

Use of Isocyanate Production Waste in the Preparation of Improved Waterproofing Bitumen

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ABSTRACT: Waste residue generated during the production of toluene diisocyanate was used as a modifier in making improved waterproofing bitumen. The waste particles were surface-modified with stearic acid. Various bitumen blends based on untreated particles, surface-treated particles, and a combination of an SBS elastomer and waste particles were prepared. The optimized blends were subjected to evaluate their response against temperature and frequency sweeps. It was observed that improvement of the softening point and reduction in penetration could be correlated with the blend morphology in terms of the compatibility between the waste particles and the bitumen. The increased glass transition temperature and satisfactory phase miscibility in the modified bitumen observed in MDSC and DMA traces supported these findings. The coefficient of linear thermal expansion of the modified bitumen

was found to be $1.21 \times 10^{-4}/^{\circ}\text{C}$. The rheological studies revealed that time-dependent properties of the modified bitumen were better in terms of its stiffness and elasticity than that of neat bitumen. The applicability of the Williams-Landel-Ferry (WLF) equation confirms the superior temperature-dependent response of the modified systems over the control. It was noticed that stearate-treated waste-modified bitumen gives the best results in terms of a high complex modulus and a low phase angle. The newly formulated bituminous blend based on stearate-treated waste meets the requirement of existing standard specifications for waterproofing felt. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1365–1377, 2003

Key words: compatibility; coatings; filler; rheology; waste

INTRODUCTION

The concept of using mineral fillers in the modification of bitumen has been recognized for a long time because of their cost and stiffness advantages.^{1–5} However, concerns have been raised that mineral fillers may cause mastics to exhibit excessively brittle behavior and result in cracking at low temperatures.^{6,7} Recently, considerable attempts have been made on the modification of bitumen by soft fillers, such as coke dust,⁸ recycled polymers,⁹ bentonite (volcanic ash),⁵ and carbon black,^{10,11} for road, roofing, and waterproofing applications. These modifiers have a tendency to settle out and not to stay in suspension. Consequently, the modified bitumen loses its ultimate properties and the existence of the grossly separated second phase induces high crack susceptibility. These limitations may be overcome by the surface treatment

of soft fillers through the chemical anchorage/grafting of elastomers,^{8,12,13} ozonization,¹⁴ and microfiller pallet-formation¹⁰ methods. This has resulted in improving the softening point, stiffness, flexibility, storage stability, and thermal behavior of bitumen blends. The performance of these blends can be further achieved by controlling their rheology at a critical level with polymer addition.^{15–20} The lack of good storage stability of these polymer-modified systems at elevated temperatures has received further attention.²¹ The ability of bitumen to withstand forces such as thermal expansion/contraction without cracking, the steady pull of gravity on inclines, and age/physical hardening without deformation is considered as representative of quality roofing/waterproofing materials.^{22–24}

The main objective of the present study was to investigate the suitability of isocyanate production waste as a reactive modifier in the manufacturing of improved waterproofing bitumen. In viewing the health hazard associated with its existing disposal means (ground water contamination from landfills and toxic gas emission during pyrolysis), it is thought that the presence of isocyanate traces in the waste can be effectively utilized in improving the waterproofing function of bitumen via formation of urethane linkage among —OH, —NH, and other reactive groups (bitu-

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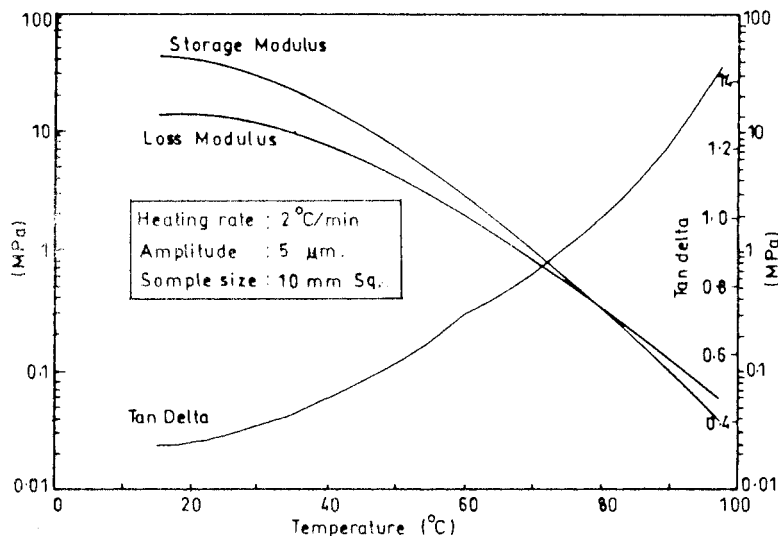


Figure 1 Dynamic mechanical curve of neat bitumen under shear sandwich mode.

men) and an isocyanate functionality. This assumption is based on the polyurethane reaction in asphalt reported by various authors.^{25–28} In previous articles,^{29,30} the phase compatibility between isocyanate production waste and bitumen was reported. It was found that the blend was more stable when waste particles were surface-modified with stearic acid.²⁹ Because of their reactive and soft nature, the behavior of these particles in bitumen is different from that of rigid and inert particles in suspension. These blends were utilized for making a waterproof roof mastic of bitumen–plastics waste. The mastic meets the Indian standard specification in terms of physicomaterial properties and waterproofing functions.³⁰

In this article, we report the effect of isocyanate production waste on the thermal and rheological properties of bitumen. The properties of bitumen blends were assessed in terms of the dispersion of waste particles and their miscibility (with bitumen), thermal expansion, and temperature/frequency dependency using the Williams–Landel–Ferry (WLF) equation.³¹ The waterproofing properties of felts prepared from these blends were also assessed.

EXPERIMENTAL

Materials

An industrial-grade bitumen was obtained from an Indian industry (softening point, 82°C; penetration at 25°C, 16 dmm; ductility at 27°C, 3 cm; flash point, 200°C; loss of heating, 0.30%). The suitability of bitumen was initially assessed for its adhesiveness and temperature susceptibility. The shear properties were obtained from dynamic mechanical spectroscopy at a rate of 2°C/min and 5 μm amplitude. The shear mod-

ulus of the sample was found to be ~40 MPa (Fig. 1). It was also observed that the $G^*/\sin \delta$ of bitumen was more than 10 kPa at 80°C (Fig. 2). This test was performed mainly as a supplement to the softening-point test. The isocyanate production waste was received from an Indian manufacturer of toluene diisocyanate (TDI). Chemically, the waste contains ~96% carbon, isocyanate traces, and other organic matters. The presence of an isocyanate moiety in the waste was confirmed by the appearance of the —NCO peak at 2267 cm^{-1} on an FTIR spectrum. It is a black powder having an average particle size of about 0.51 μm after grinding. Styrene–butadiene–styrene (kraton make) was procured from M/s Shell India Ltd. (New Delhi, India). Stearic acid and limestone dust were procured locally and used as received.

Preparation of blends

The isocyanate production waste was ground in a ball mill, dried in an oven, and sieved to obtain finer and uniform particles. Subsequently, these waste particles were treated with a stearic acid solution in carbon tetrachloride (1 wt % of waste) to avoid particle agglomeration. The slurry was agitated for 60 min, filtered on a Buckner filter, and dried at 70°C for 4 h. The blends were prepared by adding different percentages of ground waste to the bitumen. To prepare a blend, about 200 g of bitumen was heated to a fluid condition, transferred into a steel beaker, and then placed in a heating mantle. Upon reaching 180°C, a preweighed amount of waste particles was added to the bitumen and stirred gently to wet out the particles. Thereafter, the mixing of blends was carried out in a mixer at a speed of about 2000 rpm with three blades of 20-mm

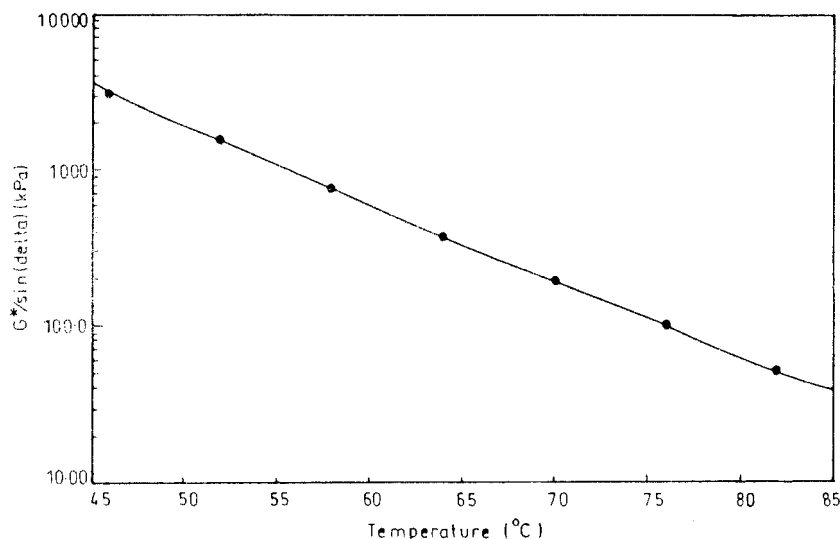


Figure 2 $G^*/\sin \delta$ versus temperature of neat bitumen at 10 rad/s.

diameter. The blending time and temperature of the mix were optimized by obtaining a plateau in the plots of the softening point/penetration versus the blending time. In another experiment, polymer-modified bitumen was prepared by adding SBS (3 wt %) to the bitumen at 180°C under constant stirring for 2 h. Thereafter, waste particles were added to it. The resultant blends were divided into several small containers and stored at room temperature for subsequent experimental testing.

Methods

Conventional tests

The softening point of the blends was measured by a ring and ball apparatus as per IS: 1205-78 using a glycerin bath.³² The penetration test was performed according to IS: 1203-78 under the condition of applying a 100-g weight on the penetration probe for 5 s at 25°C.³³

Modulated differential scanning calorimetry (MDSC)

A modulated differential scanning calorimeter (MDSC 2920, TA Instruments) was used for the characterization of phase miscibility in the blends because of its high resolution and sensitivity over standard DSC. In this technique, a cyclic heating profile (sinusoidal oscillation) is applied to the sample and reference. The resultant deconvoluted signals provide not only the total heat flow obtained from standard DSC but also separate that total into its heat capacity related to reversing and nonreversing components. The sample (12 mg) was conditioned by heating to 140°C at a rate of 10°C/min, followed by controlled cooling at a rate

of 5°C/min to the starting temperature. The DSC runs were performed from -60 to 100°C in crimped aluminum pans at a heating rate of 2.5°C/min under a nitrogen atmosphere. A slow heating rate was selected to allow for good deconvolution. Modulation with a 1°C amplitude for a 60-s period was employed. The standard DSC experiment was also performed on the samples for comparison purposes.

Dynamic mechanical analysis (DMA)

A dynamic mechanical analyzer (DMA 2980, TA Instruments) was employed to measure the viscoelastic behavior of the bitumen blends. A specimen of size 17.50 × 13 × 4 mm was mounted between the arms and tested in a single-cantilever bending mode as a function of the temperature. The sample was tested from -50 to 100°C, while heating at a rate of 2°C/min and 5 μm amplitude under a nitrogen atmosphere.

Scanning electron microscopy (SEM)

A scanning electron microscope (LEO-435 VP) was used to study the microstructural features of the blends. Before examination under the microscope, the surface of the samples was coated with a thin film of gold/palladium to render them conductive.

Thermomechanical analysis (TMA)

The thermal expansion of the bitumen blends was measured by a thermomechanical analyzer (TMA 7, Perkin-Elmer). A flat sample (18 × 7 mm, height 4–7 mm) was placed on a standard quartz expansion fixture and a flat-tipped probe (~2.5-mm diameter) was

lowered onto the sample with the predetermined force (10 mN). The sample was first conditioned by heating to its softening temperature and cooling with a loaded probe to the starting temperature to relieve the internal stress. The TMA traces were obtained between 10 and 50°C at a heating rate of 5°C/min. The change in length of the specimen versus temperature was recorded with respect to a reference body. The coefficient of linear thermal expansion was calculated from these recorded data.

Rheological analysis

The dynamic rheological measurements of samples were carried out on a stress-controlled rheometer (AR 1000, TA Instruments) using parallel-plate geometry of 20-mm diameter and a 2-mm gap. The sample was placed between the plates and oscillated at different frequencies ranging from 0.01 to 100 Hz with three points per decade. For each sample, multiple graphs of storage and loss moduli versus frequency at nine temperatures (20–100°C) were plotted on a log-log scale. Using time-temperature superposition software, each data set was shifted at a reference temperature of 50°C. The shifts were fitted according to the WLF equation. A master curve for each sample was generated, simulating a single experiment performed at 50°C on a wide frequency range. A temperature sweep was performed using plate and plate geometry (25-mm diameter and 2-mm gap) at 10 rad/s over a range of temperatures from 46 to 160°C with an increment of 6°C.

RESULTS AND DISCUSSION

Effect of loading

Figure 3 shows the effect of isocyanate waste loading on the properties of bitumen. There is a continuous increase in the softening point followed by an abrupt change in the magnitude after ~30 wt % waste addition. This is attributed mainly to the synergistic effect of the constituents following the closed packing of particles in an amorphous micellar structure of bitumen. As a consequence, the penetration decreases as the waste loading increases. After ~30 wt % waste addition, the extent of reduction in penetration of the blend is minimal. The presence of excess waste particles may contribute slightly to the stiffness of bitumen due to their soft nature. The supportive evidence for this behavior can be seen in the scanning electron micrographs [Fig. 4(a-c)]. By increasing the waste loading, the emergence of a fibrillar structure in the modified bitumen is attributed possibly to the disturbed equilibrium between the maltenes and the asphaltenes. The dominance of a fibrous-type structure

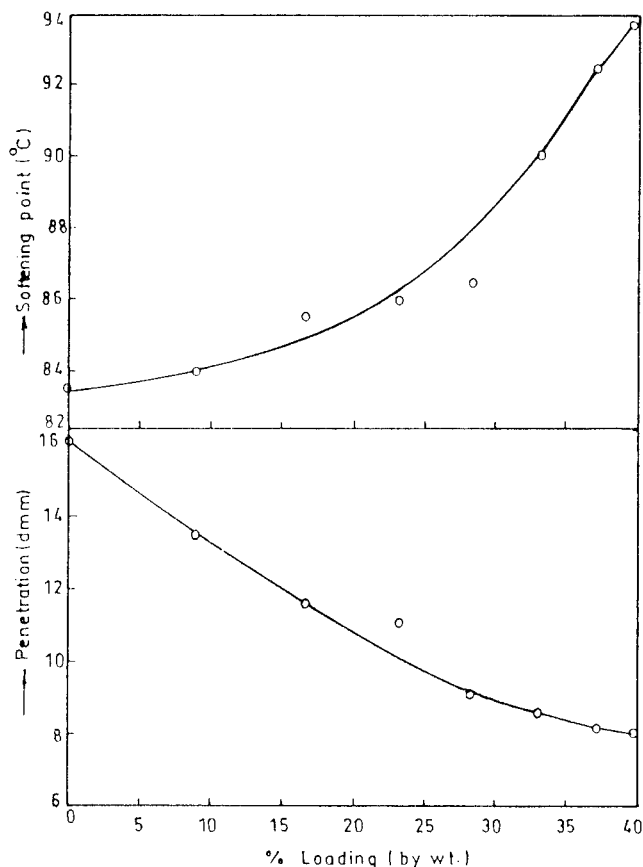


Figure 3 Effect of isocyanate waste loading on the softening point and penetration of bitumen.

is more visible at higher waste loading. It can be assumed that the strengthening effect from these fibrous structures may help in improving the mechanical properties of the binders. The particles are able to absorb low molecular weight ingredients of bitumen, which results in a relatively higher asphaltene content and a possible structural change from sol to gel. The demarcation of separated zones seems to be very apparent following the settling of the denser phase. Some particle aggregates in the oil-rich medium are also seen because of the collision of particles during the creaming process [Fig. 4(b)]. At 40 wt % loading, the extent of demarcation between the phases is comparatively less as the maltene-rich portion also contains particles [Fig. 4(c)]. This indicates that the asphaltene-waste particle associations are near saturation. The coalescence of the particles observed in all cases could be considered due to the presence of negligible Brownian motions.

To obtain an adequate blend stability, the waste particles were surface-treated with stearic acid to maintain their presence in the suspension. The resultant blend has an improved softening point and a reduced penetration with respect to the untreated ones. The distribution of treated waste particles in the

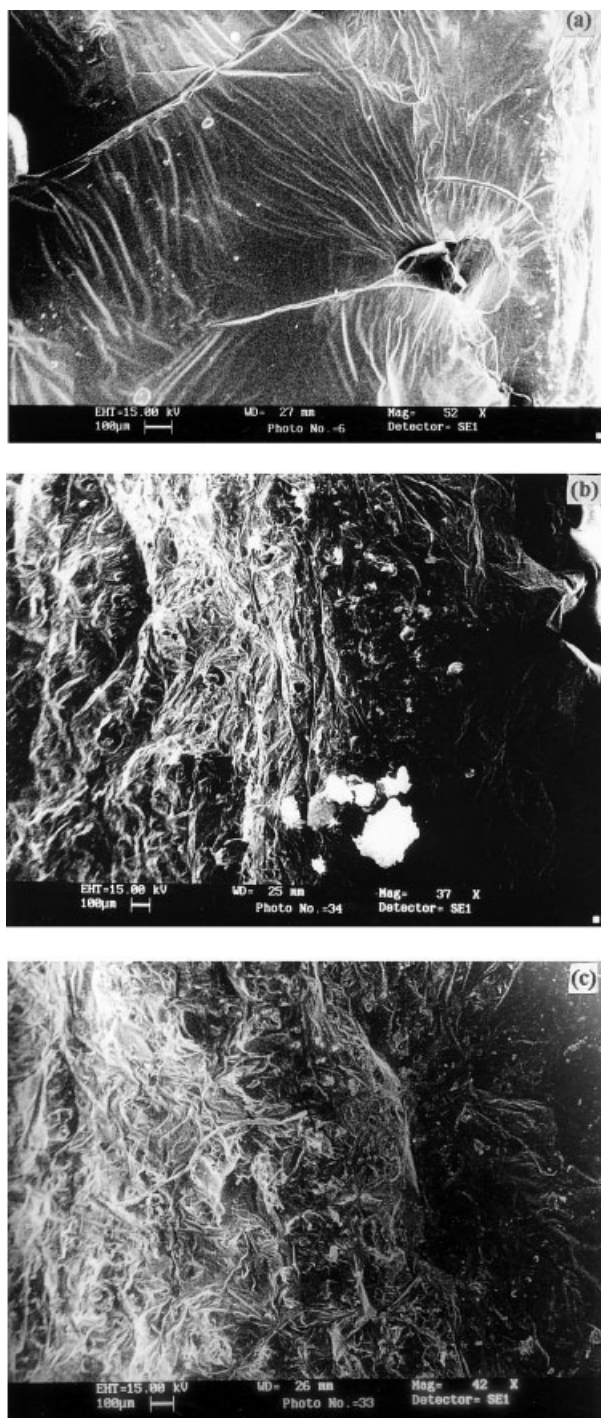


Figure 4 SEM of neat and modified bitumen showing (a) neat bitumen, (b) ~30 wt % waste particles, and (c) ~40 wt % waste particles.

bitumen seems to be nearly uniform (Fig. 5). The surface modification enhances the wetting of the particles, which, in turn, improves the strength of the binder against thermal and mechanical stresses during services. On the other hand, the optimum elasticity in the blend is imparted by adding 3 wt % of the SBS

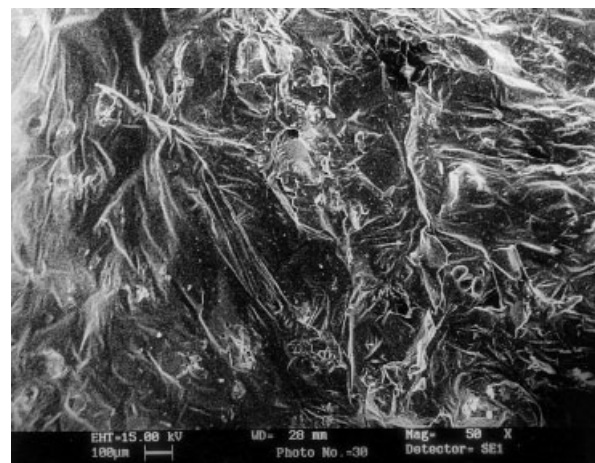


Figure 5 SEM of stearate-treated system showing fine dispersion of particles in a bitumen medium.

elastomer. Figure 6 shows the distribution of the dispersed phases (waste particles and SBS) in the bitumen medium. We assume that small cluster-type structures may be due to the entrapment of fine waste particles in the swollen SBS networks following the absorption of paraffins and aromatic constituents of the bitumen.

Blend miscibility

The miscibility of constituents in the modified bitumen was assessed by DSC [Fig. 7(a,b)]. The thermograms show glass transition temperatures near -10°C followed by an endothermic peak along with a baseline shift. The addition of waste particles increases the glass transition temperature of bitumen from -14.54 to -4.70°C . This indicates that resins/aromatics would interact with an isocyanate moiety existing in the waste, resulting in harder microstructures besides

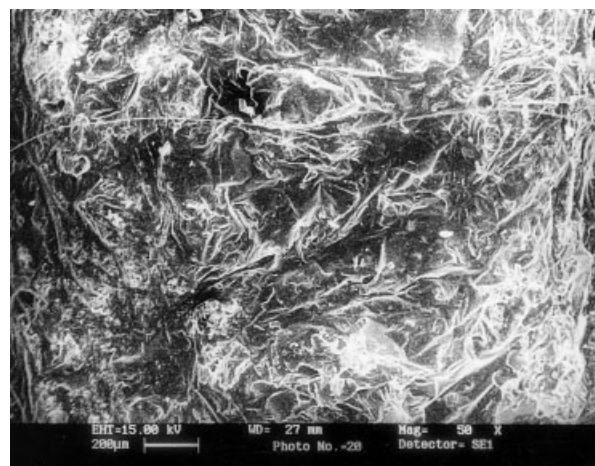


Figure 6 SEM of particle-SBS-modified bitumen blend showing dispersion of particles in a cluster form.

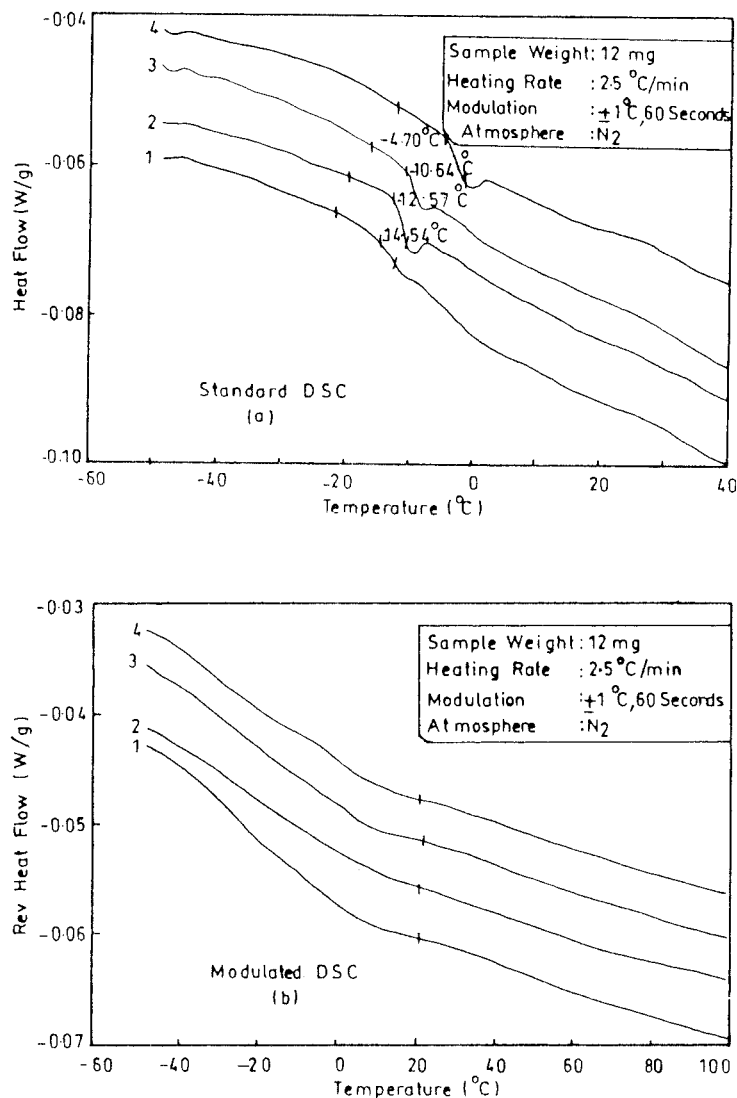


Figure 7 DSC traces of neat and modified bitumen: (1) neat bitumen; (2) untreated particle-bitumen; (3) particle-SBS bitumen; (4) treated particle-bitumen.

the filler contribution.³⁴ The increased depth of an endothermic peak in the modified bitumen could be explained on the basis of the dissolution of crystallized paraffinic fractions in the bitumen medium with respect to the control. It is noticed that the stearate-treated waste particles contribute a significant shift in the glass transition and endothermic peak temperatures, probably due to the fine dispersion of the particles as observed in SEM (Fig. 5) and their association with both maltenes and asphaltenes. This result can be used for justifying the high softening point obtained for the stearate-treated waste-modified bitumen as compared to the other systems. Between -10 and 20 °C, the reduced dissolution region in the modified bitumen is considered to be due mainly to the interactive involvement of phases as compared to the neat bitumen. Figure 7(b) shows modulated DSC curves of

neat and modified bitumen. The reversing signal (heat-capacity component) indicates the multiple subtle transitions between -40 and 20 °C. The resolved transitions in the modified bitumen are observed as a result of modulation, contrary to its conventional thermograms. The small endo peak around -10 °C as observed in the standard DSC disappeared. The presence of the broad nature of transitions after deconvolution suggests the existence of immiscible phases as observed in the SEM. Dynamic mechanical traces of the bitumen blends are shown in Figure 8. The loss modulus curves exhibit well-defined glass transition temperatures near -15 °C, with a clear indication of modifier inclusion effects as observed in the DSC thermogram. The glass transition temperature obtained from the DMA curve is comparable to the DSC trace. During the transition event, the samples undergo sig-

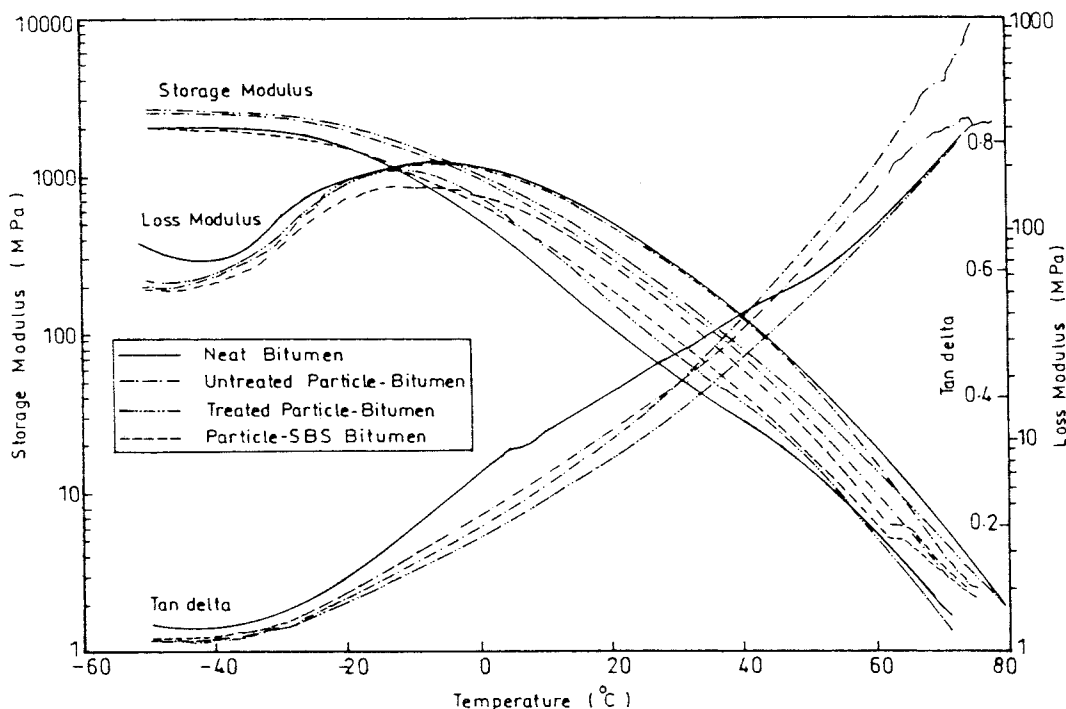


Figure 8 DMA spectra of neat and modified bitumen in a single-cantilever mode.

nificant softening, as reflected by the considerable decrease in the storage modulus. The samples show a glass plateau between -50 and -30°C in the storage modulus curves due to the limited free volume within the sample which prevents any additional molecular motions. The $\tan \delta$ curves show peak maxima near 75°C , which is supportive of its correlation with the softening point ($\sim 82^{\circ}\text{C}$). It is noticed that the storage modulus (elastic component) of the modified bitumen is higher than is the neat bitumen, whereas the loss modulus (viscous component) of the modified bitumen is lower than that of the neat bitumen. The retention of a higher modulus in the flow region of the modified bitumen may be due to the existence of molecular entanglements. The lower values of $\tan \delta$ of the modified bitumen is indicative of the superior elasticity over the control system.

Thermal expansion

To assess compatibility, the information on thermal expansion of the material is desirable to judge the dimensional stability of blends with temperature changes while selecting the contact materials. Figure 9 shows TMA traces of bitumen blends. The thermal expansion of samples increases when the temperature increases and approaches toward softening. During the phase transitions, even in an invariable aggregate state of matter, a sharp change in the dependence of expansion on the temperature was

noticed. The magnitude of the peak maxima of neat bitumen between 30 and 45°C is reduced following the addition of waste particles. This is attributed mainly to the formation of an elastic network as evidenced from the increased glass transition temperature (DSC) and the harder microstructure (SEM). As a result, changes in the length of the modified blends are comparatively less than in the unmodified system. The coefficient of linear thermal expansion of neat bitumen decreased from 1.83×10^{-4} to $1.21 \times 10^{-4}/^{\circ}\text{C}$ for the modified systems. The result obtained on the waste-modified SBS bitumen system is favorable over the other systems for use in the waterproofing of a roof.

Rheology

The rheological behavior of neat and modified bitumen under a temperature ramp is shown in Figure 10. The difference in the values of the storage moduli and $\tan \delta$ is clearly seen upon the addition of an isocyanate waste modifier. The presence of a plateau and lack of a flow region in the storage-modulus curves for the modified bitumen are supportive of the formation of the elastic network while compared with neat bitumen. The evidence on these networks can be further viewed in the $\tan \delta$ curves by the attainment of a peak contrary to neat bitumen. The extent of variation in $\tan \delta$ is more pronounced after 90°C , showing the superior temperature resistance of the modified systems. At 150°C , the value

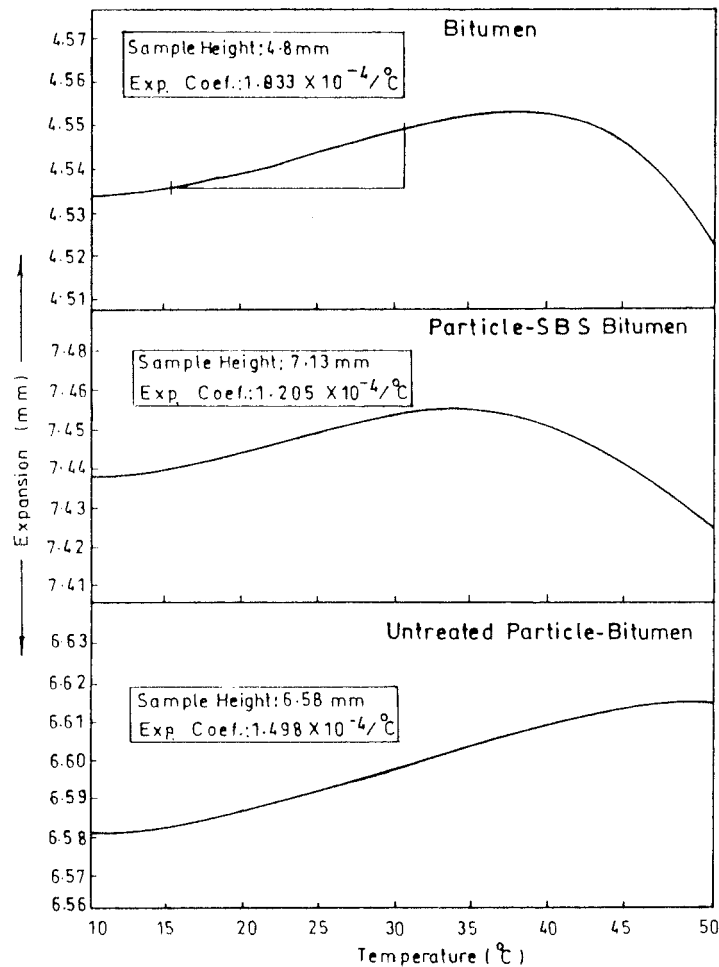


Figure 9 Thermomechanical curves of neat and modified bitumen (temperature range, 10–50°C; load, 10 mN; heating rate, 5°C/min).

of $\tan \delta$ for the neat bitumen is roughly four times that in the modified systems. Similarly, the effectiveness of the modifier on the retention of the storage modulus (modified system) is more visible after 88°C. The stearate-treated waste-modified system gives the best results in terms of a high complex modulus and a low-phase angle over the entire range of temperatures. The modification effects can be well supported by the BLACK diagram between the complex modulus and the phase angle (Fig. 11). It is well known that pure viscous liquids have a phase angle of 90°, while elastic solids possess a zero-degree phase angle. The pronounced difference in the complex moduli of neat and modified systems is noticed above 50°, due mainly to the contribution from the loss modulus. An erratic behavior in the curves between 60 and 70° is indicative of an elastic network formation due to the association of an isocyanate existing in the waste with the bitumen which could provide superior flexibility in the systems with respect to the control.

The storage modulus master curves of bitumen blends at a reference temperature of 50°C are shown

in Figure 12. It is observed that samples behave like an elastic solid at higher frequencies (shorter period) and a rubbery/liquidlike response at lower frequencies (longer period). The effectiveness of the modifier is more pronounced at low and intermediate frequencies than at higher frequencies. The stearate-treated waste and waste-modified SBS bitumen systems retained their higher storage moduli as compared to untreated waste and neat bitumen systems over almost the entire range of frequencies. The critical storage modulus for the modified systems is noticed at a frequency of ~2.2 Hz as compared to ~3.5 Hz for the neat system, showing a better time-dependent response of the modified systems. Figure 13 displays loss modulus master curves of samples at a reference temperature of 50°C. Similar to the storage modulus, the loss modulus also changes with the varying frequencies. However, the magnitude of the difference between the neat and the modified bitumen is very evident at low and intermediate frequencies. At higher frequencies,

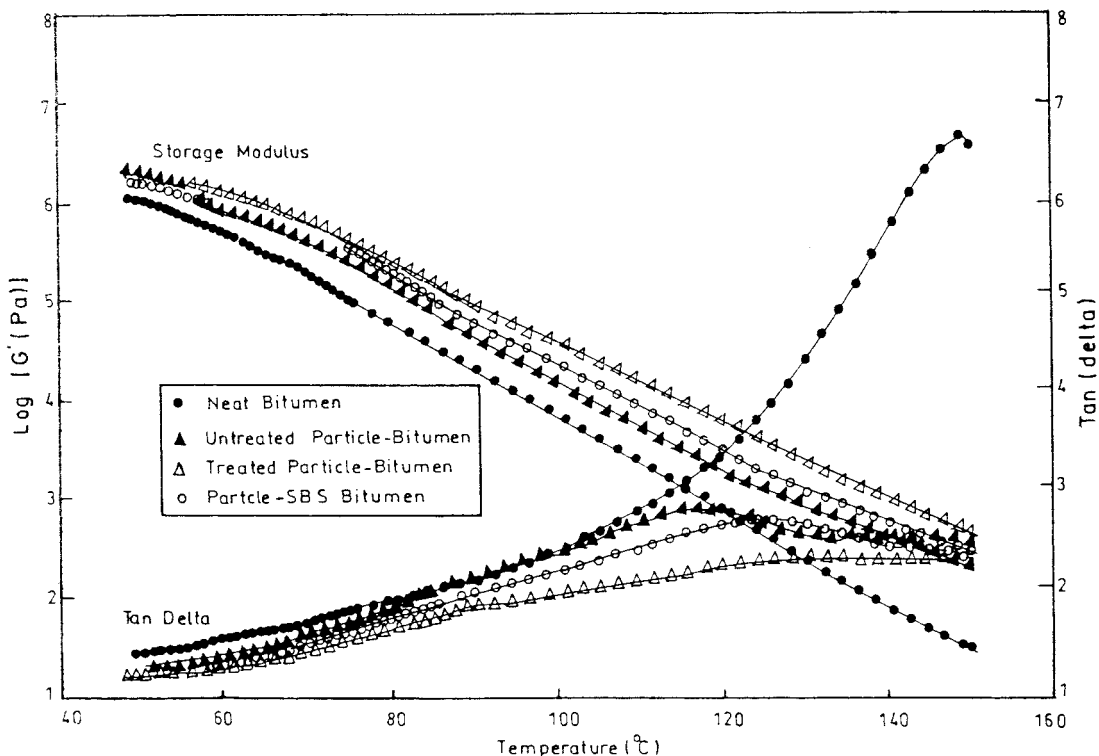


Figure 10 Storage modulus and tan δ of neat and modified bitumen as a function of temperature.

both neat and modified samples exhibit a comparable loss value. The maximum energy dissipation in the modified systems is observed at a frequency of ~ 1.5 Hz as compared to ~ 3.7 Hz for the neat bitu-

men, showing the presence of a less viscous component over a period of time. The loss tangent master curves of bitumen blends are shown in Figure 14. It is observed that the loss tangent of the modified

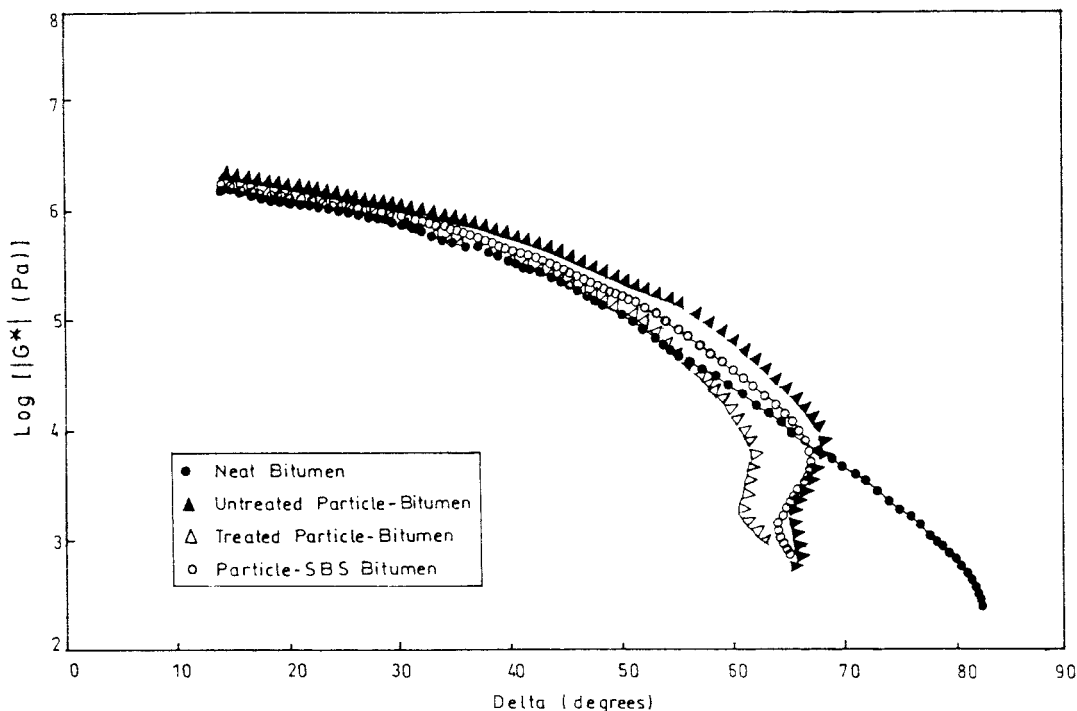


Figure 11 BLACK diagram: complex modulus versus phase angle for neat and modified bitumen from temperature ramp.

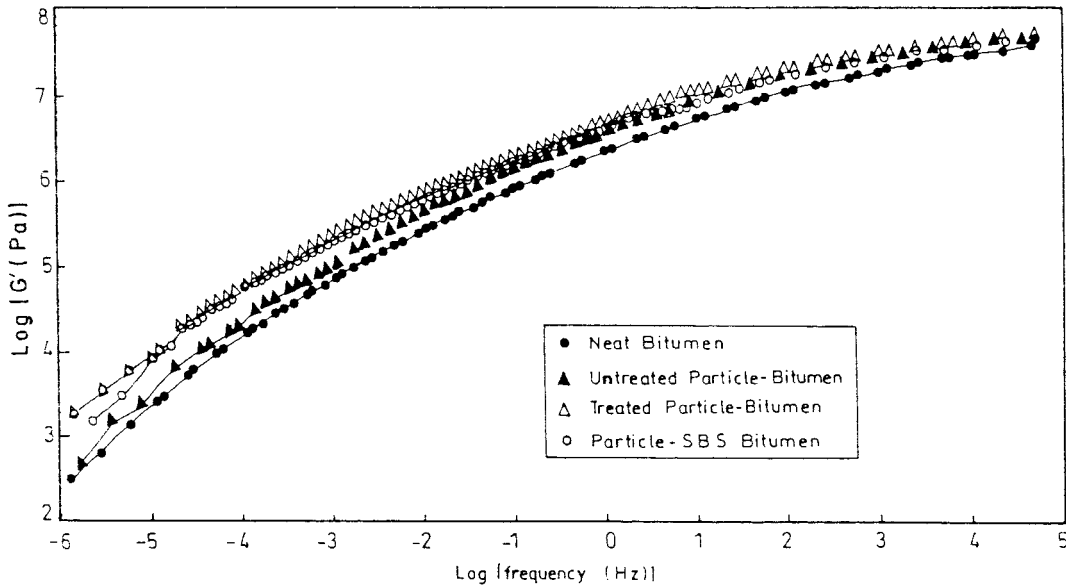


Figure 12 Storage modulus master curves for neat and modified bitumen at a reference temperature of 50°C.

binders is lower than that of the neat bitumen. This gives an indication of the modifier effect in improving the elasticity of the blends. The plateau region in the intermediate frequencies again supports the presence of molecular entanglement. It is noticed that the action of the modifier at lower frequencies is more pronounced than at higher frequencies as reported earlier.³⁵ At low frequencies, the ratio of loss to the storage moduli for the stearate-treated blend is the lowest, showing its superiority (elasticity) over other systems.

The temperature dependency of the modified bitumen is assessed by the following 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 °C); T_0 , the reference temperature (K or °C), and C_1 and C_2 , the experimental constants. The verification of the WLF equation on the bitumen was confirmed pre-

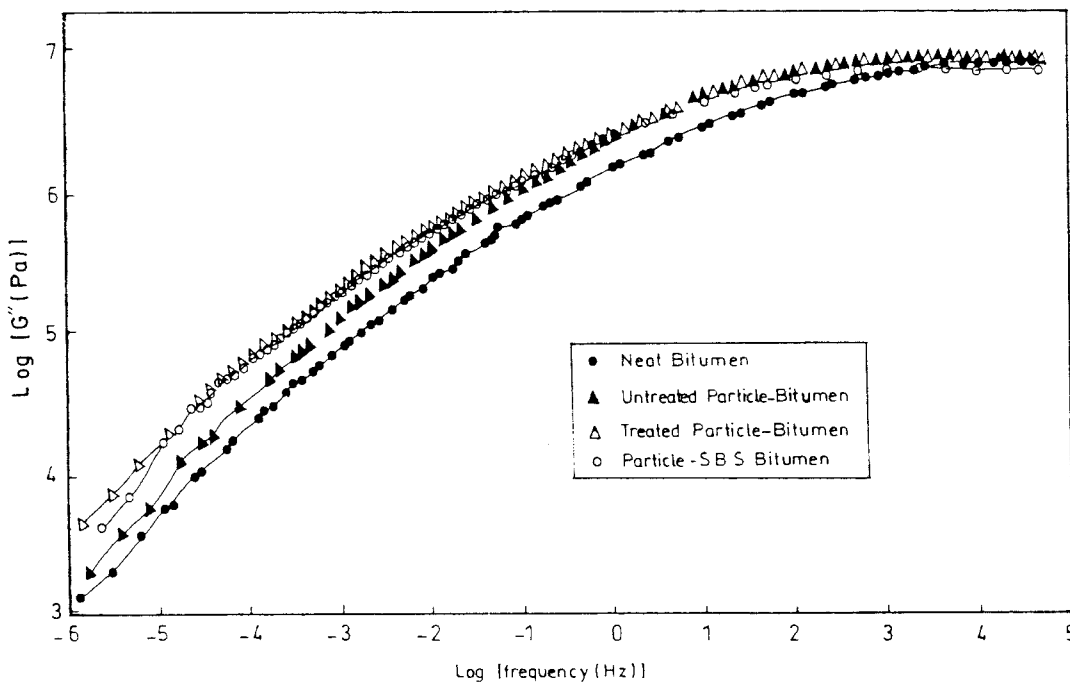


Figure 13 Loss modulus master curves for neat and modified bitumen at a reference temperature of 50°C.

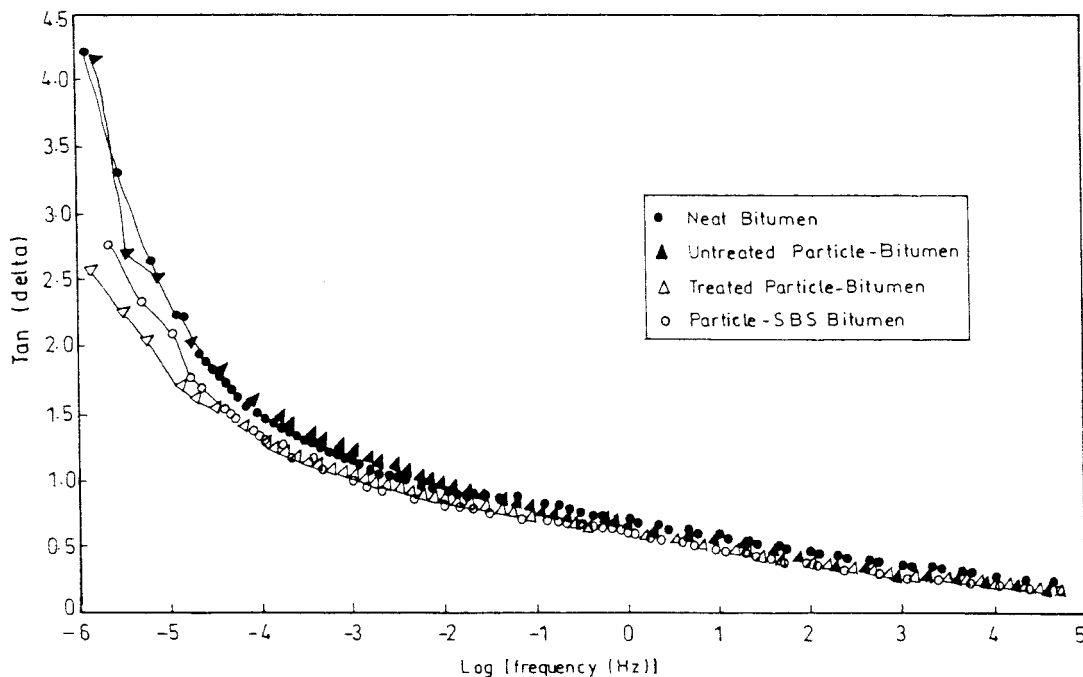


Figure 14 Tan δ master curves for neat and modified bitumen at a reference temperature of 50°C.

viously by several workers at temperatures well above the glass transition temperature.³⁵⁻³⁹ The shift factors for both neat and modified bitumen are calculated by shifting the curves horizontally to superimpose overlapping data. It is mentioned that the shift factor is a measure of how a material's frequency response changes with the variation of temperatures. The values of experimental constants C_1 and C_2 are in the range of 17-28 K and 206-307 K, respectively. The selected reference temperature is

50°C (323.1 K), which the material will see in use. The measured shift factors are fitted to the WLF equation with experimental constants through a nonlinear least-square analysis to obtain theoretical shift values. It is observed that the plot is slightly curved, showing that the frictional free volume increases linearly with respect to the temperature (Fig. 15). The good fit between the shift factors obtained from the WLF equation (solid line) and experimental (circle) shows the validity of the model.

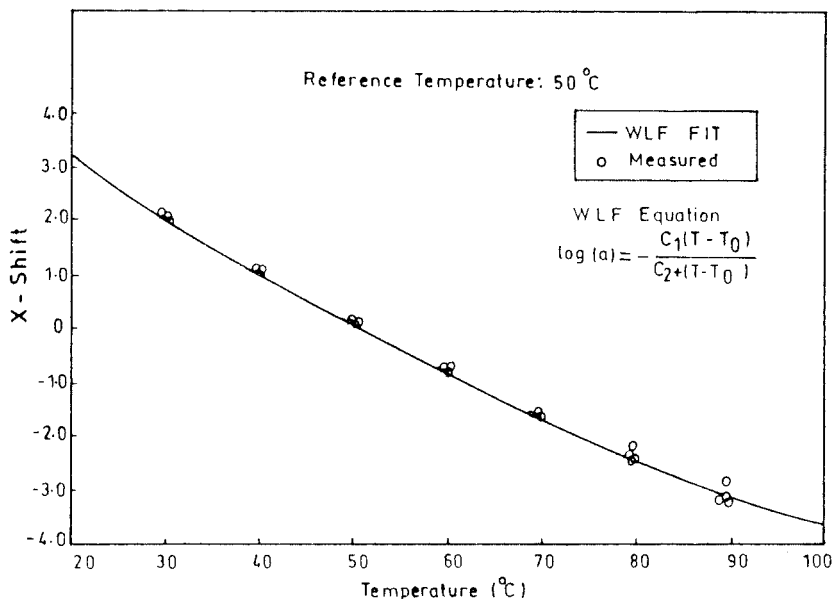
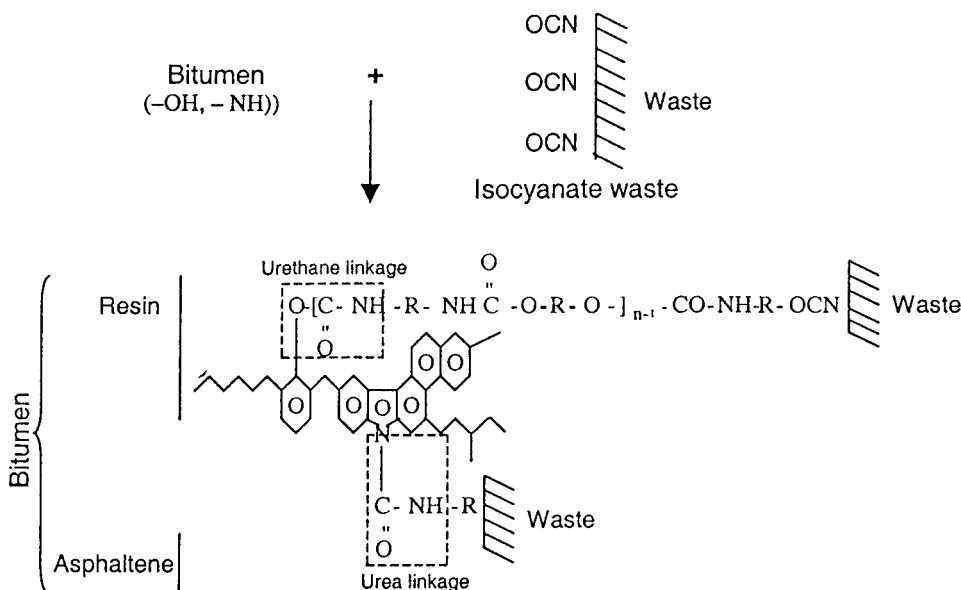


Figure 15 Measured shift factors and WLF fit for neat and modified bitumen.

Waterproofing coating

The modified bitumen is subsequently compounded with a pulverized mineral stabilizer (limestone), anti-aging additives (hydroquinone and phenylamine), an antistripping agent, and rosin. The properties of

the compounded waterproofing bitumen are given in Table I. It is noticed that urethanized bitumen formation could be responsible for a reduced moisture uptake of the binder. The reaction between the bitumen and the isocyanate can be depicted as follows:



It is well known that bitumen contains a small amount of moisture. The moisture may react with the isocyanate traces to form urea derivatives along with

foamy domains which help in achieving the thermal insulation along with the waterproofing system. The coefficient of thermal expansion of the modified bitu-

TABLE I
Comparative Properties of the Modified Bitumen vis-à-vis BIS Specification (IS: 1322- 93, Specification for Bitumen Felt for Waterproofing and Damp-proofing)

Property	Required value (IS: 1322-93)	Obtained value
A. Waterproof coatant		
Filler content maximum (%)	42	40
Softening point (°C)	105	108
Penetration at 25°C (dmm)	7	12
Moisture-vapor transmission ($g\ m^{-2}\ 24\ h^{-1}$), ASTM E96-53T	—	11.29
Water-impermeability test (IS: 5913-95)	—	Impermeable
Water absorption (%)	—	0.51
Coefficient of thermal expansion ($/^{\circ}C \times 10^{-4}$ ASTM E 831- 93)	—	1.2
DMA (ASTM D 4065-82)		
(single-cantilever mode)		
Storage modulus (MPa)	—	220
Loss tangent	—	0.35
B. Felt		
Base	Hessian mat	Nonwoven sisal mat
Bitumen content, minimum (%) kg/10 m ²	12.1	13
Breaking strength (kg)	72	95
Pliability test	No cracking on unrolling	Pass
Storage sticking test	Damage-free during separation of layers	Pass
Heat-resistance test	No melting of coatant	Pass
Pressure-head test	Leakage-free	Pass
Water absorption test maximum (%)	5	4.94

men is also reduced as compared to the neat bitumen. The thermal conductivity of the mastic prepared from these binders is $0.228 \text{ kcal m}^{-2} \text{ h}^{-1} \text{ }^\circ\text{C}^{-1}$, contrary to conventionally used materials such as $0.446 \text{ kcal m}^{-2} \text{ h}^{-1} \text{ }^\circ\text{C}^{-1}$ for the mud phuska, $0.628 \text{ kcal m}^{-2} \text{ h}^{-1} \text{ }^\circ\text{C}^{-1}$ for lime concrete, and $0.155 \text{ kcal m}^{-2} \text{ h}^{-1} \text{ }^\circ\text{C}^{-1}$ for the polymer concrete. The waterproofing felt was prepared using these blends (diluted in naphtha) and natural fiber fabrics (jute/sisal weight: 400 g/m^2). The reason for using a high softening point and a low-penetration bituminous top layer is to maintain foot traffic at all temperatures without any damage during outdoor work. The retention of the penetration value ($\sim 17 \text{ dmm}$) at 60°C is still enough to work. The prepared felt was evaluated for its various properties (Table I). The waterproofing felt meets the requirements specified in IS:1322-93.⁴⁰ A weathering evaluation is under progress.

To explore the recycling possibility of these modified bitumens, an experiment on the extraction of its bituminous portion was made. It is found that the resultant residue is quite brittle due to physical/chemical hardening and also to the loss of maltenes constituent during the recovery process. It is desirable to upgrade the extracted residue with oil and other modifiers for reuse as a saturant in roofing and become a part of a new roofing membrane. Bituminous mastics, cut back/paint, and sealing compounds would be other areas of recycled bitumen for effective utilization.

CONCLUSIONS

The results indicate that isocyanate production waste can be effectively utilized as a modifier along with other additives in the manufacturing of waterproofing bitumen. The modified binders exhibit superior properties such as a high softening point, reduced penetration, high stiffness, low coefficient of linear thermal expansion, and reduced moisture uptake. At low temperatures, phase separation in the blend seems to be minimal as observed by DSC and DMA. The master curves generated from rheological parameters indicate the retention of higher stiffness and elasticity in the modified bitumen over a period of time (frequency) as compared to the neat system. The prepared blend can be satisfactorily used in making a waterproof compound and felt.

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