Physical and Rheological Characteristics of Liquid Natural Rubber Modified Bitumen

N. RADHAKRISHNAN NAIR,[1] N. M. MATHEW,[1] SABU THOMAS,[2] PRABHA CHATTERJEE,[3] M. A. SIDDIQUI[4]

[1] Rubber Research Institute of India, Kottayam 686 009, India

[2] School of Chemical Sciences, Mahatma Gandhi University, Priyadarsini Hills P.O., Kottayam 686 650, India

[3] Indian Institute of Chemical Technology, Hyderabad 500 007, India

[4] Cochin Refineries Ltd., Ambalamugal 682 302, India

Received 31 October 1996; accepted 12 September 1997

ABSTRACT: Polymer modification of commercially available bitumen has been attempted by the incorporation of liquid natural rubber (LNR) of medium viscosity. Both soft and blown bitumens have been studied. Physical and rheological characteristics of the samples were investigated. Improvement in physical properties such as shear strength and ductility in the case of blown bitumen and resistance to flow in the case of soft bitumen were observed. It was also found that as a result of addition of LNR, the activation energy of flow increases in the case of soft bitumen and decreases in blown bitumen. © 1998 John Wiley & Sons, Inc J Appl Polym Sci 68: 53–61, 1998

Key words: liquid natural rubber; bitumen; rheology; polymer modification

INTRODUCTION

Bitumen by itself has become inadequate in many applications due to the changed perception on paving binders in recent years. Traffic factors have increased with respect to both load and volume. Higher pressures are employed for tires, and higher costs demand construction of thinner pavements. Hence, modification of bitumen by different techniques has become a topic of interest. Modification using polymers is a widening area due to the viscoelastic contribution of the polymer to the bitumen properties. The changes are aimed at addressing major problems, such as high-temperature permanent deformation, load-associated fatigue cracking, low-temperature thermal cracking, etc. Aging is the hardening of bitumen over time and temperature. Polymers have been found to reduce hardening and moisture susceptibility and improve the adhesion of the binder to aggregates. Use of rubber by a French bitumen company for laying pavements as early as in 1902 has been documented.[1] Most bitumen binders were classified by a viscosity-graded system. The viscosities at 60 and 135°C are important to the application and use of bitumen binders. The viscosity-graded system has been replaced by the penetration system in the 1960s. A needle is loaded with either 100 g (25°C) or 200 g (4°C). The depth of penetration is measured and expressed in one hundredth of a centimeter. The penetration at 4°C is used to describe the low-temperature properties of bitumen binders. Other tests used to characterize bitumen binders are ring and ball softening point (ASTM D113).

There are a large variety of polymers currently

Correspondence to: N. Radhakrishnan Nair.

Journal of Applied Polymer Science, Vol. 68, 53–61 [illegible]

CCC [illegible]

being used in the bitumen paving industry. The purpose of modification depends on the problem it addresses or the type of bitumen mixture to be modified. The extent of improvement may, however, be quite different, depending on the source of bitumen, the effect of origin of the petroleum, etc. Modification with rubber improves the properties of bitumen. The effect on the bitumen is expressed most clearly in the toughness/tenacity test. Blown bitumen, also known under the name of "mineral rubber," is generally not considered suitable for blending with rubber.[3]

Modification with rubber permits bitumen, even of low quality, to acquire attractive properties. This makes it possible to lay down suitable road paving, using relatively inexpensive bitumen. Natural rubber (NR) is a potential candidate among various polymers for blending with bitumen. Because of its photosynthetic origin and renewability, it is ecologically friendly. It is one of the polymers with which bitumen modification has been successfully carried out. NR is obtained as latex from the plant *Hevea braziliensis*. Addition of NR to bitumen has been attempted in different ways. One of the earliest methods is the addition of latex, stabilized with alkali, to molten bitumen under vigorous stirring. Water evaporates, and NR becomes mixed with the bitumen.[4] Addition of rubber in powder form has also been attempted. These include ground vulcanized rubber powder from the rejections of various dry rubber and latex products.[5]

NR latex is the most effective additive to bitumen and the cheapest, but difficulties arise due to its water content. Vulcanized and lightly vulcanized powders are convenient to use. Smoked sheet or crepe rubber can be used by masticating and dispersing in fluxing oil. The present investigation is on the addition of liquid natural rubber (LNR) for improving the properties of bitumen binders and encapsulating materials. The addition of polymer in this form is simple as a result of the dry nature of LNR, due to which problems of frothing and fall in temperature associated with latex addition are eliminated. LNR also readily mixes with bitumen. This method can be easily adopted as one of the unit operations in a petrochemical complex to manufacture modified bitumen. Stabilizing agents incorporated into the latex can also be dispensed with. Further, NR in the latex form is a premium grade, whereas depolymerized rubber can be prepared starting even from scrap rubber that is considered inferior for many structural and engineering applications.

MATERIALS AND METHODS

Bitumen

Bitumen, the residue left over after the distillation of petroleum, characteristically contains very high molecular polar species, called asphaltenes, soluble in a wide range of solvents. Asphalt is used extensively for paving and waterproofing. Crude oils from different sources contain different amounts of asphalt, and their properties vary. Asphalt produced for the paving industry is normally a blended product so as to achieve the specifications. Asphalt is converted into a harder product by air contact at 200–270°C. The modification involves dehydrogenation and polymerization reactions. The heteroatoms like sulfur reacts preferentially with oxygen leaving less polar substances, which increases incompatibility. Industrial emulsions prepared from blown bitumen have applications outside the road building industry. Casein, gelatin, blood albumin, etc., are used as peptizing agents in these cases. The emulsions have found a wide variety of applications, such as surface coatings for asphalt pavements, for built-up roofs, and for other weatherproof coverings. For the present study, normal and blown bitumens were used. The soft bitumen, 80–100 grade, was a product of Cochin Refineries Ltd., Cochin. Blown bitumen was of grade 5, on the penetration scale, and was supplied by Bituminex Ltd., Ambalamugal. It was prepared by removing the volatile fragments, such as gas oils, by heating to 300 to 350°C and also by the application of vacuum for 3–4 h.

Liquid Natural Rubber

The LNR was of medium viscosity grade with a Brookfield viscosity of 1,60,000 mPa s. It was prepared starting from ISNR-5 by thermal depolymerization technique, as suggested by Claramma et al.[6] Its production involves size reduction of the NR molecules by the combined action of mechanical, chemical, and thermal energies. NR was first masticated on a two-roll mill incorporating peptizing agents and then heated in a depolymerizer at an elevated temperature to produce LNR.

being used in the bitumen paving industry. The purpose of modification depends on the problem it addresses or the type of bitumen mixture to be modified. The extent of improvement may, however, be quite different, depending on the source of bitumen, the effect of origin of the petroleum, etc. Modification with rubber improves the properties of bitumen. The effect on the bitumen is expressed most clearly in the toughness/tenacity test. Blown bitumen, also known under the name of "mineral rubber," is generally not considered suitable for blending with rubber.[3]

Modification with rubber permits bitumen, even of low quality, to acquire attractive properties. This makes it possible to lay down suitable road paving, using relatively inexpensive bitumen. Natural rubber (NR) is a potential candidate among various polymers for blending with bitumen. Because of its photosynthetic origin and renewability, it is ecologically friendly. It is one of the polymers with which bitumen modification has been successfully carried out. NR is obtained as latex from the plant *Hevea braziliensis*. Addition of NR to bitumen has been attempted in different ways. One of the earliest methods is the addition of latex, stabilized with alkali, to molten bitumen under vigorous stirring. Water evaporates, and NR becomes mixed with the bitumen.[4] Addition of rubber in powder form has also been attempted. These include ground vulcanized rubber powder from the rejections of various dry rubber and latex products.[5]

NR latex is the most effective additive to bitumen and the cheapest, but difficulties arise due to its water content. Vulcanized and lightly vulcanized powders are convenient to use. Smoked sheet or crepe rubber can be used by masticating and dispersing in fluxing oil. The present investigation is on the addition of liquid natural rubber (LNR) for improving the properties of bitumen binders and encapsulating materials. The addition of polymer in this form is simple as a result of the dry nature of LNR, due to which problems of frothing and fall in temperature associated with latex addition are eliminated. LNR also readily mixes with bitumen. This method can be easily adopted as one of the unit operations in a petrochemical complex to manufacture modified bitumen. Stabilizing agents incorporated into the latex can also be dispensed with. Further, NR in the latex form is a premium grade, whereas depolymerized rubber can be prepared starting even from scrap rubber that is considered inferior for many structural and engineering applications.

MATERIALS AND METHODS

Bitumen

Bitumen, the residue left over after the distillation of petroleum, characteristically contains very high molecular polar species, called asphaltenes, soluble in a wide range of solvents. Asphalt is used extensively for paving and waterproofing. Crude oils from different sources contain different amounts of asphalt, and their properties vary. Asphalt produced for the paving industry is normally a blended product so as to achieve the specifications. Asphalt is converted into a harder product by air contact at 200–270°C. The modification involves dehydrogenation and polymerization reactions. The heteroatoms like sulfur reacts preferentially with oxygen leaving less polar substances, which increases incompatibility. Industrial emulsions prepared from blown bitumen have applications outside the road building industry. Casein, gelatin, blood albumin, etc., are used as peptizing agents in these cases. The emulsions have found a wide variety of applications, such as surface coatings for asphalt pavements, for built-up roofs, and for other weatherproof coverings. For the present study, normal and blown bitumens were used. The soft bitumen, 80–100 grade, was a product of Cochin Refineries Ltd., Cochin. Blown bitumen was of grade 5, on the penetration scale, and was supplied by Bituminex Ltd., Ambalamugal. It was prepared by removing the volatile fragments, such as gas oils, by heating to 300 to 350°C and also by the application of vacuum for 3–4 h.

Liquid Natural Rubber

The LNR was of medium viscosity grade with a Brookfield viscosity of 1,60,000 mPa s. It was prepared starting from ISNR-5 by thermal depolymerization technique, as suggested by Claramma et al.[6] Its production involves size reduction of the NR molecules by the combined action of mechanical, chemical, and thermal energies. NR was first masticated on a two-roll mill incorporating peptizing agents and then heated in a depolymerizer at an elevated temperature to produce LNR.

Table I Formulation of Blends

Sample No.	Percent of Bitumen	Percent of Blown Bitumen	Liquid Natural Rubber
B0	100	Nil	Nil
B5	95	Nil	5
B10	90	Nil	10
B20	80	Nil	20
B30	70	Nil	30
BB0	Nil	100	Nil
BB5	Nil	95	5
BB10	Nil	90	10
BB20	Nil	80	20
BB30	Nil	70	30

Preparation of Samples

LNR was incorporated into bitumen by melt blending. The bitumen was first heated to an easily flowable consistency, and LNR was added slowly under stirring and was homogenized properly. Formulations of the blends are given in Table I.

Viscosity Measurements

For the measurement of viscosity of the soft bitumen samples, a Haake rotational viscometer was used. The sensor system used was MV1. The viscosity of the blown bitumen samples was measured on a capillary rheometer attached to a Zwick UTM. Viscosities were measured over a range of temperature and shear rate to study the flow behavior on the modification of bitumen with LNR.

Lap Shear Test

The lap shear test was used to determine the room temperature cohesive strength of modified bitumens and also to study the thickening process.[7] Two aluminum strips of 1 mm thick were overlapped by 2.5 cm and firmly bonded together with a drop of molten bitumen. The test pieces were held in position with alligator clips until ready for testing. The samples were bonded together and tested after 24 h of conditioning. The test was carried out on a Zwick Universal Testing Machine. The speed of the crosshead was 5 mm/min.

Softening Point

This test was carried out as per IS 1205-1958. A ring and ball softening point apparatus was used.

Ductility

Ductility of the samples was determined according to the test specified in IS 1208-1958. The method consists of measuring the distance in centimeters to which a briquette specimen of the material elongates before breaking, when its two ends are pulled apart at a rate of 50 mm/min at 27 ± 0.5°C.

Penetration

Standard penetration tests on the samples were conducted as per IS 1204-1958 in a container having a depth greater than 15 mm. A needle thoroughly cleaned with benzene was used. The test was conducted at 25°C, applying a 100-g load for 5 s, and the depth was measured and expressed in 1/100th of a centimeter.

RESULTS AND DISCUSSION

Liquid Natural Rubber

For the modification of bitumen, a LNR sample in the medium viscosity range was chosen in order to have a compromise between the blending process and the strength characteristics. The physical strength of NR decreases on depolymerization, and the low-molecular-weight samples exhibit more viscosity rather than elastic properties. On the other hand, more viscous LNR samples are difficult to mix with other liquids, so the optimum molecular weight of LNR has to be chosen to optimize between processability and properties of the resultant compounds.[8] The molecular weight details of the LNR sample are given in Table II. Molecular weights ($\bar{M}_n$ and $\bar{M}_w$) were determined

Table II Properties of LNR

Property	Measurement
$\bar{M}_n$	5,057
$\bar{M}_w$	33,360
$\bar{M}_w/\bar{M}_n$	6,598
Brookfield viscosity (mPa s)	160,000

by steric exclusion chromatography (SEC) in THF on a Waters 1500 instrument fitted with 5 μm styragel columns (0.7 × 120 cm) of different pore sizes (100, 3× 500, and 1000 Å) calibrated with polystyrene standards.

A wide range in the elution time of the polymer molecules indicated a broad molecular weight distribution. This is also evidenced from the polydispersity index (M_w/M_n).

Softening Point

The observations are given in Table III. The softening points were found to be in the range of 29–53°C for soft, and 96–110°C for blown bitumen. The increasing trend in the softening temperatures with an increase in the LNR content up to 10%, and a subsequent fall on further addition, were observed. The softening point was the highest on addition of 10% of LNR. The softening point is a measure of the capability of the material to resist cold flow even at higher ambients. Hence, the addition of LNR increases the service temperature of bitumen for different applications.

Ductility

Ductility of the samples measured at 27°C on the soft bitumen samples showed a continuously decreasing trend with increasing concentration of LNR. Ductility is the ability of a material to yield to tensile strains without collapsing. Bitumen is a thermoplastic material and is often subjected to variable mechanical reactions. The properties are affected by the conditions of loading and by the presence of solvents remaining from distillation or purposely added. Mechanical resistance to deformation and mode of failure are influenced by the low-molecular-weight materials. With much of the low-molecular-weight substances being removed during the process of preparation, the blown bitumen appeared less ductile. The presence of NR was found to make the soft bitumen sample less ductile. In the case of blown bitumen, a slight improvement was noticed with 10% of LNR (Table IV).

Table III Tests on Bitumen as per BIS

Sample No.	Softening Point (°C)	Ductility (at 27°C/cm)	Penetration Index at 25°C
B0	43	>150	80
B5	44	92	85
B10	53	26	119
B20	39	25	260
B30	29	25	340
BB0	96	3	5
BB5	107	3	5
BB10	110	4	18
BB20	105	3	30
BB30	100	3	40

Table IV Shear Stress at Different Shear Rates for Soft Bitumen

Shear Rate (s^{-1})	4	8	150	300
B0	—	35	49	142
B5	—	40	61	117
B10	32.5	42	63	119
B20	5.3	67	100	233
B30	24	40	67	175

Penetration

The penetration tests on the samples were done at 25°C, and the values are given in Table III. The values were found to increase with the increased loading of LNR. Penetration measurement gives an indication about the resistance of the material to indentation. The test revealed that the samples were rendered softer by LNR at 25°C. In the case of BB0 and BB5, no difference was noticed; but, at higher loadings, the increasing trend prevailed. Thus, LNR was found to impart relative softening of the samples at low temperatures and reduction in temperature susceptibility at high temperatures.

Lap Shear

Figure 1 shows the results of lap shear test. In both the soft and hard samples, an appreciable increase was noticed in the force for shear failure on incorporation of LNR. Peak strength was noticed around 10% of LNR to soft bitumen and 5% of LNR to hard bitumen. The shear test in the present case has led to breakage within the material rather than pealing of the bitumen from the substrate, and so the values directly reflect the strength of the samples. Any sign of cleavage of

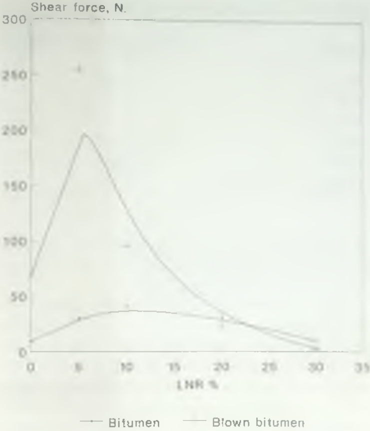

Figure 1 Influence of LNR on shear strength.

the material from the substrate was not visible. The blown bitumen samples were brittle, and, therefore, a slow test speed of 5 mm/min was used.

Viscosity Studies

Effect of Shear Rate

Table IV shows the shear stress values of the soft bitumen samples at different shear rates measured at 100°C. In general, the viscosity values showed an increasing trend with increasing shear rate.

Among different compounds, at low shear rates, the values were in a close range, but, at high shear rates, B10 showed the highest shear stress value. Table V shows the corresponding values for the blown bitumen samples. Shear stress increased with increasing shear rates.

The rate was high initially and decreased gradually. The downward trend in the shear stress with shear rate curve may be attributed to the pseudoplastic nature of the composite. An upward trend in the shear stress values of BB5 over the other samples showed that the addition of small quantities of LNR increased the resistance to flow. Addition of larger quantities of LNR caused a decline in the stress values. Particularly, at high shear rates, a shear stress stabilizing trend was noticed as being most prominent for BB0, a Bingham plastic behavior of bitumen. The compound with 30% LNR appeared closely to Newtonian behavior. Mildly dilatant behavior was observed at a high shear rate. Soft material could be checked only in the lower shear rate, whereas blown material was tested at higher shear rates. The soft material showed bingam plastic behavior because the curves do not originate from zero. It is also observed with the addition of LNR. Initially, the viscosity increases, but later, it decreases. This may be attributed to the presence of low-molecular-weight constituents present in soft bitumen, which makes the rubber particle swell, thereby increasing the viscosity. Once the rubber content is above a minimum amount, this effect is not observed, and rubber obviously act as flow promoter. The mild dilatent behavior may be due to the interaction of rubber with the low-molecular-weight material in the soft bitumen. However, this effect is not significant because of the lower shear rate range explored.

In the case of blown bitumen, the interaction of low-molecular-weight material with rubber is not observed as expected since the blowing process has removed the low-molecular-weight constituents. LNR acts as a flow promoter in this case also. Initially, at lower shear rates, a Newtonian behavior is seen, but, later on, the viscosity decreases with the amount of LNR and shear rate. When the rubber content is low, a different behavior is seen, which may be due to the interaction of the rubber with residual low-molecular-weight material present in the blown bitumen.

Effect of Temperature

Temperature dependence of the soft bitumen samples at an arbitrary shear rate, 15 s^{-1} is presented

Table V Shear Stress at Different Shear Rates for Blown Bitumen

Shear Rate (s^{-1})	10	35	85	165	835
BB0	1.12	3.59	5.96	7.15	7.30
BB5	1.34	2.71	4.23	9.45	7.45
BB10	0.66	1.94	3.38	5.97	5.97
BB20	0.30	0.96	1.99	4.48	4.48
BB30	0.17	0.40	0.50	0.90	1.74

Table VI Influence of Temperature on Shear Stress (Soft Bitumen)

Temperature (°C)	B0	B5	B10	B20	B30
90	155	185	217	270	83
100	49	76	63	100	67
110	32	35	48	90	59
120	18	22	26	48	32

in Table VI. All samples showed a decrease of viscosity with an increase in temperature. At all temperatures, the shear stress values were the highest for the sample containing 20% LNR. The general trend was that the shear stress increased from B0 to B20 and then declined. For the sample BB30, with 30% LNR, a steady decrease in shear stress with an increase in temperature was noticed, but the stress values were the lowest. For samples with a low LNR content, the rate of reduction in viscosity was higher at low temperatures. Table VII shows the corresponding values for blown bitumen samples.

A gradual decrease in the stress values was observed for the samples on increasing LNR content. The rate of reduction in the low-temperature region was found to decrease with increasing LNR/bitumen ratio. Higher quantities of LNR rendered the bitumen too soft at low temperatures.

Effect of Temperature on Viscosity

Viscosity on logarithmic scale versus reciprocal of temperatures was plotted on the absolute scale. Activation energy of flow was calculated from the slope of the lines. The viscosity at higher temperature obey the Arrhenius equation, as follows:

$$\eta = Ae^{-E/RT} \qquad (1)$$

Table VII Influence of Temperature on Shear Stress (Blown Bitumen)

Temperature (°C)	BB0	BB5	BB10	BB20	BB30
70	11.4	10.49	8.56	2.31	0.90
80	4.33	4.45	4.98	1.19	0.80
90	3.38	2.48	1.19	0.67	0.40
100	1.73	1.94	0.80	0.59	0.39

Table VIII Activation Energy of Flow

Sample	Activation Energy (kcal/mol)
B0	24.75
B10	25.79
B30	36.38
BB0	2892
BB10	2573
BB30	1438

where E is the activation energy of flow, and T is the absolute temperature. The activation energy values are given in Table VIII.

For soft bitumen, the activation energy increases with increasing LNR content. The observation in the case of blown bitumen was the opposite. With increasing LNR content, the activation energy was found to decrease considerably. Bitumen is a complex mixture consisting of asphaltenes predominant in high-molecular-weight fractions surrounded by substances of several chemical structures with varying functionalities from polar aromatic to nonpolar aliphatic.[9] Due to its presence in soft bitumen, swelling of the added polymer is likely to cause an increase in viscosity. With the blown bitumen samples during the process of blowing or oxidation, most of the low-molecular-weight fractions are removed. As a result, the influence of the polymer might be less.

Evaluation of Superposition Shift Factor

The time temperature superposition principle applies to bitumen samples. The experimental flow curves for log τ_w versus $\dot{\gamma}_w$ were plotted at temperatures of 70, 80, 90, and 100°C for the compounds BB0, BB5, and BB10. The method of superposition has been done by arbitrarily choosing 80°C as the reference temperature. The values of superposition shift factors were obtained by choosing log shear rates 2, 2.5, 3, and 3.5 s^{-1} on the reference temperature flow curve and shifting the corresponding points (constant shear rate) on the flow curve for other temperatures to coincide with the shear stresses. The values of the shift factors were calculated from the following equation:

$$a_T = \tau_w(\text{ref})/\tau_{(T)} \text{ (constant } \gamma_w) \qquad (2)$$

where a_T is the shift factor, $\tau_w(\text{ref})$ is the shear stress at reference temperature, and $\tau_{(T)}$ (con-

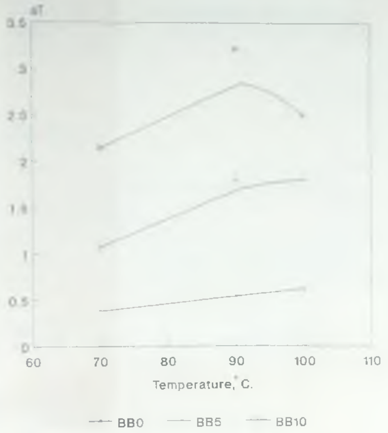

Figure 2 aT versus temperature.

stant γ_w) is the shear stress at a particular temperature. The average values of shift factors were calculated[10] and are plotted in Figure 2. Using the appropriate average value of the shift factors, a master flow curve at 90°C was constructed and is given in Figure 3. The shear rate temperature

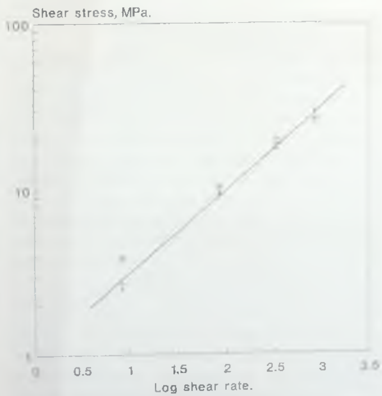

Figure 3 Super position master curve.

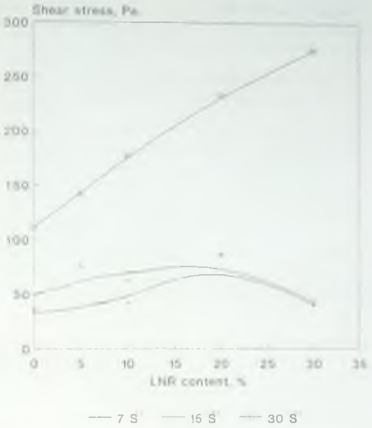

Figure 4 Effect of LNR on shear stress at 100°C (B).

superposition method is a useful tool in predicting the viscosities of polymer melts at any required temperature by determining the viscosity at a reference temperature.

Effect of LNR Content

Figure 4 represents the change in the shear stress of soft bitumen compounds with a LNR content. The values were recorded at 100°C. At lower loadings and lower shear rates, the values were almost steady. In general, the stress values showed an increasing trend with increasing loading of LNR. Dissolution of LNR in the low-molecular-weight components of bitumen can cause thickening and, hence, lead to high shear rates needed to maintain the same flow rate. Figure 5 shows the corresponding parameters for blown bitumen. In this case, a general decrease in shear force was observed with increasing LNR content. This may be due to the volumetric contribution of LNR, which has a significantly low viscosity than blown bitumen at 100°C. Figures 6 and 7 give the influence of LNR loading on viscosity at different temperatures of the soft and blown bitumen respectively. As is evident from Figure 6, the viscosity of the compounds increased up to 20% loading and subsequently decreased. The increase in viscosity

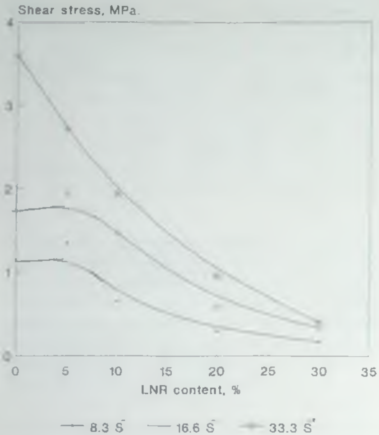

Figure 5 Effect of LNR on shear stress at 100°C (BB).

could be attributed to the dissolution of LNR and the subsequent thickening. A decrease in viscosity above 20% may be due to limiting solubility and

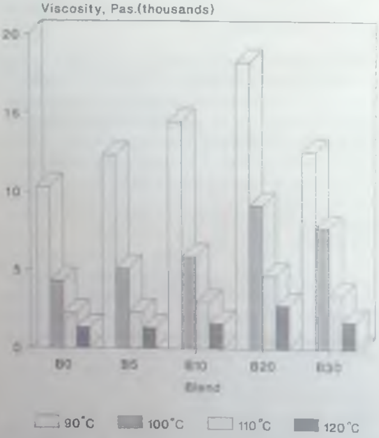

Figure 6 Effect of LNR on viscosity at 15 s^{-1} (B).

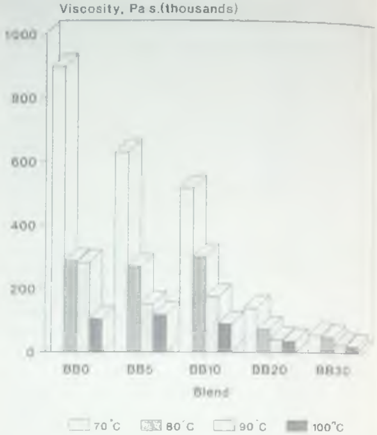

Figure 7 Effect of LNR on viscosity at 16.6 s^{-1} (BB).

existence of free LNR in the mixture. On the other hand, a gradual decreasing trend in viscosity was observed with increasing LNR content in blown bitumen irrespective of the loading. Considerable reduction was noticed above 10%.

SUMMARY AND CONCLUSIONS

Polymer modification of bitumen was studied using LNR obtained by the depolymerization of natural rubber. LNR of molecular weight (M_w) around 33,000 was used. The effect of LNR on soft bitumen as well as blown bitumen was studied. An increase in softening point was observed by the addition of 5 to 10% (w/w) of LNR. Ductility decreased in the case of soft bitumen, while some improvements were noticed in the case of blown bitumen at 10% loading. Penetration values consistently decreased in both the cases. Resistance to shear increased on the addition of LNR and was maximum in the region of 5 to 10% (w/w) of rubber. It was also observed that shear stress for all the bitumen samples increased with increasing shear rate. For soft bitumen, the temperature dependence on viscosity was prominent up to 100°C and subsequently marginal. Maximum viscosity resulted on addition of 20% LNR. Activation energy of flow of soft bitumen increased, while that of blown bitumen decreased on addition of LNR.

REFERENCES

1. D. C. Thompson, in *Bitumenous Materials: Asphalt, Tars and Pitches*, Vol. 1 A. J. Hosberg, Ed., Robert Kreiger Publishing Co., 1979.
2. V. P. Puzinauskas, *Properties of Asphalt Cements*, Research Rep 80, Asphalt Institute, Nov. 1980.
3. L. H. Lewandowski, *Rubb. Chem. Technol.*, **67**, 447 (1994).
4. J. Shim Tom, K. A. Kennedy, M. R. Pigott, and R. T. Woodhams, *Rubb. Chem. Technol.*, **53**, 88 (1980).
5. R. D. Thompson, *MRPRA Technical Bulletin No. 9*, 1962.
6. N. M. Claramma, N. Radhakrishnan Nair, and N. M. Mathew, *Ind. J. Nat. Rubber Res.*, **4**(1), 1 (1992).
7. L. Ciplijauskas, M. R. Piggott, and R. T. Woodhams, in *Ions in Polymers*, Advances in Chemistry Series 187, Adi Eisenberg, Ed., American Chemical Society, Washington, DC, p. 171 (1980).
8. I. R. Gelling and P. G. Mente, *Current Development in Product Manufacture*, RRIM, Kuala Lumpur, 1993, pp. 193–205.
9. R. S. Winnifold and R. A. Witherspoon, *Fundamental Aspects of Petroleum Chemistry*, 1967, p. 261.
10. J. S. Anand, *Int. Plast. Eng. Technol.*, **1**, 25 (1994).