

# Rheological Investigation of the Influence of Acrylate Polymers on the Modification of Asphalt

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**ABSTRACT:** The effect of ethylene, ethylene acrylate and glycidyl methacrylate (EA) terpolymer, and ethylene butyl acrylate (EBA) copolymer on asphalt modification was investigated at 4, 6 and 8% polymer concentrations. Both melt state rheology and asphalt concrete mix (ACM) were investigated. In the melt state analysis, dynamic shear rheology, storage stability, artificial ageing, and performance grading (PG) were studied. The PG grading of polymer modified asphalt (PMA) is correlated to the elastic properties of the polymers. Both resins improved the rheological properties, reduced the temperature susceptibility, showed better storage stability, and increase the upper grading (performance) temperature of the base asphalt. The two polymers showed similar ageing characteristics with little influence on flow activation energy. In asphalt concrete mix analysis, Marshall stability, stripping (durability), resilient modulus, and per-

manent deformation tests were performed. Polymer-modified asphalt concrete mix (PMACM) has increased percent retained stability and the resilient modulus when compared with ACM. The elastic modulus of PMA and the resilient modulus of their ACM followed the same trend. Weak influence on water sensitivity was observed, but excellent rutting resistance was obtained for PMACM over ACM. EA (much cheaper than EBA) produced satisfactory properties of PMA and superior ACM properties when blended with the high asphaltenes Arabian asphalt. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 3446–3456, 2006

**Key words:** acrylate polymer; polymer modified asphalt; storage modulus; performance grading; storage stability; asphalt concrete mix

## INTRODUCTION

Asphalt is widely used as an adhesive material in many fields,<sup>1</sup> especially in pavement construction. A little amount of asphalt (4–6% by weight) is usually needed for acceptable pavement performance.<sup>2,3</sup> Asphalt concrete pavements, however, suffers from different kinds of distresses like low temperature cracking, rutting, fatigue, etc.<sup>4–6</sup> Rutting is the permanent deformation caused by repeated dynamic loads. Moreover, increasing traffic volume, high traffic load, and weather accelerate the pavement deterioration.<sup>2</sup> So, asphalt binder should be stiff enough to resist rutting, flexible at low temperature to avoid thermal cracking, and should have time independent properties as well as good fatigue and stripping resistances. Base asphalt is not capable of doing so; hence, modified asphalt is used. Among the different types of asphalt modification, polymer modification is done enormously.

In many of the previous studies, asphalt was modified with selected polymers and the performance was

evaluated for polymer-modified asphalt (PMA).<sup>7–16</sup> In these studies, the effects of polymer type and content on compatibility, storage stability, rheology, and ageing were investigated by rheological techniques. Polymer modification increased the complex shear modulus ( $G^*$ ) of asphalt at intermediate and high temperatures and had little influence on  $G^*$  and elastic modulus ( $G'$ ) at very low temperatures. Compatibility and storage stability were found to depend on polymer content, polymer type, and characteristics of base asphalt. Some researchers also introduced elementary sulfur in PMA and significant improvement in performance was observed.<sup>17–19</sup>

The differential scanning calorimeter (DSC) was used to investigate the glass-transition temperature of PMA.<sup>20,21</sup> The addition of small amount of polymer acts as a plasticizer and lowers the glass-transition temperature of base asphalt. The effect of functional groups (acetate and acrylate) and grafted polymers on PMA and improvement in rheological properties was examined.<sup>22</sup> The polymer modification of asphalt is strongly manifested in the viscoelastic properties of PMA.<sup>13,23</sup> Performance of PMA depends on ageing of asphalt, oil absorption by polymer particles, and interaction of polymer particles with asphaltenes along with other factors.<sup>8,12</sup>

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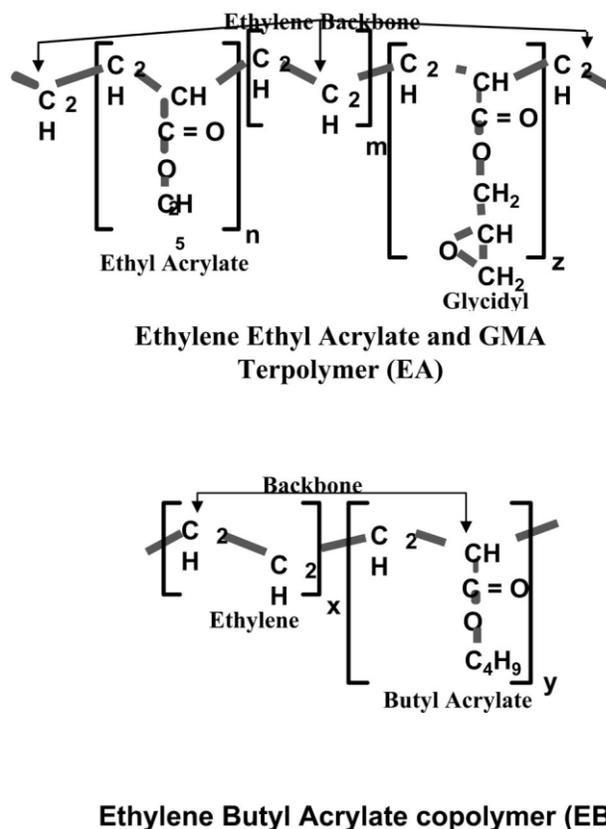
Usually, the improvement of asphalt properties due to polymer modification is evaluated by comparing the properties of asphalt concrete mix (ACM) to polymer-modified asphalt concrete mix (PMACM).<sup>24–29</sup> Moreover, some researchers attempted to correlate the solid-state properties of base asphalt and PMA to that of ACM and PMACM, respectively.<sup>30,31</sup>

In this research, polymer modification of asphalt was carried out using two different acrylate polymers with different acrylate content, and a comprehensive evaluation was performed to investigate the improvement in asphalt due to the modification. This evaluation contained two parts: study of the upgrade of asphalt performance due to polymer modification and its implication on the properties of ACM and PMACM. Most of the previous work has either focused on the rheology of PMA or the properties of ACM. In this study, we will try to examine the possibility of correlation between the properties of modified asphalt and their ACMs. Also, most of the previous work was carried out in cold climates (Canada and Sweden), where lower temperature properties of PMA were of great interest.<sup>4,21,22,32</sup> In this study, the high temperature performance is of interest for hot weather such as Arabian Gulf. In addition, most of the previous work has used polyethylene, ethylene vinyl acetate, or styrene butadiene styrene polymers. Data on acrylate polymers is limited,<sup>4,22</sup> regardless of its commercial use in some US roads, such as Oregon, Oklahoma, etc. Furthermore, the use of the previous polymers was limited to North American or European asphalts.

## EXPERIMENTAL

### Materials

Two resins of acrylate polymers were used in this study. One was ethylene, ethyl acrylate, and glycidyl methacrylate terpolymer (EA) containing more than 99% ethylene acrylate. The other polymer was ethylene and butyl acrylate copolymer (EBA) containing 27% butyl acrylate (Fig. 1). Both polymers are commercial polymers and are marketed by DuPont as asphalt modifiers. These polymers were used in USA with ELF asphalt (50/70 penetration grade); however, they are yet to be tested with Arabian asphalt. Density, melting point, melt index (MI) at 190 °C/2.16 kg as provided by DuPont are given in Table I. Number-average ( $M_n$ ), weight-average ( $M_w$ ) molecular weights, and molecular weight distribution (MWD) were measured by a gel permeation chromatography (GPC) and results are shown in Table I. Details of the GPC characterization procedure are given in a recent publication.<sup>7</sup> The low density of EA is likely due to the high acrylate content. Asphalt, used in this study, was obtained from Saudi Aramco, Riyadh Refinery; and



**Figure 1** Molecular structure of EA terpolymer and EBA copolymer.

the results of the elemental analysis and asphaltene content of base asphalt were mentioned elsewhere.<sup>7</sup> Asphalt used in this study contains about 30% asphaltenes as determined by the method of El-Mubarak et al.<sup>33</sup> Fourier transform infra red (FTIR) analysis of base asphalt showed very narrow peak at the wavelength of  $3000\text{ cm}^{-1}$ , which indicates the smaller amount of  $\text{—COOH}$  group.

Limestone aggregates were collected from local sources (see Table II for details about size distribution). The mix design was done according to Marshall method (ASTM D 1559) of mix design.

### Sample preparation

Flat discs of as received polymer were prepared in a Carver press for rheological tests. A molding temperature of  $\sim 20^\circ\text{C}$  above the melting point of each polymer was selected. Details of sample preparation in the Carver press are given elsewhere.<sup>7</sup>

PMA samples were prepared by blending pre-weighed polymer with asphalt at  $160^\circ\text{C}$ . The blending took place in a high shear blender ( $\sim 2500\text{ rpm}$ ) for a fixed time. The blending time was determined as 10 and 15 min for EA and EBA, respectively. This time was determined according to the procedure outlined

TABLE I  
Characterization of Polymers

Polymer type	Density (g/cm <sup>3</sup> )	Melting point (°C)	Melt index (g/10 min)	$M_w$ (kg/mol)	$M_n$ (kg/mol)	MWD
EA	0.576	52	8	91	16.16	5.61
EBA	0.926	94	4	80	18.98	4.23

in a previous publication.<sup>7</sup> ACM and PMACM were prepared according to Marshall mix design method (ASTM D 1559). Table III shows the details of mix design, and values were obtained by following the standard test procedures. Standard cylindrical Marshall specimens (100 × 62.5 mm<sup>2</sup>) were prepared for ACM and PMACM tests.

### Rheological characterization

Rheological tests of as received polymer, pure asphalt, and PMA were carried out in a strain controlled Advanced Rheometric Expansion System (ARES) rheometer. Nitrogen environment was used to avoid any possible degradation. Parallel plate geometry with a diameter of 25 mm and a gap of 1.5 mm was used in ARES rheometer. Strain amplitude of 20% was selected following separate strain sweep tests on asphalt, polymer, and PMA samples. This value was in the linear viscoelastic range.

Samples of 4% EBA-PMA from two different batches were tested for reproducibility by performing frequency sweep tests to check for possible degradation. Good agreement of both viscous and elastic properties between two batches was observed, which indicates excellent reproducibility of the measurement. Dynamic frequency and temperature sweep tests were performed on all melts and test details were described elsewhere.<sup>7</sup>

### Storage stability test

This test helps in assessing the miscibility of polymer-asphalt blend, which is critical for storage and final use of PMA. The storage stability of the modified

asphalt was evaluated according to Hussein et al.<sup>7</sup>  $G^*$  values at 76°C and 10 rad/s were measured in ARES rheometer for the top and the bottom samples and the difference was calculated. This temperature represents the required upper service temperature in the Gulf countries.<sup>2</sup> The test was carried out for PMAs containing 4% polymer. Samples were obtained and tested after zero and 72 h of continuous mixing at 160°C

### Rolling thin film oven test

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. The AASHTO T240 procedure was followed to perform the RTFO test for PMA with 4% polymer. After completing the simulation, samples were collected for rheological testing in ARES. Moreover, performance grading (PG) of the 4% PMA was carried out according to AASHTO Designation: MP1.

### Marshall stability test

Marshall stability was evaluated by measuring the compressive load required to break the ACM or PMACM specimen in a Marshall testing machine.<sup>20</sup> The load was applied on the specimen at a constant deformation rate of 51 mm/min (2 in./min), and the load at failure was obtained (ASTM D1559). Six specimens were immersed into a water bath at 60°C. After 40 min (initial condition), three specimens were tested and the average compressive load required for break-

TABLE III  
Marshall Mix Design Method

Sieve size (inches)	Mix formula (% passing)	SHRP limits (% passing)	Job mix formula	Specification limits
1	100	100		
3/4	87	80–95		
4	55	48–62		
10	38	32–45		
40	21	16–26		
80	13	8–18		
200	6	4–8		
			Optimum asphalt content (%) (60/70 penetration grade asphalt)	5.3 5.3 ± 0.3
			Marshall test results (75 blows, compaction temperature 150°C)	
			Stability (Kg)	1804 800 min.
			% Air voids (total mix)	4.4 4.0–6.0
			Flow (mm)	3.2 2.0–4.0
			% Voids filled with asphalt	74 70–80
			Stability loss (%)	16.2 20 max.
			Void in mineral aggregates	16.04 –

ing the sample was determined. The remaining three specimens were kept for 24 h (final condition) and the average compressive load was measured.

**Stripping test (Lottman test)**

This test shows the resistance of ACM and PMACM sample to water induced damage(AASHTO T283). It involves measuring the indirect tensile strength (ITS) at a constant deformation rate of 51 mm/min. ITS test was performed on compacted asphalt mixtures before and after saturation and accelerated water conditioning. Three specimens were immersed into water bath at room temperature for 2 h, and the average initial ITS was determined. For the measurement of the final average ITS, another three specimens were immersed in water under vacuum (67.73 kPa) to achieve 60% saturation, then samples were kept in a water bath at 60°C for 24 h, and finally immersed in another water bath at room temperature for 2 h. The three samples were tested to determine final ITS.

**Resilient modulus**

Resilient modulus (ASTM D 4123) shows the pavement response in terms of dynamic stresses and corresponding strains. It is one of the important parameters for pavement design. A static load of about 10 lb<sub>f</sub> (44.5N) was applied to hold the specimen in place, and a repeated load in the linear range was applied at a frequency of 1 Hz. The resulting horizontal deformation was measured at 50°C.

**Permanent deformation (rutting) test**

Permanent deformation measurements were performed on ACM and PMACM at 50°C. The stress was controlled to produce a 150 initial μ-strain (10<sup>-6</sup> in/in strain) level and make sure that it is in the linear deformation range. This stress was used repeatedly at a frequency of 1 Hz. The deformation was measured by linear variable differential transducer and data were collected using a data logger. The data were collected at every 5 s for the first 100 load repetitions, every 10 s for the next 100 repetitions, then every 15 s for the following 100 repetitions, and finally every 30 s up to the sample failure. Results were analyzed to compare the accumulated deformation because of repeated load in both ACM and PMACMs.

The rheological characterization, storage stability, and RTFO test were performed on asphalt and PMA. On the other hand, Marshall stability, durability (Lottman test), measurement of resilient modulus, and rutting tests were carried out on asphalt concrete mixes.

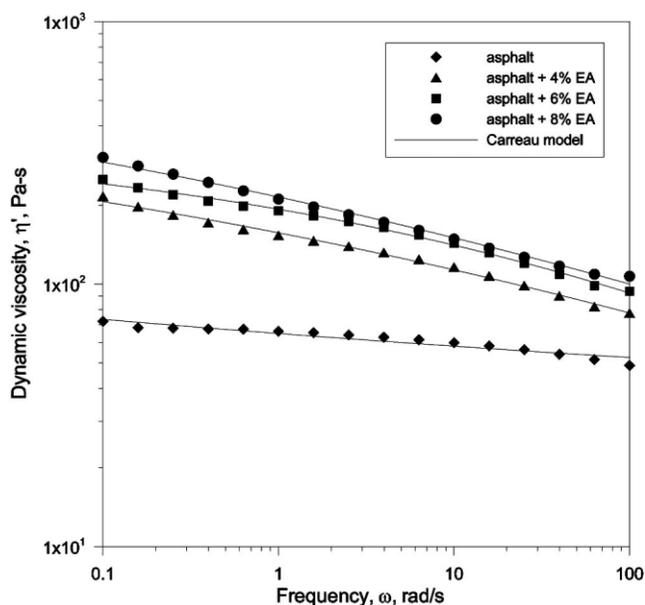


Figure 2 η' (ω) for EA modified asphalt at different EA concentrations (T<sub>test</sub> = 76°C).

**RESULTS AND DISCUSSION**

**Rheological characterization**

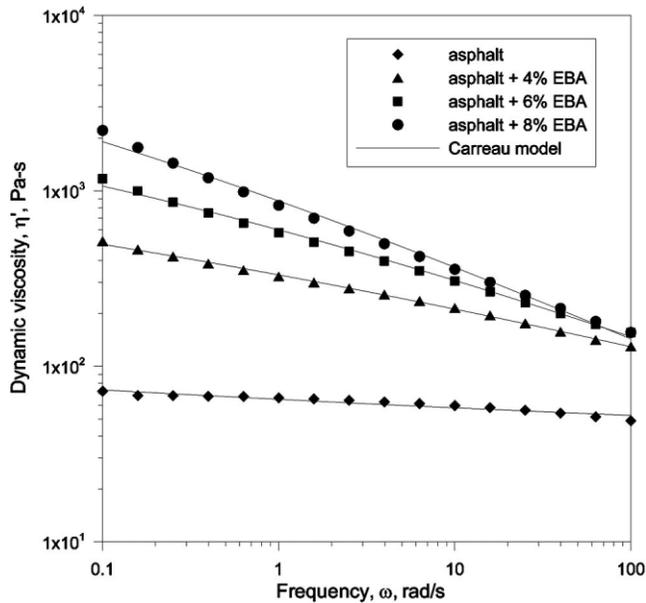
The results of dynamic frequency sweep tests on as-received polymer provided power law indices of 0.43 and 0.48 for EA and EBA, respectively. So, EA displayed higher shear thinning behavior than EBA, which explains the low blending time (10 min) determined from the separate measurement of G\* as a function of time. Moreover, Table I shows that MFI of EA is higher than that of EBA; hence, less time was needed for blending of EA polymer. This observation supports the results of the dynamic shear rheology.

The dynamic viscosity, η<<, for EA-PMA are given in Figure 2 as a function of frequency, ω. Results are shown for the 4, 6, and 8% polymer content as well as base asphalt. Base asphalt showed typical Newtonian behavior over almost the entire ω range, but PMA displayed non-Newtonian behavior, which was more pronounced at high polymer concentrations. Similar behavior was observed for asphalt modification with other polymers.<sup>7,34,35</sup> At low ω (ω = 0.1 rad/s), η' of the 4% EA modified asphalt is ~3 times higher than that of base asphalt; while at high ω (100 rad/s), η' was ~2 times higher. Also, η' increased at high polymer content; however, at high ω the effect of polymer concentration was not pronounced.

The shear thinning behavior of PMAs can be described by Carreau model:

$$\frac{G''}{\omega} = \eta' = \frac{\eta_0}{(1 + (\lambda_c \omega)^2)^s} \tag{1}$$

where, s is a parameter related to the slope of the shear-thinning region and λ<sub>c</sub> is a characteristic time of

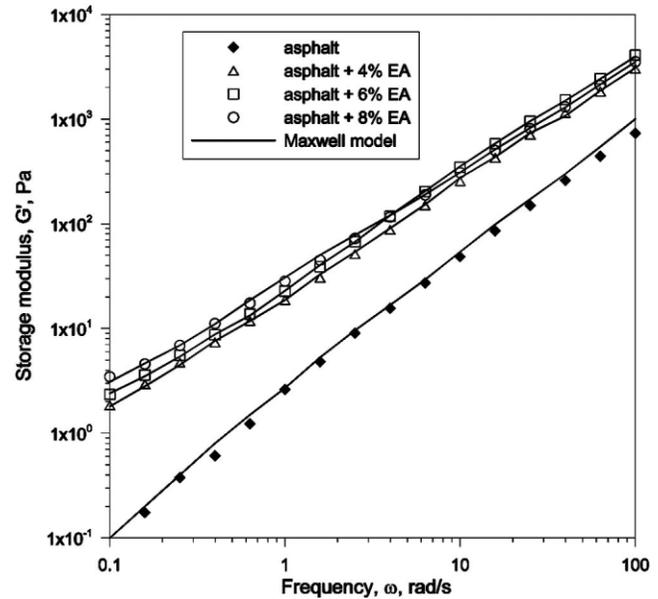


**Figure 3**  $\eta'(\omega)$  for EBA modified asphalt at different EA concentrations ( $T_{\text{test}} = 76^\circ\text{C}$ ).

the material. Excellent fit of Carreau model was observed for asphalt and PMAs as shown in Figure 2.

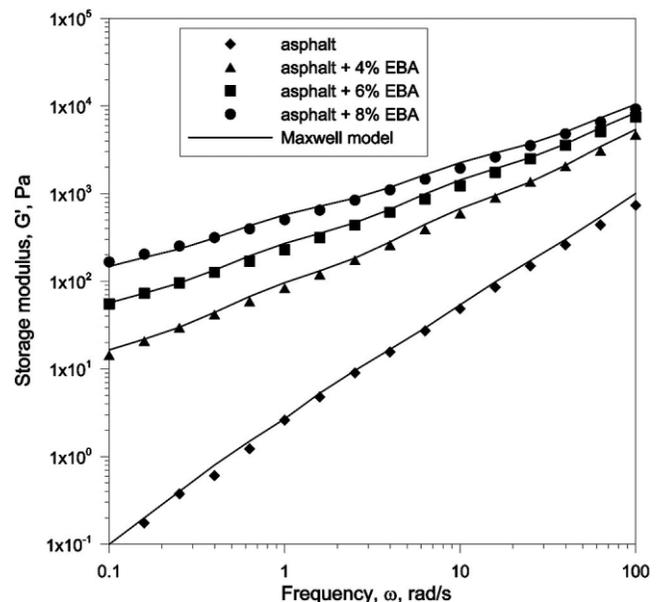
Data for  $\eta'(\omega)$  of EBA PMA at three different polymer concentrations are presented in Figure 3. Addition of 4% of the polymer has increased  $\eta'$  of PMAs at low- $\omega$  and resulted in a shear thinning behavior. The viscosity of the PMA in the range 100–0.1 rad/s is about 2–7 times that of base asphalt. For the same amount of polymer (4%), increase of viscosity due to the addition of EBA is almost twice that of EA. It should be noted that the EA terpolymer had an MFI that is twice that of EBA copolymer (see Table I).

High values of elastic modulus,  $G'$ , suggest low resistance to low-temperature cracking, because materials become harder (i.e. value of  $G'$  increases) at low temperature and crack easily. Hence, EA is expected to have better low-temperature cracking resistance than EBA as confirmed later by PG tests in the bending beam rheometer. Figures 5 and 6 show data for  $G'(\omega)$  of EA and EBA modified asphalt, respectively, at three different polymer concentrations. Polymer modification increased value of  $G'$  of base asphalt. The value of  $G'$  for the 4% EA PMA was more than four times that of base asphalt and it increased at higher polymer contents. The influence of polymer content was not that much strong for EA, since the test temperature ( $76^\circ\text{C}$ ) is above the melting point of EA ( $52^\circ\text{C}$ ). Therefore, a weak influence of polymer concentration on  $G'$  is evident. For EBA, the increase in  $G'$  with the increase of polymer concentration is attributed to its high melting point ( $94^\circ\text{C}$ ). Similar improvements were observed in previous research.<sup>1,9,10</sup> So, EBA shows higher  $G'$  at low  $\omega$ , which suggest better

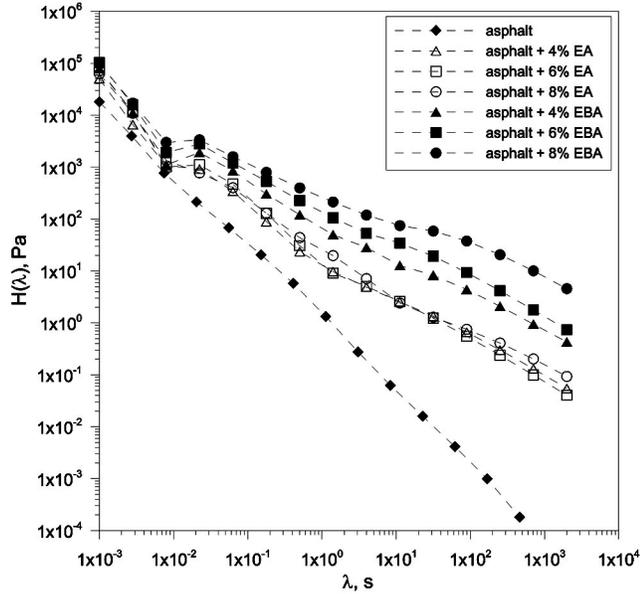


**Figure 4**  $G'(\omega)$  for EA modified asphalt at different EA concentrations ( $T_{\text{test}} = 76^\circ\text{C}$ ).

flexibility. According to the principle of time–temperature superposition, this behavior corresponds to long service time or higher temperature, which is needed in hot climate. The slopes of  $\log G'$  versus  $\log \omega$  at low  $\omega$  were 1.43, 1.04, 0.81, and 0.6 for base asphalt, the 4, the 6, and the 8 wt % EA PMA (see Fig. 4), respectively. However, for the 4, 6, and 8% EBA modified asphalt, the slopes are 0.76, 0.61, and 0.48, respectively, (see Fig. 5). It can be observed that for the same polymer content, the slope for EBA-PMA was less than that of



**Figure 5**  $G'(\omega)$  for EBA modified asphalt at different EBA concentrations ( $T_{\text{test}} = 76^\circ\text{C}$ ).



**Figure 6** Relaxation spectrum of asphalt and PMAs ( $T_{\text{test}} = 76^\circ\text{C}$ ).

EA-PMA. So, EBA shows higher  $G'$  at low  $\omega$ . So, the melt rheology of EBA-PMA suggests that EBA is expected to show better deformation resistance at high temperature.

Analysis of viscoelastic data was extended to mechanical spectra to obtain a detailed overview of rheological properties because of polymer modification of asphalt.  $G'(\omega)$  was described by the generalized Maxwell model. In the linear viscoelastic range, the model leads to the following expressions for  $G'$  as a function of  $\omega$ :

$$G' = \sum_i \frac{H_i \lambda_i^2 \omega^2}{1 + \lambda_i^2 \omega^2} \quad (2)$$

where  $\lambda_i$  and  $H_i$  are relaxation time and elastic modulus of  $i^{\text{th}}$  Maxwell element. Here, 7 sets of Maxwell elements were considered to avoid any problems concerning the evaluation of fitting parameters  $\lambda_i$  and  $H_i$ . Under these conditions, the model was able to describe the mechanical spectra of all asphalt and PMAs in Figures 4 and 5.

Figure 6 shows the relaxation spectra,  $[H(\lambda)]$ , of asphalt and PMAs at  $76^\circ\text{C}$ . In this case, 15 sets of Maxwell elements were considered to get good fit. It can be observed that  $H$  for base asphalt has rapidly decreased with the increase of  $\lambda$ . It means decrease in elastic properties for asphalt is high with time. This decrease is less for PMAs and the 8% EBA PMA showed the least decrease. EBA copolymer has shown a slower rate of decrease in  $H$  with  $\lambda$  and  $H(\lambda)$  for EBA is always higher than that of EA. This suggests that

EBA modified asphalt has maintained higher values of elastic properties and loses its elasticity at a slower rate in comparison with EA-PMA. These results are consistent with our previous data for  $G'$  of EBA-PMA shown in Figure 5.

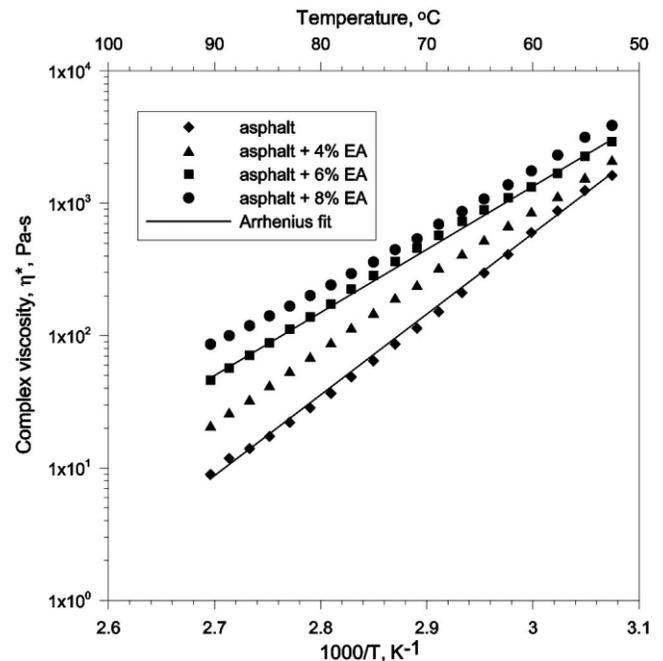
Figures 7 and 8 show the results of  $\eta^*(T)$  obtained from temperature ramp tests for EA and EBA PMA, respectively.  $\eta^*$  was found to increase significantly for the 4% EA PMA, and this increase was higher for high EA content. At higher temperatures ( $\sim 70^\circ\text{C}$ ), the influence of polymer content on  $\eta^*$  was noticeable. At high temperature, high values of  $G^*$  ( $G^* = \eta^* \omega$ ) are needed. Higher value of  $\eta^*$  indicates high rutting resistance at higher temperature. Because higher value of  $\eta^*$  shows better resistance from getting melt at higher temperature. Although 4% EBA showed better increase in  $\eta^*$ , 6 and 8% EBA PMA showed similar increase in  $\eta^*$  (Fig. 8).

Viscosity–temperature relationships of PMAs can be expressed by the well known Arrhenius equation.

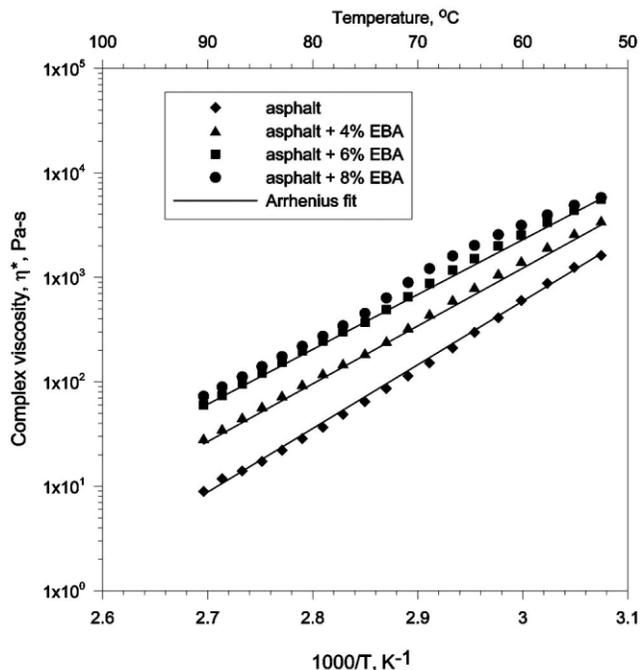
$$\frac{G^*}{\omega} = \eta^* = A e^{E_a/RT} \quad (3)$$

where  $E_a$  is the flow activation energy,  $A$  is the pre-exponential term, and  $R$  is the universal gas constant.  $E_a$  is an important factor that strongly influences the viscosity. The data given in Figures 7 and 8 showed good fit to Arrhenius equation.

To prevent high temperature rutting, asphalt should be more elastic at elevated temperature. One of the



**Figure 7**  $\eta^*(T)$  for EA modified asphalt at different EA concentrations ( $\omega = 10 \text{ rad/s}$ ).



**Figure 8**  $\eta^*(T)$  for EBA modified asphalt at different EBA concentrations ( $\omega = 10$  rad/s).

objectives of polymer modification is the lowering of  $E_a$  of base asphalt. So, viscosity changes with temperature should be low and relatively high  $\eta^*$  (or  $G^*$ ) is desirable at high temperature. Temperature ramp tests data were also used to obtain  $E_a$  and  $A$  from eq. (3). Figure 9 shows the plot of  $E_a$  versus polymer concentration. A good linear relation between  $E_a$  and weight fraction of polymer was obtained for both polymers and the relations are displayed on the plot. The 8% EA reduced  $E_a$  of base asphalt from 114 kJ/mol to as low as 82.96 kJ/mol. On the other hand, the addition of 8% EBA reduced  $E_a$  to 99.4 kJ/mol. So, for the 4% polymer concentration, the influence of EA and EBA on activation energy is comparable.

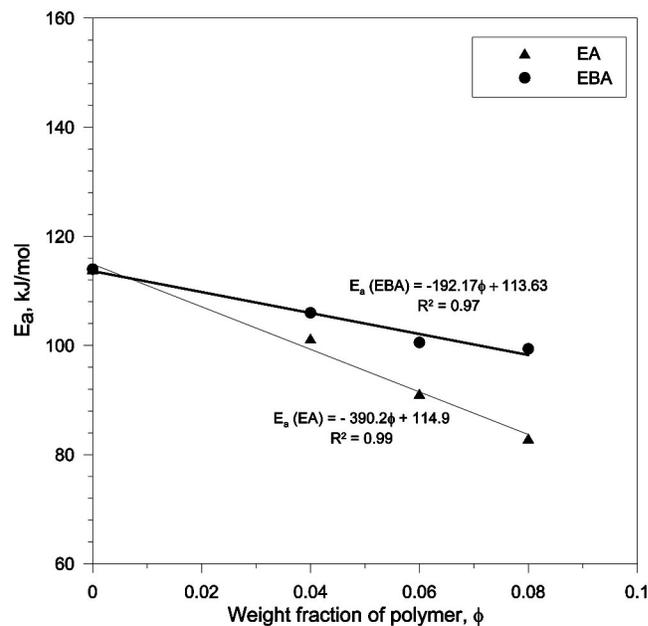
According to Strategic Highway Research Program (SHRP), PMA should have a minimum  $G^* / \sin \delta$  of 1 kPa at its upper service temperature. Base asphalt showed a  $G^* / \sin \delta$  of 1 kPa at 70.96°C. However, the 4% EA and the 4% EBA PMA showed the same value at 79.48°C and 85.46°C, respectively. So, further analysis was performed on the 4 wt % polymer samples since both PMAs satisfy the SHRP specifications at this concentration.

### Storage stability

Addition of polymer increases the complexity of asphalt since asphalt contains different phases.<sup>23,36,37</sup> Practically, asphalt is stored at elevated temperature, which accelerates the phase separation of PMA into asphalt and polymer-rich phases. Initially, the blend

was homogeneous, and there was no difference in  $G^*$  value between the top and the bottom of the container. After 72 h of continuous mixing at 160°C (storage temperature) in the presence of air, all polymers showed  $G^*$  values that are high both at the top and at the bottom. Moreover, there was a difference in  $G^*$  value between the top and the bottom. The percent differences were 8.81 and 16.06% for EA-PMA and EBA-PMA, respectively. The high temperature and long mixing time would result in considerable oxidation that would eventually lead to the observed increase in  $G^*$ . So, phase separation in EBA-PMA was higher than that of EA-PMA. However, both PMAs showed good storage stability that is within the acceptable limit of 20%.<sup>38</sup>

Also, relaxation spectra were used in Figure 10 ( $\lambda^*H(\lambda)$  vs.  $\lambda$ ) to observe the immiscibility of asphalt polymer blend. In this kind of plots, a single phase pure component shows a single peak, which reflects the complete homogeneity, but multi phase systems show more than one peak. In our study, the 4% of EA and EBA PMA were compared with base asphalt. At low  $\lambda$  ( $\sim 0.001$  s), base asphalt showed a broad peak, a characteristic of the multiphase nature of asphalt constituents. Both PMAs showed similar behavior at low  $\lambda$ . The low  $\lambda$  peak ( $\lambda \sim 0.01$  s) is likely due to the low Mw asphalt phase, while higher peaks represent the polymer phase. For EBA, the second peak was observed to be broader than that of EA. This implies that EBA PMA has great tendency for phase separation in comparison to EA-PMA. Similar behavior was observed in storage stability, where the percentage difference in  $G^*$  value between the top and the bottom



**Figure 9** Plot of  $E_a$  vs. weight fraction of polymer.

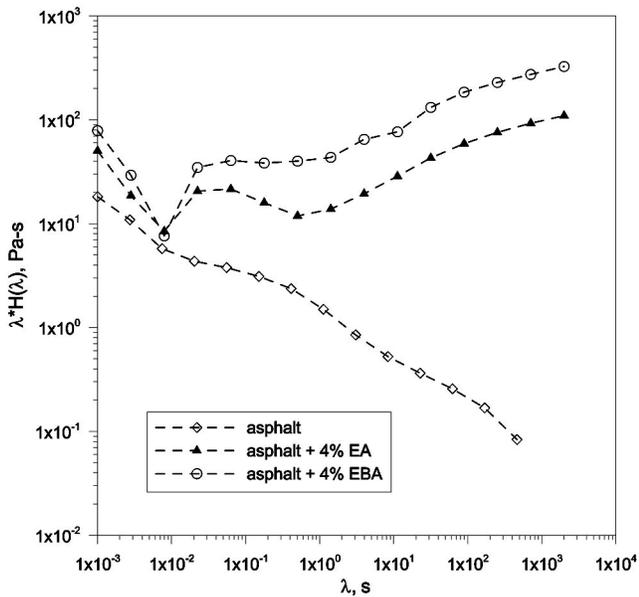


Figure 10 Plot of  $\lambda^*H(\lambda)$  vs.  $\lambda$  for asphalt and 4% of EA and EBA PMA ( $T_{test} = 76^\circ\text{C}$ ).

samples was higher for EBA-PMA. Thus, rheological test reflects exact behavior of time consuming (72 h) storage stability test. This kind of analysis may be used to predict miscibility between polymer and asphalt without doing storage stability test.

The supplier of the polymer resins claimed that no percent difference was observed between the top and the bottom for the polymers in the storage stability test. The reason could be the  $-\text{COOH}$  content. Asphalt, used in this study, contains small amount of  $-\text{COOH}$  group. So, insufficient reaction between  $-\text{COOH}$  and the polymers were allowed to occur to form homogeneous phase.

**Rolling thin film oven test**

Figure 11 shows the effect of short term ageing on base asphalt and PMAs. It is clear that ageing increases  $\eta^*$  with little or no influence on flow activation energy (the lines are almost parallel). The viscoelastic properties of aged specimens are generally higher than those of unaged ones. High ageing temperature ( $160^\circ\text{C}$ ) favors the volatilization of low  $M_w$  constituents of asphalt and degradation of the polymer. High  $M_w$  constituents remain in the asphalt. Polymer degradation can lead to either cross-linking or chain scission depending on the chemistry of the polymer degradation.<sup>39</sup> The rheological changes of aged asphalt depend on the combined effect of asphalt oxidation and polymer degradation. The polymer degradation is influenced by polymer type and concentration, molecular structure, residual catalyst, etc. In this case, cross-linking is favored, which is likely due to the formation

of free radicals as a result of the combined effect of heat and shear.

**Performance grading of PMA**

The PG of local PMA should have a PG of 76–10.<sup>2</sup> The  $76^\circ\text{C}$  refers to the upper service temperature, while the  $-10^\circ\text{C}$  is the lower temperature. The PG for base asphalt is 64–22. For the 4% EA-PMA and the 4% EBA-PMA, the PG was 76–16 and 82–10, respectively. So, modified asphalt showed higher service temperature in comparison with base asphalt. EBA polymer showed higher upper service temperature than that of EA polymer ( $82^\circ\text{C}$  vs.  $76^\circ\text{C}$ ). On the other hand, EA modified asphalt displayed lower upper grading temperature than that of EBA. The more viscous EBA has increased the upper service temperature. So, the PG grading of PMA is correlated to their elastic properties.

Polymer modification improved the performance of base asphalt at every melt state analysis described so far. EBA polymer increased the value of rheological properties like  $G'(\omega)$ ,  $\eta'(\omega)$  and  $\eta^*(T)$  compared to EA. But the influence on  $E_a$  was comparable. Moreover, better storage stability was observed for EA polymer. In general, addition of 4% of EA or EBA resulted in acceptable performance. However, EBA showed better PG and  $G'$  that are important for high temperature performance.

**Marshall stability test**

The required compressive loads to fail ACM and PMACMs samples are presented in Table IV. For sta-

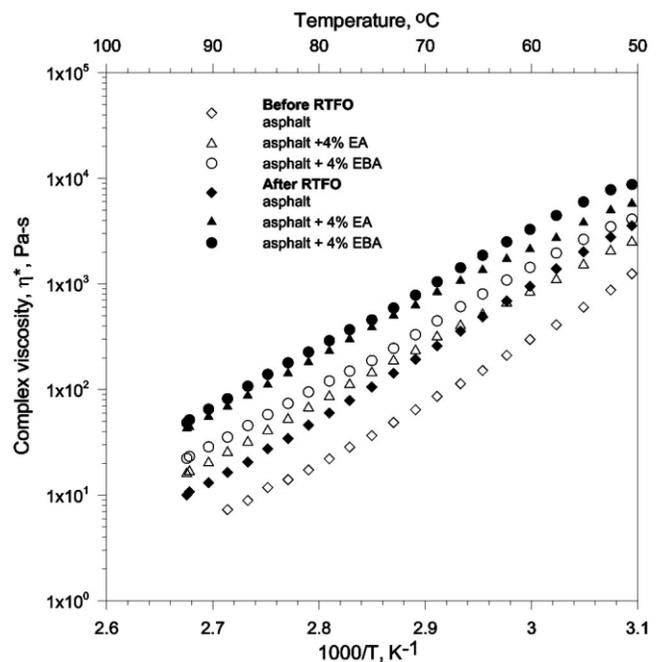


Figure 11 Effect of ageing on  $\eta^*(T)$  ( $\omega = 10 \text{ rad/s}$ ).

**TABLE IV**  
**Marshall Stability and Stripping Tests Result**

Mix type	Condition	Average load/ITS	Standard deviation	% Loss
Marshall stability test				
ACM	Initial	19.93	0.41	34.01
	Final	13.15	1.39	
EA-PMACM	Initial	14.70	2.98	9.95
	Final	13.23	0.33	
EBA-PMACM	Initial	13.72	3.71	14.70
	Final	11.70	1.35	
Stripping test				
ACM	Initial	10.75	0.02	36.26
	Final	6.68	4.05	
EA-PMACM	Initial	12.25	1.56	30.93
	Final	8.46	1.09	
EBA-PMACM	Initial	10.75	0.65	32.28
	Final	7.29	1.03	

bility loss, three specimens for each condition (initial and final) were used and the average compressive load, with standard deviation, is reported in Table IV. The stability of PMACMs was less than that of ACM. The percent loss in compressive load due to conditioning at high temperature is reported in Table IV. This loss was the highest for ACM and the least for EA PMACM. The percent loss for EBA PMACM was in the acceptable 20% limit.<sup>36</sup> So, the percent retained stability for PMACMs was higher than that of ACM, while EA modified asphalt had better Marshall stability. For the 4% PMA, the results given in Figures 3–6 indicate that EBA-PMA had higher viscous and elastic properties than EA-PMA, followed by base asphalt. The results of the Marshall stability do not correlate with the melt rheology of their PMA.

### Stripping test (Lottman test)

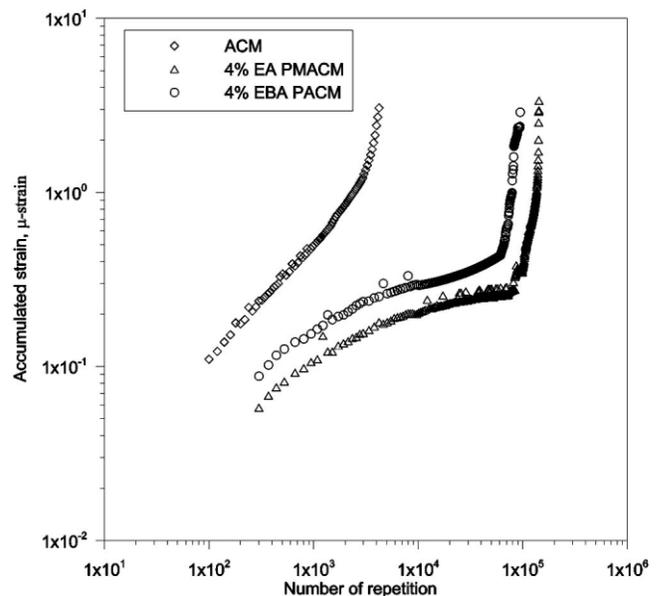
The average indirect tensile strength (ITS) for ACM and PMACMs is shown in Table IV. Three specimens of each sample were used, and the standard deviation is reported for the initial and final conditions along with percent loss due to accelerated water damage. The percent loss in ITS was obtained for EBA- and EA-PMACMs, and compared with ACM. Values of the percent loss are in the range of 31–36%. Accelerated saturation by using vacuum and long time exposure in high temperature water bath weakened the bond between PMACM and aggregates resulting in the loss of ITS. It is quite clear that the water sensitivity properties of asphalt and PMAs are similar. So, polymer modification had no significant influence on the stripping properties of ACM. The water stripping in ACM is more of a chemical rather than a physical property. So, we did not attempt to correlate it with rheological properties of PMA.

### Resilient modulus ( $m_r$ )

Resilient modulus obtained at 50°C for ACM, EA PMACM, and EBA PMACM are 66.15, 90.79, and 116.73 kilo-lb<sub>f</sub>/per square inch (ksi), respectively. Polymer modification increased  $M_R$  of base asphalt by 37.2% and 76.46% for EA and EBA, respectively. Similar behavior was obtained for PMACM in the previous studies.<sup>40,41</sup> Here, we attempted to check for a possible relationship between the resilient modulus of ACM and the elastic modulus of PMA. Qualitatively, the trend of the increase in  $G'$  in asphalt, EA-PMA, and EBA-PMA was the same as that of their corresponding ACMs. Therefore, there exists a qualitative relationship between  $G'$  of PMA and  $M_R$  of PMACM.

### Permanent deformation (rutting) test

Figure 12 shows the results of accumulated strain vs. the number of repeated loads. Polymer modification decreased the deformation of concrete mix, i.e., increased the rutting resistance. Similar observations were reported for modification with other polymers.<sup>25,42</sup> Lower deformation of PMACM indicates the elastic nature of PMA, which is attributed to polymer modification. The slopes and antilogs of intercepts were obtained in the linear region. The slopes were 0.6, 0.2, and 0.2 for ACM, EA, and EBA PMACMs, respectively. Antilogs of the intercepts were 0.0045, 0.0205, and 0.0316 for ACM, EA, and EBA PMACMs, respectively. PMACM showed less accumulated strain in comparison with ACM, which suggests improvement in rutting resistance because of the addition of polymers. Although the slope of both PMACMs is the same, but the antilog of intercept is



**Figure 12** Rutting curve at 150 initial microstrain ( $\mu$ -strain) and 50°C.

smaller for EA-PMACM, which suggests higher rutting resistance. Therefore, the more elastic EBA-PMA showed the lower rutting resistance than EA-PMA. So, there is no correlation between the melt rheology and the permanent deformation properties of the ACM.

At the high number of repetitions, the deformation was gradual for ACM, while PMACMs showed rapid deformation. Both polymers contain rigid carbonyl group, which bears double bond and makes the polymer highly elastic and tough. After a certain number of repeated load, PMACM breaks. The critical number of repeated loads is 70,000 and 110,000 for EBA and EA-PMACM, respectively. The number of repeated loads required for the failure of the ACM was 4255. These values indicate the high rutting resistance behavior of EA-PMACM. Also similar endurance limit for EA was claimed by the supplier.

The overall performance of the high acrylate content EA-PMACM is superior to that of EBA in rutting resistance and Marshall stability. However,  $M_R$  of EBA-PMACM was higher than that of EA-PMACM. The water stripping properties of the two polymers are comparable with that of ACM. In general, EBA showed better PMA properties, while EA displayed better ACM properties.

### CONCLUSIONS

Ethylene acrylate copolymer and ethylene butyl acrylate terpolymer of different acrylate content were used to modify asphalt, and the performance of the two polymers was studied. The following conclusions are drawn on the basis of this investigation:

1. The addition of EA and EBA significantly increased the viscoelastic properties ( $G'$  and  $\eta'$ ) of the asphalt. EBA modified asphalt showed about twice the increase in rheological properties ( $G'$  and  $\eta'$ ) in comparison to EA. This ratio is the same as the ratio of the MFI of EA to that of EBA.
2. Flow activation energy of asphalt was reduced from 114 to 101 and 106 kJ/mol due to addition of 4% of EA and EBA, respectively. The temperature sensitivity of asphalt has improved. Both EBA copolymer and EA terpolymer modified asphalts showed acceptable storage stability results (<20% difference in  $G^*$ ) at 160°C. EA-PMA was found to have better storage stability in comparison to EBA. The storage stability results are in agreement with the predictions of the plots  $\lambda^*H(\lambda)$  vs.  $\lambda$ , where a broader peak was obtained for EBA-PMA.
3. Both asphalt and PMA hardens due to ageing. At the same polymer concentration, EBA-PMA showed higher upper service temperature (82°C) than EA (76°C). However, both polymers satisfy the required PG.
4. Marshall stability test showed that both PMACMs retained a percent stability some what higher than that of ACM. However, the addition of the polymer did not influence the water stripping properties of base asphalt.
5. The  $M_R$  of EBA-PMACM was the highest, which indicates the less deformation at early life of the pavement. Higher rutting resistance was obtained for PMACMs in comparison to ACM. Accumulated deformation was the smallest for EA-PMACM, which implies higher elastic behavior for EA-PMA among the two studied polymers.

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