

Polymer-Modified Bitumen of Recycled LDPE and Maleated Bitumen

B. Singh,¹ Lokesh Kumar,¹ M. Gupta,¹ G. S. Chauhan²

¹Polymers, Plastics and Composites Division, CSIR—Central Building Research Institute, Roorkee 247667, India

²Department of chemistry, Himachal Pradesh University, Shimla, India

Correspondence to: B. Singh (E-mail: singhb122000@yahoo.com)

ABSTRACT: Maleated bitumen was prepared by the reaction of penetration grade bitumen (80/100) with maleic anhydride at 150°C for 2 h under nitrogen atmosphere. The effectiveness of maleation was assessed in bitumen–recycled low-density polyethylene (LDPE) blends in terms of their softening point and elastic recovery. It was observed that the softening point and elastic recovery of the blends increased after maleation of the base bitumen owing to the formation of an asphaltene-linked-LDPE system. To obtain the desired elasticity, a recoverable composition was worked out with the help of maleated bitumen, recycled LDPE and styrene–butadiene–styrene. The storage stability of the blends was assessed in terms of their difference in softening points, rheological parameters, and microstructure of the top and bottom portions of test tube samples. The difference in softening point of the recoverable maleated bitumen blend was 5°C as compared to 60°C for the base bitumen blend. The phase angle was also reduced to 7.4° at 70°C compared with the 44.30° for the base bitumen blend. Scanning electron micrographs indicate that polymers existed in both the top and the bottom portions of the aged test tube maleated blend samples. The stability of the blend was further improved when LDPE is colloidal milled with maleic anhydride in the blend preparation. Roofing bitumen was also made with maleated bitumen containing 9 wt % recycled LDPE content. Based on the rheological data, it was found that the maleated bitumen–LDPE blend exhibited superior time-/temperature-dependent response and higher creep recovery compared with the base bitumen blend. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: maleated bitumen; recycled LDPE; storage stability, SEM; rheology

Received 29 April 2011; accepted 13 January 2012; published online

DOI: 10.1002/app.36810

INTRODUCTION

In recent years, the use of recycled polymers has been recognized for bitumen modification^{1–10} because of their favorable economics and environment friendly disposal in making built-up roof membrane and pavement construction. Depending on their nature, recycled polymers are able to influence the rheological properties of bitumen at their specified level in a micronized form and the optimum mixing conditions. One of the issues addressed in the system is the incompatibility of recycled polymers and bitumen.^{2,4,9} When recycled polymers are added into bitumen, the phase separation will arise probably because of their high molecular weight and also inadequate maltenes for solvation. As a result, heterogeneous mixtures are formed without cohesion and ductility. Consequently, the poor storage stability is arised in the system that makes it unsuitable for use in roofing, paving, and other industrial specialty products. The compatibility of constituents in the systems can be improved either by ozonization¹¹ and chemical anchorage/grafting of reactive monomers onto recycled polymers¹²/functionalization of recycled polymers^{1,6} or by modification of the bitumen by reactive species^{13–17} to form a polymer-linked bitumen system. These systems, however, require

adequate rheological stability to obtain satisfactory blend endurance in the use conditions.

In the present study, recycled low-density polyethylene (LDPE) was used as a partial replacement of virgin polymers in the polymer-modified bitumen. Introducing recycled polymers alone into bitumen cannot improve its low-temperature flexibility.^{1,9,18} To achieve this behavior, a recoverable bituminous composition with recycled LDPE and styrene–butadiene–styrene (SBS) combination was formulated, aiming at to satisfy the minimum specified level of softening point (60°C) and elastic recovery (50% at 15°C).¹⁹ Although this system has advantages in the property improvement, the large amount of SBS copolymer requirement makes it too expensive. It is now desirable that the quantity of polymers needed is reduced and the physical properties of the modified bitumen are enhanced when its components are at least imparts chemical bond to each other through the use of a coupler. Therefore, maleated bitumen (maleic anhydride group attached bitumen) was chosen in the formulation in preference over the conventional bitumen. It is expected that the maleated bitumen provides adequate storage stability to the system by forming chemical interactions between the anhydride (maleic) functionality of bitumen and the surface

hydroxyl groups of LDPE. Previously, the combination of recycled polymers and elastomers/plastomers (SBS, ethylene vinyl acetate, ethylene propylene diene monomer, *etc.*) has been reported for the bitumen modification to obtain satisfactory performance under varying conditions.^{2,20–23} The most polymers are only physically dispersed into the bitumen that results in a poor interphase adhesion between the blend constituents.¹⁹ In our earlier report,¹¹ recycled polyvinyl chloride (PVC) treated with hydrogen peroxide has been used in the SBS-modified bitumen (~70 wt %) for waterproof roof mastics preparation. The activation of PVC particles by peroxidation method improved their compatibility with the bituminous binders. The resulting mastics meet requirements of commercial specification (IS: 3037-91). In the previous study, attempt on producing bituminous blends with maleated bitumen and recycled LDPE has not received much attention, necessitating a thorough examination of their formulations and performance.

In this article, we report the properties of polymer-modified bitumen made with recycled LDPE, SBS copolymer/natural rubber, and maleated bitumen. The storage stability of these blends was studied by measuring the difference in softening point, microstructure, and rheological parameters of the top and bottom portions of aged samples. Roofing bitumen made with higher percentage of recycled LDPE was also examined for various properties with respect to its end-use applications.

EXPERIMENTAL

Materials

The penetration grade bitumen (softening point, 39°C; penetration, 140 dmm; elastic recovery, <7%) was obtained from an Indian refinery. Recycled LDPE in a micronized form was obtained from packaging waste of the local recycling plants (density, 0.91 g cm⁻³; average particle size, 0.20 mm; MFI, 0.5–0.7 g/10 min). SBS (Kraton D 1101) was obtained from M/s Shell India. It is a linear polymer in the powder form with 31% styrene and 16% diblock copolymer by weight. Maleic anhydride (Aldrich make) was obtained from the local market.

Preparation of Samples

Maleated Bitumen. A known amount of bitumen was heated in a stainless steel kettle at 150°C and refluxed for 30 min to remove its residual moisture. Subsequently, the maleic anhydride (1, 2, 3, 5, and 10 wt %) was added gradually in the molten bitumen under a constant stirring for 2 h. The reaction is carried out under nitrogen atmosphere. The resulting bitumen samples were stored in an airtight container.

Maleated Bitumen–LDPE Blends. The maleated bitumen was preheated at 170°C in a laboratory mixer. Recycled LDPE particles were added gradually and mixed well with the help of stirrer at a low level for 30 min followed by a high-speed mixing (~3000 rpm) for the remaining period (1.5 h). The various maleated bitumen blends were prepared with different percentages of recycled LDPE (3, 5, 7, and 9 wt %).

In another attempt, recoverable formulations of the polymer-modified bitumen were prepared using optimized maleated bitumen–LDPE blend, SBS copolymer, and natural rubber. In a process, SBS copolymer was added to the maleated bitumen and stirred well at 170°C. The resulting blend was then mixed

with recycled LDPE at a specified level at 180°C for 2 h at a speed of ~3000 rpm. The blends have been optimized as a function of modifiers (SBS, 1, 2, 3, and 5 wt %; natural rubber, 2, 4, and 6 wt % and castor oil, 5 and 10 wt %). The blends were stored in containers for further work.

Test Methods

Softening Point and Penetration Tests. The softening points of the base and maleated bitumen blends were measured by a ring and ball method as per ASTM D 36-09. In this test, two disks of sample were cast into a shouldered ring and then they were heated at a constant rate in a glycerin bath. The temperature at which bitumen disks soften and sag downward under the weight of a standard steel ball was noted as a softening point.

The penetration test was performed according to ASTM D 5-06 under the condition of applying a 100 g weight on the penetration probe for 5 s at 25°C and reported in tenths of millimeters.

Elastic Recovery. The elastic recovery of the bitumen–LDPE blends was determined according to ASTM D 6084-06. In this test, the specimens were elongated up to 100 mm at a speed of 50 mm/min at 15 and 25°C and cut it into two halves at the mid point. After 60 min, the length of the recombined specimens was recorded by placing an elongated cut half of the piece back into position just touching the fixed half of test specimen to record the length of the recombined specimen.

Storage Stability. The storage stability test of the bitumen–LDPE blends was carried out as per IRC SP 53-2002 (Indian Roads Congress, Standard specification, Special Publication 53, India). The molten samples screened through 600- μ m sieve were poured into vertically held aluminum tubes (136.7 \times 25.4 mm). The sealed tubes were placed in an oven at 163°C for 48 h and then subjecting them in a freezer at 6.7°C for 4 h. The aged tubes were cut into three equal parts. The upper and lower ends of tubes were then melted into separate small beakers and tested for their softening point, microstructure, and rheological properties.

Scanning Electron Microscopy. The morphology of the maleated bitumen–LDPE blends was examined by a Scanning electron microscope (Leo 435 VP). Before examination, the samples were coated with Au/Pd to render them conductive.

Rheological Test. The rheological test of the bitumen blends was carried out on a stress-controlled rheometer (Bholin, Gemini 200, United Kingdom) using 25-mm parallel plate geometry with 2 mm gap under flow and oscillation modes. The viscosity of samples was measured in the range between room temperature and 180°C under flow mode. A temperature sweep was performed using plate and plate geometry at 10 rad/s over a range of temperature from (–) 6 to 100°C with an increment of 6°C. Under frequency sweep, the measurements were taken from 20 to 100°C temperatures with an increment of 10°C at frequencies ranging from 0.01 to 100 Hz with three points *per* decade. The strain of 0.05 was selected in the linear viscoelastic region over the entire temperature and frequency range. Using time–temperature superposition software, the master curves for storage and loss moduli of base bitumen and maleated bitumen–LDPE blend were generated, simulating a single

Table I. Effect of Maleic Anhydride on the Properties of the Base Bitumen^a

Maleic anhydride content (wt %)	Softening point (°C)	Penetration (dmm)
0	39 ± 1.9	140 ± 7.1
1	40 ± 2.1	132 ± 6.6
2	42 ± 2.1	125 ± 6.3
3	44 ± 2.2	115 ± 5.8
5	48 ± 2.4	70.16 ± 3.5
10	56 ± 2.8	60.80 ± 3.1

^aStandard deviation, ±5%.

experiment performed at 60°C as reference temperature on wide frequency range.

The creep test of samples was carried out at 60°C by applying 100 Pa pressure on the samples for 60 s. The stress was then relieved and the recovery of deformation was monitored.

RESULTS AND DISCUSSION

Effect of Maleic Anhydride

Effect of maleic anhydride on the properties of the base bitumen is summarized in Table I. The addition of maleic anhydride increases the softening point and reduces the penetration of the base bitumen. The difference in the properties was more pronounced when the base bitumen is modified with higher percentage of maleic anhydride (~ 10 wt %). This has resulted owing to the reactions involving the active maleic anhydride double bond and condensed aromatic ring systems in the bitumen.^{15,24,25} Because of this association, the viscosity of the maleated bitumen was also higher than the bitumen without maleic anhydride. This indicates that maleation phenomenon is favorable for making less temperature susceptible bitumen because of its stiffening effect.

The efficacy of maleic anhydride was further assessed in the bitumen–recycled LDPE blends (Table II). The increase observed with maleated bitumen is attributed to the enhanced interaction within the system. The maleated bitumen would interact with LDPE through its anhydride functionality to form asphaltene-linked LDPE system, reducing asphaltene flocculation and oil bleeding. A possible interaction between maleated bitumen and LDPE is shown in Scheme 1. Extending the mixing time during blend preparation also arrests these problems. The level of interaction can also be easily viewed in scanning electron micrograph (SEM) in which the LDPE particles seem to be embedded in the maleated bitumen besides their satisfactory dispersion. Contrary to this, the base bitumen-based system shows that LDPE particles exist in unbonded state with their coherence on the surface and the microstructure seems to be heterogeneous [Figure 1(b,c)]. The enhanced consistency and reduced temperature susceptibility of the maleated bitumen systems would make it a potential candidate over the base system for roofing/paving.

Optimization of Composition

The optimization of recycled LDPE content in the maleated bitumen was made with respect to its use in the actual condition

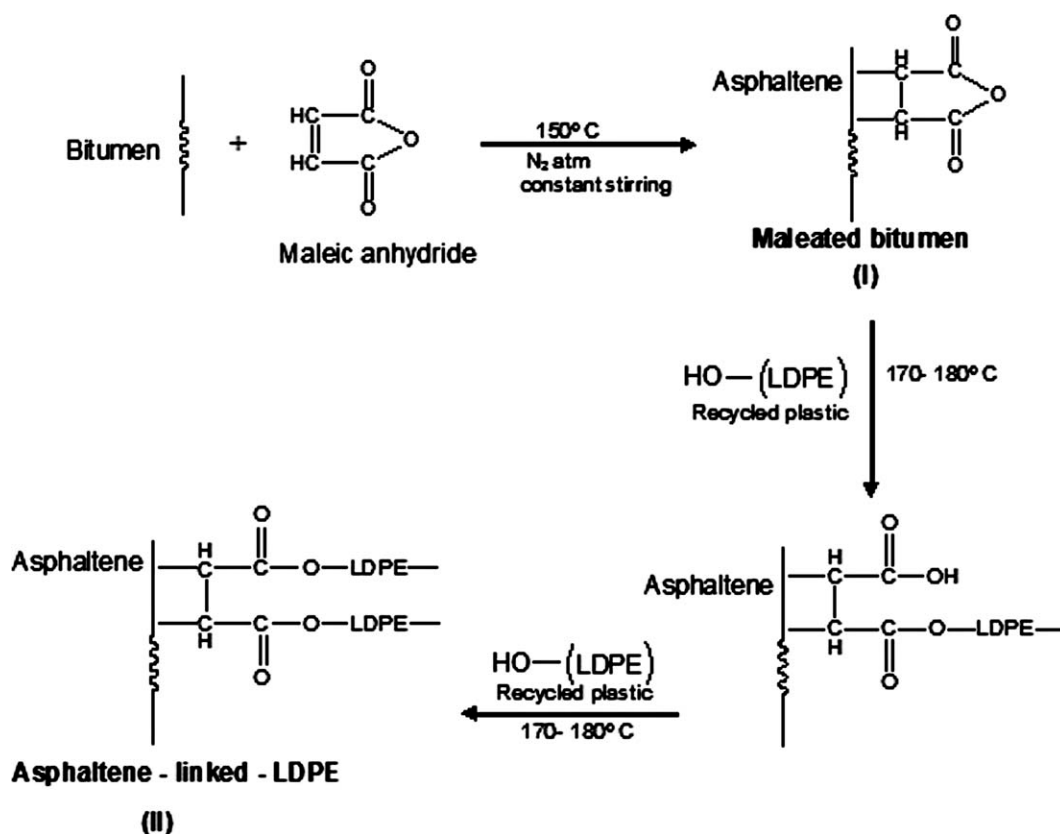
(Figure 2). The addition of recycled LDPE to the bitumen increases both the softening point and the elastic recovery of the resulting blends. Contrary to this, the penetration decreases with increasing LDPE loading. Other studies also supported the similar trends on adding recycled polymers into bitumen.^{2,18,20,26} Increasing the level of maleic anhydride increases the elastic recovery of the resulting blends beside their softening points. Such interaction suggests that the bitumen blend with 2 wt % maleic anhydride has shown superior behavior than the blend containing 1 wt % maleic anhydride. As shown in Figure 1, SEM images indicate a clear difference in the morphology of bitumen blends as the LDPE content increases. In 3 wt % LDPE blend, the microstructure was relatively smooth with a slight demarcation of boundary between particles and bitumen [Figure 1(c)], whereas in the case of 5 wt % LDPE blend, the particles were large, swollen and also slightly flattened posing stability problems²⁷ [Figure 1(d)]. At higher loading (7 wt %), coalescence of swollen particles was visible. Because of solubility of LDPE in bitumen owing to its short chain, the blend exhibited irregular shape islands of polymer-rich phases with a dispersed bitumen phase [Figure 1(e)]. The LDPE particles may absorb light fractions of bitumen. As a result, LDPE tends to aggregate and formed a network structure with a continuous polymer phase. Such kind of microstructure is usually suited for roofing. However, this alone is not sufficient for such applications, as the blend also required an adequate elastic recovery at low temperatures.

The recoverable compositions composed of maleated bitumen recycled LDPE and elastomers (SBS and natural rubber) were prepared while maintaining an optimum balance between the softening point, elastic recovery, and workable viscosity and also control its stability (Table III). When SBS was added to the maleated bitumen–LDPE blend, the softening point, penetration, and elastic recovery of the resulting blends increased with increasing SBS concentrations. At elevated temperature, SBS behaves as a viscous liquid allowing uniform coating of LDPE particles during mixing. Upon cooling, physical crosslinking of SBS polymer blocks reformed and strength and elasticity is restored.²⁸ About 105% increase in elastic recovery was noticed when the bitumen–LDPE blend is modified with 5 wt % SBS level probably owing to its contribution in the formation of network structure.²⁹ At low temperatures, these blends retained their elastic recovery at a specified level (50%) even at 2 wt % SBS addition. This is attributed mainly to the changed

Table II. Effect of Maleic Anhydride (2 wt %) on the Properties of the Bitumen–LDPE Blends (LDPE 3 wt %)^a

Property	Base bitumen–LDPE blend	Maleated bitumen–LDPE blend
Softening point (°C)	49 ± 2.5	60 ± 3.1
Penetration (dmm)	72 ± 3.6	58 ± 2.9
Elastic recovery (%)	22 ± 1.1	36 ± 1.8

^aStandard deviation, ±5%.



Scheme 1. Schematic representation of interaction between maleated bitumen and recycled LDPE.

characteristics of the modified bitumen to those of the elastomer type, which could be stressed and would recover. To make it cost-effective, natural rubber was used in place of SBS in the maleated bitumen-LDPE system. The desired level of elastic recovery in the system was achieved at a level of only 4 wt % natural rubber addition at 15°C. The softening point of the resulting blend was maintained when elemental sulfur (1.5%) was used as a crosslinker to the natural rubber. It is known that sulfur chemically crosslinks the rubber molecules and chemically couples the natural rubber and bitumen through sulfide and polysulfide bonds.³⁰ Beyond this (6 wt % natural rubber), the satisfactory behavior was not achieved owing to nonuniform dispersion and poor compatibility with the bitumen because of its high molecular weight. Because of this, the blend storage was unstable and also sensitive to decomposition. To reduce the viscosity, the bitumen blend was plasticized with castor oil (up to 10 wt %). It is observed that besides viscosity reduction, castor oil enhances the elastic recovery of the resulting blends because of its interaction with the asphaltene fraction of the bitumen. It is also noted that softening point of blends decreases with increasing castor oil content. Based on these results, a recoverable bitumen formulation has been optimized comprising 2 wt % SBS, 3 wt % recycled LDPE, and maleated bitumen (maleic content, 2%).

Storage Stability Studies

To find out phase separation, the storage stability of the bitumen blend systems was studied in terms of their softening

point, rheological changes, and microstructural features. It is specified that the difference between softening point of the top portion and softening point of bottom portion shall not differ by more than 4°C.¹⁹ As summarized in Table IV, maleated blend exhibited the difference in softening point of the top and bottom portions was 16°C compared only with 60°C for the base bitumen blend. This would suggest a substantial phase separation between the polymer and the bitumen as viewed under SEM [Figure 3(a,b)]. The base bitumen blend exhibited polymer-rich phase in the top portion (in which the bitumen was dispersed) and asphaltene rich continuous bitumen phase in the bottom portion of aged samples. Creaming process is dominant owing to higher buoyant force.²¹ Contrary to this, the maleated bitumen blend showed polymer dispersion in both the top and the bottom portions of the tubes. Fine-dispersed particles along with some agglomerates were viewed in the bottom portion of the aged samples. This indicates that the presence of maleic anhydride contributes substantially in the improvement of storage stability of the resulting system. In the case of SBS/natural rubber-based bitumen blends, the difference in the softening point of its top and bottom portions was further reduced to 5°C for SBS system and 6°C for the natural rubber. The small difference in softening point compared with the specified value (4°C) can be considered to be within experimental error. It is believed that interaction between the SBS/natural rubber and the LDPE with maleic anhydride in the blend favors its storage stability. The addition of SBS/natural rubber improves the viscoelastic properties of the bitumen blends owing to the presence of the

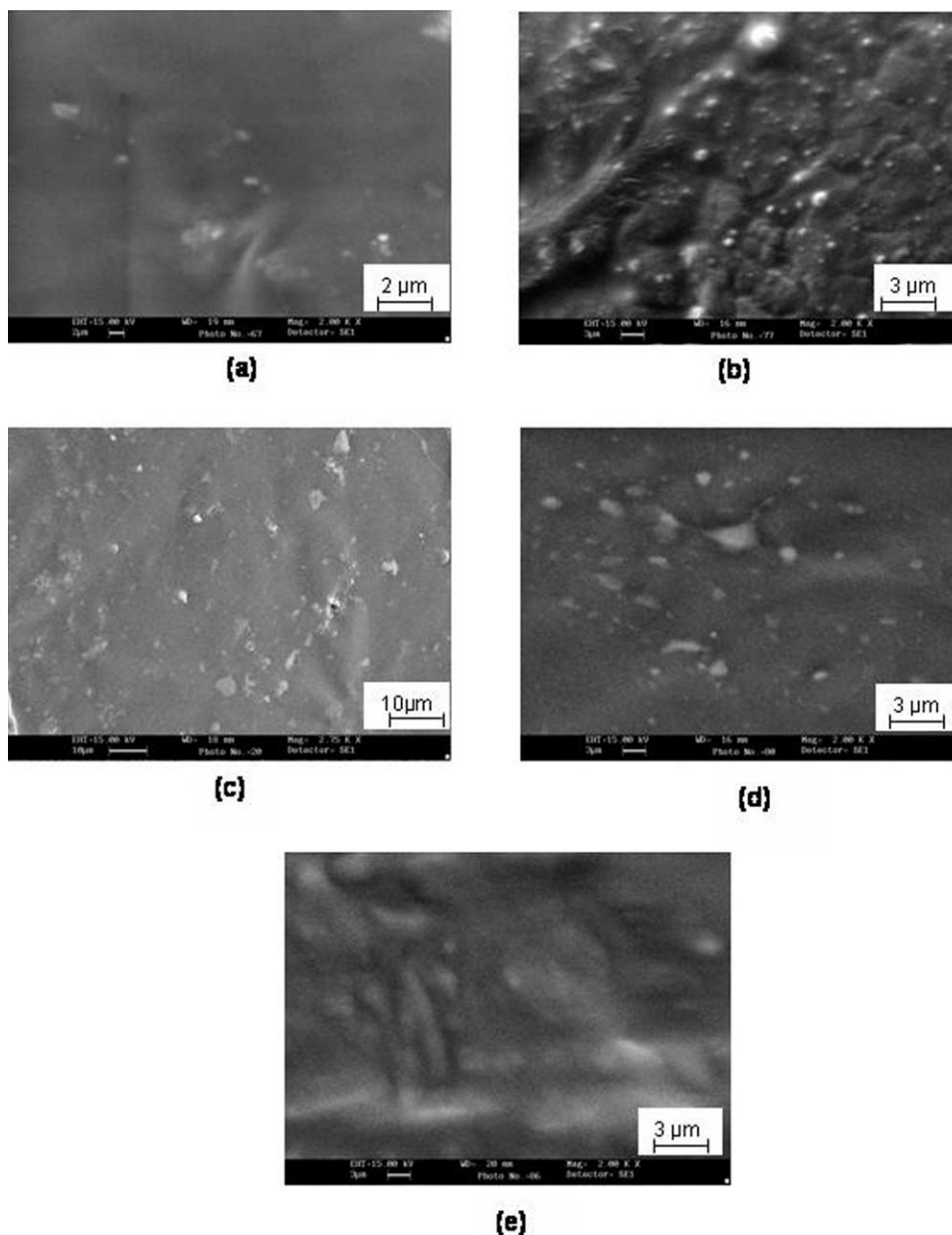


Figure 1. SEM images of bituminous blends (a) base bitumen (b) base bitumen + 3 wt % LDPE (c) maleated bitumen + 3 wt% LDPE (d) maleated bitumen + 5 wt % LDPE (e) maleated bitumen + 7 wt% LDPE.

more viscous polymer phase besides solubility of LDPE at higher temperatures. Diffusion of aromatics and saturates in the polymer phase also contributes to the increase of asphaltenes in the matrix.²⁰ As a result, the shifting from sol-to-gel colloidal structure occurred. The improved viscoelasticity may cause delay in the phase separation phenomenon. SEM showed that LDPE particles were dispersed in both the top and the bottom portions of tube samples [Figure 4(a,b)]. However, in the bottom portion, asphaltene is still in a dominant phase, whereas in the top portion, bitumen dispersed in a continuous polymer phase.

Figure 5 shows rheological changes in the unaged and aged bitumen-LDPE blends. It is seen that base bitumen blend exhib-

ited a clear large difference in the complex modulus of the top and bottom portions of aged tube samples over the entire range of temperatures. At low temperatures, the complex modulus of the top portion was less and phase angle was more than the bottom portion of aged tube owing to the fact that polymer may slow down the approach of a binder to an elastic solid.²⁹ The bottom portion behaves like a viscous liquid without any elasticity at higher temperatures as the phase angle practically reached 90°. The difference in the phase angle of the upper and lower part of the tube is 44.30° at 70°C. It is noted that the behavior of bottom portion of the test tube remains close to that of the unaged sample, showing lack of uniform LDPE particles dispersion in the blend. This indicates that molecular association between the bitumen and the LDPE does not exist.

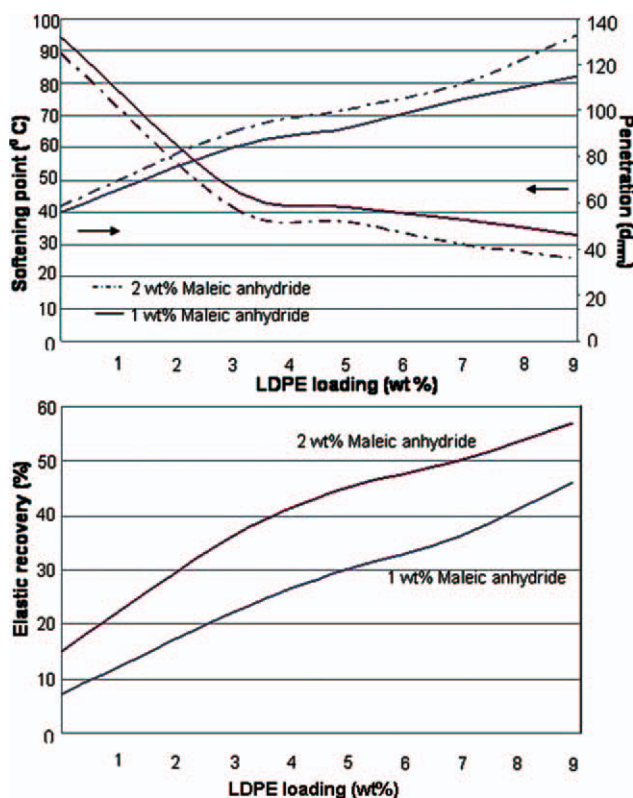


Figure 2. Effect of recycled LDPE addition on the properties of maleated bitumen-LDPE blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

As a result, phase separation in the blend occurred. On the other hand, recoverable maleated bitumen-LDPE blend showed

a small difference in the rheological parameters of the top and bottom portions of test tube compared to the base bitumen blend. At low temperatures, the complex modulus and phase angle of both the unaged and aged samples (top and bottom) were nearly the same, showing that their structure in this region did not change with thermomechanical conditions. The extended glassy region and a plateau in the complex modulus curve were observed, showing a dominant polymer network within the blend. The effectivity of modifier in the blend was more pronounced at higher temperatures. The lesser slope in the intermediate region of complex modulus curve was observed with respect to the base bitumen. The phase angle decreased to the level of 68° at 80°C compared to 88° for the base bitumen blend, showing a more elastic behavior. The difference in the phase angle of the top and bottom portions also remained 7.4° at 70°C only as against to 44.30° for the base bitumen blend (Table V). The coupling of maleated bitumen and LDPE particles occurred during blend preparation at higher temperatures. Hence, the stability of blend was achieved. The improvement in the compatibility of phases can also be supported with the help of SEM and ring and ball softening point data as described above. It is believed that maleated bitumen-LDPE blend seems to be rheologically stable and exhibiting reduced temperature susceptibility characteristic.

Attempts have also been made to improve storage stability of the maleated bitumen-LDPE blend by pretreating recycled LDPE with the maleic anhydride and also pyrophosphoric acid and milled with gilsonite—a natural asphalt. It is found that the difference in the softening points of the top and bottom portions of maleic anhydride and acid-treated LDPE blends was 2.5 and 4°C , respectively. SEM of maleated LDPE blend shows that the size of LDPE particles was in the range of 538 – 868 nm and distributed uniformly in the bituminous matrix [Figure 6(a)]

Table III. Effect of Modifiers on the Properties of Maleated Bituminous Blends (2 wt % Maleic anhydride + 3 wt % LDPE)^a

Modifier content (wt %)	Softening point ($^\circ\text{C}$)	Penetration (dmm)	Elastic recovery (%)	
			15°C	25°C
Control	60 ± 3.1	58 ± 2.8	30.3 ± 1.5	36 ± 1.8
SBS				
1	63 ± 3.1	48 ± 2.4	40 ± 2.1	45 ± 2.3
2	66 ± 3.3	47 ± 2.4	50 ± 2.5	53 ± 2.7
3	69 ± 3.5	45 ± 2.3	56 ± 2.8	62 ± 3.1
5	71 ± 3.6	44 ± 2.2	70 ± 3.5	74 ± 3.7
Natural rubber (1.5 wt % elemental sulfur)				
2	45 ± 2.3	85 ± 4.3	45 ± 2.3	47 ± 2.3
4	53 ± 2.7	56 ± 2.8	52 ± 2.6	56 ± 2.8
6	56 ± 2.8	54 ± 2.7	53 ± 2.7	58 ± 2.9
Castor oil				
5	52 ± 2.6	72 ± 3.6	40 ± 2.1	53 ± 2.7
10	45 ± 2.3	76 ± 3.8	46 ± 2.3	56 ± 2.8

^aStandard deviation, $\pm 5\%$.

Table IV. Storage Stability Test of Various Bitumen–LDPE Blends^a

System	Softening point (°C)		
	Top	Bottom	Difference
Bitumen–LDPE blend	112 ± 5.6	52 ± 2.6	60
Maleated bitumen–LDPE blend	77 ± 3.9	61 ± 3.1	16
SBS modified maleated bitumen–LDPE blend (2 wt % SBS)	68 ± 3.4	63 ± 3.1	5
Natural rubber-modified maleated bitumen–LDPE blend (4 wt % natural rubber)	54 ± 2.7	48 ± 2.4	6

^aStandard deviation, ±5 %.

On the other hand, microstructure of the acid-treated LDPE blend exhibited creaming of few LDPE particles along with its agglomeration at some places [Figure 6(b)]. The particle size was in the range of 690 nm–1.05 μm. The bitumen blend was

also prepared with pretreated LDPE in a laboratory mixer. The particle sizes observed under SEM for the maleic anhydride and acid-treated LDPE particles were 744 nm–1.95 μm and 916 nm–1.61 μm, respectively, which are larger than the milled samples. In a colloidal mill, LDPE particles are passed through very small gaps between the rotor and the stator under the action of centrifugal force. This reduces LDPE particle size to a level of submicron scale. Because of this fact, the milled LDPE gives better storage stable bituminous system than the laboratory mix samples.

Roofing Bitumen

Roofing bitumen was prepared using maleated bitumen and recycled LDPE content (9 wt %). It is observed that viscosity of the maleated bitumen–LDPE blend was significantly higher than the base bitumen at all temperatures (Figure 7). Above 160°C, the viscosity of maleated bitumen blend reduced to a level of 3 Pa s. According to the specification,³¹ it is stated that the workability of blend is adequate during handling/preparation of built-up roof membrane. The softening point and penetration of the maleated bitumen blend were 95°C and 22 dmm, respectively. The elastic recovery of the maleated bitumen–LDPE blend was in the range of 57–60% as against the elastic recovery

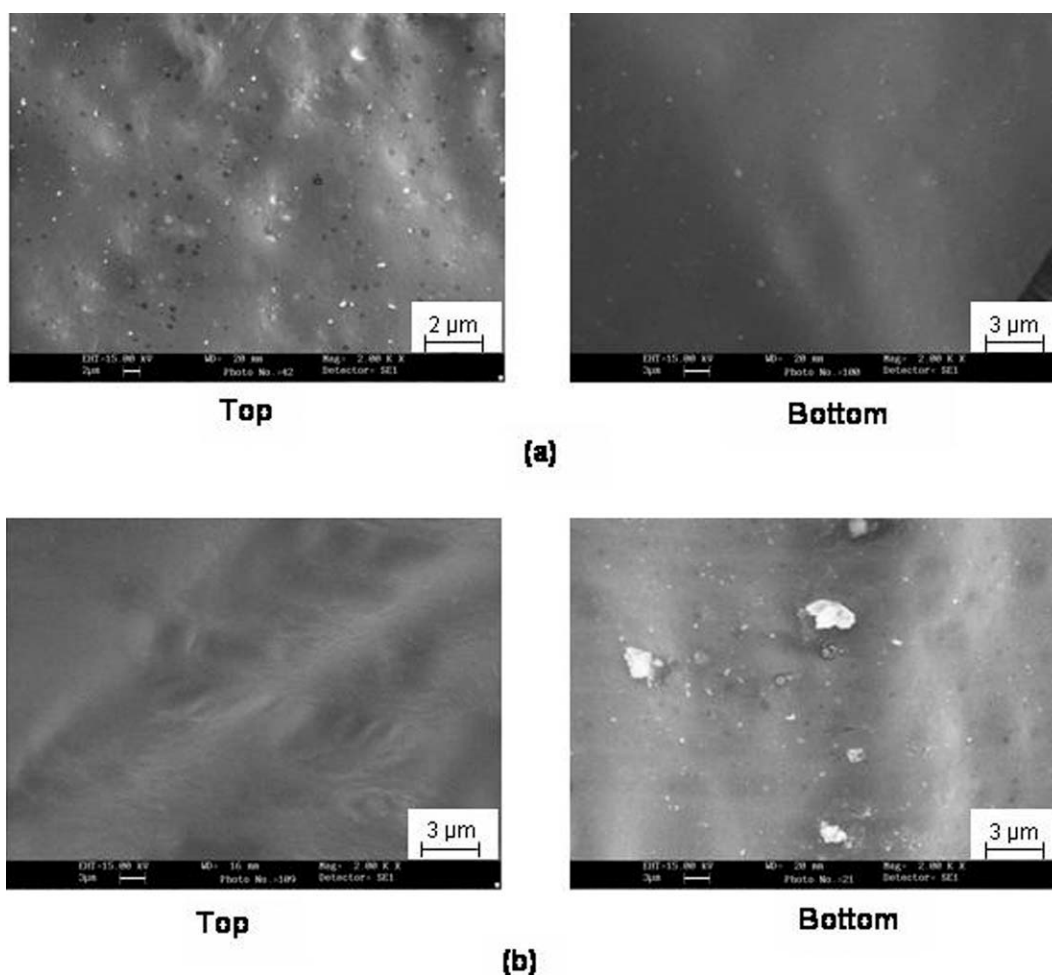


Figure 3. SEM images of the top and bottom portions of bituminous blends after storage stability test (a) base bitumen–recycled LDPE (b) maleated bitumen–recycled LDPE.

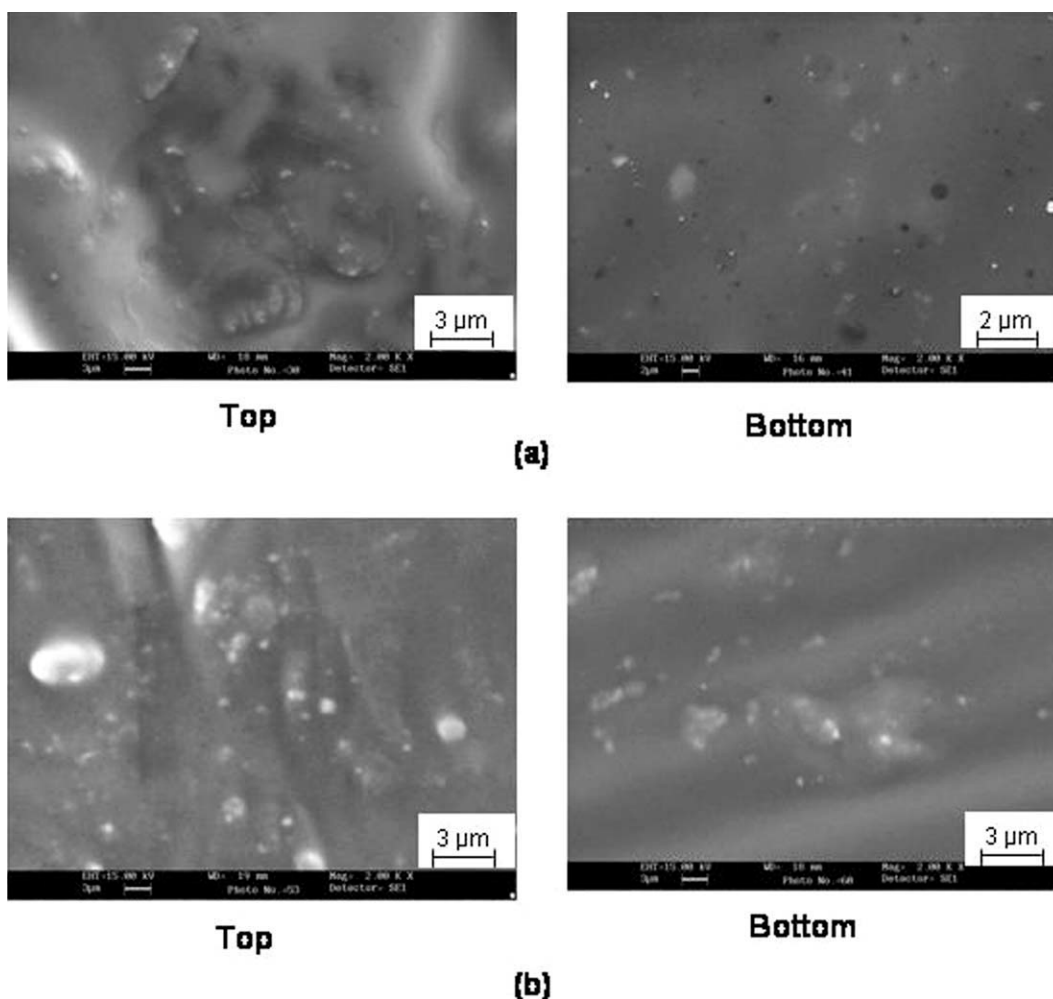


Figure 4. SEM images of maleated bitumen–LDPE blends modified with elastomers after storage stability test (a) SBS modified (b) natural rubber modified.

of 46% for the base bitumen blend. SEM images showed that microstructure of maleated bituminous blend is changed from bituminous to polymeric type (Figure 8). Recycled LDPE particles are swelled owing to absorption of light fraction of bitumen and tend to aggregate in the form of a network structure. As seen in rheological test, the phase angle of the maleated bitumen blend was 77° compared to 89° for the base bitumen at 80°C supportive of its elasticity. The storage and loss moduli of the maleated bitumen blend were significantly higher than the base bitumen at all temperatures. Using time–temperature superposition, a master curve was constructed for the base and maleated bitumen blends at a reference temperature of 60°C (Figure 9). At low frequency (high temperature), the difference in the storage modulus was much more apparent. The plateau in the curve could be attributed to the possible formation of molecular entanglement among the macromolecular components. The presence of probable high-molecular-weight reaction products such as maleic anhydride–bitumen copolymer/adduct and asphaltene-linked LDPE phases mentioned in Scheme 1 could provide superior properties to the maleated bitumen blend compared to the base bitumen. Because of the chemical

interaction between hydroxyl group of LDPE and anhydride portion of maleated bitumen (Scheme 1), the blend exhibited higher storage and loss moduli than the base bitumen/blend at high frequencies. By adopting maleation of bitumen, the blend retained higher storage and loss moduli at low and high frequencies. It is noted that the maleated bitumen blend has less frequency-dependent response than that of the base bitumen.

The temperature dependence of the shift factor for the base bitumen and maleated bitumen–LDPE blend composition is assessed using Williams–Landel–Ferry (WLF) equation:

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

where a_T is the shift factor; T , the temperature (K or $^\circ\text{C}$); T_0 , the reference temperature (K or $^\circ\text{C}$); and C_1 and C_2 , the experimental constants. The values of experimental constants for C_1 and C_2 for base bitumen are 26.33 and 284.9 K, respectively, with the standard error of 9.330, whereas C_1 and C_2 for maleated bitumen blend composition are 24.48 and 275.2 K, respectively, with the standard error of 6.606. It is observed that

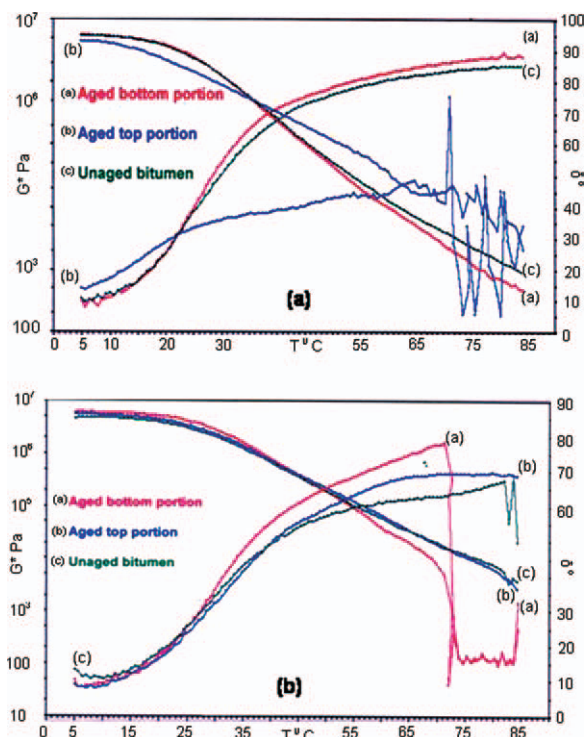
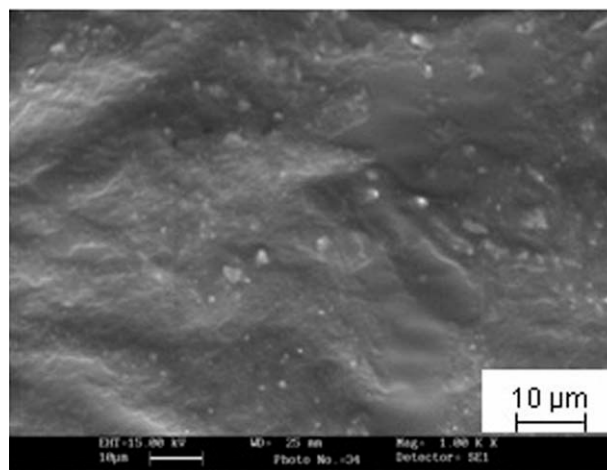


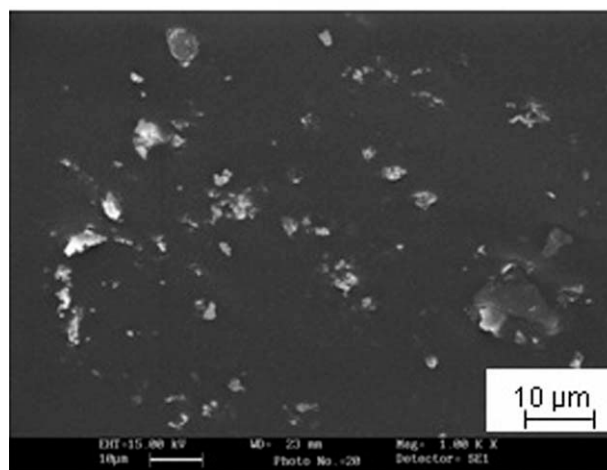
Figure 5. Complex modulus and phase angle of bituminous blends (a) base bitumen–recycled LDPE (b) maleated bitumen–LDPE. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

shift factor plot is curved, showing that the frictional-free volume increases with respect to the temperature. The maleated bituminous blend had lesser slope than the neat bitumen, showing its superior temperature behavior (Figure 10). The good fit between the shift factors obtained from the WLF equation (solid line) and experimental (circle) shows the validity of the model.

Creep response of the maleated bitumen blend at 60°C is shown in Figure 11. It gives information on the degree of deformation of the blend as a function of time under stress. The initial response under applied stress was mainly indicative of elastic deformation, whereas at longer time the deformation was owing



(a)



(b)

Figure 6. SEM images of bitumen blends prepared under colloidal mill (a) maleated bitumen–LDPE blend (b) acid-treated bitumen–LDPE blend.

to both the viscous and the elastic elements. The compliance curve below the yield value for the maleated bitumen blend tends to the horizontal, showing a fixed elastic deformation.

Table V. Rheological Properties of Top and Bottom Portions of Bitumen Blends After Storage Stability Test

Property	Base bitumen-LDPE blend			SBS-modified maleated bitumen-LDPE blend (2 wt % SBS)		
	Fresh	Aged		Fresh	Aged	
Complex modulus (G^*) Pa		Top	Bottom		Top	Bottom
5°C	5.27×10^6	4.32×10^6	5.35×10^6	4.43×10^6	5.20×10^6	5.67×10^6
25°C	2.32×10^6	1.36×10^6	2.38×10^6	2.95×10^6	3.28×10^6	4.0×10^6
70°C	4059	17,102.6	2511.10	19,784	18,417	6517
Phase angle (°)						
5°C	10.50	13.7	9.1	12.9	8.7	9.9
25°C	38.10	33.1	39.9	25.2	23.3	24.9
70°C	83	41.6	85.9	69.1	69.1	77.50

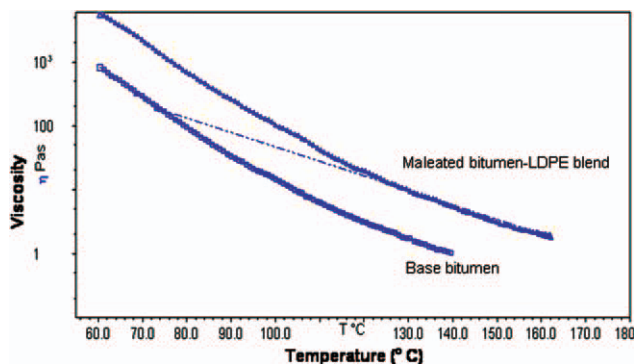


Figure 7. Viscosity versus temperature curves for the base bitumen and maleated bitumen-LDPE blend. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Contrary to this, the base bitumen breaks under stress after certain time, showing its low elasticity. The slope in the maleated bitumen curve is nearly constant and did not flow, whereas the slope in the base bitumen compliance curve increased showing

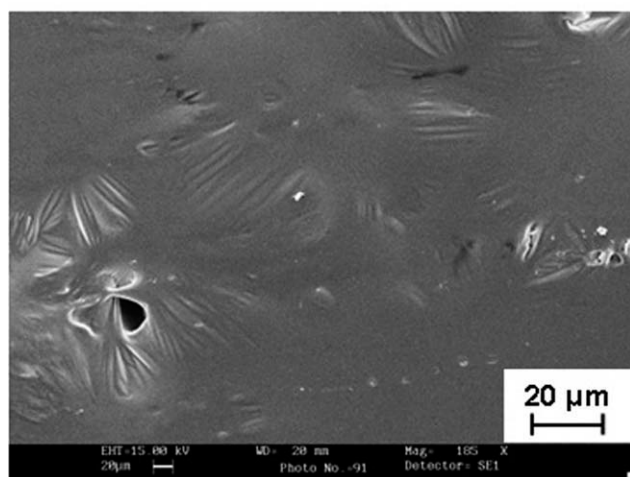
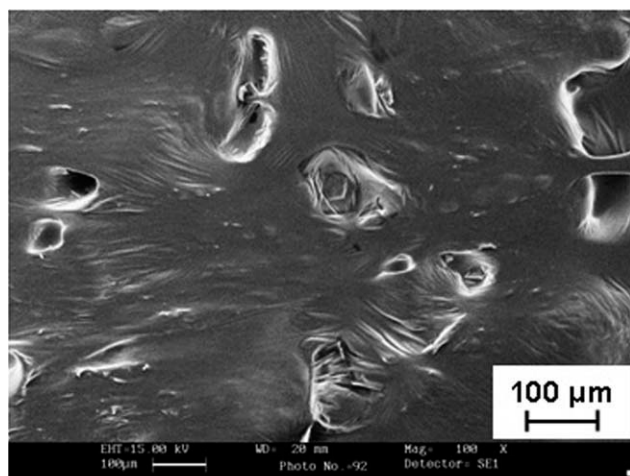


Figure 8. SEM image of maleated bituminous blend with 9 wt% LDPE content.

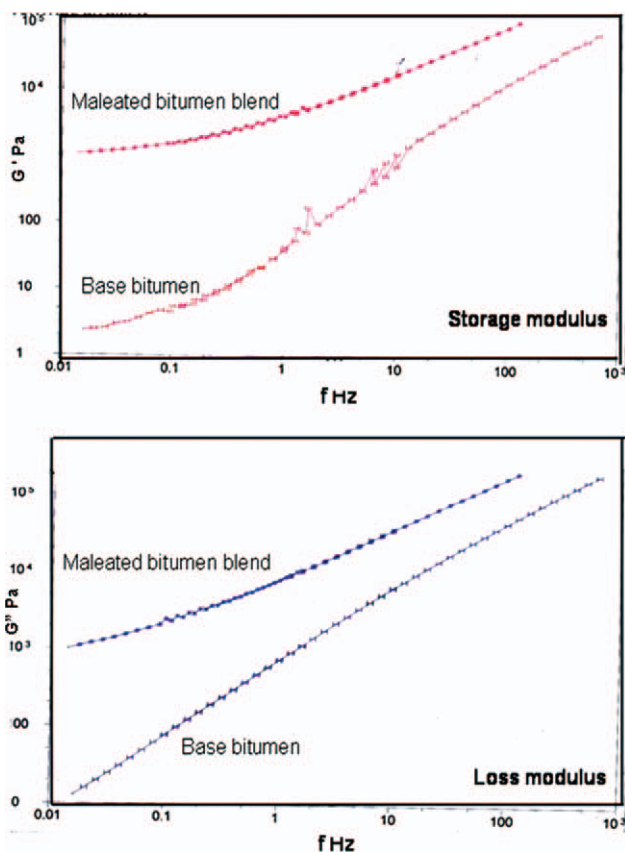


Figure 9. Storage modulus and loss modulus master curves of base bitumen and maleated bitumen-LDPE blend at reference temperature of 60°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

its viscous flow. As seen in the curve, the base exhibited larger creep compliance than the maleated bitumen. This indicates that maleated bitumen blend has shown less temperature susceptibility than the base bitumen. After the removal of stress, the bituminous material was recoiled owing to its inherent elasticity. It is found that the creep recovery of maleated bitumen blend was higher than the base bitumen attributable to the existence of bitumen-polymer network formation. It is observed that the maleated bitumen blend possessed adequate endurance to maintain the shape of roofing under service condition.

CONCLUSIONS

The results indicate that maleated bitumen can be effectively employed as an alternative to base bitumen in minimizing the phase separation *via* its coupling with LDPE and consequently, the improved performance of maleated bitumen-LDPE blends during storage/application. The increase in the degree of maleation leads to increasing viscoelastic properties of the resulting blend systems. Using maleated bitumen, the recoverable blends composed of recycled LDPE and SBS exhibited adequate softening point and low-temperature flexibility. The storage stability of these blends is expected to be more stable when processed it under a colloidal mill. Because of superior temperature resistance

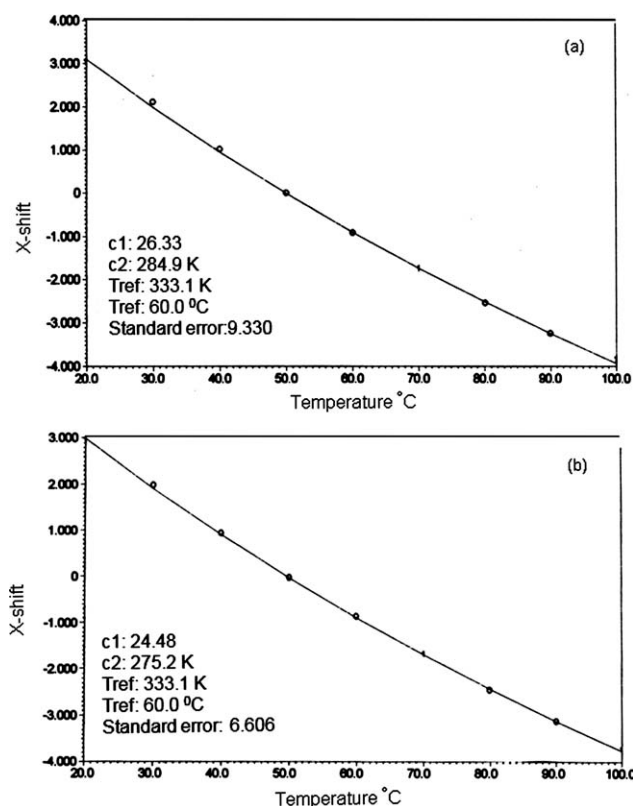


Figure 10. Plots of shift factor versus temperature (a) base bitumen (b) maleated bitumen-LDPE blend. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

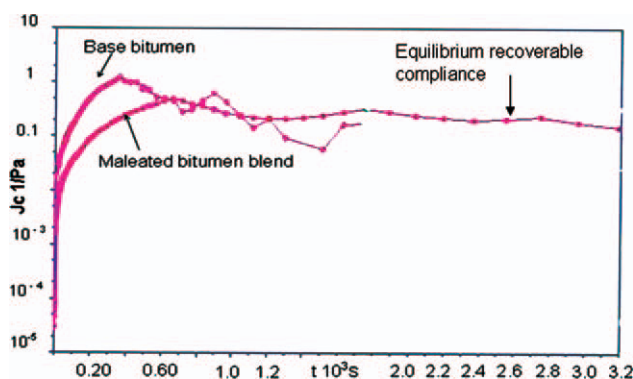


Figure 11. Creep test of base bitumen and maleated bitumen-LDPE blend. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and reduced creep compliance, the maleated bitumen blends with 9 wt % LDPE can be suitably used for producing built-up roofing membrane. It is suggested that the optimum formulation of recoverable blend is necessary to meet the requirements of commercial specifications for desired end-use applications.

ACKNOWLEDGMENTS

This article forms part of a Supra Institutional Project of CSIR R & D programme (Govt. of India) and is published with the permis-

sion of Director, CSIR-Central Building Research Institute, Roorkee.

REFERENCES

1. Boutevin, B.; Pietrasanta, Y.; Robin, J. J. In *Grafted Copolymers and Their Use in Polymer Blends: Recycling of PVC and Mixed Plastics Waste*, Mantia, F. P. La., Ed.; Chemical Technology Publishing: Toronto, Canada, 1996.
2. Murphy, M.; Mahony, M. O.; Lycett, C.; Jamieson, I. *J. Mater. Civ. Eng.* **2001**, *13*, 306.
3. Navarro, F. J.; Partal, P.; Garcia-Morales, M.; Martin-Alfonso, M. J.; Martinez-Boza, F.; Gallegos, C.; Bordado, J. C. M.; Diogo, A. C. *J. Ind. Eng. Chem.* **2009**, *15*, 458.
4. Al-Dubabe, I. A.; Al-Abdul Wahhab, H. I.; Asi, I. M. Ali, M. F. *J. Mater. Civ. Eng.* **1998**, *10*, 161.
5. Tappeiner, W. J.; Male, A. G. *SPE Tech. Pap.* **1993**, 860, ANTEC.
6. Yousefi, A. A.; Ait-Kadi, A.; Roy, C. *J. Mater. Civ. Eng.* **2000**, *12*, 113.
7. Navarro, F. J.; Partal, P.; Martinez-Boza, F. J.; Gallegos, C. *Polym. Testing* **2010**, *29*, 588.
8. Panda, M.; Mazumdar, M. *J. Mater. Civ. Eng.* **2002**, *14*, 527.
9. Yeh, P. H.; Nien, Y. H.; Chen, J. H.; Chen, W. C.; Chen, J. S. *Polym. Eng. Sci.* **2005**, *45*, 1152.
10. Fang, C.; Zhou, S.; Zhang, M.; Zhao, S.; Wang, X.; Zheng, C. *J. Vinyl. Addit. Technol.* **2009**, *15*, 199.
11. Singh, B.; Gupta, M.; Tarannum, H. *J. Appl. Polym. Sci.* **2003**, *90*, 1347.
12. Jun, L.; Yuxia, Z.; Yuzhen, Z. *Constr. Build Mater.* **2008**, *22*, 1067.
13. Singh, B.; Gupta, M.; Kumar, L. *J. Appl. Polym. Sci.* **2006**, *101*, 217.
14. Polacco, G.; Stastna, J.; Biondi, D.; Antonelli, F.; Vlachovicova, Z.; Zanzotto, L. *J. Colloid. Interface. Sci.* **2004**, *280*, 366.
15. Kang, Y.; Wang, F.; Chen, Z. *Chem. Eng. J.* **2010**, *164*, 230.
16. Wang, Q.; Liao, M.; Wang, Y.; Ren, Y. *J. Appl. Polym. Sci.* **2007**, *103*, 8.
17. Rojas, J. M.; Hernandez, N. A.; Manero, O.; Revilla, J. *J. Appl. Polym. Sci.* **2010**, *115*, 15.
18. Yousefi, A. A.; *J. Appl. Polym. Sci.* **2003**, *90*, 3183.
19. Becker, Y.; Mendez, M. P.; Rodriguez, Y. *Vis. Technol.* **2001**, *9*, 39.
20. Ait-Kadi, A.; Brahimi, B.; Bousmina, M. *Polym. Eng. Sci.* **1996**, *36*, 1724.
21. Garcia-Morales, M.; Partal, P.; Navarro, F. J.; Martinez-Boza, F. J.; Gallegos, C. *Polym. Eng. Sci.* **2007**, *47*, 181.
22. Hesp, S. A.; Woodhams, R. T. In: *Polymer Modified Asphalt Binders*, Wardlaw, K. R., Shuler, S., Eds.; ASTM Publications STP 1180: Philadelphia, 1992; p 20.
23. Fang, C.; Li, T.; Zhang, Z.; Wang, X. *Polym. Compos.* **2008**, *29*, 1183.
24. Herrington, P. R.; Wu, Y.; Forbes, M. C. *Fuel* **1999**, *78*, 101.

25. Boucher, J. J.; Wang, I. H.; Romine, R. A. *Am. Chem. Soc. Div. Pet. Chem. Preprints* **1990**, 35, 556.
26. Serfass, J. P.; Joly, A.; Samanos, J. In: *Polymer Modified Asphalt Binders*, Wardlaw, K. R., Shuler, S., Eds.; ASTM Publications, STP 1180, Philadelphia PA, **1992**. p 281.
27. Fawcett, A. H.; Mc Nally, T. P. *Polym. Eng. Sci.* **2001**, 41, 1251.
28. Airey, G. D.; Singleton, T. M.; Collop, A. C. *J. Mater. Civil Eng.* **2002**, 14, 344.
29. Lu, X.; Isacson, U. *Constr. Build. Mater.* **1997**, 11, 23.
30. William, A. G.; Baton, L. R. U.S. Pat., 5,672,642, **1994**.
31. Indian Roads Congress Special Publication 53, Guidelines on use of Polymer and Rubber Modified Bitumen in Road Construction, New Delhi, India, **2002**.