Influence of polymer structure and amount on microstructure and properties of polyethylene-modified asphalt binders

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Abstract In recent years, the use of polyethylene (PE) for asphalt modification has been gaining increased attention due to the environmental sustainability and cost-saving benefits. To optimize the performance of the PE-asphalt blends, it is necessary to understand the polymer-binder interactions and their impact on the properties of the modified asphalt binder. In this study, low-density polyethylene (LDPE) with low and high melt flow index (MFI), i.e., LDPE4 and LDPE70, were blended with Pen 60-70 asphalt binder in dosages ranging from 1 to 5 wt.%. PE Wax was also added to the binder or the PE-binder blend to enhance dispersion. The dispersion of PE in the binder and the phase stability of the modified binder were investigated by optical microscope. The equivalent diameter of PE domains increased with time and the polymer dosage level. The addition of PE wax improved the polymer dispersity in the LDPE4 blends. The polymer dispersity in LDPE70 blends was good without adding PE Wax, attributed to the higher

MFI value (low molecular weight) of LDPE70. In addition, to understand the stability of polymer modified binder, the steady shear viscosity-temperature profile of these binders was studied using a rotational viscometer. The dynamic rheological properties and performance of the PE-binder blends were evaluated using the dynamic shear rheometer. Based on the microstructure, all other rheological and performance properties, it was concluded that the 3% LDPE70 binder has better polymer dispersity, better low and high temperature performance characteristics.

Keywords Polymer modified asphalt binder · Optical microscopy · Low-density polyethylene · Rheological properties · Viscosity-temperature profile

1 Introduction

Asphalt modification using plastics started in the early 1980's [1]. Initial works involved the use of polyethylene (PE) alone without other additives; continuous agitation was required to prevent separation of PE from asphalt until asphalt mixture is laid. Early research studies focused on the characterization of PE modified asphalt mixture and pavement performance evaluation [2–6], while many of the recent studies focused on improving stability of the PE-binder blend [7–10]. When blending PE with asphalt

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binder, it is necessary first to understand the interaction between PE and asphalt binder and how the addition of PE impacts the thermal and rheological behavior of the binder.

Low-Density Polyethylene (LDPE) is the most commonly used PE polymer for asphalt modification [11–14]. The properties of PE modified binders are highly dependent on the mixing conditions [15, 16]. Polacco et al. [17] reported that long high-shear mixing changes the asphalt binder's molecular weight and chemistry and significantly influences the polymer swelling. Dalhat et al. [16] recommended a mixing temperature of 50 °C above the PE melting temperature, but not exceeding 190 °C to avoid binder oxidation at high temperatures. Based on the blend viscosity, dynamic modulus (G^*) values and phase angle (δ) values, the optimum blending time, blending speed, and LDPE dosage was selected as 30 min, 1300–5000 rpm, and 3–5%, respectively [16, 18–20].

The properties of polymer-modified binders are influenced by many factors: the type and properties of polymer, polymer size, binder source, and blending conditions. The stability/compatibility of polymer modified binder (PMB) depends on the capability of polymer swelling with maltene molecules and asphaltene content [21]. Some polymers like PE have low miscibility/solubility in binder, resulting in the separation of the two components. Polacco et al. [12] reported that the polymer - binder compatibility is enhanced when the asphalt binder with high aromatic content and low asphaltene content is used [16, 22]. In a study conducted by Liang et al. [23], optical microscopic analysis was carried out on PE modified asphalt binder, and the phase separation of PE and asphalt binder was simulated using phase-field model coupled with the Navier–Stokes equation. They concluded that LDPE disperses better in the binder than HDPE. In another study, Ho et al. [7] combined PE Wax with LDPE/HDPE/recycled PE to improve the binder-PE compatibility. Their results revealed that a very low molecular weight (M_w) PE with wide molecular weight distribution (MWD) and high melt flow index (MFI) has less tendency to separate from asphalt binder [9].

The addition of PE reduces the amount of asphalt binder used and improves the high temperature performance properties of asphalt binder/mix [3, 4, 16, 19, 20]. The major challenge with PE modified asphalt is the phase separation/storage

stability. When PE is blended with the binder, they tend to separate, because PE is a nonpolar and nonaromatic polymer. This low compatibility between PE and binder leads to storage stability issues. In addition, the reason for the low compatibility could be the differences in molecular structure, density, molecular weight, and viscosity of the polymer and bitumen components. Hence, by controlling these parameters, the phase separation can be reduced.

This study evaluates the efficacy of using locally produced PE polymer as a modifier for asphalt binders. This aim is achieved by analyzing the dispersion of the polymer domains in the LDPE modified binders and improving the compatibility between the LDPE and binder with the addition of PE wax. Therefore, the study focuses on the following tasks:

- Analyzing the thermal properties of polymer-binder blends.
- Analyzing the dispersion of polymer in the polymer-binder blends and investigating the phase stability after mixing.
- Identifying the instability of PMB from the viscosity-temperature profiles.
- Analyzing the impact of the polymer type and addition level on the steady and dynamic rheological properties of the polymer-binder blends.
- Determining the grade of polymer blended binders based on the high, intermediate and low temperature performance characteristics.

2 Materials and methods

2.1 Materials

A base binder of pen 60-70 grade was used in this study. Two different LDPE samples and one PE wax sample were supplied by Qatar Petrochemicals Company (QAPCO) and used as a modifier to the asphalt binder. PE wax is a very low molecular weight by-product of the LDPE polymerization process (molecular weight: 6000). The two LDPE materials have different properties: LDPE4 has low MFI of 4g/10 min, LDPE70 has high MFI of 70 g/10 min.

2.2 Blend processing

The blends were produced by adding the polymer to asphalt binder at different concentrations ranging from 1–5 wt.%. The blend is designated as x% LDPE y, where x is the polymer concentration in the blend and y is the polymer MFI. Blends containing both LDPE and PE wax are designated as x% LDPE y+ z% wax, where z is the weight percentage of the PE wax in the blend. The polymer-binder designations are 1% LDPE4, 2% LDPE4, 3% LDPE4, 4% LDPE4, 5% LDPE4, 3% LDPE70, 5% LDPE70, 3% PE wax, 2% LDPE4+1% wax, 4% LDPE70+1% wax. The blending procedure was as follows: (1) the binder was preheated at 180 °C for 1 h, (2) the polymer (LDPE pellets and/or PE wax) were added to the binder and kept the blend in an oven at 180 °C for 30 min, and (3) the polymer-binder blend was mixed using a shear mixer operating at 2000 rpm, 180 °C for 1 h.

2.3 Thermal properties of polymer and polymer–binder blends

Thermogravimetric Analyzer (TGA) was used to determine the thermal stability of the PE-asphalt blends. This test was carried out using Perkin Elmer's Pyris 6 instrument by heating 15 mg of the sample from 30 to 550 °C at a rate of 10 °C/min under N_2 . Then, the percentage of mass loss was determined as a function of temperature. The decomposition temperatures corresponding to 5% mass loss ($T_{0.05}$) were 356, 368, 360, 375 °C for Pen 60-70, 3% LDPE4, 3% PE wax and 2% LDPE4+1% PE wax, respectively. LDPE modification enhanced the thermal properties of the blend. The TGA experiment was not carried out on LDPE70 blends because the decomposition temperatures of LDPE4 blends were substantially higher than that of its use temperature. Hence, the Differential Scanning Calorimetry (DSC) tests were carried out to characterize the thermal behavior of the polymer-modified blends.

The thermograms of polymers, polymer modified binders were collected using Perkin Elmer's Jade DSC machine. Then, the thermo-mechanical properties (melting point temperature (T_m), and heat of fusion (ΔH_f)) were determined as shown in Table 1. The melting point and heat of fusion of LDPE+binder was lower than that of the corresponding LDPE polymer. The reduction in ΔH_f could be due to the disruption of

the crystalline structure caused by the swelling of polymers [24]; thus, smaller crystallites result in the lower melting point of polymer modified binder.

2.4 Microstructural and rheological characterization of polymer-binder blends

2.4.1 Optical microscopy

The optical microscope images of all the binders were captured by preparing the samples on a microscope glass slide using the heat and cast approach [25, 26]. Then the samples were cooled at room temperature and imaged at 30, 60, 90, and 150 min post-blending. The optical images were captured using Zeiss AxiVert 40 MAT fitted with ERc5s camera. The size of each image was 2560×1920 pixels (1083 μm × 809 μm). To check the uniformity in polymer dispersion, minimum five images were captured for each binder.

2.4.2 Steady-shear (rotational) rheology

The steady shear viscosity of the base binder and PE asphalt binders was measured at different temperatures using Brookfield rotational viscometer utilizing SC 4-27 spindle. About 10.5 grams of asphalt binder sample were poured in the rotational viscometer containers. To analyze the stability of PE-blended binders and the state of phase separation, the viscosity hysteresis of the binders was measured during temperature decrement and increment. In this test, PE-blended binders were sheared at 20 rpm and the viscosity was measured at 160, 145, 130, 115, 100, 100, 115, 130, 145 and 160 °C. The binder blends were sheared for 15 min at each temperature. Out of the total 15 min, the first 5 min were considered as pre-shearing time and the last 10 min were the actual testing time as shown in Fig. 1a. The experimental data capture of time, temperature, and viscosity of 3% LDPE4 binder are presented in Fig. 1b. In this last 10 min, the viscosity at 6th, 7th, and 8th min were averaged and reported.

2.4.3 Dynamic rheology

Dynamic rheological experiments were conducted using dynamic shear rheometer (DSR) for the selected polymer blends. The viscoelastic properties of PE-binder blends were determined using the frequency

Table 1 Melting point and heat of fusion values obtained from DSC data

Material	Peak melting point (°C)	ΔH_f (J/g)
<i>Plain binder</i>		
Pen 60-70	72.3	0.04
<i>Plain polymer</i>		
LDPE4	119.3	65.3
LDPE70	111.8	44.8
PE wax	102.1	1.43
<i>LDPE+binder</i>		
5% LDPE4	103.8	5.3
5% LDPE70	94.4	4
<i>LDPE+ PE wax+ binder</i>		
2% LDPE4+1% wax	100.1	1.8
4% LDPE70+1% wax	94.1	4.2
3% wax	81.8	0.17

sweep test. While the rutting resistance of blends were evaluated using the multiple stress creep and recovery (MSCR) test [27], the fatigue failure cycles were determined using the linear amplitude sweep (LAS) test [28]. Finally, the PE-binder blends were graded based on their high and low-temperature performance characteristics [29]. The repeatability of each test was checked by conducting at least two trials, and the percentage difference between the two trials was less than 5% from the mean.

2.4.3.1 Frequency sweep test In this test, the unaged PE-binder blends were oscillated at a frequency range of 15–1 Hz (rate: 1 Hz/s), at different temperatures in the range of 25–65 °C (increment interval: 10 °C). At each temperature, the ratio of peak stress to strain and the time lag between stress–strain curves were used to calculate the dynamic modulus (IG^*) and phase angle (δ), respectively. The temperature isotherms were shifted individually to a reference temperature and constructed master curves.

2.4.3.2 Multiple stress creep and recovery (MSCR) test [27] To compare the rutting behavior of all short-term aged (RTFO) binders, the MSCR test was carried out at a single temperature of 64 °C. In this test, two stress levels of 0.1 and 3.2 kPa were applied [27]. The binders were subjected to 10 creep loading and recovery cycles at each stress level; the loading time is 1 s and recovery is 9 s. For each cycle, the non-

recoverable creep compliance (J_{nr}) was measured and their average for each stress level was reported.

2.4.3.3 Linear amplitude strain sweep test (LAS) [28] Using this test, the fatigue response of all long-term (PAV) aged binders was determined at a single temperature of 25 °C. In this test method, first, the frequency sweep was conducted to determine the linear viscoelastic parameters. In continuation, the linear strain amplitude sweep test was conducted to determine the damage parameter. The test parameters were selected as prescribed in AASHTO TP 101 [28]. In LAS test, the strain increased linearly from 0 to 30% in 31000 cycles (3100 s). The peak shear stress and strain values were captured at each second.

2.4.3.4 Performance grading (PG) [29, 30] The PG high temperature grading was determined by testing unaged and RTFO (short-term) aged binders as per ASTM D6373 [29], started from 52 °C with an increment of 6 °C until the failure criterion ($G^*/\sin \delta \leq 1$ kPa for unaged or ≤ 2.2 kPa for RTFO aged binders) is reached. The strain levels used for unaged and RTFO (short-term aged) samples were 12% and 10%, respectively. The PAV (long-term) aged binder was used to determine the PG intermediate temperature by conducting the tests from 31 °C with a decreased interval of 3 °C until the failure criterion is reached ($G^* \times \sin \delta \geq 5000$ kPa). The selected strain level for PAV aged sample was 1%.

(a) Test protocol

(b) Time, temperature, and viscosity of 3% LDPE4 blend

Fig. 1 Temperature sweep test protocol and experimental data

To determine the PG low temperature, bending beam rheometer (BBR) was used. The temperature corresponding to a creep stiffness of ≤ 300 MPa and m-value of ≥ 0.3 were used to assign the PG low

temperature grade. In addition, as per AASHTO M332 [30], the traffic grade was assigned based on the non-recoverable creep compliance value at PG high temperature obtained from the MSCR test.

3 Results and discussion

3.1 Optical microscopy- polymer distribution analysis

The optical micrographs of unmodified binder, LDPE4, LDPE70 and PE wax blends were captured after 30, 60, 90, and 150 min of blending as shown in Figs. 2 and 3. The PE domains started agglomerating within 30 min of blending and the particle size increased over a period of time (60, 90 and 150 min). As the dosage of LDPE4 increased in the blend, the PE material formed large particles (Fig. 2) whereas the addition of LDPE 70 did not significantly increase the particle size (Fig. 3a–h). The images of 3% PE wax blended binder are similar to the base Pen 60-70 binder (Fig. 2a). When the PE wax was introduced to LDPE4 blend, the dispersion of the polymer improved in the binder (Fig. 3i–l). In the case of LDPE70, the addition of PE wax did not actually improve the polymer dispersion, and the polymer agglomeration was observed (Fig. 3m–p). At least five images were captured for each blend. The percentage of polymer particle size distribution was analyzed using Imagej and Avizo software.

In this study, the optical microscope images were thresholded to identify the LDPE polymer domains in the asphalt binder. The distinguish between PE domain, and asphalt binder was not only noticed with an optical microscope, but it was also able to identify with Atomic Force Microscope (AFM) analysis, and the images were presented in a recent study conducted by Aljarrah and Masad [25]. From the optical microscope images, the equivalent diameter of LDPE domains was determined and the percentage of polymer particle size distribution was measured through the pixel count. The volume-weighted average diameter (D_v) is calculated using the following Eq. 1.

$$D_v = W_{vi} D_i = \frac{D_i^4}{\sum_i D_i^3} \quad (1)$$

where $W_{(v,i)}$ is the volume fraction of PE domain with diameter D_i , $W_{(v,i)} = \frac{v_i}{\sum_i v_i} = \frac{D_i^3}{\sum_i D_i^3}$.

As the dosage (addition level) of LDPE4 increased in the blend, the PE material agglomerated and formed large domains (Fig. 4a) whereas the addition of

LDPE70 did not significantly change the PE domain size (Fig. 4b). As shown in Fig. 4, the polymer agglomeration depends on LDPE's dosage, the melt flow properties of LDPE, and the time duration. This polymer size increased over a period of time, and the shift in the range of polymer size from 30 to 90 min was 120 μm to 173 μm for 3% LDPE4 and 256 μm to 292 μm for 5% LDPE4 blend (Fig. 4a). This increase in size of polymer domain size represents the phase separation of LDPE4 and asphalt binder materials [31]. In the case of LDPE70 (Fig. 4b), the polymer domain size was not significantly changed with the polymer dosage, and the average PE domain sizes were between 27–34 μm at 30 min, 48–52 μm at 90 min. This better stability of LDPE70-blend is due to the high MFI of LDPE70. The excellent mobility and flow properties of LDPE70 is because of the shorter molecular chains and lower entanglement density in the melt state compared to LDPE4. This observation agrees with the previous reports that indicated the addition of polymers with a high MFI and low molecular weight could increase the polymer dispersion in the binder [7, 11].

To reduce the phase separation and make the polymer and binder more compatible, PE wax was introduced to the blend. With the addition of $\geq 3\%$ LDPE4 dosage, the polymer agglomeration increased rapidly with time and hence, the total polymer content was limited to 3% for LDPE4 blends with PE wax. In the case of LDPE70 blends, the total polymer content was limited to 5% (with or without PE wax), because the polymer agglomeration was not significant up to 5% dosage.

When 1% of PE wax was introduced to 2% LDPE4 blend, the dispersion of the polymer in the binder improved, as shown in Fig. 4a. For the 3% LDPE4 blend, the diameter of the polymer domains was $\approx 120 \mu\text{m}$ after 30 min and reduced to 59 μm after adding 1% PE wax to the blend. A similar finding was reported in the work conducted by Ho et al. [7]. In case of LDPE70, the addition of wax obstructed the uniform dispersion of LDPE70. The polymer diameter of 4%LDPE70+1%PE wax was higher than that of the 5%LDPE70 blend (Fig. 4b). This could be due to the inherent flow properties of the high MFI LDPE70.

(a) pen 60-70 base binder

(b) 1% LDPE4, 30 min

(c) 1% LDPE4, 60 min

(d) 1% LDPE4, 90 min

(e) 1% LDPE4, 150 min

(f) 2% LDPE4, 30 min

(g) 2% LDPE4, 60 min

(h) 2% LDPE4, 90 min

(i) 2% LDPE4, 150 min

(j) 3% LDPE4, 30 min

(k) 3% LDPE4, 60 min

(l) 3% LDPE4, 90 min

(m) 3% LDPE4, 150 min

(n) 4% LDPE4, 30 min

(o) 4% LDPE4, 60 min

(p) 4% LDPE4, 90 min

(q) 4% LDPE4, 150 min

(r) 5% LDPE4, 30 min

(s) 5% LDPE4, 60 min

(t) 5% LDPE4, 90 min

(u) 5% LDPE4, 150 min

◀ **Fig. 2** Optical images of base binder & LDPE4- binder composites as a function of dosage and storage time

Fig. 3 Optical microscopy images of LDPE70 blends, LDPE4+PE wax, LDPE70+PE wax blended binder samples

Fig. 4 Volume-weighted average polymer diameter (PE4—LDPE4; PE70—LDPE70; PE4/W (2/1)—2%LDPE4+1%wax; PE70/W (4/1)—4%LDPE70+1%wax)

Fig. 5 Viscosity of PE blended binders

3.2 Viscosity-temperature profile

Figure 5 shows the average viscosity of LDPE4 and LDPE70 blends. This test was not conducted for 5% LDPE4 binder because it was too viscous, and the

torque value exceeded the allowable limit of 90% at 100 $^{\circ}\text{C}$ with the same spindle speed of 20 rpm. For each blend, two viscosity curves can be seen in Fig. 5. The lower viscosity curve was obtained during temperature decrement (160–100 $^{\circ}\text{C}$), and the upper curve was captured during temperature increment (100 to 160 $^{\circ}\text{C}$). As the LDPE dosage increased, a significant difference in the viscosity values was identified during the temperature decrement and increment. The area between these two curves and the normalized area values are plotted in Fig. 6.

As shown in Fig. 6, the area between the viscosity curves increased with the LDPE4 dosage. The 4% LDPE4 binder area was 3.4 times higher than that of the base Pen 60-70 binder. It is worth noticing that the high viscous flow activation energy and non-newtonian behaviour of the polymer in the binder blend. The binder blend system might undergo some structural changes as a function of temperature, and hence the area under the viscosity-temperature hysteresis loop curve increases with the increase of polymer content in the binder blend. This phenomenon depends on polymer type, molecular weight (M_w) and molecular weight distribution (MWD). The 3 and 5% LDPE70 blends' area did not significantly vary due to the higher MFI of LDPE70.

The addition of PE wax reduced the viscosity of LDPE4/70 blends. The viscosity hysteresis area of the 3% LDPE4 blend was 2.6 times the area of the Pen 60-70 binder, while the area of the 2% LDPE4+1% PE wax was only 1.5 times that of the Pen 60-70 binder. The large hysteresis area represents the instability of the blends with higher percentages of LDPE4. In addition, the improved stability of LDPE4 blend with

Fig. 6 Area under viscosity hysteresis curves

the addition of PE wax is confirmed by the lower hysteresis area.

The high-temperature behavior of the LDPE70 blend (with or without PE wax) was not significantly influenced by the polymer dosage. From Fig. 6, the area of the viscosity hysteresis increased gradually with LDPE content up to 3% LDPE4 content; after that, a rapid increment was observed. The addition of LDPE70 did not significantly change the viscosity hysteresis area with dosage. Hence, we limited the dosage of LDPE4 to 3% with PE wax and LDPE70 to 5% (with or without PE wax). For further study, Pen 60-70, 3% LDPE4, 5% LDPE4, 3% LDPE70, 5% LDPE70, 2% LDPE4+1% PE wax, 4% LDPE4+1%PE wax and 3% PE wax binders are analyzed.

3.3 Frequency sweep test—dynamic modulus

At each temperature of 25, 35, 45, 55, and 65 °C, the storage (G') and loss modulus (G'') values were recorded, and the dynamic modulus ($|G^*|$) and the

phase angle (δ) were calculated. The dynamic modulus curves were shifted to a reference temperature of 35 °C using RHEA software [32] as shown Fig. 7. From Fig. 7a, the Pen 60-70 base binder has the lowest dynamic modulus and the modulus of 3% PE wax and 2% LDPE4+ 1% PE wax seem to be identical.

The addition of a low molecular weight PE wax softens the binder blend, which lowers the dynamic modulus. Above 3% LDPE4 dosage, there is no change in the dynamic modulus of LDPE4 blends. In the case of LDPE70 blends (Fig. 7b), the 3% LDPE70 has the lower dynamic modulus values than the 3% PE wax blend at lower frequencies and the modulus of 5% LDPE70 and 4% LDPE70+1% PE wax blends were approximately the same. As the ΔH_f of these blends is very close, the crystalline structures form physical cross-links in the amorphous phase, thus increases the storage modulus and both the loss modulus and phase angle decreases.

In Fig. 7, for constructing master curves at a reference temperature of 35 °C, the temperature dependent shift factors were determined using WLF Eq. 2 [33].

Fig. 7 Master curves of dynamic modulus at 35 °C versus frequency calculated using TTS of data measured at 25 °C (pentagon), 35 °C (star), 45 °C (triangle), 55 °C (circle), and 65 °C (square), shift factors in subplots

$$\log a_T = \frac{C_1(T - T_0)}{C_2 + (T - T_0)} \quad (2)$$

where a_T is the shift factor; T is the temperature in °C; T_0 is the reference temperature; C_1 and C_2 are constants. First, the temperature isotherms were

shifted to a known reference temperature and the horizontal shift factors were determined using the time–temperature superposition principle (TTSP). Then, the material constants C_1 and C_2 were determined by fitting shift factors against temperatures.

Using these constants, the master curve can be constructed at any reference temperature, and the temperature-dependent shift factors are presented in inset plots of Fig. 7. The LDPE blended binders have the least slope of shift factors. Based on the slope of the shift factors, 3% PE wax binder has more temperature susceptibility whereas the addition of LDPE4 and LDPE70 reduced the temperature susceptibility of the binders.

3.4 Multiple stress creep and recovery Test

Figure 8a, b show the strain response during the creep and recovery cycles of LDPE4 and LDPE70 blends at 64 °C. Out of all binders, the unmodified binder has higher strain values. With the addition of higher dosage of LDPE4 and LDPE70, the total strain was reduced. In Fig. 8b, the identical strain response of 3% PE wax and 3% LDPE70, 4% LDPE70+1% PE wax and 5% LDPE70 was seen.

The non-recoverable creep compliance (J_{nr}) values were calculated for PE-binder blends by following the equations given in ASTM D7405 [27] and the obtained values are presented in Fig. 9. The results indicate that the J_{nr} values decreased with increase in the dosage of LDPE 4 and LDPE70. The inclusion of polymeric chains in the asphalt binder restricts the deformation and is in proportion to the molecular weight of polymers. High molecular weight LDPE4 restricts the deformation more when compared to low molecular weight LDPE70 polymer. When compared LDPE4 and LDPE70 binders in the inset plot (Fig. 9), the J_{nr} values of 3% and 5% LDPE70 binders were slightly higher than 3% and 5% LDPE4 binders. However, the difference was not as significant as the J_{nr} values of all four samples were less than 1.5 kPa^{-1} . As per AASHTO M332 [30], at 64 °C, the traffic grade of 5% LDPE4 was 'E' which represents extremely heavy traffic and the remaining three binders (3% LDPE4/70, 5% LDPE70) have 'V' grade that represents very heavy traffic.

3.5 Linear strain amplitude sweep test

For determining the fatigue life of binders, the slope of storage modulus was determined from the frequency sweep test, and the damage accumulation was calculated from the linear strain amplitude sweep test data.

Figure 10 shows the applied shear stress and the calculated dynamic modulus values plotted against the increased strain amplitude (0–30%). In Fig. 10a, the stress increased up to a specific strain value, thereafter a sudden drop was seen, whereas the dynamic modulus values gradually decreased (Fig. 10b). The fatigue failure point was defined as the cycle corresponding to the 1. peak shear stress (or) 2. 50% reduction in the dynamic modulus values whichever occurs first.

From Fig. 10a, 5%LDPE4 sample was able to take more oscillatory load, and at the same time, a sudden drop in the stress values was observed from the peak point. Though the dynamic modulus of LDPE70 blends was lower than LDPE4 blends, the rate of reduction in the oscillatory stress was slow for LDPE70 blends.

As described in AASHTO TP101 [28], the LAS test data were analyzed using the Viscoelastic Continuum Damage Theory (VECD) [34]. The damage accumulation of the PE-binder blends was calculated using Eq. 3.

$$D(t) \cong \sum_{i=1}^N [\pi \gamma_o^2 (C_{i-1} - C_i)]^{\frac{\alpha}{1+\alpha}} (t_i - t_{i-1})^{\frac{1}{1+\alpha}} \quad (3)$$

where t is time in seconds. γ_o is applied strain (%). $C(t) = \frac{|G^*(t)|}{|G^*|_{\text{initial}}}$. α is inverse slope of the storage modulus. The damage at failure point (D_f) was calculated from the $C(t)$ at peak shear stress (or) at 50% reduction in dynamic modulus, whichever occurs first. The equation used to calculate the fatigue life N_f was $N_f = A(\gamma_{\text{max}})^{-B}$, where $A = \frac{f D_f^k}{k(\pi C_1 C_2)^\alpha}$, $B = 2\alpha$ and γ_{max} is the binder strain (2.5, 5%).

Figure 11 shows the fatigue life determined at the strain levels of 2.5 and 5%. The fatigue performance of LDPE70 blends was better than the LDPE4 blends. High molecular weight and densely packed molecules in LDPE4 decrease the mobility of the polymer chains during fatigue loading, leading to brittle failure. On the contrary, LDPE70 with low molecular weight has increased chain mobility, leading to experience shear yield and ductile failure. This type of failure phenomenon favors the low M_w LDPE for improved fatigue life compared to high M_w LDPE. With an increased dosage of LDPE70, the ductile-brittle transition occurs at an early stage, and hence 5%LDPE70 binder blend shows less fatigue life than 3%LDPE70. The 3% LDPE70 blend has greater fatigue life than the

(a) LDPE4 blends

(b) LDPE70 blends

Fig. 8 Strain response during creep and recovery cycles at 64 °C

remaining binders. A similar low temperature performance was confirmed for the 3% LDPE70 blend by the performance grading test discussed in the following section.

3.6 Performance grading-temperature sweep test

The critical PG high temperatures were determined based on the $G^*/\sin\delta$ value of 1 kPa for unaged binders and 2.2 kPa for RTFO aged binders. The

binders have PG continuous temperature in the range of 67–74.9 °C for unaged binders, and 66.7–75.6 °C for RTFO aged binders (Table 2). However, for Pen 60-70 and 3% wax blend, the continuous temperatures were less than 70 °C and these binders were graded as PG64 and all the remaining binders were graded as PG70. The PG intermediate continuous temperature was in the range of 23.9–30.2 °C ($G^*/\sin\delta$ is 5000 kPa).

Fig. 9 Non-recoverable creep compliance (J_{nr}) at 64 °C

Fig. 10 Stress, strain and dynamic modulus values in LAS test

The BBR failure temperature for Pen 60-70 and 3% LDPE70 binders were -12°C (temperature corresponding to stiffness ≤ 300 MPa, slope ≥ 0.3) and

their PG low-temperature grade was -22°C . All the remaining LDPE blends have a PG low temperature of -16°C (BBR failure temperature is -6°C). Based on the non-recoverable creep compliance (J_{nr}) value, the standard traffic grade 'S' was assigned because all the binders have (J_{nr}) values greater than 2 kPa^{-1} at their PG high-temperature. Out of all the binders, the 3% LDPE70 content has improved both the high and low-temperature performance characteristics (PG 70S-22), and its low-temperature PG grade was the same as that of the Pen 60-70 base binder.

4 Conclusions

In this study, polyethylene (PE) modified binders were prepared with various wt% compositions of LDPE polymers. PE wax was also added in certain wt% to improve the polymer dispersion and to reduce the agglomeration. The interaction between the LDPE chains and the asphalt binder was analyzed using thermal stability, microscopic, rheological, and mechanical tests. Based on the polymer particle size analysis and viscosity profiles, selected dosages of LDPE4 and LDPE70 were used for the rheological and mechanical testing. Based on the obtained results, the following conclusions are drawn:

- From thermo-mechanical properties, the blends containing LDPE4 have a higher melting point and heat of fusion than LDPE70 blends. The addition of PE wax to the LDPE blends significantly influenced the enthalpy, which could negatively

Fig. 11 No. of fatigue failure cycles of LDPE blends

impact the low-temperature properties of the blend containing PE wax.

- The polymer dispersity in the binder was highly dependent on the dosage level of the polymer and storage time. In the case of LDPE4, the polymer content was limited to 3%, above which a large size polymer agglomerates were observed. The addition of a higher dosage of LDPE70 (5%) did not significantly influence the polymer particle (domain) size distribution.
- The addition of PE wax to the LDPE4 blend improved the polymer dispersity but did not improve the dispersity of the LDPE70 polymer due to the inherent flow properties of the high MFI LDPE70 polymer.

- The area of the viscosity hysteresis curves increased gradually with LDPE4 loading up to 3%, thereafter a rapid increase was observed. The addition of higher dosages of LDPE70 (3-5%) did not significantly change the area of viscosity hysteresis. Hence, the dosage of LDPE4 was limited to 3% (with PE wax) and LDPE70 to 5% (with or without PE wax).
- The LDPE4 blends with greater than 3% dosage have similar dynamic modulus values. The stiffness of LDPE70 blend was lower than that of the PE wax blend. From the slope of the shift factors versus temperature, the LDPE blended binders have lower temperature susceptibility than the base binder.

Table 2 Performance grade of different binders

Parameter	Pen 60-70	3% Wax	2%LDPE4+ 1% wax	3%LDPE4	5% LDPE4	3% LDPE70	4% LDPE70+ 1% wax	5% LDPE70
PG HCT (unaged)	67	68	70.9	72.4	74.1	70.9	73.2	74.9
PG HCT (RTFO)	66.7	68.6	71.1	73.60	75.6	71.6	72.4	73.1
PG high grade	64	64	70	70	70	70	70	70
PG ICT (PAV)	23.9	25.2	27.4	27.4	30.1	27.6	29.8	30.2
PG intermediate grade	25	28	28	28	31	28	31	31
BBR failure temp.	−12	−6	−6	−6	−6	−12	−6	−6
PG low grade	−22	−16	−16	−16	−16	−22	−16	−16
J_{nr} at PG high	3.188	2.307	4.581	3.37	2.257	3.94	3.26	3.07
PG grade	64S-22	64S-16	70S-16	70S-16	70S-16	70S-22	70S-16	70S-16

*HCT- high critical temperature, ICT- intermediate critical temperature

- From the MSCR results, the non-recoverable creep compliance decreased with the increase in the dosage of LDPE. However, all the binders' traffic grade was "S" (standard traffic) at their PG high temperatures. At a constant temperature of 64° C, 5% LDPE4 has better rut resistance.
- In the LAS test, though the LDPE4 blends could take more oscillatory loading, they failed early at fewer cycles than the LDPE70 blends. The addition of PE wax deteriorated the fatigue life of the LDPE blends. The fatigue performance of the 3% LDPE70 blend was better than all the remaining binders.
- Among all blend formulation, the 3% LDPE70 blend has improved both the high and low-temperature performance characteristics (PG 70S-22), and its low temperature PG grade was the same as the Pen 60-70 base binder.

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Declarations

Conflicts of interest The authors declare that there is no conflict of interest.

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