Natural Rubber Modified Asphalt

Mazlina Mustafa Kamal\textsuperscript{1*}, Kamarul Ariffin Hadithon\textsuperscript{1} and Rohani Abu Bakar\textsuperscript{1}

\textsuperscript{1}Stesen Penyelidikan RRIM LGM, 47000 Sungai Buloh, Selangor
\*Corresponding author: mazlina@lgm.gov.my

Abstract. The asphalt binder is modified using natural rubber (NR) based on cup lump to improve its performance and service life due to intense load and weather induced stress. A source of PG 60-70 asphalt was used for preparing a natural rubber modified asphalt, (NRMA). The rheological characteristics of the NRMA was analyzed using dynamic shear rheometer (DSR) according to Superpave test protocol. The presence of the NR also was investigated by thermogravimetric analysis (TGA) and Fourier infra-red spectroscopy (FTIR). Results showed that the conventional properties of the base bitumen such as penetration, softening point, and temperature susceptibility improved with addition of NR. The DSR analysis exhibited that the presence of elastic NR within the bitumen network increases the viscosity, stiffness and reduces temperature susceptibility which consequently enhances the rutting property.

1. Introduction
Asphalt is a thermoplastic and viscoelastic material. It exhibits elastic solid at low temperature and /or during rapid loading and as viscous fluid at high temperatures or during slow loading. Hence, improvement in bitumen binder quality is prerequisite to minimize stress cracking at low temperature and permanent deformation, at high service temperature. Vast interest in modified bitumen in road pavement has been growing rapidly over the years. Many methods and techniques have been used to upgrade the road service life.

Blending polymers into bitumen is one of the most promising method to improve the performance of the binder [1-6]. The three common polymers are block copolymers, thermoplastics, synthetic and natural rubbers and others. Currently, the most commonly used polymer is the, styrene –butadiene – styrene (SBS) which usually added 3% to 6% by weight of the bitumen phase [1]. Many factors must be considered when using a polymer modified bitumen binder such as of crude bitumen source, polymer microstructure and, mixing [1]. Therefore, the understanding of the interaction of asphaltene and maltene with polymer is crucial in order to ensure the improvement of the overall asphalt performance [7-8].

This work is also part of Malaysian National Key Economic Area Entry Points Projects (NKEA) in rubber to increase the usage of natural rubber in Malaysia and reduce the import of raw rubber. Recently, International Tripartite of Rubber Producing Country (ITRC) consensuses at the inter-ministerial level to strategize the application of rubberised road to increase the usage of NR affecting the global supply and demand of rubber. Therefore, this natural rubber in asphalt for road pavement in Malaysia is a good move to increase domestic usage to stabilize rubber price and reduce the impact on about 300,000 smallholders. The utilization of cup lump rubber in road construction will expect to boost domestic rubber demand for rubber. Due to that, a collaboration work has been initiated and Memorandum of Agreement (MOU) has been signed between Public Works Department

[Note: The original text has been marked as a figure with content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI. Published under licence by IOP Publishing Ltd]
(JKR) and the Malaysian Rubber Board (MRB) to undertake joint research in the use of the cup lumps as an additional material in bitumen. In the present work, the fundamental characteristics of the natural rubber modified asphalt (NRMA) has been determined using conventional methods. The chemical characteristics and rheological properties of the NRMA were analysed by means of Fourier transform Infra-Red transform (FTIR) and dynamic mechanical analysis using a Dynamic Shear Rheometer (DSR).

2. Materials and methods

Bitumen with penetration grade of 60/70 and natural rubber is supplied by Shell Sdn Bhd and MRB. In this experiment, a mixture of 95:5 ratio of bitumen to rubber is used. The bitumen is heated to 160°C prior mixing and natural rubber is added gradually into the bitumen until the mixture become essentially homogenous. The modified bitumen sample is prepared by means of a high shear laboratory type mixer rotating at 1100 rpm. A commercial modified bitumen PG76 was used as a comparison.

Penetration and Softening Point: The conventional parameters such penetration grade and softening point of the neat bitumen and modified bitumen were determined in accordance to ASTM D5-86 and ASTM D36-95.

Viscosity: The viscosity of the binder was measured using Brookfield viscometer at a shear rate of 6.8/s with a rotational of 20 rpm with the Brookfield Spindle of 27 at a temperature of 135°C as recommended by Superpave (SHRP).

Dynamic Shear Rheometer: Dynamic Shear Rheometer (DSR) was used to measure the rheological characteristics of unaged and aged of the binder samples at intermediate temperature terms of G* and the phase angle (δ) in accordance with Superpave requirements, AASHTO 315

ATR-FTIR: The functional groups of the modified binder were investigated using ATR-FTIR Nicolet 6700 spectrometer (Thermo Scientific) with 32 scans at a resolution of 4 cm⁻¹ in the range of 4000 – 600 cm⁻¹.

3. Results and Discussion

The effect of NR based cup lump on the conventional binder properties on the softening and penetration properties can be seen in Table 1. A decrease in penetration and increase in softening point is observed with NRMA. Hence, the incorporation of rubber increases the stiffness and temperature susceptibility of the binder. This result is similar with some previous result with ENR addition [9].

| Bitumen Type | Penetration (dmm) | Softening(°C) |
|--------------|------------------|---------------|
| Bitumen 60/70 | 50               | 54            |
| NRMA         | 45               | 60            |
| PG 76        | 60               | 81.5          |

Viscosity or the flow characteristics of the asphalt binder is used to provide some assurance in pumpability, mixability and workability at the hot mix facility. The temperature–viscosity charts are therefore used for estimating mixing and compaction temperature in mix design as a reference [10]. The specification established by SHRP indicating that asphalt viscosity should not exceed 3 Pa-s at 135°C. Therefore, the low viscosity enhances the pumpability and constructability of the binder.

Figure 1 presents the influence of temperature on the binder’s viscosity. As shown in Figure 1, it can be observed that the viscosity values reduce as the test temperature increases for PG 60/70 and both modified asphalt binder. It also indicates that the base binder has the lowest viscosity values at
test temperatures while the modified binder shows the highest viscosity. The viscosity of the NRMA is greater by 2-fold as compared to neat asphalt binder, PG 60/70 at that particular concentration. This is due to that the NR begins to form a localized network structure and begin to interact to form continuous network throughout the binder. The network reinforces the asphalt structure, resisting deformation.

There is scarce information and study on the bitumen – rubber interaction available, and hence increase in binder viscosity cannot be accounted for only by existence of the rubber swelling particles [11]. There is a possibility of attraction between rubber and asphalt, but the strength and nature of the attraction vary. Interactions can be classed as chemical or physical. By far the most widespread and important of these are the physical interactions which have profound effects on properties. The physical interactions can be non-specific or specific. The non-specific physical interactions may well be the strongest present in a system and provide reinforcement such as dipole-induced dipole interactions. Here a polar group interacting with a non-polar group can induce a dipole by the negative charge repelling the electron cloud in the non-polar group. The strength of the interaction here depends on both polarity of the polar group and polarisability of the non-polar group. Polarisability can be considered as the “looseness” or mobility of the electron cloud which allows it to be influenced by the polar group. A tightly held electron cloud is not very polarisable. In elastomers the most common highly polarizable groups are the double bonds present in the unsaturated elastomers such NR and in the aromatic rings of asphalt structure.

In the final example the induced dipole-induced dipole interaction is the result of momentary fluctuation in the distribution of the electron cloud in groups which can result in instantaneous polar interactions and a net attraction between the groups. Although this interaction considered very weak, it is also might contribute for the strong interactions between asphalt and unsaturated elastomers like NR.

![Figure 1. Viscosity of Asphalt Binder](image)

The influence of rubber on complex modulus (G*) of rubberised binder versus temperature at 1.5 Hz for asphalt binder is shown in Figure 2. The G* represents the total resistance deformation under dynamic loading. In general, greater rigidity of binder is favoured for the high temperature pavement application. Figure 2 shows that the shear modulus of neat bitumen is the lowest at low temperatures compared to other modified bitumen. The G* of all binders decreases as the temperature continuously increases (T>52°C). Unlike the neat bitumen, the isochronal plots of modified bitumen show greater G* even at high temperature which reflects to the material strength and rigidity.
Figure 3 shows the influence on phase angle of modified bitumen in relation to its elasticity at high temperature. Findings suggested that, the phase angle properties follow the same trend. Compared with the PMB binder the phase angle of NRMA increases continuously with temperature. The phase angle clearly illustrates that Natural Rubber addition improved elastic response of the neat bitumen. The increase in elastic response at high temperatures can be attributed due to continuous rubber network structure formation when disperse in the bitumen that influence the properties of the binder [12]. To resist rutting and fatigue damage, more elasticity is favourable at high temperature. In general, a predominant viscous behaviour is expected when the phase angle approach 90° while, complete elastic when the value of phase angle is 0°.

In general, the requirement value established by SHRP is determined as the temperature at which the $G^*/\sin \delta$ is greater than 1 kPa for unaged binder and minimum of 2.2 kPa for short term aged binder to minimize rutting. Figure 4 shows the effect of rubber on the Superpave rutting parameter of both unaged and aged binder at various temperatures in comparison to unmodified binder. Figure 4 shows that the unmodified binder contributes $G^*/\sin \delta$ values are higher than 1.0 kPa (unaged condition) and 2.2 kPa (RTFO aging condition) at 64°C, while NRMA and PMB at 76°C and 82°C accordingly. The results suggest that addition rubber could increase elasticity and rutting resistance of asphalt. A similar trend was observed by Ali et al (2013)[13], where it was found that the addition of high crumb rubber increased the value of $G^*/\sin \delta$ thus improved the aging resistant and durability. The high value of shear modulus and low phase angle is important in determining the performance of deformation properties [14].
The FTIR spectra of neat bitumen, CMB and Natural Rubber are given in Figure 5. As expected, the spectra of neat bitumen and CMB are similar to each other and the typical absorbance peaks are listed in Table 2. Compared with neat bitumen, NR brought a new absorbance peak of 839 cm\(^{-1}\) corresponding to the =C-H, but the peak of 1660 cm\(^{-1}\) corresponding to the C=C is not observed due to small ratio of Natural Rubber in CMB.

![Figure 5. FTIR Spectra of (a) neat bitumen 60/70 b) CMB and c) Natural Rubber](image)

**Table 2. Absorbance peaks of bitumen [5]**

| Wavenumbers (cm\(^{-1}\)) | Functional group               |
|---------------------------|--------------------------------|
| 2920, 2850                | C-H aliphatic stretching       |
| 1600                      | C=C aromatic stretching        |
| 1456                      | C-H of -(CH\(_2\)) - bending  |
| 1376                      | C-H of CH\(_3\) bending       |
| 1030                      | S=O sulfoxide stretching       |
| 862, 807                  | C=C of alkene stretching       |
| 746, 720                  | C-H or C-S bending             |

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 6 shows the curves of TG analysis. TGA curves show that there are clearly three areas of weight loss between 250 and 450°C in modified bitumen samples. The first weight loss between 350-420°C corresponds to 14% of the total weight and is attributed to the decomposition of Natural Rubber. The next mass losses of 66% and 20% which have an initiating mass loss temperature of 420°C to 480°C and 480°C to 850°C is characterized by the decomposition of saturates and aromatic hydrocarbons while the later decomposition is referred to aromatics hydrocarbons, resins and asphaltenes of bitumen of bitumen respectively [15]. Finally, at higher temperatures more than 850°C is mainly due to asphaltenes and non-combustible filler.
4. Conclusion
The rheological properties of bitumen for road application is improved by means of NR rubber modification as proven by both conventional and rheological parameters $G^*$, $\delta$ and $G^*/\sin \delta$ obtained by DSR measurements. Addition of NR, $G^*$, $\delta$ and $G^*/\sin \delta$ increases as well as the elastic response. The increases are more pronounced with changes in temperature. The presence of NR in the modified bitumen is proven by TGA and IR analysis.

5. References
[1] McKay K W, Gros W A and Diehl C F 1995 The influence of styrene–butadiene diblock copolymer on styrene–butadiene–styrene triblock copolymer viscoelastic properties and product performance J. Appl. Polym. Sci. 56 947- 958
[2] Adedeji, A, Grunfelder T, Bates F S, Macosko C W, StroupGardiner M and Newcomb D E 1996 Asphalt modified by SBS triblock copolymer: structures and properties Polym Eng Sci 36 1707
[3] Lu X and Isacsson U 2001 Modification of road bitumen with thermoplastic Polym Test 20 77- 86
[4] Ait-Kadi A, Brahimi H and Bousmina M 1996 Polymer blends for enhanced asphalt binders Polym Eng Sci. 36 1724
[5] Gonzalez O, Pena J J, Munoz M E, Santamari’a A, Pe´rezLepe A, Marti’nez-Boza F and Gallegos C 2002 Influence of Polymer Concentration on the Microstructure and Rheological Properties of High-Density Polyethylene (HDPE)-Modified Bitumen Energy & Fuels 16 1256
[6] Airey G D 2003 Rheological properties of styrene butadiene styrene polymer modified road bitumens Fuel 82(14) 1709
[7] Martinez-Boza F, Partal P, Conde B and Gallegos, C 2000 Influence of temperature and composition on the linear viscoelastic properties of synthetic binders Energy & Fuels 14(1) 131-137
[8] Wloczysiak P, Vidal A, Papirer E and Gauvin P 1997 Bitumen and Bitumen modification: A Review on Latest Advances J. Appl. Polym. Sci. 65 1595-1607

Figure 6. TG thermogram of Bitumen 60/70, Natural Rubber and CMB
[9] Ramez A. Al-Mansob, Amiruddin Ismail, Nur Izzi Md Yusoff, Che Husna Azhari, Mohamed Rehan Karim, Aows Alduri, and Mojtaba Shojaei Baghini 2014 Rheological characteristics of Epoxidised Natural Rubber modified bitumen. *Applied Mechanics and Materials* **505-506** 174-179

[10] Lewandoski L H 1994 Polymer Modification of Paving Asphalt Binders *Rubber Chemistry Technology* **67** 447-480

[11] Presti D L 2013 Recycled tyre rubber modified bitumens for road asphalt mixtures: A Literature review *Constr. Build. Mater.* **49** 863–881

[12] Yong Wena, Yuhong Wanga, Kecheng Zhaoa and Agachai Sumaleeb (2015) The use of natural rubber latex as a renewable and sustainable modifier of asphalt binder *Int. J. Pavement Eng.* **18(6)** 547–559

[13] Ali A H, Mashaan N S and Karim M R 2013 Investigations of physical and rheological properties of aged rubberised bitumen *Adv. Mater. Sci. Eng.* **2013** 1–8

[14] Parvez M A, M. AL-Mehtel M, Al-Abdul Wahhab H I, Hussein I A 2014 Utilization of sulfur and crumb rubber in asphalt modification, *J. Appl. Polym. Sci.* **131** 40046

[15] Jimenez:Mateos J M, Quintero L C and Rial C 1996) Characterization of petroleum bitumens and their fractions by thermogravimetric analysis and differential scanning calorimetry *Fuel* **75** 1691 -1700