Polyethylene Dispersions in Bitumen: The Effects of the Polymer Structural Parameters

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ABSTRACT: Polymer-modified bitumens are very important to the transportation sector. Polyethylene is one of the most used polymers in bitumen modification. The effects of the structural parameters of polyethylene on its dispersion in bitumen and the performance of the resulting polymer-modified bitumens were studied. With the addition of different polyethylenes to bitumen, the performance of bitumen at high temperatures increased as the polymer melt-flow index (MFI) decreased. At low temperatures, the performance of bitumen decreased as the polyethylene MFI decreased. Furthermore, a decrease in the polyethylene MFI intensified its dispersion instability. At very low MFIs, the dispersions were unstable, even under the very high shear forces applied by a double mixer. Moreover, changes in the polyethylene MFI did not improve the dispersion stability at an elevated temperature (165°C). © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 3183–3190, 2003

Key words: polyethylene (PE); melt; dispersions

INTRODUCTION

The tailoring of polymers to bitumen and the use of polymer-modified bitumens (PMBs) are routine in some countries, and PMBs have attained worldwide popularity in the paving and roofing industries.[1–28] However, mixing materials with extremely different viscosities at high temperatures is not an easy task, and special mixers are needed.[21,24,29] The roles of the polymer structure and rheological properties are of primary importance. Using conventional mixers at very high speeds is not fruitful, and the necessarily long mixing times induce disastrous structural changes in bitumen.[22,24] This is mainly due to the very large difference in the viscosities of the polymer and bitumen at high temperatures, which inhibits polymer particle breakup under shear. However, in large scales, using these types of mixers is out of question. The proper mixer for large scales is a colloidal mill, in which polymer granolas and bitumen are passed through very small clearances and gaps at high temperatures (160–200°C). In PMB plants, polymer granolas are suspended in bitumen with a conventional low-speed mixer, and then the resulting suspension is sucked into the colloidal mill. Under the action of centrifugal force from the mill, the polymer is forced to pass through very small gaps between the mill's rotor and stator. This disintegrates the polymer granolas and reduces the polymer particle size in the bitumen medium to micrometer and submicrometer scales. In a laboratory, this can be accomplished with very high shear homogenizers (disintegrators). Even with these mixers, dispersing some polymers in bitumen is not possible. Among the different polymers used in bitumen modification are polyolefins such as polyethylenes [PEs; low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), and high-density polyethylene (HDPE)],[6,21–27] polypropylenes (isotactic and atactic), and their copolymers.[17,28] The three major groups of PEs have frequently been used in bitumen modification without any attention being paid to controlling polymer structural factors governing their behavior in bitumen and the performance of the resulting PMBs. Thermoplastic polymers are usually characterized by their melt-flow index (MFI). This index portrays the architecture of the polymer molecular structure. Therefore, it is expected that this property could be used as a criterion for the selection of a thermoplastic polymer for bitumen modification.

In this article, we highlight the existing correlation between a polymer's MFI, its ability to be dispersed in bitumen, and the PMB performance.

EXPERIMENTAL

Materials

Two LDPE grades, one LLDPE grade, and six HDPE grades, all from Iranian petrochemical companies, were used. The HDPEs, along with available informa-

TABLE I
Available Physical Properties of PEs[30]

PE type	Grade	Manufacturer	MFI[a]	Crystallinity (%)[b]	Density (g/cm^3)
LDPE	LF0450	BIPC	4.5	47.6	0.92
	LF200	BIPC	2	?	0.92
LLDPE	LL209	Arak PC	0.9	48	0.92
HDPE	HD5620	Arak PC	20	?	0.955
	HD13	Arak PC	7.2	71	
	HD3840	Arak PC	4	52.5	0.938
	HD3848	Arak PC	2.8	64	
	HBX35	BIPC	0.34	66	
	EX3	Arak PC	0.15	61	0.944
	HRB	Recycled	9.9	—	
	HRM	Recycled	0.89	—	

BIPC = Bandar Imam Petrochemical Co.
[a] 190°C/2.16kg; g/10 min.
[b] XRD method.

tion, are described in Table I. Two recycled HDPEs were also used (Table I).

Bitumen (60/70 penetration grade) from Tehran's refinery was purchased, and all modifications were carried out on it. Some available information on this bitumen is reported in Tables II and III.[31]

Procedures

The polymers were mixed with bitumen at 170°C with a Polytron 6000 (Kinematika Co., Littau/Luzerne, Switzerland) equipped with a PD-TA3030 as a disintegrating head. Because this mixer was not able to disperse high-viscosity PEs in bitumen, a propeller-type mixer was added to the mixer set (Fig. 1). Because of the action of the high-shear mixer, the temperature increased up to 180°C during a 30-min period of mixing. At the end of the mixing, the mixture was transferred into metallic cans via a drain valve. The metallic cans were put in a cold-water container during the transfer period and remained in it until the PMBs cooled to room temperature. Stability and optical microscopy samples were taken during the transfer period. The percentages of the polymer added to bitumen were fixed at 3 and 5 wt %. To avoid any emulsification effect, no stabilizing agent was added to the PMBs.

Morphological analysis

A 5–10-mg sample of bitumen was heated and slowly pressed between glass slides, and then micrographs

TABLE II
Tehran's Refinery 60/70 Penetration-Grade Bitumen Properties

Penetration at 25°C (0.1 mm)	Softening point (°C)	Frass breaking point (°C)	PI	PG
39	54	−8	−0.625	70-16

TABLE III
Tehran's Refinery 60/70 Penetration-Grade Bitumen Composition[30]

Saturates (%)	Naphthene aromatics	Polar aromatics (%)	Asphaltenes (%)
15.83	39.58	35.43	10.26

(with a Zeiss FX Jenapol optical microscope, Germany) were taken with a camera.

Emulsion stability analysis

After the mixing period, part of the prepared mixture was transferred into glass test tubes (15 cm × 1 cm). The tubes were immediately covered and put in an air-circulating oven at 165 ± 5°C for 48 h. The tubes were then taken from the oven, ice-cooled to room temperature, and stored in a freezer. After 24 h, the bottoms of the tubes were broken. The samples of the upper and lower parts were then viewed with the Zeiss FX Jenapol optical microscope.

Penetration tests

The penetration tests were carried out at 25°C according to ASTM D 5-73. Bitumen was thermostated in a water bath, and the penetration of a standard needle under a total standard load (100 g) was measured and reported in tenths of millimeters.

Ring-and-ball test (softening-point temperature)

The softening points (ring-and-ball test) of different straight and modified bitumens were measured according to ASTM D 36-76. In this test, two disks of bitumen were cast into shouldered rings, and then the disks were trimmed for the removal of excess bitumen. In the next step, the disks were heated at a constant rate (5°C/min) in a water bath with a special apparatus.

Frass test

Frass breaking-point tests were performed according to the IP-80 standard. A sample of 0.40 ± 0.01 g of bitumen was weighed on a flat standard steel plaque. The plaque and bitumen were gently heated to form a uniform film of bitumen on the plaque. Then, the plaque was put on a flat and horizontal surface to ensure the uniformity of the bitumen film, and it was covered with a watch glass. The tests were carried out with the apparatus mentioned in IP-80. The Frass breaking point was defined as the temperature at which a break or a crack appeared on a thin layer of asphalt coating the steel plaque. The plaque was sub-
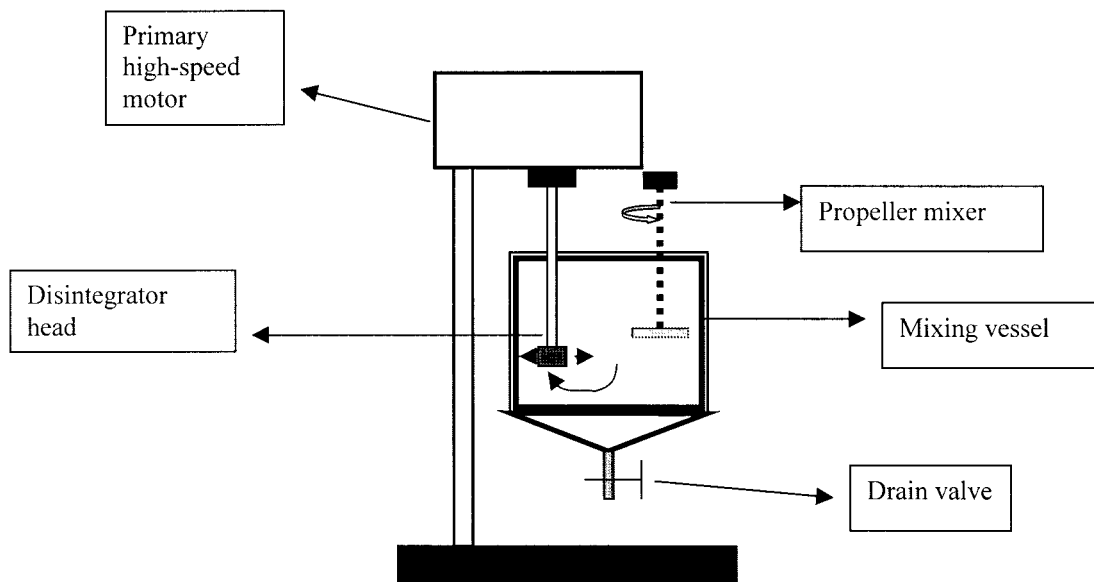
Figure 1 High-speed and high-shear double-mixer set.

jected to successive flexions under determined cooling conditions.

Rheological measurements

Rheological measurements were performed on a Rheometric Scientific ARES constant-strain rheometer (New Jersey) in the linear viscoelastic zone of the polymers at 180°C.

Penetration index (PI)

PI is a measure of the temperature susceptibility of bitumen. For all bitumens, PI is calculated as follows:[32]

$$PI = \frac{20 - 500A}{1 + 50A}$$

$$A = \frac{\log 800 - \log(\text{Pen at } 25°C)}{T_{R\&B} - 25}$$

PI is the slope of changes in the bitumen consistency curve,[32] Pen is penetration, and $T_{R\&B}$ is softening point temperature. The consistency of changes in bitumen depends on the sign and magnitude of PI. For paving-grade asphalt, a PI value of approximately 1 is ideal for the temperature susceptibility of bitumen.

Performance-grade (PG) estimation

In the past, an empirical correlation was found between the Strategic Highway Research Program high-temperature criterion for performance obtained by dynamic shear rheometry (T_{DSR}) and the softening point of bitumen.[25] This can be expressed as the first of the following equations:
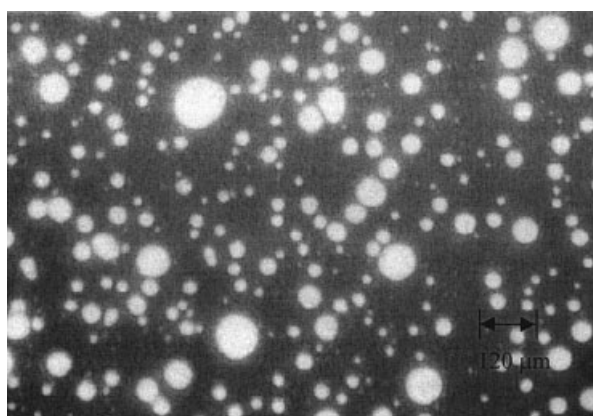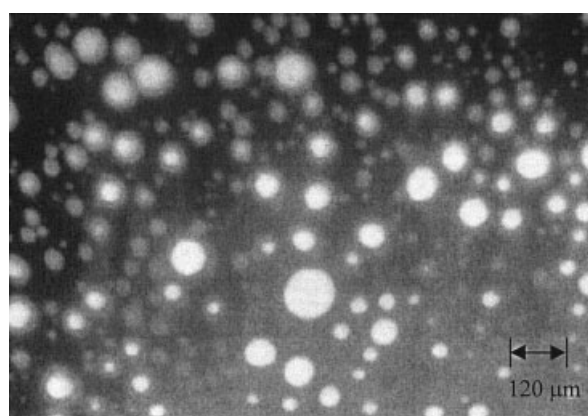

Figure 2 State of dispersion of 5% LF0450 in bitumen.
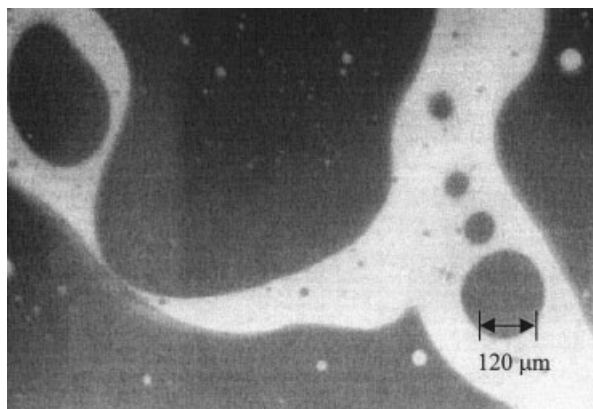

Figure 3 State of dispersion of 5% LF200 in bitumen.

Figure 4 State of dispersion of 5% LL209 in bitumen.

$$T_{DSR} \cong T_{R\&B} + 20$$

$$T_{BBR} \cong 2(T_{Frass})$$

$$PG = T_{DSR} + T_{BBR}$$

Another idea concerns finding a correlation between the low-temperature criterion for performance of the Strategic Highway Research Program system (T_{BBR}) and the Frass breaking point (T_{Frass}). Some experimental data were already accessible,[22] and so the second of these equations was proposed.[33,34] Using these equations, we were able to roughly estimate the PG of bitumen with conventional tests.

RESULTS AND DISCUSSION

Morphology

The state of dispersion of LDPEs in bitumen is represented in Figures 2 and 3. The MFIs of these polymers were different (2.5 units; Table I; for brevity, the images of 3% blends are not included). However, at both polymer concentrations (3 and 5%), no clear difference
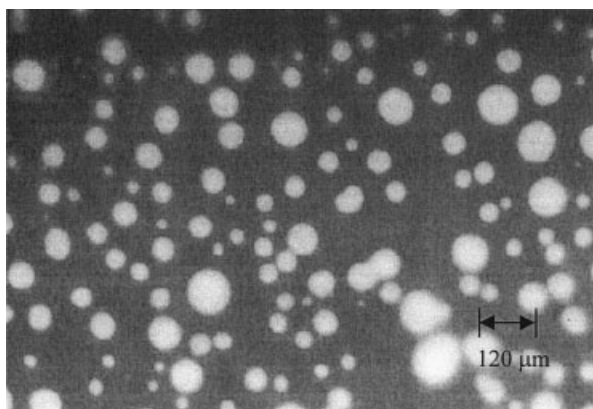
could be observed. The LLDPE that was used (LL209) had an MFI of 0.9, and it was very difficult to disperse it in bitumen. It is clearly shown in Figure 4 that very small particles and a continuous polymer phase coexisted. This resulted from the large difference between the rheological properties of this PE and bitumen at the temperature of mixing. In fact, a large difference between the material to be dispersed and the matrix results in the rotation of dispersed materials under shear. A rotating particle does not break up and in a low-shear region coalesce with other particles.

The state of dispersion of different grades of HDPE at a concentration of 5% is shown in Figures 5–10. No large difference was observed among high-MFI PEs (from 20 to 3.9 units; Figs. 5–8). Despite some irregularities in the shapes of the particles for 5% 3848, all the other particles were rounded in bitumen and were more or less of the same diameter. Moreover, small and large particles coexisted. As a matter of fact, small particles presented their real diameters, whereas the large ones were flattened; their real diameter in bitumen was much smaller than what appeared in pictures.[22,24] At a lower MFI, the preparation of a blend of bitumen and 5% PE became very difficult. For this
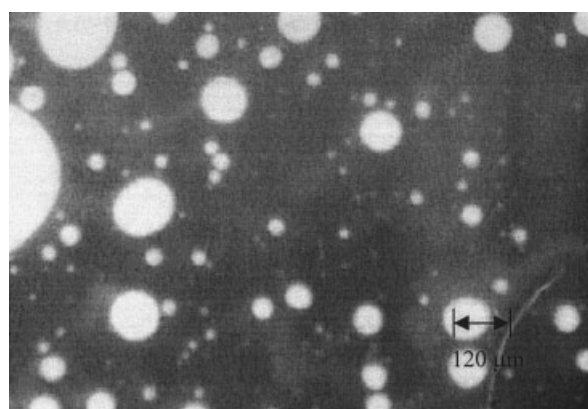

Figure 6 State of dispersion of 5% HD13 in bitumen.

Figure 5 State of dispersion of 5% HD5620 in bitumen.

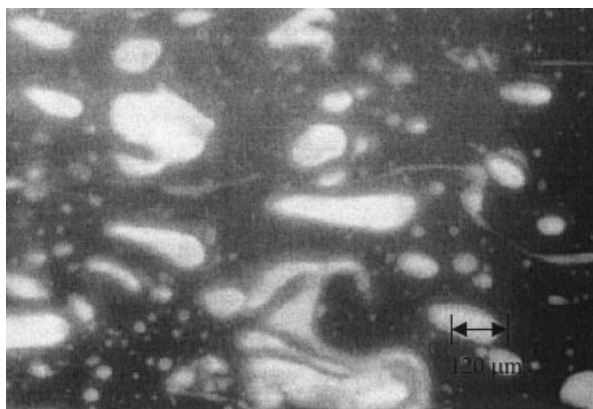**Figure 7** State of dispersion of 5% HD3840 in bitumen.

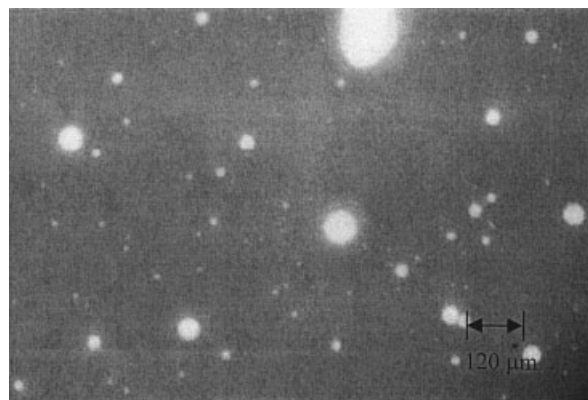**Figure 8** State of dispersion of 5% HD3848 in bitumen.

Figure 10 State of dispersion of 3% EX3 in bitumen.

reason, in the case of 5% HBX35 (Fig. 9), a continuous polymer phase formed in which bitumen was dispersed. In the 3% blend of this polymer, very large particles formed. The observed morphology was mainly due to a very low MFI (0.34; Table I). Even with the very strong high-shear double mixer used in our laboratory, the preparation and characterization of 5% EX3 (MFI = 0.15; Table I) were not attainable, and the polymer was precipitated in the bottom of the mixing vessel. The state of dispersion of 3% EX3 is reported in Figure 10. It may seem that the polymer was well dispersed in bitumen. In fact, a very small portion of the polymer was mixed, and the rest of the polymer was precipitated under shear. The micrographs clearly show that the MFI of the polymer affected its dispersion in bitumen. As a matter of fact, MFI is a rheological parameter that shows the ability of a polymer to flow and is a direct indication of its molecular weight. We can conclude that as the PE chains shortened (higher MFI) or became more branched, the solubility of PE in bitumen increased.

Unfortunately, at least for the studied materials, the degree of polymer crystallinity did not correlate with the ability of the polymer to be dispersed in bitumen

(Table I and Figs. 5–12). The results of two recycled PEs (MFI = 9.9 and 0.89) are also consistent with this conclusion (Figs. 11 and 12). As a general conclusion, dispersing a polymer with an MFI of less than 1 in bitumen is very difficult, and resulting blends will not have very good engineering properties.

In the case of PMBs, it is very important to have a stable dispersion of polymer inclusions in the bitumen medium under quiescent conditions. Stable polymer–bitumen dispersions could be reheated many times and would be commercially attractive. The results of stability tests do not show any effect of the PE MFI on the stability of the dispersion. This can be considered a drawback for PE-modified bitumen (the optical microscopy pictures are not shown for the sake of brevity).

Performance-estimating tests

The different properties of the base bitumen are summarized in Tables II and III. It is surprising to see a 60/70 penetration-grade bitumen possessing a penetration value of around 40. This result was double-checked with two apparatus at 25°C according to ASTM D 5. This could be due to some difficulties in
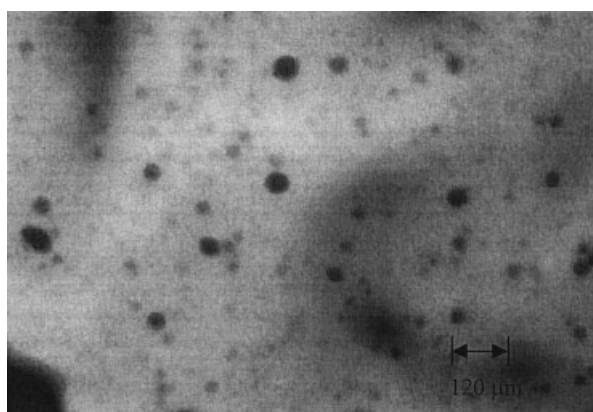

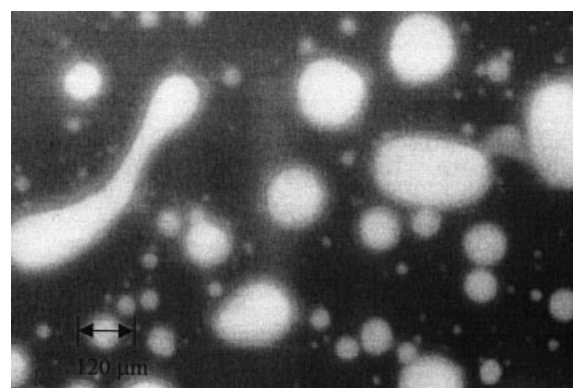**Figure 9** State of dispersion of 5% HBX35 in bitumen.

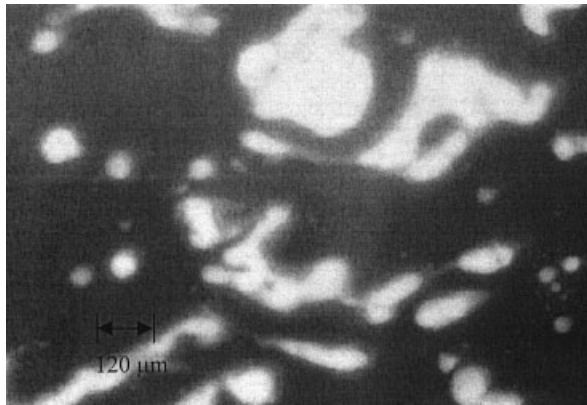**Figure 11** State of dispersion of 5% HRB in bitumen.

Figure 12 State of dispersion of 5% HRM in bitumen.

TABLE IV
LDPE- and LLDPE-Modified Bitumens

Blend	Penetration (0.1 mm)	Softening point (°C)	Frass breaking point (°C)	PI	PG
3% LF0450	34	63.5	−9	0.909	82-16
5% LF0450	24	69.3	−4	1.11	88-4
3% LF200	25	62.3	−4	0.049	82-4
5% LF200	16	67.6	−3.5	0.169	82-4
3% LL209	37	62.8	NP	0.909	82-?
5% LL209	19	99	NP	4.643	118-?

NP = sample preparation was not possible.

refining the corresponding crude. The softening and Frass points were the same as those reported by other workers.[31] A negative PI is an indication of high-temperature susceptibility for this bitumen. However, with the proposed empirical relations, a PG of 76-16 was estimated for this bitumen.

The results for 3 and 5% blends of different LDPEs in the base bitumen are listed in Table IV. With the PE concentration increasing from 0 to 3 to 5%, the penetration of bitumen decreased, whereas its softening point and Frass breaking point increased. An increase in the PI of bitumen was also observed. The PG of PMBs also decreased at low temperatures and increased at high temperatures. For 3% LF0450, the performance at low temperatures remained unchanged.

Because of difficulties in the preparation of Frass samples for 3 and 5% LL209, the estimation of the low-temperature performance of these blends was not possible. It can be concluded for these polymers that LLDPE profoundly improved the performance of bitumen at high temperatures, whereas the low-temperature properties of bitumen deteriorated. This was mainly due to the different rheological properties of this polymer, which is portrayed with a low MFI and high dynamic viscosity in Figure 13. The higher MFI and lower dynamic viscosity of LF0450 PE were responsible for its lesser effect on the bitumen properties. As a general rule, when polymer chains are branched and the polymer MFI is higher, its dispersion in bitumen is finer.

The results of conventional tests along with the PI and estimated PG of HDPE-modified bitumens are reported in Table V. Here again we clearly observe the
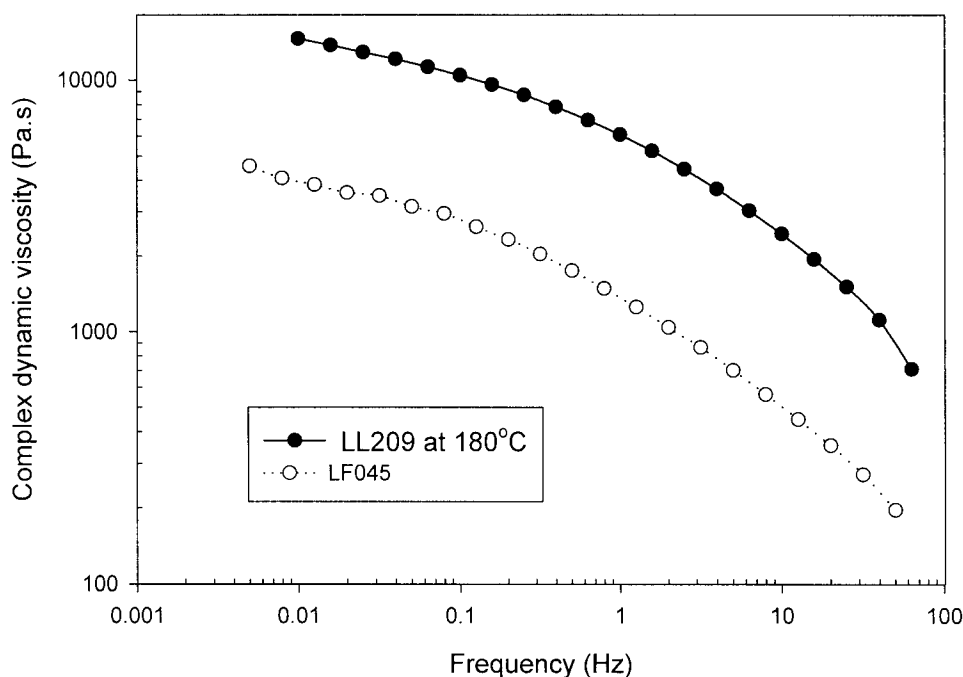

Figure 13 Complex dynamic viscosity of LDPE (LF045) and LLDPE (LL209) at 180°C.

TABLE V
LDPE- and LLDPE-Modified Bitumens

Blend	Penetration (0.1 mm)	Softening point (°C)	Frass breaking point (°C)	PI	PG
3% HD5620	20	64	−5	0.163	84-10
5% HD5620	15	68.5	−4.6	0.169	88-4
3% HD13	22	65.9	−4	0.344	82-4
5% HD13	19	68	−3	0.526	88-4
3% HD3840	12	61.5	−5	−1.428	76-10
5% HD3840	32	67.8	−8	1.538	82-16
3% HD3848	16	63.7	−4	−0.476	82-4
5% HD3848	25	67.6	0	0.909	82+2
3% HBX35	8.4	91.5	NP	2.244	106-?
5% HBX35	20	121	NP	6.67	136-?
3% EX3	15	70.5	NP	0.526	88-?
5% EX3	12	NP	NP	?	?
3% HRB	33	61.6	−9	0.526	76-16
5% HRB	27	66.5	−5	0.909	82-10
3% HRM	46	61.6	−4	1.32	76-4
5% HRM	25	73	NP	1.764	88-?

NP = sample preparation was not possible.

effect of the polymer MFI on the bitumen properties. A reduction in the polymer MFI resulted in lower penetration and higher softening points. A discrepancy was observed for the EX3 polymer that was related to the precipitation of the polymer during mixing, which resulted in lower polymer concentration. The dynamic viscosities of some HDPEs are reported in Figure 14. HDPE3840 and HDPE3848 were not very different from each other. For the rest of the polymers, the measured viscosities were in complete agreement with the reported MFIs. The difference in the dynamic viscosities of HDPEs also confirmed a large difference between the rheological properties of these polymers even at very high frequencies, which corresponded to high shear rates. In fact, low-MFI polymers are very entangled, and dispersing them in bitumen is difficult.

For recycled PEs, the observed properties were very consistent with the order of their MFIs. The bitumen modified with HRB recycled PE had very good properties. However, the Frass breaking point of 5% HRB bitumen moved to higher temperatures. This polymer's effects on the bitumen properties seemed to be very similar to those of LF0450. That is, an LDPE with MFI = 4.5 acted as an HDPE with MFI = 10. However, this conclusion is not consistent with an HDPE having a higher MFI such as HD5620. For the HRM recycled polymer, which had a much lower MFI, some difficulties were observed in its dispersal. The properties of the blends of this HDPE were more or less similar to those of LL209 (MFI = 0.9; Table I). The reason lies in the similarity between the MFIs and rheological properties of these two polymers. As shown in Table I, the MFI for the HRM polymer was about 0.89, whereas the MFI was 0.9 for LL209. However, the complex viscosity measurements (Figs. 13 and 14) indicated similar values and rheological behaviors for these polymers. This comparison results in the following conclusion, that the MFI is a reliable rheological
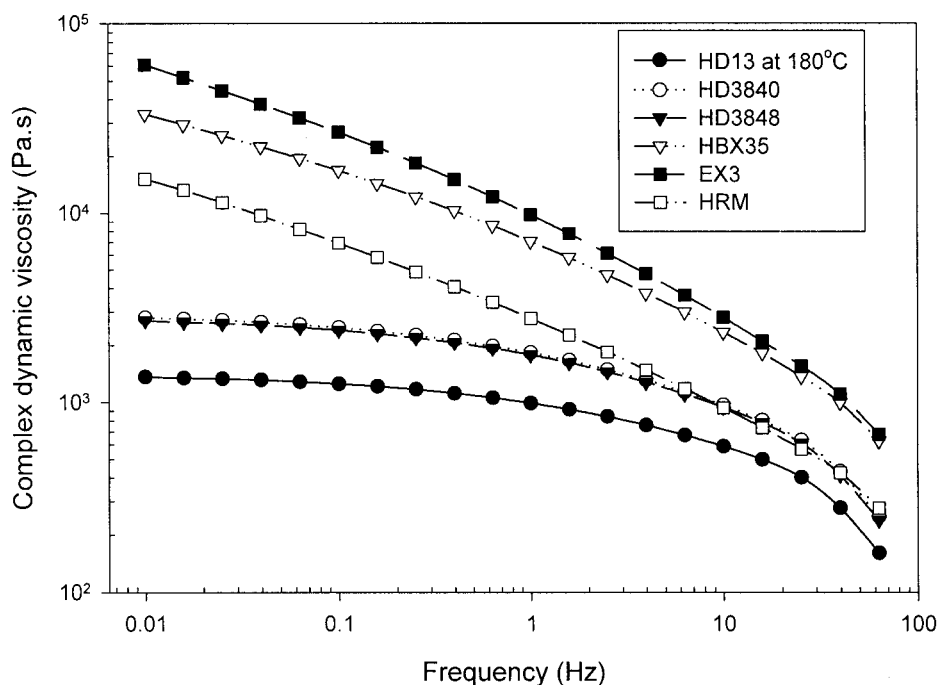

Figure 14 Complex dynamic viscosity of different HDPEs at 180°C.

factor for evaluating the effect of a polymer on the bitumen properties and performance.

CONCLUSIONS

The structural parameters of polymers intensively affect their dispersion in bitumen. Branched PEs such as LDPEs easily disperse in bitumen. For linear PEs, the extent of compatibility decreases as MFIs of HDPEs decrease. The stability of dispersions of HDPEs follows the same trend. For HDPEs of very low MFIs (<1), the dispersion is unstable even under the action of a high-shear double mixer. High-MFI polymers improve the high-temperature performance of bitumen to a lesser extent. However, with these polymers, the low-temperature properties of bitumen deteriorate less. The structural parameters of the polymer do not affect the high-temperature instability of PE–bitumen dispersions. No correlation between the PE crystallinity and melting point has been found.

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