Chapter 7.

PHYSICAL AND RHEOLOGICAL CHARACTERISTICS OF LIQUID NATURAL RUBBER MODIFIED BITUMEN

The results of this chapter have been communicated to the Journal of Applied Polymer Science.
7.1. INTRODUCTION

Bitumen by itself has become inadequate in many applications due to changed perception and working environment. Traffic factors have increased with respect to both load and volume. Higher pressures are employed for tyres and higher costs demand construction of thinner pavements. Bitumen based coatings are used in a number of anticorrosive applications. Composites based on bitumen are used for water-proofing buildings. It is also used for sealing joints of underground cables. 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. Ageing is the hardening of bitumen over time and temperature. Polymers have been found to reduce hardening, moisture susceptibility and improve 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 viscosity graded system. The viscosities at 60 and at 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 The viscosity graded system has been replaced by the penetration system in the sixties[2]. Other tests used to characterize bitumen binders are ring and ball softening point [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. NR is a potential candidate among various polymers for blending with bitumen. It is one of the polymers with which bitumen modification has been successfully carried out. 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 gets mixed with the
bitumen[4]. Addition of rubber in powder form has also been attempted. These include rubber powder from the rejections of various dry rubber and latex products[5-6].

NR latex is the most effective additive to bitumen, 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 a study on the addition of NR, in liquid form, for imparting desirable properties on bitumen binders and encapsulating materials. The process of polymer addition has been made easy by simple melt blending on account of the easy miscibility of LNR and bitumen. The mixing process is rather simpler than latex addition as little precaution is needed to prevent lump formation, fall in temperature due to water, frothing due to evaporation, etc. 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 which is considered inferior for many automotive/ engineering applications.

Polymer modification of commercially available bitumen has been attempted by the incorporation of LNR of medium viscosity. Both soft and blown bitumens were 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 the case of blown bitumen.
7.2. MATERIALS AND METHODS

7.2.1. Bitumen

Two types of bitumen, normal and blown, were used. The soft bitumen, 80-100 grade, was a product of Cochin Refineries Ltd., Cochin. Blown bitumen was of 5 grade, on the penetration scale, supplied by Bituminex Ltd, Ambalamugal. It was prepared by removing the volatile fragments like gas oils by heating to 300 - 350°C and also by the application of vacuum for 3 to 4 h.

7.2.2. Liquid natural rubber

The LNR was of medium viscosity grade with Brookfield viscosity 1,60,000 mPa.s. It was prepared starting from ISNR 5 by thermal depolymerization technique as suggested by Claramma et al.[7].

7.2.3. Preparation of samples

Table 7.1. Formulation of blends.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>% of bitumen</th>
<th>% of blown bitumen</th>
<th>Liquid natural rubber</th>
</tr>
</thead>
<tbody>
<tr>
<td>B0</td>
<td>100</td>
<td>Nil</td>
<td>Nil</td>
</tr>
<tr>
<td>B5</td>
<td>95</td>
<td>Nil</td>
<td>5</td>
</tr>
<tr>
<td>B10</td>
<td>90</td>
<td>Nil</td>
<td>10</td>
</tr>
<tr>
<td>B20</td>
<td>80</td>
<td>Nil</td>
<td>20</td>
</tr>
<tr>
<td>B30</td>
<td>70</td>
<td>Nil</td>
<td>30</td>
</tr>
<tr>
<td>BB0</td>
<td>Nil</td>
<td>100</td>
<td>Nil</td>
</tr>
<tr>
<td>BB5</td>
<td>Nil</td>
<td>95</td>
<td>5</td>
</tr>
<tr>
<td>BB10</td>
<td>Nil</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>BB20</td>
<td>Nil</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>BB30</td>
<td>Nil</td>
<td>70</td>
<td>30</td>
</tr>
</tbody>
</table>
LNR was incorporated into bitumen by melt blending. The bitumen was first heated to easily flowable consistency and LNR was added slowly with stirring and was homogenized properly. Formulations of the blends are given in Table 7.1.

7.2.4. 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 were measured on a capillary rheometer attached to a Zwick UTM. Viscosity was measured over a range of temperature and shear rate to study the flow behaviour on modification of bitumen with LNR.

7.2.5. Lap shear test

Lap shear test was used to determine the room temperature cohesive strength of modified bitumen and also to study the thickening process[8]. Two aluminium strips, 1mm 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 as shown in Figure 7.1 and tested after 24 h conditioning. The test was carried out on a Zwick universal testing machine with the crosshead travelling at 5 mm per minute.

7.2.6. Softening point

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

7.2.7. Ductility

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

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

7.3. RESULTS AND DISCUSSION

7.3.1. 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 ease of blending and strength characteristics. The physical strength of NR decreases on depolymerization and the low molecular weight samples exhibit more viscous rather than elastic properties. On the other hand more viscous LNR samples are difficult to mix with other liquids. Hence, an LNR of optimum molecular weight has to be chosen to optimize between processability and properties of the resultant compounds [9]. The molecular weight details of the LNR sample are given in Table 7.2. Figure 7.2 is the GPC chromatogram of the sample.

Table 7.2. Properties of LNR

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\bar{M}_n$</td>
<td>5,057</td>
</tr>
<tr>
<td>$\bar{M}_w$</td>
<td>33,360</td>
</tr>
<tr>
<td>$\bar{M}_w/\bar{M}_n$</td>
<td>6.598</td>
</tr>
<tr>
<td>Brookfield viscosity, mPa.s.</td>
<td>1,60,000</td>
</tr>
</tbody>
</table>

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.
7.3.2. Softening point

The observations are given in Table 7.3. The softening points were found to be in the range 29 to 53°C for soft, and 96 to 110°C for blown bitumen. On addition of small quantities of LNR to soft bitumen, the softening point increased. But around 10 parts, this property showed a reversing trend and at 30 parts loading, the softening point was much lower than that of the unmodified bitumen. For the blown bitumen samples also, a steady increase in softening point was observed with a maximum value around 10 parts. However, the subsequent decrease was not prominent as in the case of soft bitumen. Sample containing 30 parts of LNR had a higher softening point than the unmodified bitumen. Softening point is a measure of the resistance to cold flow. Hence, addition of LNR increases the service temperature of bitumen for different applications.

Table 7.3. Tests on bitumen as per BIS

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Softening point, °C</th>
<th>Ductility, at 270°C, cm.</th>
<th>Penetration at 250°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>B0</td>
<td>43</td>
<td>&gt;150</td>
<td>80</td>
</tr>
<tr>
<td>B5</td>
<td>44</td>
<td>92</td>
<td>85</td>
</tr>
<tr>
<td>B10</td>
<td>53</td>
<td>26</td>
<td>119</td>
</tr>
<tr>
<td>B20</td>
<td>39</td>
<td>25</td>
<td>260</td>
</tr>
<tr>
<td>B30</td>
<td>29</td>
<td>25</td>
<td>340</td>
</tr>
<tr>
<td>BB0</td>
<td>96</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>BB5</td>
<td>107</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>BB10</td>
<td>110</td>
<td>4</td>
<td>18</td>
</tr>
<tr>
<td>BB20</td>
<td>105</td>
<td>3</td>
<td>30</td>
</tr>
<tr>
<td>BB30</td>
<td>100</td>
<td>3</td>
<td>40</td>
</tr>
</tbody>
</table>
7.3.3. 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. Much of the low molecular weight substances having been removed during the process of preparation, the blown bitumen appeared less ductile. Presence of NR was found to make the soft bitumen sample is less ductile. In the case of blown bitumen a slight improvement was noticed with 10 parts of LNR (Table 7.3).

7.3.4. Penetration

The penetration tests on the samples were done at 25°C and the values are given in Table 7.3. The values are found to increase with increasing loading of LNR. Penetration 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, an increasing trend prevailed. Thus LNR was found to soften the samples at low temperatures and reduce temperature susceptibility at high temperatures.

7.3.5. Lap shear

Figure 7.3 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 parts of LNR in soft bitumen and 5 parts of LNR in 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 the material from the
substrate was not visible. The blown bitumen samples were brittle and therefore, a slow test speed of 5 mm per minute was used.

7.3.6. Viscosity studies

7.3.6.1. Effect of shear rate

Figure 7.4 shows the plot of 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 the 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. Figure 7.5 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 curvature of the shear stress-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 decline in the stress values. The viscoelastic behaviour of bitumen are governed by both solid and continuous phases[10]. Asphaltenes are suspended in a colloidal manner within a matrix which contains a variety of chemical compounds like resins. Addition of large amounts of LNR increases the proportion of soft continuous phase and enhances the flow behaviour. Particularly at high shear rates a shear stress stabilizing trend was noticed, most prominently for BB0, the Bingham plastic behaviour of bitumen. The compound with 30 parts of LNR appeared closer to Newtonian in behaviour.

7.3.6.2. Effect of temperature

Temperature dependence of the soft bitumen samples at an arbitrary shear rate, 15 s\(^{-1}\) is presented in Figure 7.6. All samples showed a decrease of viscosity with increase in temperature. At all temperatures the shear stress values were the highest for the sample containing 20 parts of LNR. The general trend was that shear stress increased from B0 to B20 and then declined. For the sample BB30 with 30 parts of LNR a steady
decrease in shear stress with increase in temperature was noticed, but the stress values were the lowest. For samples with low LNR content the rate of reduction in viscosity was higher at low temperatures as was evidenced by the slope of the curve. Figure 7.7 shows the corresponding values for blown bitumen samples. A gradual decrease in stress values was observed for the samples on increasing LNR content. The slope of the curves 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.

7.3.6.3. Effect of temperature on viscosity

Figures 7.8 and 7.9 are the plots of viscosity on logarithmic scale vs reciprocal of temperatures expressed on the absolute scale. Activation energy of flow has been calculated from the slope of the lines. The viscosity at higher temperature obeys the Arrhenius equation

$$\eta = A e^{-E/RT}$$  \hspace{2cm} (7.1)

where $E$ is the activation energy of flow and $T$ the absolute temperature. The activation energy values are given in Table 7.4.

### Table 7.4. Activation energy of flow.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Activation energy, kCals/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>B0</td>
<td>24.75</td>
</tr>
<tr>
<td>B10</td>
<td>25.79</td>
</tr>
<tr>
<td>B30</td>
<td>36.38</td>
</tr>
<tr>
<td>BB0</td>
<td>2892</td>
</tr>
<tr>
<td>BB10</td>
<td>2573</td>
</tr>
<tr>
<td>BB30</td>
<td>1438</td>
</tr>
</tbody>
</table>
For soft bitumen the slope of the lines increases with increase in LNR content indicating that the activation energy increases with increasing LNR content. The observation in the case of blown bitumen was on the contrary. 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 several substances of different chemical structure with varying functionalities from polar aromatic to nonpolar aliphatic[11]. Due to their presence in soft bitumen, swelling of the added polymer is likely to cause 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.

7.3.6.4. Evaluation of superposition shift factor

The experimental flow curves for log $\gamma_w$ vs $\tau_w$ were plotted at temperatures 70, 80, 90 and 100°C for the compounds BBO, 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 equation

$$\Delta T = \tau_w^{\text{ref}} / \tau(T) \quad \text{(constant } \gamma_w)$$

where $\Delta T$ is the shift factor, $\tau_w^{\text{ref}}$ is the shear stress at reference temperature and $\tau(T)$ (constant $\gamma_w$) is the shear stress at a particular temperature. The average values of shift factors were calculated[12] and are plotted in Figure 7.10. Using the appropriate average values of the shift factors a master flow curve at 90°C was constructed and is given in Figure 7.11. The shear rate temperature 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.

7.3.7. Effect of LNR content

Figure 7.12 represents the change in the shear stress of soft bitumen compounds with 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 low molecular weight components of bitumen can cause thickening and hence, can lead to high shear rates needed to maintain the same flow rate. Figure 7.13 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 7.14 and 7.15 give the influence of LNR loading on viscosity at different temperatures of the soft and blown bitumen respectively. As is evident from Figure 7.14, the viscosity of the compounds increased up to 20 parts loading and subsequently decreased. The increase in viscosity could be attributed to the dissolution of LNR and the subsequent thickening. Decrease in viscosity above 20 parts may be due to limiting solubility and existence of free LNR in the mixture. On the other hand a gradually decreasing trend in viscosity was observed with increasing LNR content in blown bitumen irrespective of the loading. Considerable reduction was noticed above 10 parts.
References


Fig. 7.1. Test samples for lap shear test
Fig. 7.2. GPC Chromatogram of LNR sample
Fig. 7.3. Influence of LNR on shear strength
Fig. 7.4. Shear stress vs shear rate at 100 °C (B)
Fig. 7.5. Shear stress vs shear rate at 100 °C (BB)
Fig. 7.6. Shear stress vs temperature at 15 s⁻¹ (B)
Shear stress, MPa.

Fig. 7.7. Shear stress vs temperature at 16.6 s\(^{-1}\) (BB)
Fig. 7.8. Viscosity vs 1/T K (B)
Fig. 7.9. Viscosity vs 1/T K (BB)
Fig. 7.10. Shift factor vs temperature
Fig. 7.11. Superposition maser curve
Fig. 7.12. Effect of LNR on shear stress at 100 °C (B)
Shear stress, MPa.

Fig. 7.13. Effect of LNR on shear stress at 100 °C (BB)
Viscosity, Pas.(thousands)

Fig. 7.14. Effect of LNR on Viscosity of soft bitumen (15 s-1)
Fig. 7.15. Effect of LNR on viscosity of blown bitumen (16.6 s⁻¹)