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Influence of M_w of LDPE and vinyl acetate content of EVA on the rheology of polymer modified asphalt

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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 °C. The optimum blending time (OBT) for each polymer was determined following a separate investigation. OBT was influenced by M_w , MWD, and polymer structure. The influence of M_w 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 modifica-

tion increased flow activation energy (E_a) but EVA modification decreased E_a . Both VA content and M_w 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 M_w 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.

Keywords Polymer-modified asphalt · Rheology · LDPE · EVA · Storage stability

Introduction

Asphalt is used as a 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 addition 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 additives or a chemical modification for high-temperature as well as low-temperature applications (Isacsson

and Zeng 1998; Lu and Isacson 2001; Lu et al. 1998; Fawcett et al. 2000a, b, Johansson and Isacson 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 a few are suitable for asphalt modification (Lu and Isacson 2001). These polymers should resist the degradation at asphalt mixing temperatures (about 160 °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 (García-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 and 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 M_w 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 M_w (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 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

Two LDPEs and two 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 °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 °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 CH₃/1,000C 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

Table 1 Characterization of polymers

Polymer	Density (g/cm ³)	MFI (g/10 min)	Melting point (°C)	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

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 (PG) 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 min 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

Eight hundred grams of asphalt were heated at 160 °C for 50 min. Oil bath was used to control the temperature. Preweighed 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 3,000 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 in diameter and 2 mm in thickness and tested within 24 h.

Polymer specimen preparation

Before rheological testing, as received polymers were given a controlled thermomechanical history (molding) in a Carver press, Twenty five millimeter in 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 Fig. 1. The agreement of both viscous and elastic properties shows the excellent reproducibility of these measurements. The frequency sweep was carried out at 76 °C in the range 100–0.1 rad/s. Temperature sweep test was done over the temperature range 50 °C–100 °C at 5 °C/min ramp rate (to avoid long exposure time at high temperature) and a frequency $\omega = 10$ 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 °C–90 °C at a step of 10 °C. In all temperature sweep tests, 2.5 microns/°C were used as tool thermal expansion coefficient following a separate calibration experiment.

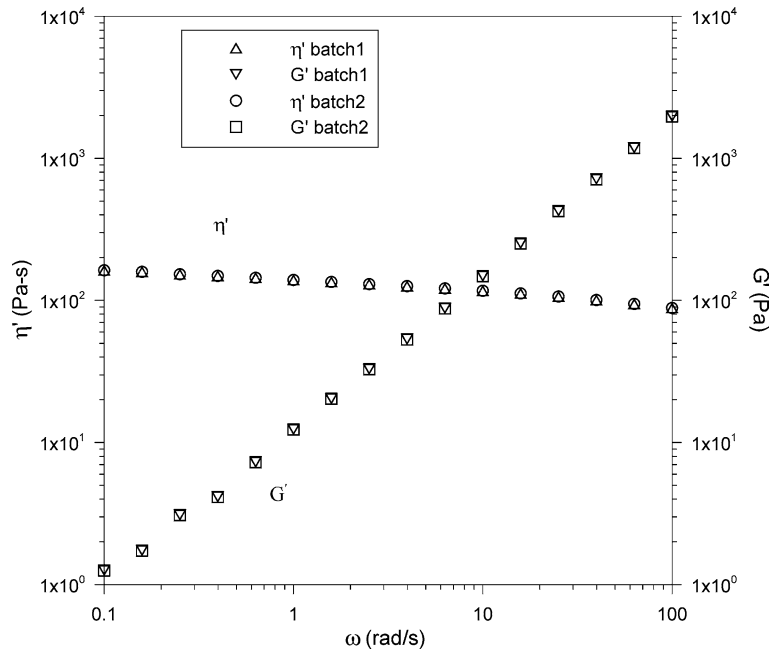
Storage stability test

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 °C for continuous agitation at 500 rpm. After 72 h, 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 °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

Rolling thin film oven test (RTFO) was used to perform ageing of asphalt binders according to ASTM D 2872 procedure. This test simulates the ageing process that

Fig. 1 Batch reproducibility test, $\eta'(\omega)$ and $G'(\omega)$ for 4% LDPE1 and asphalt blend. ($T=76\text{ }^\circ\text{C}$, $\gamma^\circ = 20\%$)



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 $163\text{ }^\circ\text{C}$ for 85 min. 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

Performance grading 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 $110\text{ }^\circ\text{C}$ and oxygen was supplied continuously following strategic highway research program (SHRP) B-005 test procedure. After 20 h, 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 ($12.4\text{ cm} \times 1.2\text{ cm} \times 0.6\text{ cm}$) were prepared to find the lower temperature limit of PG using a Fisher's Bending Beam Rheometer (BBR).

Results and discussion

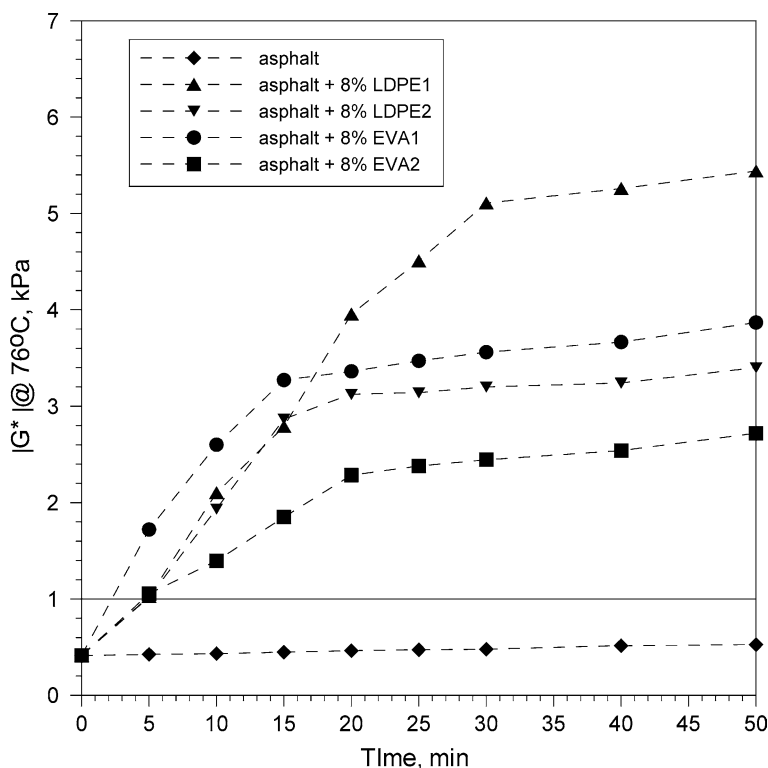
Optimum blending time

The values of $|G^*|$ are shown in Fig. 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 min, 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 M_w) reached the steady state faster than LDPE1 (high MFI, low M_w), 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-law

Fig. 2 Blending-time determination



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 M_w polymer) in comparison with LDPE1 (the low M_w 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 Fig. 3, which reports the dynamic viscosity (η') at 76 °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_0 , 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 Fig. 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 are found to decrease more in comparison to LDPE–PMAs. The effect of polymer concentration on $\eta'(\omega)$ (filled symbol) and $G'(\omega)$ (open symbol) of LDPE1 is shown in Fig. 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 $\eta'(T)$ was studied by performing temperature sweeps on LDPE1 PMA at three different polymer concentrations. The results are shown in Fig. 6. At high temperatures (~ 90 °C), the 8% LDPE1 PMA showed a sudden

Fig. 3 $\eta'(\omega)$ of the asphalt and polymer-modified asphalts at 76 °C ($\gamma^\circ = 20\%$)

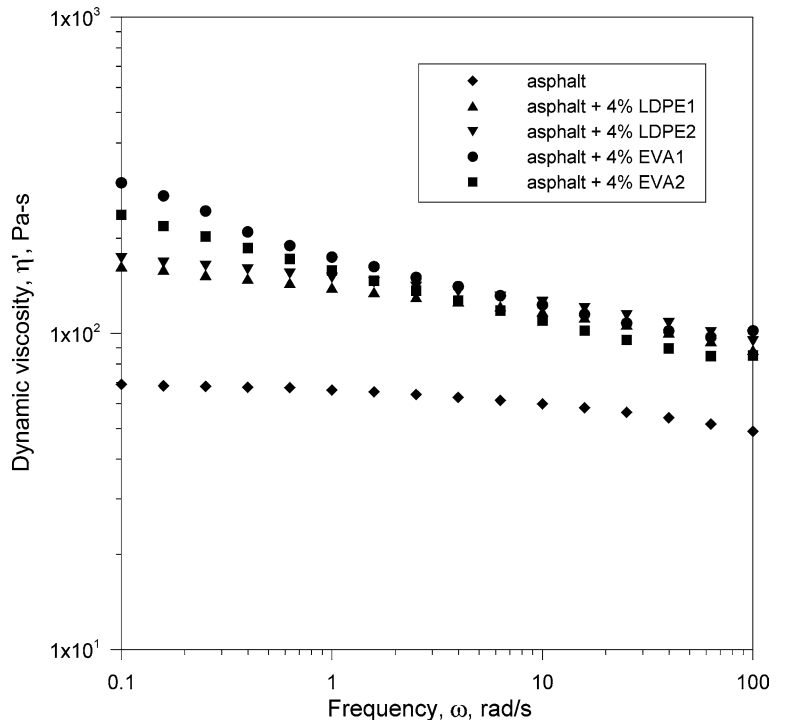
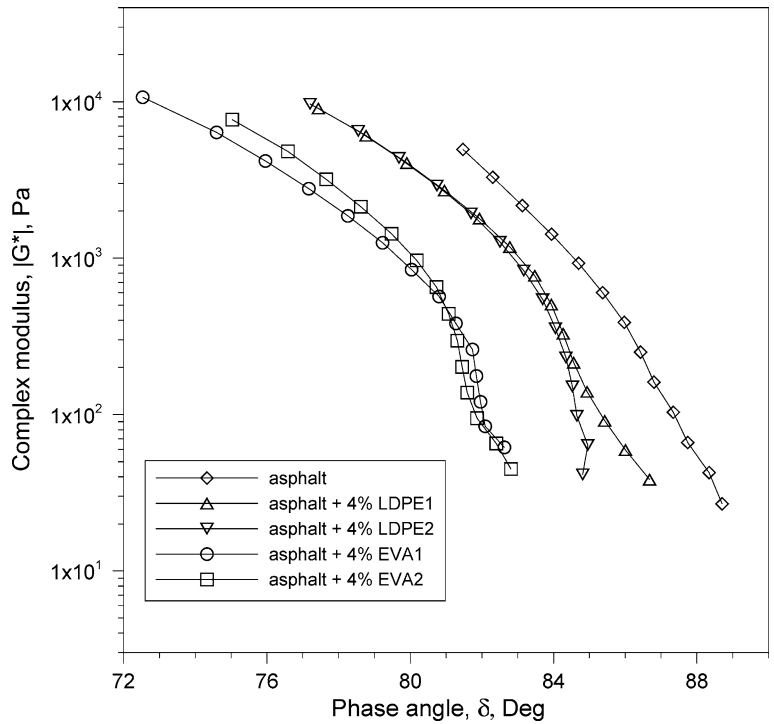


Fig. 4 G^* as a function of δ . ($T=76$ °C)



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% poly-

mer 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

Fig. 5 Effect of polymer concentration on $\eta'(\omega)$ and $G'(\omega)$ at 76 °C ($\gamma^\circ = 20\%$)

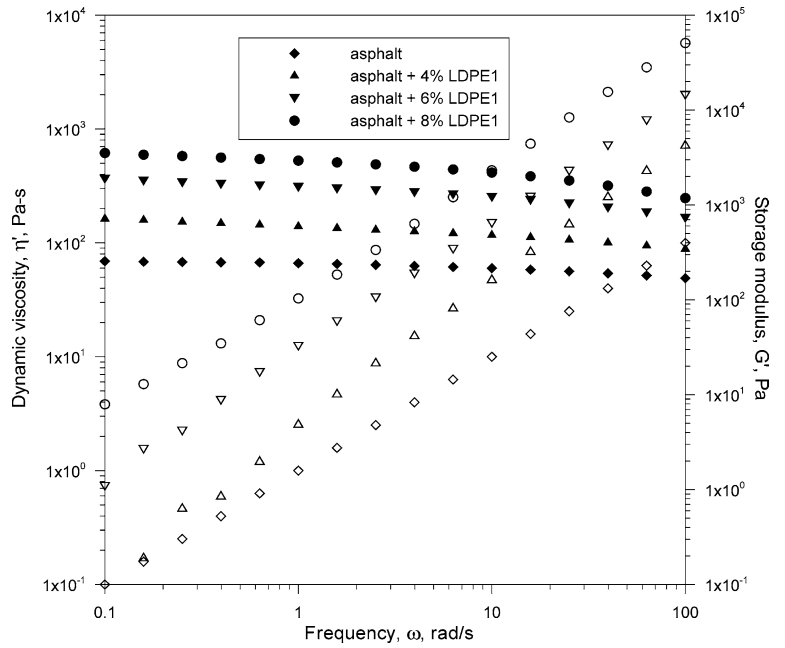
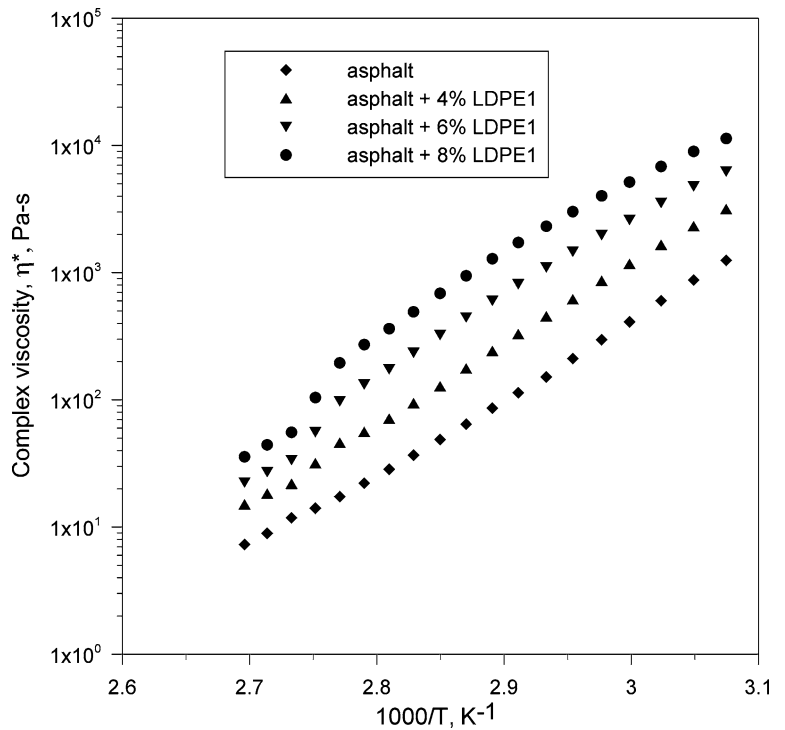


Fig. 6 Effect of polymer concentration on $\eta^*(T)$ ($\omega = 10$ rad/s, $\gamma^\circ = 20\%$)



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 semi-solid 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 Arrhenius equation.

$$\eta^* = Ae^{E_a/RT} \quad (1)$$

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 OBT 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 the viscosity of PMA due to the increase in temperature from 50 °C to 60 °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 °C to 60 °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. 2003a, b; Zupancic and Zumer 2002; Carreau et al. 2000). TTS is used to explain this behavior. For TTS, Williams-Landel-Ferry (WLF) equation is used.

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

where, C_1 and C_2 are constants and $T_{R \geq T_g + 100}$ °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 °C. The temperature dependence of the shift factor, a_T , is given in Fig. 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 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'

Table 2 Comparison of arrhenius parameters for modified asphalt

Material type	Polymer (wt%)	A (Pa s)	E_a (kJ/mol)	η^* (Pa s), at 50 °C	η^* (Pa s), at 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

Fig. 7 $G'(\omega)$ master curve for all polymer modified asphalt at $T_{ref} = 70^\circ\text{C}$

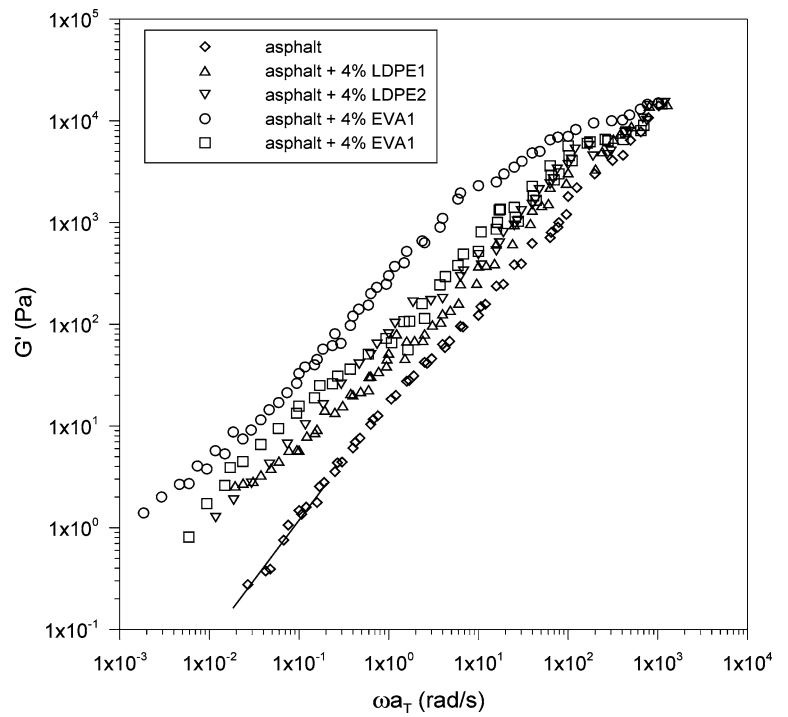
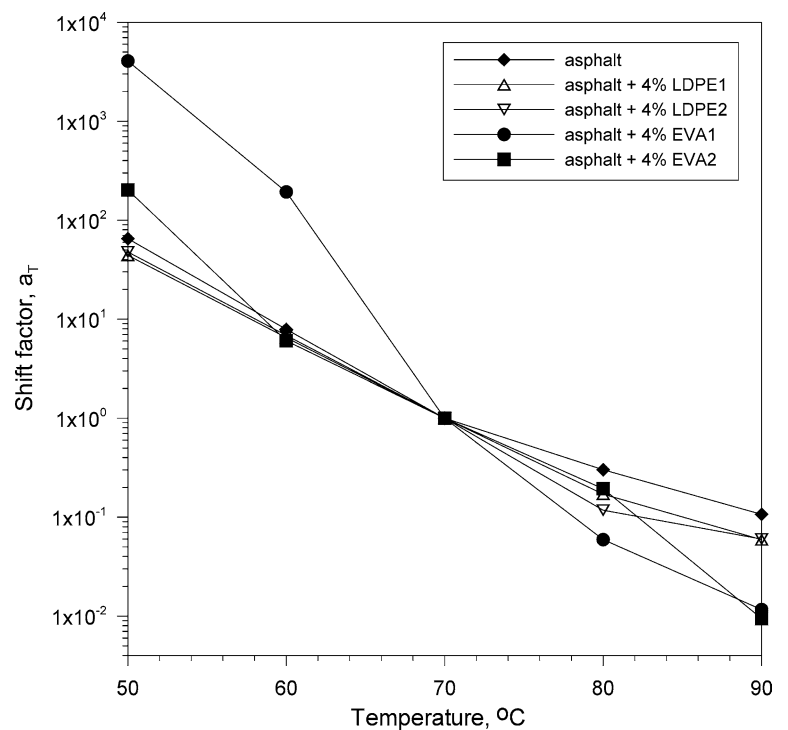


Fig. 8 a_T versus T ($T_{ref} = 70^\circ\text{C}$)



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 Fig. 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. Four percent of all polymers were used and measured $|G^*|$ increased after 72 h of continuous mixing at 160 °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 VA content leads to poor storage stability. However, the 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 M_w 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 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 Figs. 9 and 10 suggests that both the M_w 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 min).

Performance grading

According to SHRP, the highest PG in the Kingdom is 76–10. Performance grading 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 °C. Moreover, all PMAs with 4% polymer concentration satisfied the lower limit of –10 °C.

Conclusion

The influence of M_w of LDPE and the vinyl acetate content of EVA on modification of asphalt were investigated. OBT for EVA-modified asphalt was found to be lower than that of LDPE-modified asphalt due to the

Fig. 9 Effect of LDPE on the asphalt binder ageing ($\omega = 10 \text{ rad/s}$, $\gamma^\circ = 20\%$)

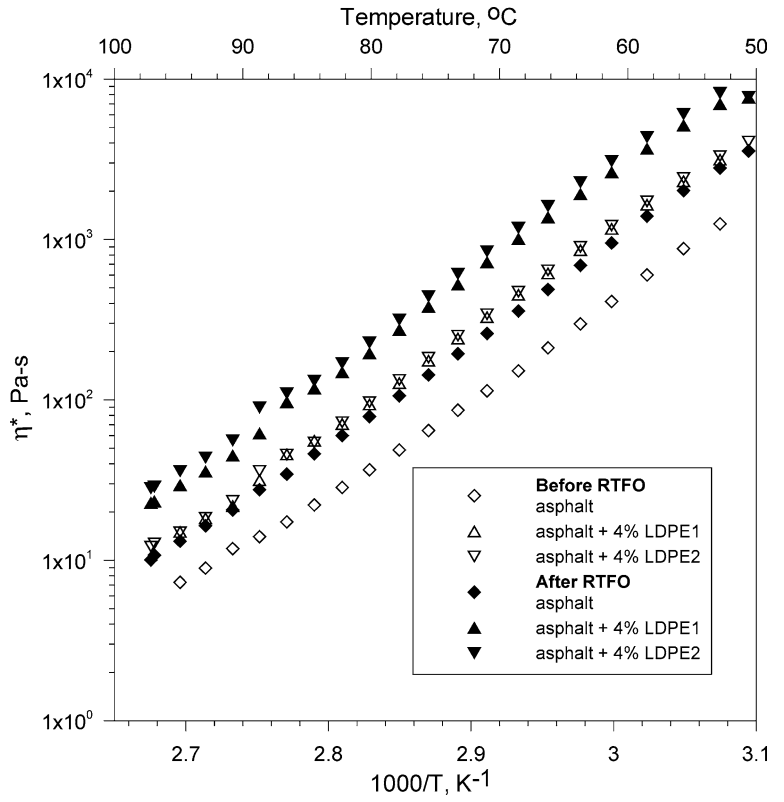
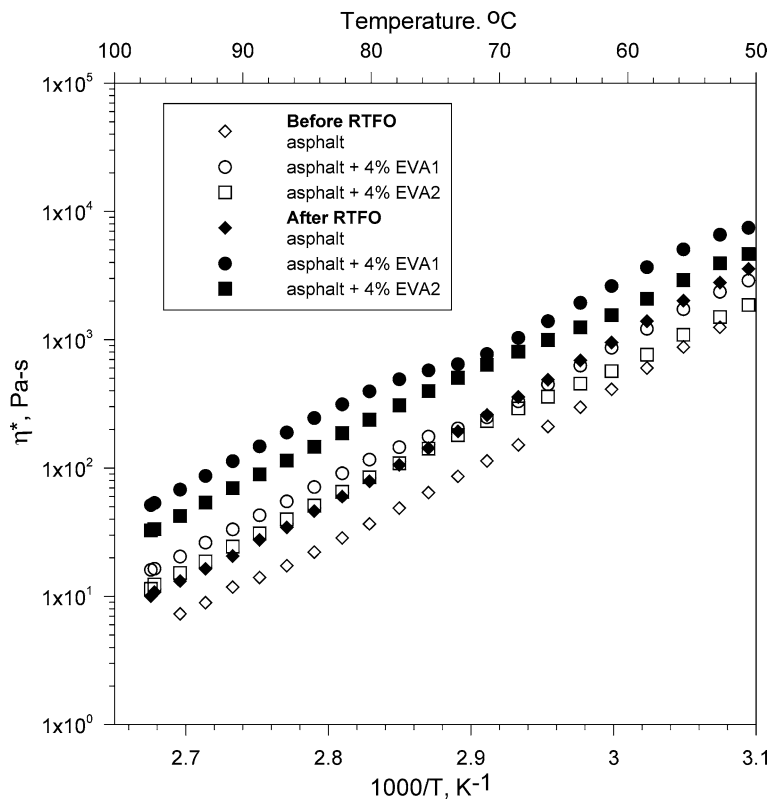


Fig. 10 Effect of EVA on asphalt binder ageing ($\omega = 10 \text{ rad/s}$, $\gamma^\circ = 20\%$)



difference in M_w . For EVA polymers with similar M_w , higher MWD (or PDI) resulted in shorter blending times in the high-shear blender. So, both M_w 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 M_w displayed higher extent of immiscibility with the asphalt used in this study. Comparison of EVA1 (low VA content) and LDPE1 (low M_w) 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 M_w or VA content. Both the M_w 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 min) according to ASTM D 2872 test procedure. The PG 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 °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 M_w showed better compatibility with asphalt and higher elasticity. Otherwise, the M_w of LDPE showed little or no influence on temperature sensitivity (flow activation energy) or the upper service temperature. Finally, the M_w 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.

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