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Thermal Behaviour and Improved Properties of SBR and SBR/Natural Bitumen Modified Bitumens

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ABSTRACT

One problem of polymer modified bitumens (PMBs) concerns the poor compatibility between polymer and bitumens. Natural bitumen (NB) is often used for bitumen modification in order to obtain improved performance of the respective bitumen mixtures. This paper presents the results of NB modified bitumens with improved properties, prepared by incorporating styrene butadiene rubber (SBR). The effects of SBR and SBR/NB on the conventional, rheological, thermal, and morphological properties of the modified bitumens were studied. It was found that 2% content of NB shows marked improvement in high temperature properties by increasing the softening point in SBR/NB modified bitumen, while SBR of 3% content in SBR/NB modified bitumens shows significant effect on the low temperature properties and the aging resistance. The morphology in accordance with TG-DTG and DSC analysis indicated that compatibility and thermal properties were improved with a homogeneous and stable mix structure in modified bitumens. FTIR analysis shows few new weak peaks for modified bitumens indicating that physical alteration is the main change in the modified bitumens.

Key Words:

natural bitumen;
SBR;
modified bitumen;
rheological properties;
DSC;
TGA-DTGA;

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INTRODUCTION

Bitumen is a viscous liquid, or a solid, consisting essentially of hydrocarbons and their derivatives. It is soluble in trichloroethylene and is substantially non-volatile and softens gradually when heated. In addition, bitumen is a colloidal system, where the highest molecular weight components, i.e., the asphaltene micelles and the lower molecular weight maltenes (i.e., aromatics, saturates, and resins) are dissolved in the saturated hydrocarbon mixture [1]. The so-called "sol" type bitumen has high content of resins and aromatics which means high solvating ability and, therefore, good mobility of asphaltene micelles. In contrast, the lower the resin and aromatic content (and solvating ability) the higher is the tendency of micelles to aggregate until a continuous network is formed where the lighter components are restricted to fill the intermicellar voids, resulting in what is called a "gel" type bitumen [2,3]. In this case, the chemical composition of bitumen deeply affects the internal structure, which is of fundamental importance from a rheological point of view.

Pavement defects, such as rutting at high temperatures, crack initiation and propagation in the low temperature region, are due not only to traffic loads but also to the thermal susceptibility of bitumen [4]. The use of polymer modified bitumens (PMBs) to achieve better pavement performance has been studied for a long time. The properties of PMBs are dependent on the polymer characteristics, content and bitumen nature, as well as the blending process. Elastomers and plastomers are typically used in bitumen modification, such as styrene butadiene rubber (SBR), styrene butadiene styrene triblock copolymer (SBS) and polyethylene (PE) [5-8].

SBR has been widely used as a binder modifier [9-11]. An Engineering Brief from 1987 available at the US Federal Aviation Administration website [5] describes the benefits of SBR modified asphalt in improving the properties of asphalt concrete pavement and seal coats. Low-temperature ductility is improved, viscosity is increased, elastic recovery is improved, adhesive and cohesive properties of the pavement are improved. According to Becker et al., SBR latex polymers increase the ductility of asphalt pavement [12], which allows the pavement to be more flexible and crack resistant at low temperatures, as found by the Florida Department of Transportation. SBR modification also increases elasticity, improves adhesion and cohesion, and reduces the rate of oxidation, which helps to compensate for hardening and aging problems [13]. SBR has a significant effect on the results of the ductility test at both 4ºC and 25ºC; while SBR modified asphalts have high ductility at all temperatures the SBS modified asphalts tend to have lower ductility [14].

Bitumens may present either elastic or viscous behaviour, or a combination of both, depending on the temperature and the time over which the bitumen is observed. An adequate viscoelastic response of the bitumen is fundamental to ensure a good performance of the road pavement. SHRP Highway Research Program [15] proposes a series of tests which involve rheological methods to replace conventional less reliable trials [16].

Base bitumens (unmodified) usually have a glass transition temperature around -20ºC. It can be observed that the transition from a viscoelastic to a Newtonian liquid above 60ºC . Pavement temperatures during the service life are between -30ºC and 60ºC (except for extreme climates, where they can be as low as -40ºC and as high as 80ºC), and paving bitumen is usually characterized by its dynamic material functions [17]. At high temperatures, when bitumen (between 140ºC and 180ºC) is pumped or poured, it behaves as a classical Newtonian fluid and thus its shear viscosity is of practical interest. By addition of several percentages of polymer, a marked increase in complex modulus (G^*) is obtained at high temperature (low frequency). By further increase in polymer content the complex modulus is increased [4]. The addition of polymer results in a significant decrease in phase angle, especially over the range of intermediate to low angular frequency. Although the addition of polymer increases both the storage and loss modulus of bitumen, it is more effective in increasing the storage modulus. Typically, a blend of NB and base bitumen is adopted in the production of NB modified bitumens [18].

NB can be found in different forms, e.g., bitumen deposits, lake bitumen, or rock bitumen, and in different degrees of purity which depends on the proportions of bitumen and other mineral contents. The high asphaltene content and high molecular weight of NB are thought to function mainly as a “solution thickener”, giving improved stiffness and deformation resistance. Natural rock bitumen has a completely different nature, being formed by the impregnation of oil into limestone. The bitumen content is typically about 10-35% by weight of the rock, and usually a chemical or solvent extraction process is required to commercially exploit the material.

NB is well known for its consistent properties, stability and durability. It is widely used for bridge and airport applications. The most famous source of lake asphalt is the Trinidad Lake Asphalt (TLA). It occurs naturally on the island of Trinidad which is composed of a mixture of bitumen and minerals of the following composition: soluble bitumen (53-55%), mineral matter (36-37%) and other (9-10%) [19]. A comparison of the components and characters of different natural bitumens is shown in Table 1.

Widyatmoko et al. investigated Uintaite or TLA modified base bitumen and PMBs (heavily modified with elastomers and plastomers with the content higher than 10%) from a series of assessments of

Table 1. Comparison of different natural bitumens in the world.

Natural bitumen	Softening point (ºC)	Penetration (25ºC, mm)	Maltenes (%)	Asphaltenes (%)	Nitrogen (%)
TLA	93-99	0-4	63-66	33-37	higher than 3%
NB (Xinjiang Province)	130-160	0-5	67.55	32.45	2.95
Gilsonite	176	0	54.8	43.6	3.3

"empirical" and rheological properties. The results showed that NB reduces or increases the conventional and rheological values in the content range 10-70% [19]. The prospective reserve of NB is about 10 million tons in Kalamay, Xinjiang Province. It is quite different from TLA or Gilsonite in chemical composition (Table 1). Consequently, the physicochemical properties, thermal, and rheological properties are significantly different in NB or NB modified bitumen with/without the polymer. However, despite considerable research in this area, NB/PMBs blends have not been yet comprehensively characterized, due to the complex nature and interaction among NB, base bitumen, and polymer system especially from a series of assessments of thermal behaviour at relatively lower content (no more than 5%) [20]. Thus, there have been no reports on thermal properties about the preparation of the SBR modified bitumen with improved properties by using NB obtained in Xinjiang Province.

In our previous work, the classical properties of SBR modified asphalts with different modifiers were characterized [21-22]. In the present work, the preparation and properties of SBR and SBR/NB modified bitumens are studied. For comparison, bitumens modified by directly adding SBR before and after the presence of NB are also studied. The conventional, rheological (dynamic shear rheometer), morphology (optical microscopy and scanning electronic microscopy) and thermal characteristics (thermal gravimetric analysis and differential scanning calorimetry) of these blends are determined in this study. The high temperature storage stability is also studied.

EXPERIMENTAL

Materials

AH-90 paving bitumen was obtained from the Lanzhou Petroleum Bitumen Factory, Gansu Province, China. SBR was produced by the Lanzhou Petrochemical Co., Ltd., China. It was a star-like SBR, containing 27.3 wt% styrene, 0.64 wt% water soluble, 0.37 wt% volatile fraction and viscosity (ML_{1+4} 100ºC) 48-55. Natural bitumen was purchased from Mineral Factory, Xinjiang Province, China. The characteristic appearance of natural bitumen is shown in Figure 1.

Preparation of Modified Bitumens

All the modified bitumens were prepared using a high shear mixer at 165-175ºC with a shearing speed of 3000-4000 rpm for 40 min. A certain amount of bitumen (500 g) was heated to become fluid in an iron container. Then, on reaching about 170ºC, the modifier (star-like SBR and SBR/NB) was added to the bitumen. The proportions of the SBR in base bitumen was 1-3 wt%. The proportions of the SBR/NB in base bitumen were 2-3 /1-3 wt%.

NB contents have led to different distributions of SBR in the bitumen, and it has resulted in changes of properties of modified bitumen during the preparation

Figure 1. The appearance of natural bitumen in Xinjiang Province.

of the bitumen modified with SBR/NB. Therefore, the effect of SBR contents on the properties of modified bitumen is studied.

Measurement of Conventional Properties

The softening points (Ring and Ball test) of different base and modified bitumens were measured according to ASTM D 36. In this test, two disks of bitumens were cast into shouldered rings, and then the disks were trimmed to remove excess asphalt. The disks were then heated at a constant rate (58ºC/min) in a water bath using a special apparatus.

The penetration tests were carried out at 25ºC according to ASTM D 5. The bitumen was thermostatted in a water bath and the penetration of a standard needle under a standard load (50 g) was measured during 5s and reported in tenth of a millimeter.

Ductility was determined at 5ºC with an extensional speed of 1 cm/min in accordance with Chinese specification GB/T 4508.

In addition, the temperature susceptibility of the modified bitumen samples has been calculated in terms of penetration index (PI) using the results obtained from penetration and softening point tests. Temperature susceptibility is defined as the change in the consistency parameter as a function of temperature. A classical approach related to PI calculation has been given in the Shell Bitumen Handbook [13] as shown with the following equation:

$$PI = \frac{1952 - 500\ \log(Pen_{25}) - 20 \times SP}{50\ \log(Pen_{25}) - SP - 120} \qquad (1)$$

where, Pen_{25} is the penetration at 25ºC and SP is the softening point temperature of PMBs.

Rutting Resistance Parameter (G^*/sinδ) Measurement

Rheological measurements were performed with temperature sweeps using a rheometer (Bohlin CVO100, UK). A temperature sweep was applied over the range 40-90ºC at a fixed frequency of 10 rad/s and variable strain. The strain was chosen to be as small as possible to ensure measurement in the linear region, but large enough to allow sufficient torque readings. A sample of about 1.0 g was put onto the lower plate. After the sample was heated to become molten, the upper parallel plate was lowered to contact tightly with the sample and trimmed. The final gap was adjusted to 1.2 mm. All the samples were held at a defined, constant temperature for 10 min, and then the temperature was varied in 2ºC increments. Dynamic shear modulus G^*, phase angle (δ) and G^*/sin δ were calculated. The frequency used was 10 rad/s. The complex shear modulus (G^*) is then defined as:

$$G^* = \left(\frac{\sigma_0}{\gamma_0}\right)\cos\delta + i\left(\frac{\sigma_0}{\gamma_0}\right)\sin\delta = G' + iG'' \qquad (2)$$

where,

G^* : Complex shear modulus, Pa;
G' : Storage modulus, Pa;
G" : Loss modulus, Pa;
δ : Phase angle, degree.

Viscosity Masurement

The viscosity properties of bitumen samples were determined by a rotational viscometer (Model DV-+Pro, Brookfield Engineering Inc, USA) according to ASTMD 4402.

High-temperature Storage Properties

After mixing, some of the prepared modified bitumen was transferred into a glass toothpaste tube (32 mm in diameter and 160 mm in height). The tube was sealed and stored vertically in an oven at 163ºC for 48 h, then taken out, cooled to room temperature, and cut horizontally into three equal sections. The samples taken from the top and bottom sections were used to evaluate the storage stability by measuring their softening points. When the difference between the softening points of the top and the bottom sections was less than 2.5ºC, the samples were considered to have good high-temperature storage stability, and when the softening points differed by more than 2.5ºC, the modified asphalt was taken as unstable.

Standard Ageing Procedure

The ageing of the modified polymer bitumen samples was performed using rolling thin film oven test (RTFOT, ASTM D 2872) which simulated the changes in the properties of asphalt during the plant hot mixing and the lay down process [23].

Thermal Analysis and FTIR

Thermal analysis was carried out in a high-resolution Thermobalance (TA instrument, TGA-APY-2P). The heating rate was 40ºC /min, while the heating rate was varied dynamically when a weight change occurred. When a loss of weight was detected in Hi-Res TGA technique, the heating rate slowed in response to the increasing rate of mass loss and the system maintained it at the lowest value (0.01ºC /min) until the end of the weight loss.

Approximately 15 mg of sample was heated from room temperature up to 600ºC with a continuous N_2 flow at 75 mL/min, then the sample was cooled down to 400ºC, the purge atmosphere was changed to air, and the sample was heated again until a constant weight was achieved at 800ºC. Sample weight and its rate of weight loss were continuously measured as a function of temperature. The total analysis took approximately 75 min. Differential scanning calorimetry (DSC) test thermograms were obtained using a Thermal Analyzer (DT-40, Japan) with a power compensation head. The test was carried out under flowing air of 10 mL/min and a heating rate of 10 K/min. About 2.0 mg of sample was taken in each case and respective peaks were recorded.

The infrared spectra were recorded with a Nicolet NEXUS 670 FTIR; Nicolet AVATAR 360 FTIR spectrometer. The samples were prepared by casting a film onto sodium chloride (NaCl) window from a 5% w/v solution in chloroform.

Morphological Analysis

Optical microscopy was used to study the morphology of polymer modified bitumens. A drop of heated sample was placed between two microscope slides. Samples were observed under different magnifications at room temperature in an optical Olympus microscope.

Samples were immersed in absolute alcohol in a beaker and dispersed by a low power ultrasonic instrument for half an hour. Then a drop of sample/alcohol mixture was taken out from the beaker for morphological observation. The observation was performed on a scanning electronic microscope (SEM, S-450) with a resolving power of 4.5 μm.

RESULTS AND DISCUSSION

SBR Contents Effects on Unaged and RTFOT-aged Bitumen Samples' Conventional properties

Table 2 shows the effect of SBR contents on the conventional properties of unaged and RTFOT-aged bitumens. As can be seen from Table 2, with the increase in SBR content, the softening points of the SBR modified bitumen samples increase, which imply that the properties of bitumen would be improved by SBR to some extent. When the content of SBR is fixed at 3%, the SBR modified bitumen shows the highest softening point of 53.0ºC. SBR has significant effect on increasing ductility (5ºC) in SBR modified bitumen. With the increase of SBR contents, the ductility (5ºC) of SBR modified bitumens dramatically increases. The influence of SBR on the ductility of the SBR modified bitumens is dependent on the SBR content. For the different SBR contents studied, 3% leads to the highest value of the ductility.

Bitumen mixtures with higher PI are more resistant to low temperature cracking as well as permanent deformation [6]. Modification reduces the tempera-

Table 2. Influence of SBR contents on the conventional properties of unaged and RTFOT aged bitumen samples.

SBR content (%)	Softening point (ºC)	Penetration (25ºC, mm)	Penetration index (PI)	Ductility (cm, 5ºC)	RTFOT		
					Ductility (cm, 5ºC)	Penetration ratio (25ºC, %)	Weight loss (%)
Base bitumen	47.0	74	-0.946	6.3	3.7	5	0.40
SBR 1%	49.7	62	0.032	105	31	8	0.06
SBR 2%	51.3	56	0.074	169	57	7	0.07
SBR 3%	53.0	41	0.083	200	69	6	0.05

ture susceptibility of the bitumen. Lower values of PI indicate higher temperature susceptibility. SBR modified bitumens exhibit less temperature susceptibility compared to base bitumen with increasing SBR content, especially of 3%.

Table 2 also indicates that the penetrations of the SBR modified bitumens decreases slightly. And with the increasing of SBR contents, the penetrations of modified bitumen show no evident changes. Moreover, there are no significant changes of penetration ratio and ductility (5ºC) when RTFOT ageing occurs.

The above mentioned results suggest that SBR has significant effect on low temperature (5ºC) properties with increasing ductility (5ºC) of the SBR modified bitumen samples while it has also effect on the softening points of the modified bitumen samples to some extent. Furthermore, 3% of SBR is an appropriate content of SBR modified bitumen; otherwise the industrial production cost will be high.

NB Contents Effect on Unaged and RTFOT-aged SBR Modified Bitumen Samples' Conventional Properties

An appropriate amount of SBR modified bitumen is 3% of SBR. We fixed SBR content at 2% and 3%, and used different NB contents to observe the influence of NB on the properties of SBR/NB modified bitumen.

The influence of NB content on the conventional properties before and after ageing using the RTFOT procedure of SBR/NB modified bitumen is shown in Table 3. With increasing of NB content, the softening points of the modified bitumen are significantly promoted. When the NB content is fixed at 2%, a maximum softening point (58.0ºC) is reached. The influence of NB on the softening points of the SBR/NB modified bitumens is dependent on the NB contents. However, 3% NB modified bitumens show slightly lower softening points (55.0ºC in SBR2%/NB3% and 57.6ºC in SBR3%/NB3%, respectively) compared with the modified bitumens having 2% NB content.

Moreover, no significant changes are observed in the ductility (5ºC) with increasing NB contents compared to cases of no NB present. The ductility (5ºC) of SBR/NB modified bitumens is seemingly independent of the NB contents. In addition to the increased hardness, the PI increased as well, revealing that NB additions enhance the temperature susceptibility of the modified bitumen samples compared with the case of having NB present. A notable improvement of the temperature susceptibility can be observed.

The variation in related properties of different modified bitumens by SBR/NB after short-term ageing compared with unaging samples is also listed in Table 3. The tendency of changes in the ductility after RTFOT aged closely resembles the changes of unaged samples. With the increase of SBR and NB contents the ductility increases significantly but not to the same extent as unaged sample. Meanwhile, the penetration ratio increases after the processes of RTFOT. The results indicate that with SBR3%/NB2% the modified bitumen greatly improves the ductile properties of improving aging resistance.

It can be concluded that NB has marked effect on the improvement of bitumen consistency at high tem-

Table 3. Influence of NB contents on the conventional properties of unaged and RTFOT aged SBR modified bitumen samples.

SBR content (%)	Softening point (ºC)	Penetration (25ºC, mm)	Penetration index (PI)	Ductility (cm, 5ºC)	RTFOT		
					Ductility (cm, 5ºC)	Penetration ratio (25ºC, %)	Weight loss (%)
Base bitumen	47.0	74	-0.9.46	6.3	3.7	66	0.40
SBR2%/NB1%	53.6	61	0.232	172	48	69	0.03
SBR2%/NB2%	56.3	59	0.312	176	59	76	0.10
SBR2%/NB3%	55.0	60	0.534	168	57	73	0.04
SBR3%/ NB1%	54.0	58	0.363	200	87	72	0.10
SBR3%/ NB2%	58.0	60	0.422	200	103	74	0.06
SBR3%/ NB3%	57.6	54	0.549	200	93	76	0.07

peratures while SBR has marked effect on the low temperature properties and improvement of aging resistance with increasing SBR content. Therefore, SBR/NB modified bitumen has the improved properties of increased softening points, promoting ductility, and aging resistance.

High Temperature Viscoelastic Properties

The effect of viscosity on bitumen binder's workability is very important in selecting proper mixing and compacting temperatures. As shown in Figure 2, the viscosity of all modified bitumen samples is higher than that of the base bitumen, itself. There is an obvious difference among various SBR contents when temperature is less than 160ºC. According to Superpave binder specification limits, the viscosity at 135ºC must not be greater than 3 Pa.s. Test results show that SBR/NB modified bitumen samples can meet the requirements of the related construction temperature. However, the viscosity of SBR/NB modified bitumen increases with increasing SBR content. This can be explained by the interactions between the molecules constituting the matrix and those of the polymer. The intermolecular interactions, which occurred in the blend, resulted in some changes of the matrix composition. In fact, SBR may dissolve and/or disperse into the maltenic medium, enhancing the viscosity of the mixture.

It is known that the temperature of the bitumen binders when $G^*/\sin\delta$ is equal to 1 kPa is defined as a criterion for the high temperature (good visco-

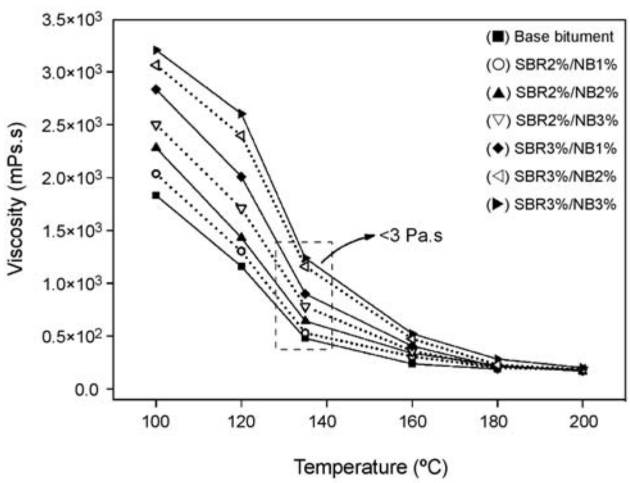

Figure 2. Viscosity of bitumen mixings with SBR/NB vs. temperature.

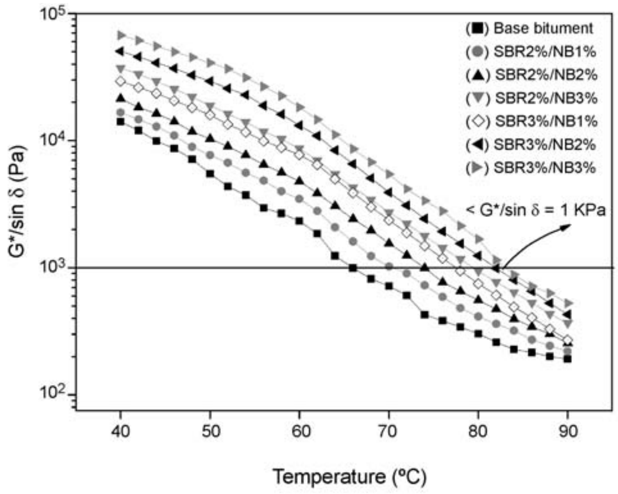

Figure 3. Curves of $G^*/\sin\delta$ vs. temperature for SBR/NB modified bitumen samples.

elastic) performance of bitumen [24]. Plots of $G^*/\sin\delta$ versus temperature are presented in Figure 3. Results reveal that the maximum temperature is improved when each modifier is added. The resulting temperature of base bitumen and modified bitumen are determined at 56ºC and above 70ºC, respectively from the data obtained. The best results are obtained when SBR3%/NB3% are mixed with base bitumen at 82ºC. This indicates that the SBR/NB modified bitumen samples have a higher performance grade than the base bitumen. It is also known that higher $G^*/\sin\delta$ values are found to correlate with higher rutting resistance.

High-temperature Storage Properties

The compatibility between polymer and bitumen is necessary during pumping, storage and applying the bitumen, and to achieve the expected properties in the pavement [25]. Stability tests can determine whether the interactions created between the polymers and the bitumen during mixing are strong enough to resist a separation of the polymer in the conditions in which it is stored. Obvious differences in the softening points are detected in base bitumen, indicating that base bitumen is unstable as shown in Table 4. With the appearance of SBR and NB, the storage stability of modified bitumen is improved significantly. No marked differences in the softening points of modified bitumen samples were observed.

Table 4. High-temperature storage stability of SBR/NB modified bitumen samples.

Content	Softening point (ºC)		S_t-S_b [a] (ºC)
	Top	Bottom	
Base bitumen	47.0	42.2	4.8
SBR2%/NB1%	53.6	51.4	2.2
SBR2%/ NB2%	56.3	54.7	1.6
SBR2%/ NB3%	55.0	53.8	1.2
SBR3%/ NB1%	54.0	52.6	1.4
SBR3%/ NB2%	58.0	57.4	0.6
SBR3%/ NB3%	57.6	57.2	0.4

(a) S_t: top softening point; S_b: bottom softening point

SBR/NB modified bitumen can be considered as a suspended system. Stoke's law demonstrates the falling velocity of the particles in a suspended system [7]:

$$V = \frac{2gr^2(\rho_0 - \rho_1)}{9\eta} \quad (3)$$

where, g is the gravitational force constant, r is the average radius of the SBR particles, ρ_0 is the density of bitumen, ρ_1 is the density of SBR, and η is the viscosity of the modified bitumen. As shown in eqn (3), there are two ways to prevent the phase separation of SBR and bitumen. One is to decrease the density difference and the other is to reduce the particle size. The density of the SBR is about 1.2 g/mL and the density of base bitumen here is 1.013 g/mL at room temperature. The density of NB is 1.04 g/mL at 15ºC. At high temperatures, the SBR particles swell in the oily fraction of the bitumen and the density difference of the SBR and bitumen becomes significant [26]. When NB is attached to polymer matrix, the density difference is decreased, thus the high-temperature storage stability is improved.

Thermal Analysis

Thermogravimetric Analysis

TGA-DTGA results are obtained by using a high-resolution TGA approach. This approach permits in a shorter experimental time with a higher resolution of the weight loss events taking place relative to traditional thermogravimetric method. Figure 4 shows the curves of TG analysis. The initiating mass loss temperature under N_2 flow is 396ºC in natural bitumen sample, indicating that natural bitumen has high stability. TGA curves show that there are clearly three areas of weight loss between 250 and 450ºC in modified bitumen samples. The first weight loss between 250-338ºC and 292-354ºC, corresponds to 11% and 9% of the total weight and is attributed to the volatilization of low boiling-point components in SBR and SBR/NB modified bitumen samples, respectively. The next mass losses of 7% and 6%, which have an initiating mass loss temperature of 340ºC and 356ºC are observed in SBR and SBR/NB modified bitumen samples, respectively.

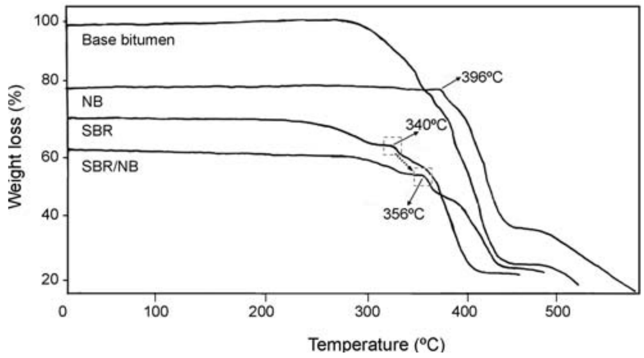

Figure 4. TGA weight loss curves of SBR modified bitumen samples before and after the addition of NB.

Furthermore, it has been observed (Figure 5) that

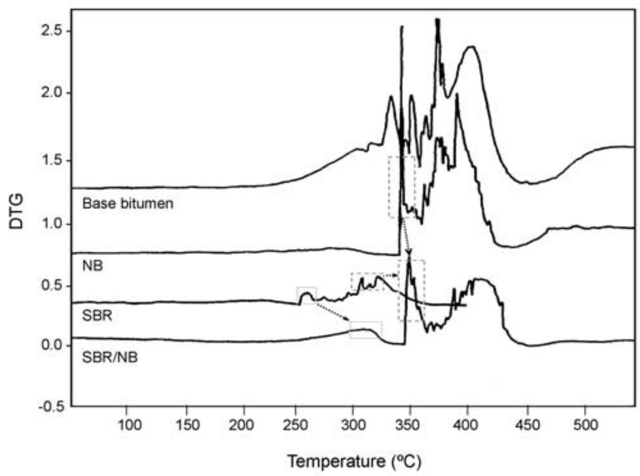

Figure 5. DTGA curves of SBR modified bitumen samples before and after the addition of NB.

the DTGA peak of SBR/NB modified bitumen shifts to a higher temperature compared to natural bitumen and SBR modified bitumen samples, indicating that the thermal stability of SBR/NB modified bitumen has been improved.

Differential Scanning Calorimetry

Bitumen exhibits a great number of exothermic peaks during DSC test for it is a complex mixture of high molecular weight hydrocarbon molecules, which indicate that plenty of ingredient transformation occurs in this temperature range. Small molecules transform at lower temperature, but large molecules transform at higher temperature. In general, morphology makes a direct approach to study polymer dispersion in the bitumen. However, it cannot determine the differences between the swelling ratios of both bitumen samples. The DSC results shed some light on this issue.

Figure 6 illustrates the results of DSC test of base bitumen and two samples containing SBR and SBR/NB. The DSC curve of base bitumen appears as a wide exothermic peak at temperature range of 385-425ºC, which is mostly decomposition temperature of base bitumen. However, the appearance of exothermic peak is postponed with a large peak value which indicates that natural bitumen has good high-temperature property. The thermal behaviour of the two modified bitumen samples is essentially dependent on temperature. SBR has slightly postponed the temperature of the appearance of exothermic peaks which appears at temperature range of 396-447ºC.

As we have expected, SBR/NB has postponed the appearance of exothermic peak more than SBR. The exothermic peak on the DSC curves is postponed towards high-temperature regions, indicating the improvement of the high-temperature property. Mechanism of improvement involves the combined function of gaseous liquid and solid mechanisms. Differences between melting peaks of SBR and SBR/NB modified bitumen samples are representative of the swelling potential of the bitumen. In that way, SBR modified bitumen will show slightly higher swelling potential. In addition, the peak temperature at which this first-order transition occurred in modified bitumen samples depends on the type of polymer and base bitumen [27-28], as can be seen in Figure 6. As a consequence, swelling effects may produce a lower melting point of SBR modified bitumen samples.

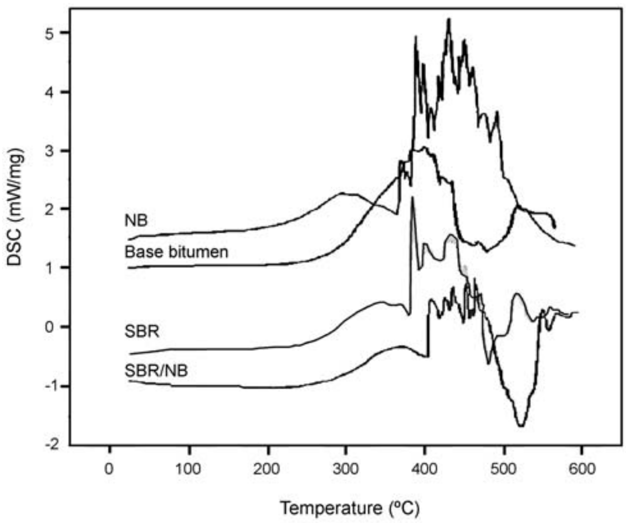

Figure 6. DSC tests of SBR and SBR/NB modified bitumen samples.

FTIR Analysis

The differences in the SBR and SBR/NB modified bitumen samples should be attributed to the structural differences. The main structural modifications that take place (during the addition of SBR or SBR/NB) in modified bitumen samples are the formation of chemical or physical interactions between polymer and bitumen. The differences in properties of base

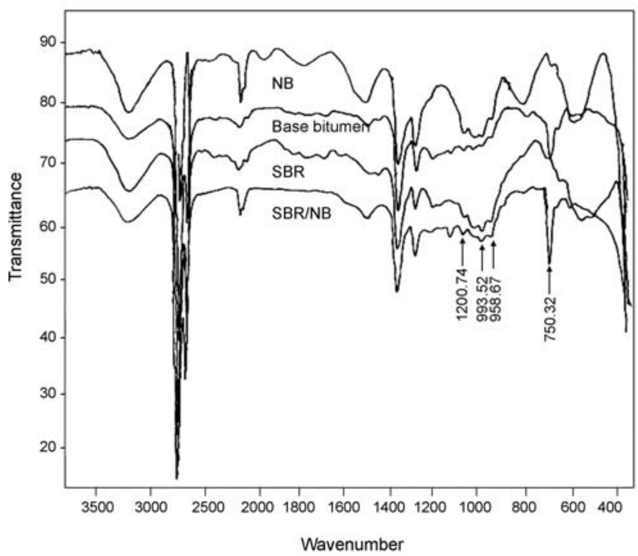

Figure 7. FTIR analysis of SBR and SBR/NB modified bitumen samples.

bitumen and SBR modified bitumen samples before and after the addition of NB imply changes in their structure. Figure 7 shows the infrared spectra of SBR modified bitumen samples before and after the application of NB. Some similarities are observed among base bitumen, SBR and SBR/NB modified bitumen samples. The spectral regions shown in Figure 7 correspond to the out-of-plane bending vibrations of aromatic =C-H and C=C groups of polystyrene at 750.32 and 700 cm^{-1}, respectively, the out-of-plane bending vibrations of =C-H of vinyl groups (993.52 cm^{-1}), and –CH=CH- at 958.67 cm^{-1} of butadiene. Bands at 1200.74 cm^{-1} correspond to $\delta_{C\text{-}H}$ aromatization. The few weak peaks show that chemical reaction is not the main change in the modification process.

Morphology

The compatibility between polymer and bitumen is critical to the properties of PMBs [29]. The morphology of PMBs is investigated using optical microscopy by characterizing the distribution and the fineness of polymer in the bitumen matrix. The morphology of SBR and SBR/NB modified bitumen samples is shown in Figures 8-11. At low polymer content (2 wt% SBR), small polymer droplets are swollen by bitumen, and as it is shown in Figure 9, lightweight

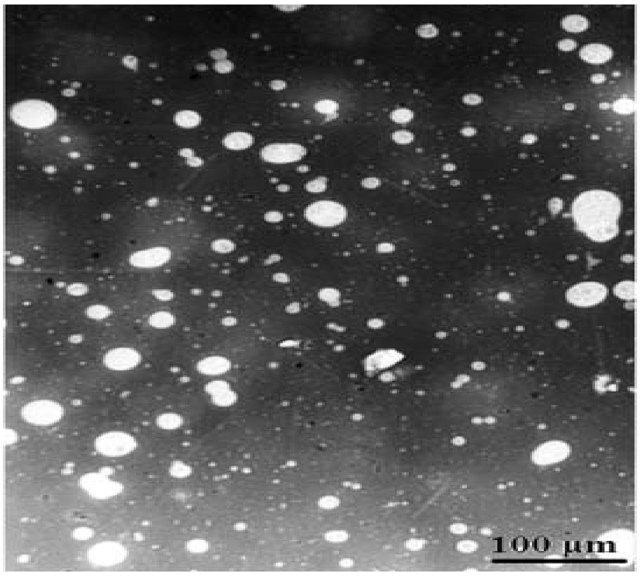

Figure 9. Morphology of SBR2%/NB2% modified bitumen by optical microscope.

fractions appear in the continuous bitumen phase. By increasing the polymer concentration (Figure 10), although polymer continuity disperses in the bitumen, a continuous polymer phase tends to appear in the studied systems. Thus, the final volume fraction of the polymer-rich phase is clearly higher than the initial one due to the swelling by maltenic components of the base bitumen. No significant changes are found with

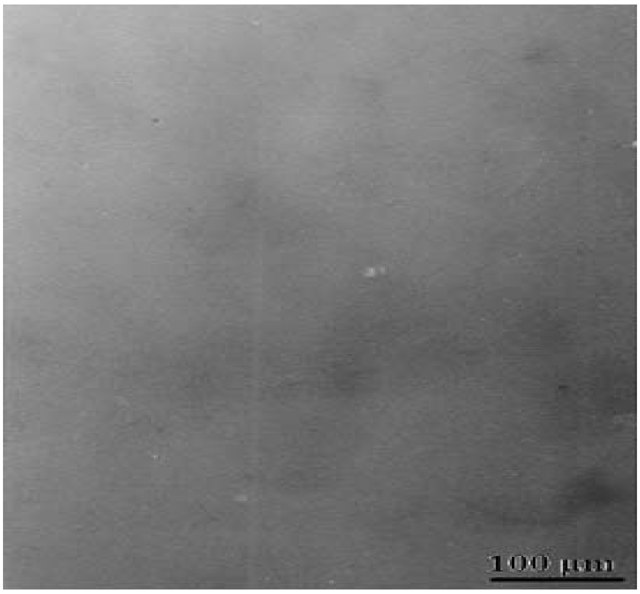

Figure 8. Morphology development of base bitumen by optical microscope.

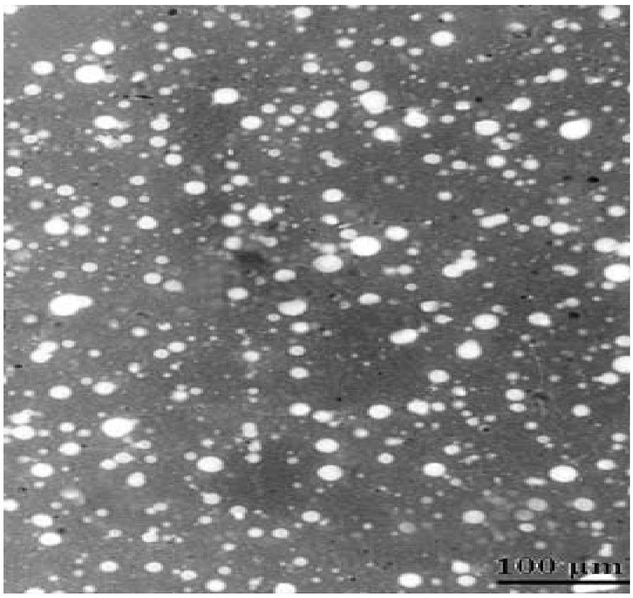

Figure 10. Morphology of SBR3%/NB2% modified bitumen by optical microscope.

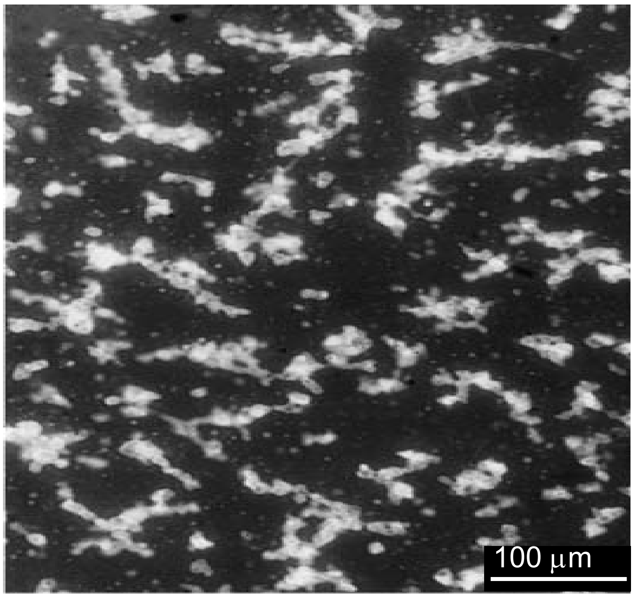

Figure 11. Morphology of SBR3%/NB3% modified bitumen by optical microscope.

the addition of NB (low content) in SBR/NB modified bitumen sample. Mouillet et al. concluded that the general trend in the SBS modified bitumen samples is when the binder becomes more homogeneous due to both polymer chain scission and a better compatibility of the smaller polymers chains with the bitumen molecules on aging [30]. However, the morphology of the polymer is quite different from the bitumen modified with 3% NB as evident in Figure 11. The results of morphology study show that 2% of NB may be the appropriate content of the SBR/NB modified bitumen samples. This is in accordance with Lesueur work [31] who concluded that the common meaning of polymer/bitumen compatibility is a system that will be homogeneous as judged by eyesighting but heterogeneous under the microscope.

Polymer/bitumen compatibility is indeed a dynamic concept and that compatible systems are those with a slow creaming rate. Since NB has high nitrogen content, a better adhesion between the binder and aggregates is accomplished in SBR/NB modified bitumen sample, thus preventing SBR droplets to coalesce.

In optical microscopy technique it is difficult to measure the real sizes of polymer inclusions in bitumen matrix. This is mainly due to the difficulty to control the thickness of viewed film of the bitumen. Scanning electron microscope (SEM) is used to analyze the shape of bitumen, surface texture, and even polymer distribution in modified bitumen.

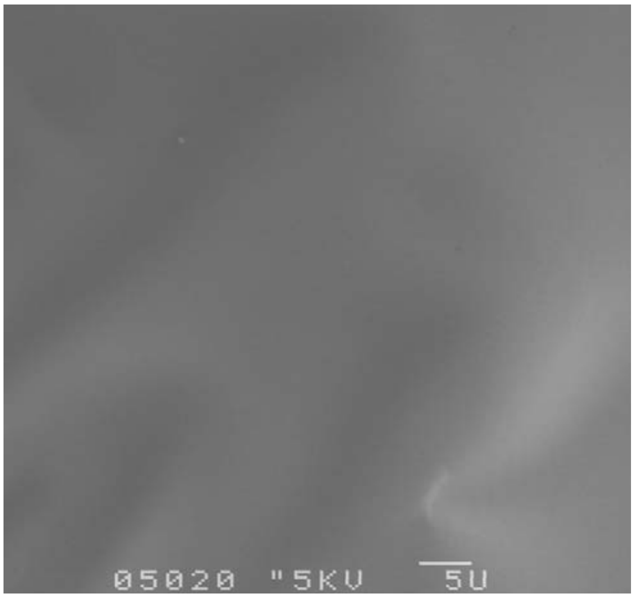

Figure 12. Morphology of base bitumen by SEM.

The SEM of a typical morphology of base bitumen is shown in Figure 12. As the content of SBR is increased up to 3 wt% the modified bitumen of relative uniformity is obtained as shown in Figure 13. It can be seen that the white SBR particles disperse in the bitumen matrix with the size of 1-3 μm. At the polymer concentration of 3 wt%, the content of maltenes (more compatible with the polymer) is probably sufficient to swell the macromolecules without inducing instability in the micellar structure of the bitumen, and the resins may stabilize the polymer-rich phase as the same as they are supposed to do with asphaltenes. The results show no sign of phase separation.

Bitumen is traditionally considered as a dynamic colloid system consisting of a suspension of high molecular weight asphaltene micelles dispersed in a lower molecular weight oily medium (maltenes) [32]. The polymer modified bitumen samples may have a tendency to separate into two phases; one is polymer-rich phase and the other bitumen-rich phase, because the introduction of any polymer disturbs the dynamic equilibrium and reduces the homogeneity of the bitumen system. The case is of utmost serious

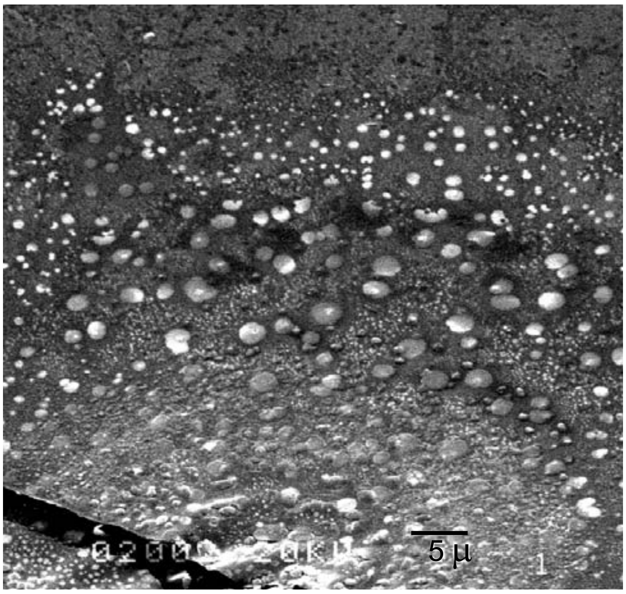

Figure 13. Morphology of SBR3%/NB2% modified bitumen by SEM.

concern under quiescent conditions at high temperature [8]. The promotion of aromatic compounds by FTIR analysis in modified bitumen indicates the improvement of compatibility between the modifier and bitumen. For SBR has high surface energy when it is compounded with NB, as chemical or physical interactions could take place during processing with selective attachment to the components of bitumen. NB gives better adhesion between SBR and natural bitumen modified bitumen. From the morphology studies, we can make assertion that physical interactions have occurred during processing. This is in accordance with the improved properties of the SBR/NB modified bitumens.

It is well known that the polymer may dissolve and/or disperse into the maltenic medium, enhancing the mechanical properties of the mixture. In this study, NB from Xinjinag province, with high nitrogen content, gives better adhesion between the binder and aggregate thus, improving the stripping and oxidation resistances. The high asphaltene content and high molecular weight of NB are thought to function mainly as a "solution thickener", giving improved stiffness, viscosity properties and deformation resistance. As we have shown above, the modified bitumen has gained improved viscoelastic behaviour with remarkable enhancement in the mechanical properties by the addition of SBR/NB.

CONCLUSION

The classical properties of SBR and SBR/NB modified bitumen, including softening point, penetration, PI and ductility before and after RTFOT aging are characterized. It is found that the NB with 2 wt% content has marked effect on the high temperature property of increasing the softening point, while 3 wt% SBR has significant effect on the low temperature properties and improvement of aging resistance of SBR/NB modified bitumen samples. The high temperature storage stability is effectively improved through the addition of NB. The morphology of SBR/NB modified bitumens shows a homogeneous and stable structure at the NB concentration range of 1 to 2 wt%. SBR has marked effect on the low temperature properties and improvement of the aging resistance with SBR content of 3 wt%.

The improved viscoelastic properties of the PMBs have been demonstrated using the rheological parameters of high-temperature viscosity and $G^*/\sin\delta$ values. TG-DTG analysis shows that SBR/NB has higher mass loss temperature than either SBR or base bitumen, indicating the improvement of stability in modified bitumen. FTIR analysis shows few new weak peaks in modified bitumen samples, indicating that the main change is physical alteration in them. DSC analysis shows the postponement of the exothermic peak towards high-temperature regions, which improved the high-temperature properties in SBR/NB modified bitumen samples.

Therefore, SBR/NB modified bitumen samples have the improved properties of increasing softening points, significantly promoting ductility, thermal-stability, and aging and rutting resistances.

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