

Bituminous Polyurethane Network: Preparation, Properties, and End Use

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ABSTRACT: Industrial-grade bitumen (85:25) was treated with 4,4'-diphenyl methane diisocyanate as a blocking agent to make it compatible with polyurethane resin. Optimization of treatment conditions for the bitumen such as isocyanate dose (~3 wt % of bitumen), reaction temperature (180°C), and treatment time (120 min) was done on the basis of estimating its residual acid value and unreacted —NCO groups. Formation of the urethanized bituminous species after treatment resulted in a reduction in the glass-transition temperature of the base bitumen from -9.63°C to -17.09°C and in moisture vapor transmission from 16.95 to 12.21 g 24 h⁻¹ m⁻². The bituminous networks were prepared from these treated/SBS-modified treated bitumen and polyurethane prepolymers by *in situ* and conventional liquid blending methods. Lack of low-temperature flexibility in the bituminous network made from the blending method restricted its use for waterproofing/sealing purposes.

Modulated differential scanning calorimetry showed the presence of two overlapping glass-transition temperatures and an endothermic peak in the *in situ* prepared networks similar to the base bitumen, evidence of a close intermixing of the bitumen constituents with the polyurethane phases. Rheological studies revealed that the SBS-modified bituminous polyurethane network exhibited superior behavior than that of other systems in terms of stiffness and elasticity over a wide range of frequencies. The compounded bituminous networks satisfied the requirements of standard specifications and can be suitably used for waterproofing purpose and sealing of concrete joints. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 217–226, 2006

Key words: polyurethanes; network; coatings; rheology; glass transition

INTRODUCTION

Polymer-modified bitumen has been practiced industrially in the manufacturing of waterproofing coatings/sealing compounds for construction uses.^{1–6} The stability of these compounds depends mainly on the dispersion of polymers and their phase compatibility with bitumen under hot storage and also over relatively long periods. Higher processing temperatures ranging from 170°C to 180°C also have caused degradation of the polymers, altering the mechanical performance of the bituminous binders. To avoid some of these disadvantages, which are linked with thermoplastic ductility, work on the development of bituminous systems has been extended to ambient curable prepolymers such as polyurethane,^{7–9} polyalkyl methacrylate,^{10,11} and phenolic resin¹² as a bitumen improver. The resulting systems did not produce synergistic properties (strength and ease of application) because of the slow reactions between the curable prepolymer reactants and the base bitumen, leading to nonintegrated heterogeneous products.¹³ The im-

provement in these blends may be achieved with the development of *in situ* generation of polymer within a matrix of bituminous material at lower temperatures, ranging from 80°C to 120°C, in the presence of flexibilizers.⁸ The potential of the resulting system can be viewed in terms of its variable viscosity, adequate elastic resiliency, and reduced thermal susceptibility. However, these curable polymers are still limited in their applicability, despite satisfying a number of the requirements as additives.

In previous studies,^{14–16} modification of waterproofing bitumen was made by styrene butadiene styrene elastomer,¹⁴ activated micronized soft plastics waste,¹⁵ and isocyanate-derived waste.^{14,16} The phase miscibility between the constituents and the time-dependent response using rheological parameters of these bituminous binders were reported. Waterproof felt and roof mastic made from these binders met the criteria of Indian standard specifications. For adequate elastic resiliency and surface tackiness (to the masonry), the use of the bituminous system with polyurethane as a dispersed phase was encouraged as a moisture barrier in the construction of commercial and residential buildings.^{7–9,13} The presence of a reactive urethane moiety in the bituminous binder was expected to improve adhesion to the different substrates, to reduce moisture penetration, and also to shorten the cure time compared to conventional bitumen. It is

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widely known that polyurethane is not compatible with bitumen.¹⁷ Phenolic and other reactive groups of bitumen react very rapidly with the free isocyanate groups of polyurethane prepolymer to form aggregates, leading to instability of the resulting system. These deficiencies may be overcome either by synthesizing the bituminous polyurethane network in the presence of plasticizers or by pretreating bitumen with modified clay,¹⁸ maleic anhydride,^{19–21} dibasic acids,²¹ and so forth prior to the mixing with polyurethane prepolymer. The end use of the resulting systems depends on their physicochemical properties in relation to compositional variables, the interactions of their constituents, and the way the product is processed.

In this article, we report the performance of a bituminous network made from the *in situ* addition of polyurethane prepolymer in a rubberized treated bituminous matrix using dibutyl phthalate as a plasticizer. Prior to use, the reactive sites in the bitumen were blocked by 4,4'-diphenyl methane diisocyanate (MDI) to make it apolar and compatible with polyurethane. The suitability of compounded bituminous networks as waterproofing coating/sealing compounds and coatants for nonwoven polyester fabric-based roofing felt is evaluated according to the existing standard specifications.

EXPERIMENTAL

Materials

Two grades of bitumen (industrial grade—softening point, 72°C; penetration, 11.8 dmm; soft grade—softening point, 39°C; penetration, 140 dmm) were obtained from an Indian company. Styrene-butadiene-styrene (SBS; Kraton) was obtained from M/s Shell Chemical Ltd. (New Delhi, India). Polyether polyol, Empeyol F 3000 (hydroxyl number, 54–56 mg KOH/g; average molecular weight, 3000; viscosity, 550 cps at 25°C), dibutyl tin dilaurate (Air Products, Allentown, PA, USA), and diazobutyl cyclo octane (Goldschmidt, Germany AG) were supplied by M/s Manali Petrochemicals (Chennai, India). The 4,4'-diphenyl methane diisocyanate (MDI), Empeyolate CR 100, was used as received (NCO content, 31%; viscosity, 150 cps at 25°C). The silane coupling agent (A-1100) was procured from M/s Union Carbide (Danbury, CT, USA). The dibutyl phthalate, carbon black, limestone powder, and cumerone-indene resin were used as received.

Preparation of blends

A known amount of bitumen was heated at 160°C in a stainless-steel kettle and refluxed for 30 min to remove its residual moisture. Thereafter, it was treated with

different percentages of MDI under constant stirring in a nitrogen atmosphere. The acid value and isocyanate content were estimated at regular intervals to determine the extent of the reaction according to IS 6746-72 and ASTM Standard D 2572, respectively. An optimum level for the treatment of bitumen such as MDI dose (~3 wt % of bitumen), reaction temperature (180°C), and reaction time (2 h) were finalized. The treated bitumen was allowed to cool at 110°C. The catalyzed polyether polyol (10–30 wt %) was added to the bitumen, thinned with dibutyl phthalate, and stirred continuously for 6–8 h. After thorough mixing, MDI was added gradually to the bitumen-polyol blend, mixed for 1–2 min. and applied to the substrates. Before adding MDI, the bitumen-polyol blend was compounded with additives such as limestone powder, cumerone-indene resin, the silane coupling agent, and carbon black.

In another experiment, the bituminous polyurethane network was prepared using SBS-modified treated bitumen as a starting material. The isocyanate-treated bitumen was mixed with SBS (~3 wt %) under constant stirring at 180°C for 2 h. Thereafter, SBS-modified bitumen-polyol blend was made following the procedure described above for preparation of the network. A conventional bituminous polyurethane network also was prepared by liquid blending of polyurethane prepolymer and treated bitumen. For the present work, polyurethane prepolymer was prepared by mixing 4,4'-diphenyl methane diisocyanate and catalyzed polyether polyol in a 1:1 molar ratio. The bitumen-polyurethane mix was stirred for 2–4 min and used for testing purposes.

Methods

The softening points of the base bitumen and its polyurethane network were measured by a ring-and-ball apparatus using a glycerin bath according to IS 1205-78. The penetration test was conducted as per IS 1203-78 under the conditions of applying a 100-g weight on the penetration probe for 5 s at -4°C and 25°C.

An FTIR spectrophotometer (Perkin-Elmer 1760) was employed to collect the spectra of the base bitumen and its treatment with MDI. The samples were dissolved in CH₂Cl₂ and spread on the KBr plate as a smeared film. The IR spectra were recorded at a resolution of 2 cm⁻¹ in the range of 4000–400 cm⁻¹. The difference between the solution and the solvent spectra provided the spectra of the neat sample.

Modulated differential scanning calorimetry (MDSC Q1000, TA Instruments) was used for the characterization of phase miscibility between constituents of the bituminous binders. In this technique, the sample is subjected to a linear temperature/time ramp with a superimposed sinusoidal temperature oscillation.

TABLE I
Properties of Isocyanate-Treated Industrial-Grade Bitumen (85:25)

Isocyanate content (%)	Acid value (mg KOH/g)	Residual NCO (%)	Softening point (°C)	Penetration (dmm)	Moisture vapor transmission (g/24 h/m ²)
0	2.81	—	72.5	11.8	16.95
3	0.28	0.34	83.50	12.4	12.21
5	0.16	0.48	88.50	11.0	33.57
10	Not detectable	0.67	95.0	9.6	48.85
20	Not detectable	1.05	98.0	8.0	54.94

tion. This condition results in a slow underlying heating rate known to improve resolution as well as a faster instantaneous heating rate that improves sensitivity. The superior base line stability and better resolution of the modulated system are the additional benefits over the conventional power compensation DSC system. The samples were conditioned by heating to 150°C at a rate of 5°C/min, followed by controlled cooling under liquid nitrogen at the same rate down to the starting temperature (−120°C). The samples were weighed into aluminum pans and then crimped using a standard sample cell. They were loaded onto the auto sampler of the instrument. Modulation with a 1°C amplitude and a 40-s period was employed. The resultant reversing (heat capacity component) and nonreversing (kinetic component) signals of samples were recorded.

The dynamic rheological measurements were carried out on a stress controlled rheometer (AR 1000, TA Instruments). The sample was placed between 25-mm-diameter parallel plate geometry with a 1-mm gap. The measurements were carried out in the temperature range of 70°C–150°C, increasing in increments of 10°C, at frequencies ranging from 0.01 to 100 Hz at 1% strain with 3 points per decade. Using time–temperature superposition software, each data set was shifted at a reference temperature of 110°C. The shifts were fitted according to the WLF equation. A master curve of complex viscosity, storage modulus, and loss modulus for the base bitumen and its polyurethane networks was generated.

Film of the base bitumen 0.2–0.4 mm thick and its polyurethane network was cast on a glass plate by an applicator. The films were subjected to the normal, heat, and cold tests according to IS 1580-98.²² The water vapor transmission of the films was measured using a pyne cup as per ASTM E 96-80. Extensibility, pour point (IS), and adhesiveness of the samples were examined in order to assess their sealing behavior in accordance with IS 1834-84²³ and ASTM D 3409-95, respectively. The sample was extended on an extension machine at a rate of 3 mm/h for a distance of 6 mm at 0°C according to IS 1834-84. The failure of sealing compounds was noted in terms of their adherence to concrete blocks and cavity formation in the

body. Elastic recovery of bituminous networks was carried out according to IS 1208-78 to a deformation of 10 cm at a rate of 5 ± 0.25 cm/min. 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 the test specimen. The bituminous felts made from polyester nonwoven fabric (weight: 207 ± 5 g/m²) and bituminous network coatant were tested for breaking strength, pliability, storage sticking, heat resistance, pressure head, and water absorption according to IS 13826-1998.²⁴

RESULTS AND DISCUSSION

Effect of blocking agent

The properties of isocyanate-treated industrial bitumen are given in Table I. As the reaction proceeded between bitumen and MDI, the acid value of the bitumen decreased continuously from 2.81 to 0.16 mg KOH/g at a level of 5 wt % MDI addition. On the contrary, unreacted —NCO content in the treated bitumen increased progressively with increases in the MDI dose. The optimum level of MDI as a blocking agent was judged on the basis of its reactivity with active hydrogen in groups typically, present in bitumen, such as —OH, —SH, —NH, and —COOH. Table

TABLE II
Residual Acid Value and Unreacted Isocyanate Content in Treated Bitumen as a Function of Reaction Time and Temperature

Reaction condition	Acid value (mg KOH/g)	Isocyanate content (%)
Temperature (°C) after 2 h		
160	0.373	0.405
170	0.313	0.387
180	0.272	0.322
Treatment time (min) at 180°C		
30	0.815	0.522
60	0.542	0.418
120	0.363	0.376
180	0.280	0.336

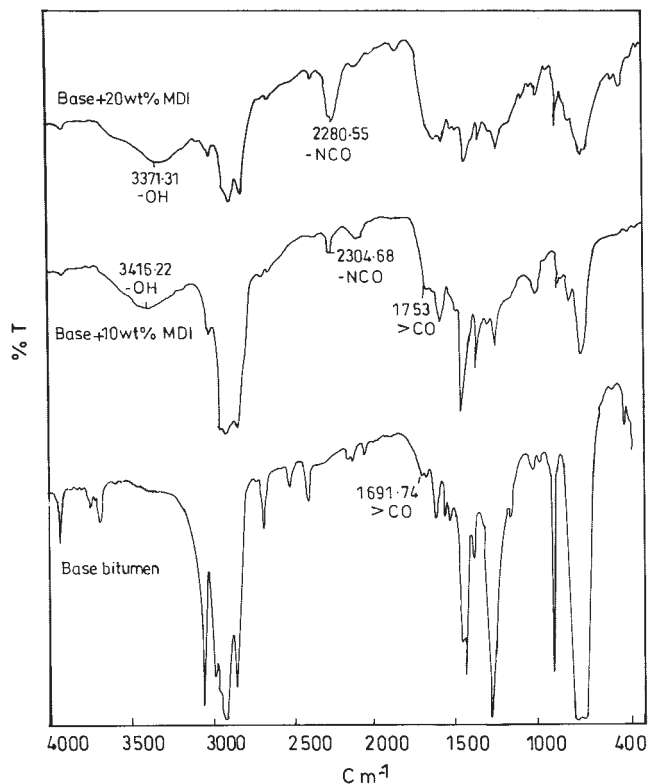


Figure 1 FTIR spectra of base and treated bitumen: (a) base bitumen, (b) base + 10 wt % MDI, and (c) base + 20 wt % MDI.

It gives the residual acid value and unreacted isocyanate groups in the treated bitumen (~ 3 wt % MDI) as a function of reaction conditions. It was found that the extent of reactivity between the base bitumen and the MDI increased with molten temperatures. At 180°C , the conversion of reactive groups into new urethanized bituminous species was maximized at the end of a 3-h reaction time. The residual acid value and unreacted —NCO content in the treated bitumen were only 0.28 mg KOH/g and 0.34% , respectively. Further confirmation of these groups was provided by the FTIR spectrum, which showed a —NCO absorption band at 2280 cm^{-1} and a sharp reduction in the peak height of $>\text{CO}$ groups at 1700 cm^{-1} (Fig. 1). On the addition of isocyanates, the softening point of the base bitumen increased and the penetration decreased (except ~ 3 wt %) following the formation of urethanized bituminous species. In addition, in the molten stage there was conversion of excess isocyanate into polyisocyanurate via an autocatalytic reaction. The formation of these phases was reflected in a regular DSC run, where several transitions at -19.70°C , -2.49°C , 5.95°C , and subtle transitions were observed. The polyisocyanurate phase adversely affected the transmission of moisture vapor (waterproofing function) of the base bitumen. At higher doses (~ 20 wt %), the transmission of moisture vapor of bitumen was con-

siderably higher ($\sim 69.15\%$). The increased height of the —OH peak in FTIR spectra supported the finding of high moisture absorption in these samples. Isocyanate concentration is not critical as long as the blocking group is readily reactive with functional groups of bitumen. At low doses (~ 3 wt %), the conversion of reactive species seems to be optimal, leaving unreacted —NCO at minimum level that is gainfully utilized in the network preparation. About a 27.96% decrease in moisture vapor transmission of the treated bitumen compared to that in the base bitumen was observed. The penetration-temperature relationships indicate that the superior temperature resistance behavior of the optimally treated bitumen over the base bitumen can be attributed to the formation of urethanized bituminous species as a result of the essential reaction between the bitumen and the MDI. It was found that there was a big drop in penetration when the base bitumen was treated with excess isocyanate doses (Fig. 2).

The suitability of isocyanate-treated bitumen was assessed as a starting material in place of the conventionally used base bitumen for making waterproofing compounds. On the basis of the generated data, the optimal doses of MDI as a blocking agent in the base bitumen could be specified at approximately 3 wt % only. Phase miscibility in the system associated with thermal events was further examined under modulated DSC (Fig. 3). The lowering of the glass-transition temperature from -9.63°C to -17.09°C in the reversing curves following the addition of MDI into the base bitumen indicated the presence of a flexible backbone.

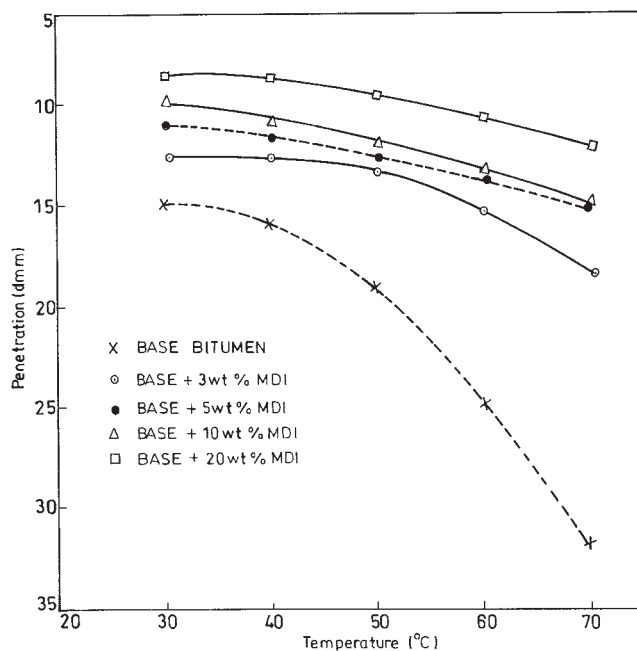


Figure 2 Penetration temperature relationships for base and treated bitumen.

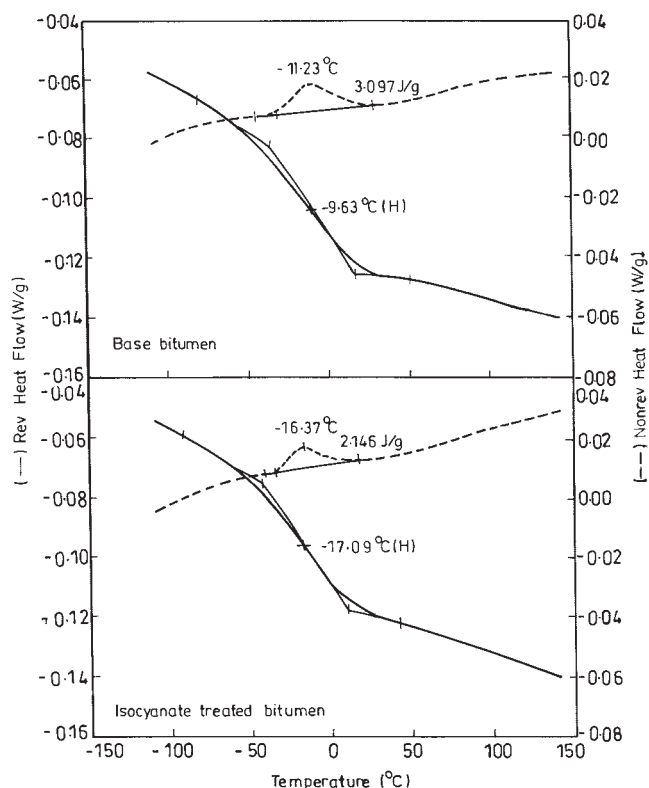


Figure 3 Modulated DSC traces: (a) base bitumen, (b) isocyanate-treated bitumen.

The glass-transition temperature arising from the resin constituent of the treated bitumen decreased from 16.95°C to 10.17°C because of the loss of resin polarity. The nonreversing signal of the treated bitumen exhibited a broad endothermic background and a reduced, shifted exothermic peak as compared to the base bitumen. The heat of fusion of the base bitumen also was reduced from 3.097 to 2.146 J/g after treatment. This would suggest that the ordering evolved during the interactive involvement of newly formed urethanized bituminous species and saturates/aromatics could be responsible for these thermal events. A lack of addi-

tional peaks in the modulated DSC trace supports that miscibility of phases existed in the treated bitumen.

Bituminous network properties

The bituminous polyurethane networks were prepared from treated bitumen by conventional blending as well as with in situ methods. The properties of these network systems are given in Table III. The bituminous network prepared by the blending method exhibited a higher softening point and lower penetration than did the network prepared with an in situ method. However, the development of brittleness, viewed at -4°C under penetration, makes this system less attractive in waterproofing uses. On the other hand, the bituminous network prepared by the in situ polymer-generated method showed a lower softening point and higher penetration than did the treated bitumen. The storage stability test indicated that the polymer phase was uniformly distributed throughout the bituminous matrix, as the top and bottom portions of aged samples exhibited comparable softening point and penetration values. The heat resistance of this network system was improved by adding SBS to the treated bitumen in order to meet the stiffening requirement for roof coatings. As a result, the consistency of the SBS-modified bituminous polyurethane network was comparable to that of the treated bitumen in softening point and penetration.

DSC studies

Modulated DSC traces of the base bitumen and its polyurethane networks are shown in Figure 4. The reversing signal showed a large decrease between -65°C and 10°C and a smaller one between 10°C to 150°C. The broad step changes in the baseline possibly indicate overlapping of two glass-transition temperatures of the amorphous phase of the bituminous system, as reported previously.²⁵ It is thought that paraffinic wax is not completely ab-

TABLE III
Physicomechanical Properties of Base Bitumen and Its Polyurethane Networks

Sample	Glass-transition temperature (°C)	Heat of fusion (J/g)	Softening point (°C)	Penetration (dmm)		Complex modulus (Pa) 110°C
				-4.0°C	Room temp.	
Bitumen	-9.63	3.10	72.50	6.20	11.80	3.40
Isocyanate-treated bitumen	-17.09	2.15	83.50	5.50	12.40	4.40
Bituminous network (<i>in situ</i>)	-17.73	2.44	66.0	6.0	14.0	2.60
SBS bituminous network (<i>in situ</i>)	-16.64	3.86	85.30	4.60	10.80	5.40
Bituminous network (blending)	-10.96	2.34	89.0	3.20	9.20	—

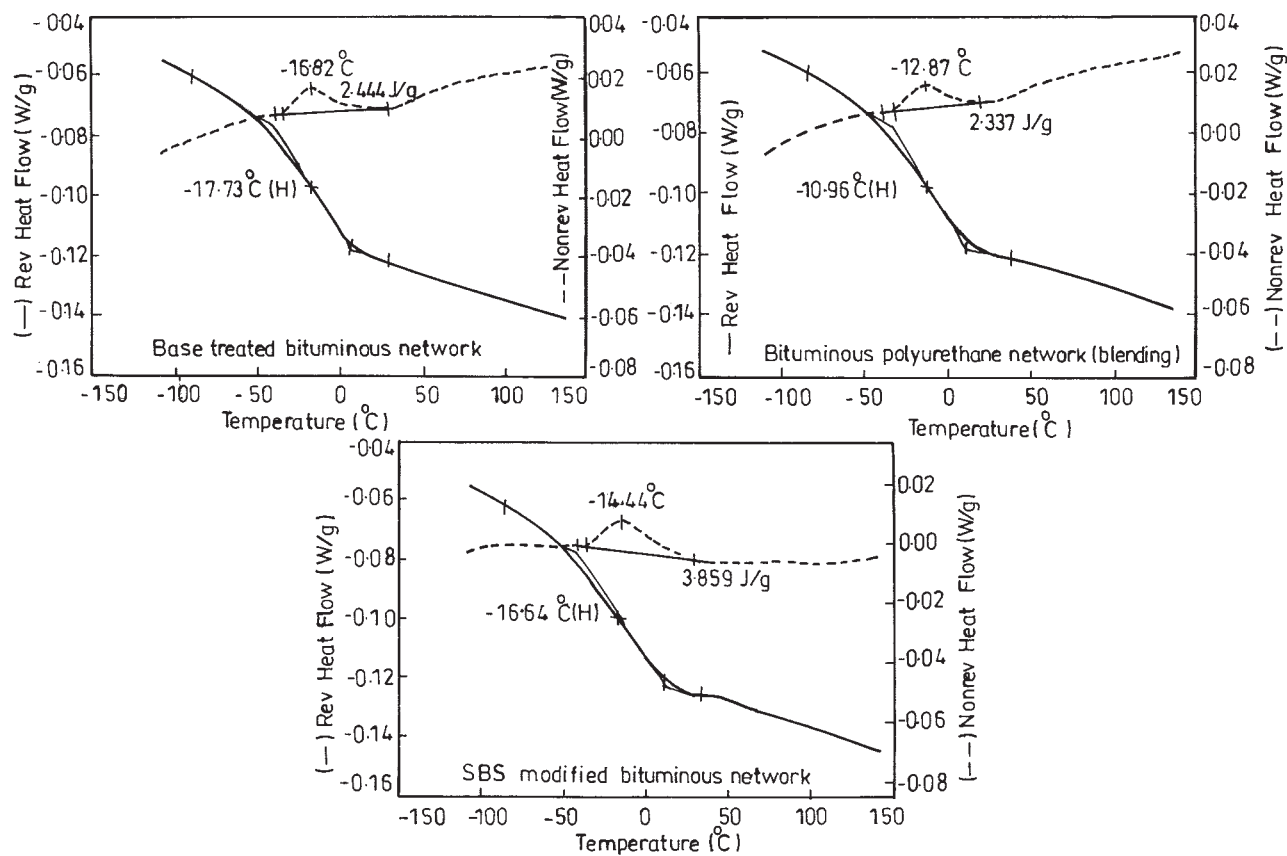


Figure 4 Modulated DSC traces of bituminous polyurethane networks: (a) base-treated bituminous network, (b) bituminous polyurethane network (blending), and (c) SBS-modified treated bituminous network.

sorbed by the aromatics, giving rise a step change. While examining the nonreversing component, an exothermic peak was observed above the baseline in the same area. Amorphous paraffin is crystallized during the glass transition of the bitumen. This resulted in a slight decrease in the apparent heat capacity of the bitumen, thus the slight shift during the glass transition. A large endothermic background also arose from the ordering of resins and asphaltenes between 20°C and 80°C. It should be mentioned that in a regular DSC, the exothermic peak is rarely seen because it is most often shadowed by glass transitions.

The in situ addition of polyurethane prepolymer in the base bitumen reduced the glass-transition temperature of the resulting network from -9.63°C to -17.73°C , showing its superior elastic behavior at low temperatures. Compared to the base bitumen, the nonreversing component of the network showed a reduced exothermic peak height along with its positional shift toward lower temperatures. The heat of fusion of the bituminous network also was reduced to 2.44 J/g from the 3.09 J/g of the base bitumen because of self-ordering of the saturates/aromatics. When SBS-modified treated bitumen was used as a starting material, the glass-transition tem-

perature of the network increased slightly, and the exothermic peak position shifted toward the higher-temperature sides, as compared to the network made only from treated base bitumen. However, the high heat of fusion of the SBS-modified bituminous network can be attributed mainly to the crystallization of both saturates as well as the SBS elastomer.⁴ In this system, the overlapping of the endotherm with higher-temperature sides also was observed. This is consistent with the results for the high softening point and low penetration of the system as described above. On the other hand, the conventionally prepared bituminous polyurethane network exhibited a glass-transition temperature (-10.96°C) comparable to that of base bitumen (-9.63°C). However, the heat of fusion of this system was low compared to those of the base- and in situ-prepared systems. Overlapping of glass-transition temperatures and an endothermic peak was found for the base bitumen and its network prepared from SBS-modified treated bitumen. However, subtle transitions were noted above 40°C in the bituminous network system. This would suggest that the intermix phases moved closer to each other but remained stationary. The storage stability test, as described above, also provided support for the physical mis-

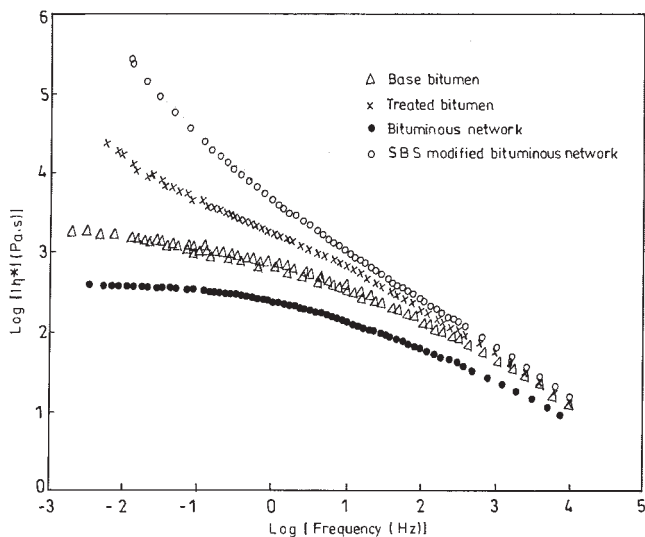


Figure 5 Complex viscosity master curves for the base bitumen and its polyurethane networks at a reference temperature of 110°C.

cibility of the constituents occurring in the network system. The reduced glass transition of the network indicated an apolar system with a flexible chain.

Rheological studies

To evaluate the contribution of polyurethane to the rheology of the base bitumen, experimental master curves of complex viscosity, shear storage, and loss moduli were constructed for the base bitumen and its polyurethane network over a wide frequency range using the time-temperature superposition principle. As can be seen in Figure 5, the base bitumen exhibited low-frequency Newtonian behavior before the shear-thinning region began. The viscosity of the base bitumen was reduced when polyurethane was synthesized within a bituminous matrix. In contrast, the network made from SBS-modified treated bitumen became nonlinear at low frequencies, and the difference in complex viscosity between the base and the bituminous network was much more apparent. At higher frequencies, the complex viscosity was found to be less sensitive to the presence of polyurethane. This may be related to the presence of high molecular weights in the network system.²⁶ These frequency scan data enabled us to assess tack (low frequency) and peel (high frequency) responses of the bituminous network over a period of time.

The master curves of shear storage and loss moduli for the base bitumen and its polyurethane networks are shown in Figures 6 and 7. The addition of polyurethane prepolymer reduced the storage and loss moduli of the base bitumen over the entire range of frequencies. This network along with its base bitumen

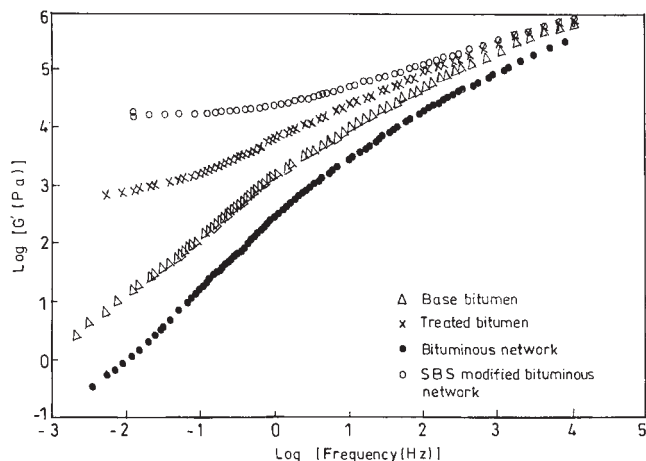


Figure 6 Shear storage modulus master curves for the base bitumen and its polyurethane networks at a reference temperature of 110°C.

was characterized by an apparent shift in the viscous terminal zone to the lower frequencies, where storage modulus measurements are meaningless. The viscosity was low enough to allow the polymer network to dominate the mechanical properties of the bituminous system. When compared to that of the other systems, the increased storage modulus of the SBS-modified treated bituminous network can be attributed to the stiffening effect of SBS elastomer and reduced temperature susceptibility of the bituminous network. At high frequencies the bituminous network exhibited a behavior similar to that of the base bitumen. A plateau observed for the treated bitumen and its SBS-modified bituminous network at intermediate frequencies indicated the formation of molecular association among the constituents of the system. As a consequence, the slope in the curves of these systems was reduced, and

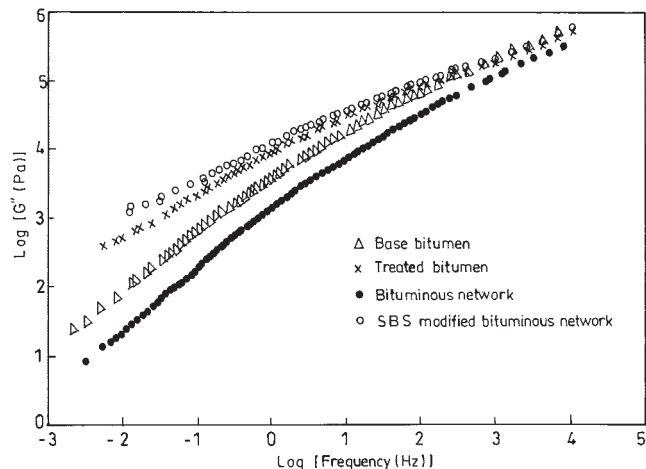


Figure 7 Shear loss modulus master curves for the base bitumen and its polyurethane networks at a reference temperature of 110°C.

TABLE IV
Waterproofing Properties of Bituminous Polyurethane Network Films as per IS 1580-98
(Bituminous Compounds for Waterproofing and Caulking Purposes—Specification)

Sample	Normal test	Heat test	Cold test	Mandrel test (Flexibility test) IS 1322-98	Moisture vapor transmission test ASTM E 96-1980 (g/24 h/m ²)
Bitumen	No slippage	4.0 mm slippage	Crack	Crack	16.95
Isocyanate-treated bitumen	No slippage	No slippage	Crack	Crack	12.21
Polyurethane-modified bitumen	No slippage	1.0 mm slippage	No cracking	No Cracking	6.13
Bitumen polyurethane blend	No slippage	No slippage	Crack	Crack	18.43
Polyurethane rubber bitumen blend	No slippage	No slippage	No cracking	No Cracking	13.78

the sample experienced fewer frequency-dependence responses. It is evident from Figure 7 that the SBS-modified bituminous polyurethane network possessed higher loss modulus than that of other bituminous systems at low and intermediate frequencies. A crossover point between the base bitumen and SBS-modified bituminous networks at higher frequencies was observed, as also reported elsewhere.^{27,28} Above this point, the loss modulus of the bituminous network was slightly reduced. This indicates that the stiffness and elasticity of the bituminous network can be attributed to its more gel-like and structured morphology. A good equilibrium between stiffness and elasticity is important to ensure satisfactory performance of the system in terms of impact and crack resistance behavior under varying conditions.²⁸

Waterproofing/sealing compounds

Coating

The properties of various bituminous systems are given in Table IV. The moisture vapor transmission of the base bitumen was reduced considerably, from 16.95 to 6.13 g m⁻² 24 h⁻¹ (64%), following the in situ addition of polyurethane prepolymer. Under normal condition, there was no slippage of film in all samples when the coated panels were kept in the vertical po-

sition at room temperature for 5 h. At 60°C, the base bitumen and its networks had 4- and 1-mm film slippage, respectively, after a 5-h exposure, whereas the films made from treated bitumen and its network made from SBS-modified bitumen retained their original position (no slippage). Under cold condition (0°C), cracks developed in the films of the base and treated bitumen samples only. However, good adherence of the film to the panel was observed for all samples. The films of bituminous networks also did not exhibit any cracks under the mandrel test (flexibility), contrary to what occurred in the films made from base and treated bitumen, wherein several fine cracks were observed. The softening point and penetration of the bituminous polyurethane network were under the permissible limits of the specification.²²

Polyester waterproofing felt

The properties of roofing felts made from nonwoven polyester fabrics and bituminous polyurethane network saturant are given in Table V. The main idea of using nonwoven fabrics over woven/knits was to obtain superior tear and puncture resistance along with sufficient elongation to accommodate building movements. The roofing felt (1.5–2.0 mm thick) possessed no cracks on being unrolled on a fairly smooth and flat

TABLE V
Properties of Polyester Felts as per IS 1322-98 (Indian Standard for Bitumen Felt
for Waterproofing and Damp Proofing—Specification)

Property	Required value (IS 1322-98)	Nonwoven polyester mat obtained value
Bitumen content, min (%) kg/10m ²	12.1	14.21
Breaking strength (kg)	72	92
Pliability test	No cracking on unrolling	Pass
Storage sticking test	No damage on the coatant during separating layers	Pass
Heat resistance test	No melting of coatant	Pass
Pressure head test	Leakage free	Pass
Water absorption test max. (%)	5	0.425

TABLE VI
Properties of Bituminous Polyurethane Network-Based Sealants as per IS 1834-84 (Specification for Hot Applied Sealing Compounds for Joints in Concrete)

Property	Required value (IS 1834-84)	Obtained value
Penetration (dmm)	15–50	29.60
Softening Point (°C)	—	56
Pour Point (°C) max.	180	103
Flow test (%) max.	5	3.80
Extensibility (mm) min	6	12
Elastic recovery (%)	—	36
Adhesion to the substrate under wet condition (%) (ASTM D 3409-75)	—	82

surface. The water absorption of the roofing felt was only approximately 0.43% when compared to Hessian felt (5%) and glass fiber felt (2%). The samples showed no sign of leakage after a 60-min exposure when subjected to a constant pressure head of water from a 300-mm height. The temperature resistance of the felts was assessed by subjecting them to $68^{\circ}\text{C} \pm 2^{\circ}\text{C}$ in a thermal chamber. Visually, there were no signs of melting of the coatant after 3 h of heat aging. Under a constant pressure of 0.7 kg/cm^2 at $55^{\circ}\text{C} \pm 2^{\circ}\text{C}$ for 18 h, the felt layers were easily separated without damaging the coatant in any way after release of the load. In another attempt, a scrim-type reinforcement in the single-ply membrane also was applied to the concrete substrate using the bituminous polyurethane network as an adhesive. After 72 h of exposure to rain, there was no surface wash of the bituminous network, and bonding between the concrete surface and the roofing membrane also was intact. These results indicate that bituminous polyurethane network-coated polyester nonwoven fabrics can be suitably used as a waterproofing felt/membrane for roofs.

Sealing compound

The suitability of using the bituminous polyurethane network as a sealing compound²³ in concrete joints to resist the ingress of water and other foreign matters (Table VI) was evaluated. Maleic-anhydride-treated 80/100 penetration-grade bitumen was used for the preparation of the network. The softening point of the base bitumen was increased from 39°C to 56°C , and the penetration was reduced from 140 to 60 dmm following the addition of maleic anhydride into the base bitumen. The reduced temperature sensitivity of the system could be explained by the formation of transient networks of bituminous species linked by hydrogen bonding and dipole-dipole interactions with maleic anhydride.²¹ The bituminous network compounded with various additives was easily

poured with a uniform consistency at 103°C into the joint space. Its nonextruding type showed enough resistance to flow out of joints during a hot summer. About a 76%–83% improvement in the elastic recovery was observed when approximately 20%–40% polyurethane was added to the base bitumen. Under extension, the adherence of the compound to both concrete blocks continued, even up to 12 mm placing, without any cavity formation, whereas the base bitumen failed through the concrete interface and also through cavity formation in the body after a 2-mm spacing. Under wet conditions, the area covered by the bituminous network on the flamed lids (as the adhesion) was approximately 82% when the sealing compound was tested as per ASTM D 3409-75. The penetration of the sealing compound was under the permissible limit of the specification.²³

CONCLUSIONS

The results indicate that *in situ* generation of polyurethane in a rubberized bituminous matrix using plasticizer as a compatibilizing agent appears to be a method preferred over conventional blending for the manufacture of waterproofing/sealing systems. The main advantages of this network are its variable viscosity behavior and short curing time. The phase miscibility between the bitumen constituents and the polyurethane resin observed in MDSC may be achieved at a desirable level by treating bitumen with a blocking agent prior to its use as a starting material. This phase mixing was again confirmed in the storage stability test, as the top and bottom portion of the network exhibited comparable softening point and penetration characteristics. The bituminous network prepared from the SBS-modified treated bitumen was stiffer and possessed the desired flexibility and time-dependent response, as viewed in the master curves constructed for complex viscosity, storage, and loss moduli using the time-temperature superposition principle. The sealing compound made of this network showed significant improvement over the base bitumen in its elastic recovery, extensibility, and adequate retention of adhesion with the substrate under wet conditions. The network films also displayed a behavior superior to those of the conventional bitumen in moisture vapor transmission and heat and cold resistance. It is suggested that bituminous polyurethane network can be used as an alternative to conventional hot bitumen systems for waterproofing/sealing purpose.

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