPE1
asphalt + 4% LDPE2
After RTFO
asphalt
asphalt + 4% LDPE1
asphalt + 4% LDPE2

Fig 10


Temperature. oC
100
90
80
70
60
50
1x10^5
1x10^4
1x10^3
1x10^2
1x10^1
1x10^0
η*, Pa-s
Before RTFO
asphalt
asphalt + 4% EVA1
asphalt + 4% EVA2
After RTFO
asphalt
asphalt + 4% EVA1
asphalt + 4% EVA2
2.7
2.8
2.9
3
3.1
1000/T, K-1