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Investigation of Rheological Properties of Asphalt Mixtures Containing Polymer Waste.

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Abstract

The objective of this study was to evaluate the rheological performance of rubberised asphalt binder with varying dosages of crumb rubber (CR), and compare these modified materials with unmodified asphalt binder. It is very important to investigate the characterization of chemical structures of the asphalt binder from a closer view for useful modifications of the virgin binder by polymer waste as modifiers. The current research employed a thin layer chromatography technique (TLC) to separate and determine the different fractions in asphalt. Nuclear Magnetic Resonance (NMR) spectroscopy was also used to characterize and confirm the chemical compositions of asphalt and its fractions. Despite of NMR spectra of asphalt is difficult to be interpreted via its structural complexity, but this technique is still able to provide useful data especially with regard to asphaltene fraction. Crumb rubber is a polymer waste which used as modifier of asphalt binder via the economic benefits and improving the rheological properties of modified asphalt binder. The rubberised asphalt binders were produced by blending the virgin asphalt with CR at various contents (3%, 5%, 10%, 15% and 20%). The effects of CR contents on the rheological behaviors of modified asphalt binder have been investigated including: penetration, softening point, ductility. Furthermore, morphological analysis of rubberised asphalt was conducted via scanning electron microscopy (SEM) to assess the effect of CR on the binder morphological structure. Based on results obtained, binder with highest CR content showed improvement in rheological properties of the modified binders in terms of decreasing in penetration, increasing in softening point values and keeping the ductility higher, unlike other CR contents which exhibited poor performance of modified asphalt.

Keywords: Polymer modified asphalt (PMA); Crumb rubber (CR); Rubberised asphalt.

1. Introduction

Asphalt binder is used as one of the important element in road pavement which extracted from crude oil through refining process [1, 2] it is one of the viscoelastic material that shows adhesive and cohesive properties with aggregates,[3] the binder is considered as only deformable element of pavement that play a very important role in pavement performance. [4, 5]

It is noteworthy that the chemical composition of asphalt binder is a kind of complex mixture of heavy organic molecules composed by hydrocarbons and metals. It mainly contains carbon (80%), hydrogen (15 %) as well as heteroatoms and metals.[6] Basically asphalt binder is composed of two main components, (a) maltenes which consists of three essential fractions, saturates, aromatics, and resins. (b) asphaltenes which mainly contains of condensed aromatic compounds that containing nitrogen, oxygen, sulfur and metals.

These two main components are integrated in a colloidal structure to determine the characteristics and performance of asphalt binder. Generally, asphaltene forms colloidal core structure which is surrounded by resins that are bridged to aromatics and dispersed in saturates. Asphaltenes and resins contribute to stiffness behaviour of binder, while

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adhesive and cohesive properties of asphalt are generally related to saturate hydrocarbons and aromatics.[6-8] Consequently, the rheological and desired performance properties of binder are determined via the properties of the individual fractions and their proportions, so rheological and mechanical characteristics is vital to predict the performance of binder with mixture in asphalt concrete.[6] Rossi and his group investigated the chemical properties of bitumen via Nuclear Magnetic Resonance (NMR) spectroscopy, they quantitatively estimated the aliphatic fragment with respect to the aromatic fragment for achieving a comprehensive understanding of the chemical characteristics of the complex materials such asphalt.[6]

Generally, the resist pavement distresses of conventional asphalt is limited due to insufficient of the durability and rheological properties therefore The target of modifying asphalt binders by polymers is to improve binder performance and properties. The road surfaces performance can be enhanced by modifying asphalt which are being developed by numerous modifiers in order to develop their performance as new technology. It is worth mention that various modifiers such as plastics, rubber and fibres have been used as additives to the unmodified asphalt binders in order to improve the performance and characteristics of pavement.[9]

As known that CR is a recycled scrap tire which is produced via crushing and grinding waste tire.[10] Over the past decades, CR started to be widely used and investigated in production of asphalt mixtures concrete for pavement. CR modified asphalt has received increasing attention in the research community as a result of its potential advantages.[10, 11]Clearly, rubberised asphalt binder is considered as one of the most reliable and effective strategy to optimise resistance to surface cracks, rutting, fatigue and reflective cracking, moisture and temperature susceptibility.[12] Moreover, it has been found that the incorporation of CR modifiers in asphalt binder have advantageous effect on the durability and pavement maintenance costs.[13] Furthermore, employing of scrap tires in asphalt manufacturing will alleviate the burden on the environment and save the energy and natural resource by using waste materials.[14]

Great progress has been achieved to improve the rheological characteristics of the rubberized asphalt binders which exhibited significantly promising performance, this can be attributed to interaction of CR Modifier with asphalt.[13]Obviously, asphalt – rubber interactions rely on mechanisms, which include swelling behaviour of rubber particle in binder components via absorbing the light oils in maltenes part of asphalt binder, and degradation behaviour (devulcanisation) of CR within liquid phase of asphalt.[15] Nevertheless, rubberised asphalt binder possesses high viscosity which negatively impacts on compatibility therefore CR and asphalt require high temperature and mixing to obtain desirable density and workability rubberised asphalt mixture.[13, 15, 16]

The rubberised asphalt has got more and more attention from the industrial societies because of its low cost and environmental benefits.[13, 17]Rubber modifiedbinders are generally produced by mixing a percentage of ground tire rubber with asphalt binder at high temperatures. Practically, a broad range of mixtures and conditions have been studied with varying degrees of success.[17]

The aim of this study is to investigate the rheological and morphological characteristics of the modified asphalts binder with CR ratios 1%,3%,5%,10%,15% and 20% wt in 100 gm. Rheological behaviors of asphalt binder were examined by different techniques in order to ascertain the effect of additives (CR) to asphalt binder performance. Furthermore, asphalt used was separated by chromatography method to evaluate the composition of asphalt used then analyzed using ^{1} HNMR for a better understanding of the chemical composition of the asphalt binder, this manner facilitates understanding of the degradation of asphalts under service conditions and this determines whether the asphalt is suitable for modification or not.

2. Experimental section

2.1 Materials and instruments

The unmodified asphalt used in all study was 40/50 penetration grad which is usually used as surface layer (binder) in pavement. It was provided by Refinery of Dourah, Baghdad, Iraq.The physical properties of unmodified asphalt used are available in Table 1.

Table 1: Physical properties of unmodified asphalt.

Properties	ASTM Standard specification	value
Ductility @ 25 °C (cm)	ASTM D113-86	100+
Softening point	ASTM D36	49-58
Penetration (25 °C , 100 g , 5 min)	ASTM D5-83	40-50
Flash point °C (min)	ASTM D92	240
Solubility in trichloroethylene (C_2HCl_3) wt. (min)		99.0
Density (g/cm^3) @ 15.6 °C	ASTM D70	1.04

In addition, CR was obtained from local supplier, and it was cord and metal free. The waste tire rubber was crushed, grounded then sieved through a 20 mesh size (0.8 mm). All common organic solvents were obtained from internal chemical stores. Regarding to instruments used, ^{1}H nuclear magnetic resonance (NMR) spectra were recorded using on Varian Inova 500 (MHz) NMR spectrometer at ambient temperature using Dimethyl sulfoxide-d (DMSO-$(CH_3)_2SO$) with tetramethylsilane (TMS) as an internal standard. Furthermore, the morphology of rubberised asphalt samples was scanned by using the scanning electron microscope (SEM) with the magnification of 2 µm in order to investigate the morphological structure of modified asphalt.

2.2 Asphalt Separation Techniques.

In this study, two different separation methods have been utilised to separate unmodified asphalt into two main fractions: maltene and asphaltene for preparation samples for the following analysis: The conventional method includes separation of asphaltene from base asphalt using organic solvent. In conical flask (100 ml), it was charged with a mixture of (1 gm) asphalt and (40 ml) n-heptane. After addition, the mixture was carefully dissolved under dark conditions then stirred vigorously at room temperature for 2 hours. The precipitate (asphaltene) was filtered off through filter paper and washed with n-heptane until became colourless. The precipitate on filter paper was dried in air. The residual solvent in asphaltene was removed under vacuum pump to afford a black – brown product (0.19 gm, 19%) as depicted in Figure 1.

Figure 1: Residual of asphaltene.

Moreover, the filtrate portion, which contains maltene fraction, was evaporated in rotary evaporator to yield a sticky black product (0.81 gm, 81%).

Column Chromatography separation technique was another separation method which has been conducted to separate the base asphalt binder into two main fractions: maltene and asphaltene. Firstly, the sample of asphalt was tested on silica gel plate (as stationary phase) using a pipette spotter, glass chamber and a suitable solvent (as mobile phase), this technique is a thin layer chromatography (TLC), which was conducted before performance of column chromatography in order to find out the optimised separation behaviour for a mixture of compounds. Asphalt binder was eluted with n-heptane, n-heptane-dichloro methan (DCM) and n-heptane-methanol respectively. Notably, TLC plate displayed four main spots as depicted in Figure 2.It is hypothesised that a spot at base line on plate should match with asphaltene portion, it was also observed that separated spots which raised from the base line on TLC plate represent a specific fraction of binder, A, B and C spots that should correspond to saturates, aromatic and resin components, respectively.

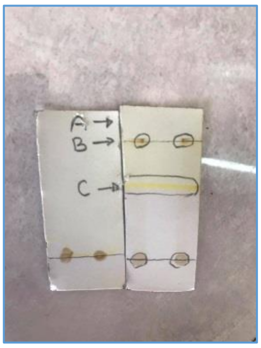


Figure 2: Fraction spots of asphalt on thin layer plate of chromatography.

The chromatographic column was set up by pyrex tube then it was packed via silica gel (Figure 3). 1 gm of the base asphalt binder solution, which partially soluble in n-heptane, was injected in the column then eluted by different co-solvents including n-heptane, n-heptane-(DCM) and n-heptane-methanol, respectively. Obviously asphaltene component stuck into the column and other components were come down as fractions as a result of polarity of solvents which were passed through the column, afterwards the eluents were combined together then evaporated in vacuum pump rotary to obtain a sticky black product (0.83 gm, 83%), the product represents maltene fraction into a base asphalt binder. the asphalt and it's separated fractions have been analysed by 1H-NMR technique.

Figure 3: The chromatographic column filled with silica gel.

2.3 Sample Preparation of CR modified asphalt.

100 gm of a base asphalt binder 40/50 pen grade was heated up to 180 ^{o}C and stirred vigorously until it was completely melted, then CR was gradually added to the asphalt and mixed for 2 hours. The base asphalt binder was heated up and blended with CR at various contents: 1, 3, 5, 10, 15 and 20 % by weight of bitumen under high speed stirring at constant temperature (180 °C) until the mixture became essentially homogenous to produce CR modified asphalt. After completion, the rubberised asphalt samples were removed from reaction container into small aluminium cans which covered with aluminium foil and stored for testing at room temperature.

2.4 Conventional tests of asphalt.

The rubberised binders were characterized by standard conventional tests, including: the softening point test (the ring and ball method), the penetration and ductility were performed in in accordance with ASTM D36,[18] ASTM D5 [19] and ASTM D113-86,[20] respectively. The results of these tests are listed inTable 2. Moreover, the penetration index (PI) value was calculated from the relation between the softening point and penetration value to predict temperature susceptibility of the modified binder. PI value is given according to following equation:

$$PI = \frac{1952 - 500 \log \quad pen \ - 20\, softening\ point}{50 \log pen - softening\ point - 120}$$

Pen represents the penetration value at the temperature of 25 °C. A lower PI value generally indicates higher temperature susceptibility.[21]

Table 2: physical data of CR modified asphalt.

Content of CR (%)	Ductility (cm) at 25 °C	Softening Point	Penetration (mm) at 25 °C	penetration index (PI) value
0	100+	51	41	-1.40
1	18	63	12	-1.10
3	19	64	12	-1.04
5	38	65	15	-0.52
10	45	66	22	0.31
15	60	66	24	0.36
20	63	63	28	0.25

2.5 Nuclear Magnetic Resonance Spectroscopy (NMR)

The chemical structure of asphalt, maltene and asphaltene were adequately verified by H^1-NMR spectra using on Varian- Inova500 (MHz) NMR spectrometers at room temperature, the H^1-NMR experiments were conducted using 15 mg of sample which diluted in 1 ml of $CDCl_3$ (chloroform-d) as solvent with tetramethylsilane (TMS) as an internal standard. The signal positions of H^1 of base asphalt and its fractions (maltene and asphaltene) are presented in Table 3. Generally, four types of H signal group have been distinguished via NMR spectra, these signal groups of measured samples correspond to proton on aromatic rings (H_{ar}), alpha-alkyl proton on C_α in aromatic rings (H_α), aliphatic proton (methyl (H_β) or farther, methylene group (H_γ) or farther from the aromatic ring .

Table 3: Proton types of asphalt and its fractions in NMR spectra.

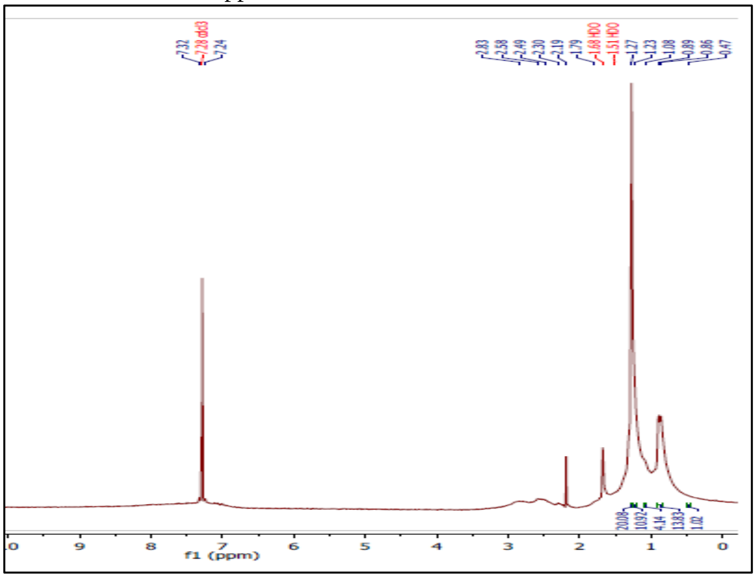
Proton types	Chemical Shift δ/ppm
Aromatic proton (H ar)	6-9
Aliphatic protons α to aromatic rings (Hα)	2-3
Aliphatic proton on C_β and the methylene beyond the C_β to aromatic rings	1-2
Aliphatic proton on Cγ and the methyl beyond the Cγ to aromatic rings	0.5-1

3 Results and discussions.

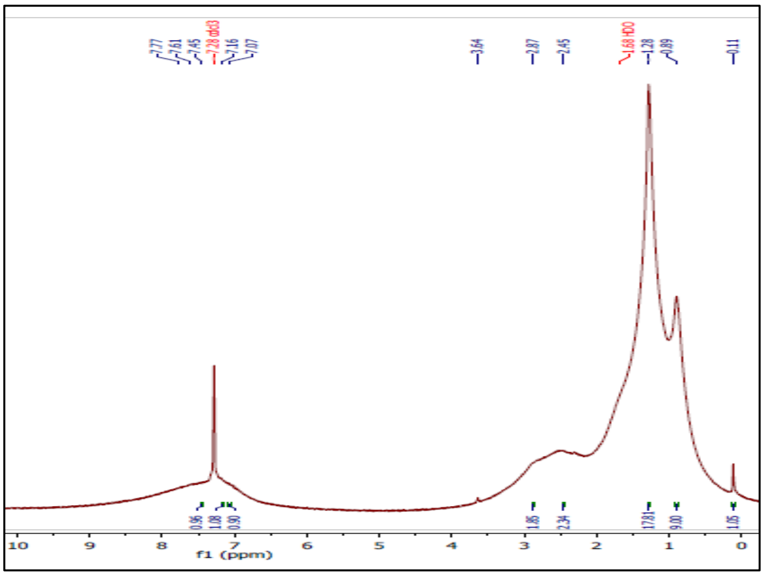
3.1 Analysis of asphalt and its fractions by ^{1}H NMR spectroscopy.

It is interesting to understand the complex natural system of asphalt and difficulties in distinction between the distinguishable differences in the asphalts with similar physical properties via ^{1}H NMR spectroscopy, the comprehensive understanding of structure of asphaltene and determining its percentage into asphalt plays an essential role to find out if this asphalt be suitable for modification or not.

The analysis of ^{1}H-NMR was performed on both maltene and asphaltene portion alongside with the 40/50 asphalt binder as shown inFigure 4. All three ^{1}HNMR spectra have displayed a very similar distribution of proton signals. However, it can be seen that higher percentage of protons in aromatic domain was present in asphaltene fraction (Figure 4b) compared to maltene fraction (Figure 4c) despite having proton in upfield region. It displayed a broad peak between 6-9 ppm in downfield region, this arises from mono, di, tri and tetra aromatic protons.[22] On the other hand, this broad peak was not exist in maltene fraction as indicated in Figure 4c. this is due to extract the asphaltene portion from asphalt binder as mentioned procedure. Obviously, the NMR spectra of maltene fraction extracted from asphalt (Figure 4c) displayed only the signals in the up-field region compared to other fractions which corresponding to protons in aliphatic domain. In this region, it can be divided to three sub-regions, the first one is between 0.5-1.0 ppm which corresponds to protons in γ-position and beyond it to aromatic rings, these signals are belonging to $-CH_2$, -CHand–CH_3 groups whether branch or linear alkenes that attached to aromatic rings. Other signals spectrum appeared between 1.0-2.0 ppm, these signals corresponded to alkyl protons in β-position of carbon and beyond it to aromatic rings. These proton signals belong to aliphatic and naphthenic chains that connected to aromatic rings, while the other –CH, -CH_2 and CH_3 groups, whose are α-position to aromatic rings, produced proton signals around 2.0-3.0 ppm. The ^{1}H NMR data of virgin asphalt, maltene and asphaltene (Figure 4a,b,c) exhibited almost similar distribution of aliphatic protons in the up-field region. However, the maltene spectrum displayed lack of proton signals in aromatic region compared to other fractions while the asphaltene fraction was characterised by a higher percentage of aromatic protons than the others.



(a)



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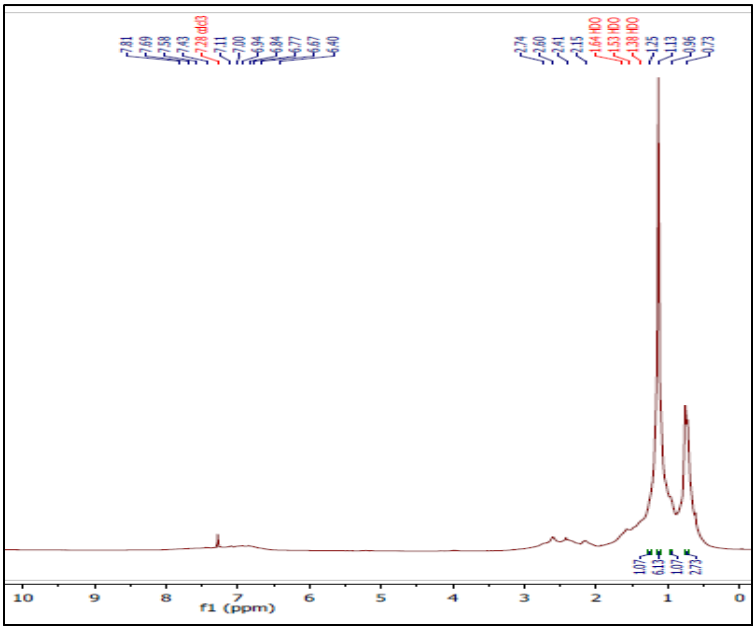


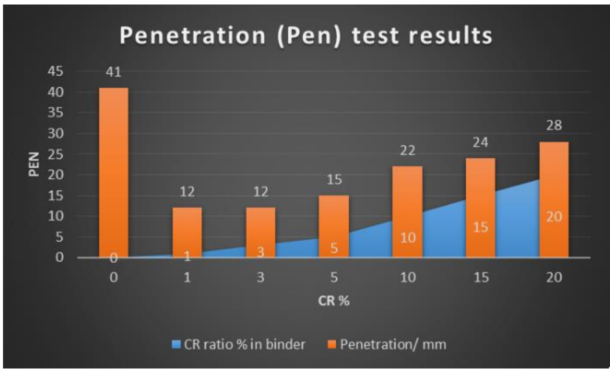
(c)

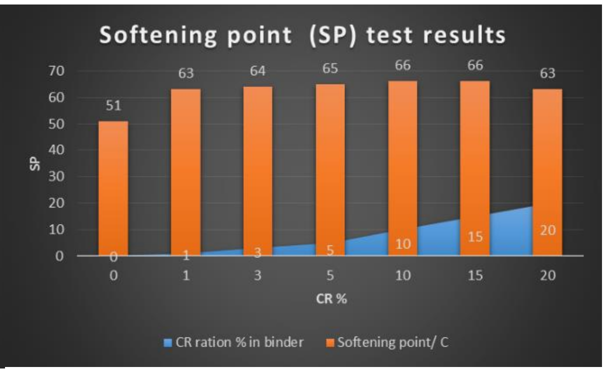
Figure 4: The 1H-NMR spectra of 40/50 asphalt in deuterated chloroform: (a) virgin asphalt; (b) asphaltene fraction and (c) maltene fraction.

Understanding of results obtained on asphalt 40/50 binder and its fractions by separation technique (83% maltene and 17% asphaltene) and ^{1}H NMR spectroscopy allows to improve the properties of binder via asphalt detailed characteristics. The complex natural system of binder is still under consideration but asphaltene content into asphalt plays an important role in determination of the mechanical properties and in general on the performance properties of the binder. Adding suitable modifier in asphalt, it would be possible to reduce or raise the aromatic content that could be the key to control the asphalt viscosity that significantly effect on mechanical properties of binder.

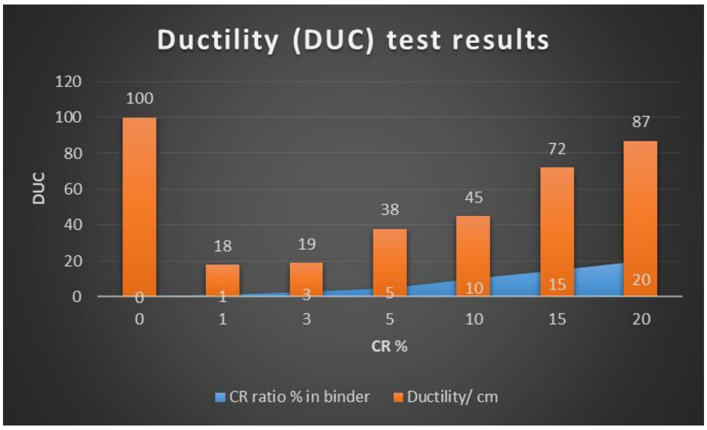
3.2 Rheological characterization.

The impact of CR is very obvious in rheological behaviour when it was combined into the virgin asphalt binder at the mixing temperature of 180°C, properties of virgin and modified asphalt are presented in Table 1andTable 2, respectively. The penetration and ductility results of various CR contents are shown in Figure 5. Surprisingly, it was noted that higher waste rubber content in binder had less effect on reducing penetration and ductility of binder compared to lower content of rubber. According to modified binder ductility results, CR ratio 1% into virgin asphalt has dramatically declined the tensile properties of binder to 18 cm compared to 100 cm of unmodified binder, but this value has increased steadily when CR ratio increased as depicted inFigure 5 c. This can be attributed to traces of sulphur into the virgin binder, combination of low contents of CR into unmodified binder would be vulcanised to produce hard clusters into bituminous material which limits its tensile properties, but increasing of CR ratios may increase the tensile properties as a resulting of softness of rubber into the rubberised asphalt via conjugated double bonds. Overall, the decrease in ductility values is due swelling of CR particles in the binder to form a viscous gel material.[23, 24] However, this is contradict with related previous studies.[13, 25] Otherwise, the softening point of modified asphalt had jumped by more than 10 degrees as CR content increased when compared with unmodified asphalt as shown inFigure 5b, which indicates that adding CR into virgin asphalt would enhance the thermal behaviour of asphalt. It is clear that the effect of rising proportion of CR on softer modified binder was considerable. Regarding to the results obtained from modified binder penetration, CR ratio of 1% and 3% decreased the penetration value at half (Figure 5a) compared to base asphalt. Furthermore, the rubberised asphalt exhibited a steady increase in penetration values as CR content increased at 5%, 10%, 15% and 20%, respectively. It is worth mentioning that lower penetration grade of asphalt binder is preferred to avoid any softening behaviour in bituminous material, which reveals that high thermal behaviour of modified asphalt would be enhanced by CR modifier.[3, 10]





(a) (b)



(c)

Figure 1: Effect of CR contents on the rheological properties of asphalt.

The values of PI are obtained from penetration and softening point results. Typically, it ranges from -3 (high susceptible asphalt to temperature) to +7 (low susceptible asphalt to temperature). Based on PI values obtained inFigure 6, CR ratio 10%, 15% and 20% in modified binder can be categorized as less susceptibility asphalt to temperature. Comparison of PI values of CR modified asphalt to its unmodified asphalt reveals the susceptibility of modified asphalt to temperature is less sensitive as a result of change its thermal behavior, which overcomes the general issues of asphalt pavement in hot climate region such as rutting and fatigue. [26]

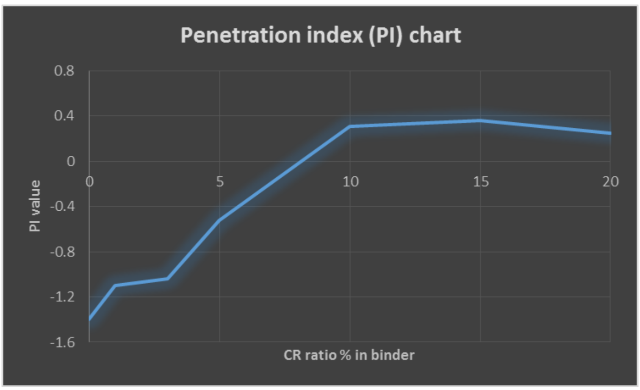


Figure 6: The values of PI of asphalt with various CR content.

In summary, incorporation of CR into base asphalt would enhance the rheological properties of asphalt and be more suitable for hot climate. Decreasing in penetration and increasing in softening point of the CR modified binder would eventually enhance the cracking and rutting resistance, anti-deformation ability and temperature susceptibility of asphalt pavement. According to the rheological results obtained, the highest CR content (20 %) by weight can be recommended to produce modified asphalt for pavement.

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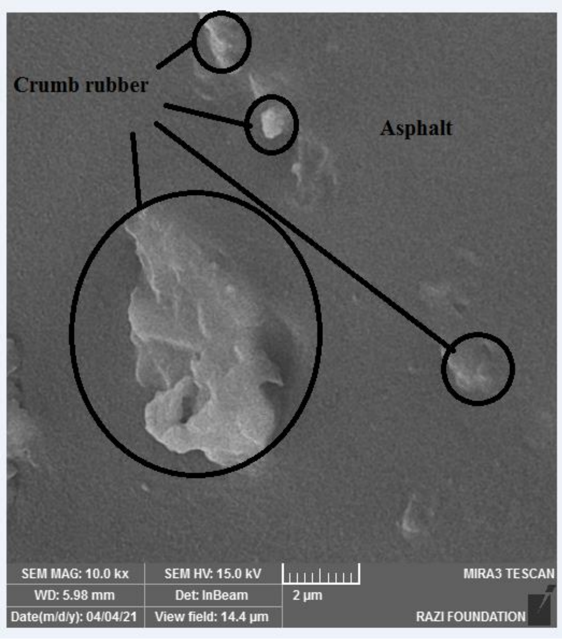
3.3 Morphological characterization.

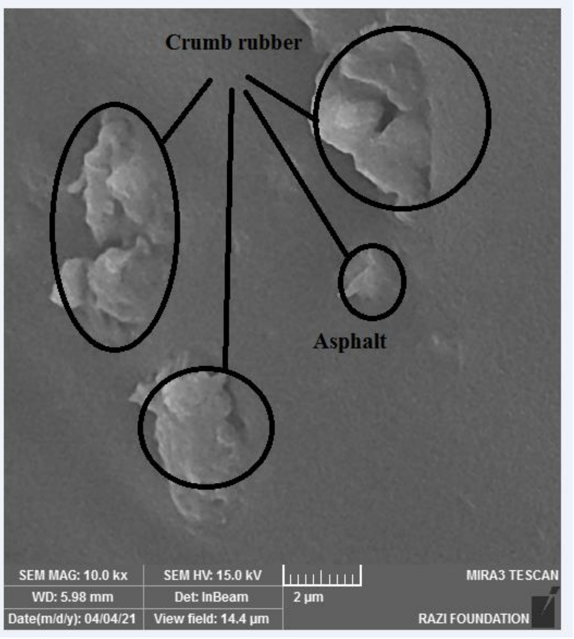
Scanning electron microscopy (SEM) is the best way to investigate and evaluate the morphological structure of modified asphalt and the effectiveness of mixing operation between CR and virgin asphalt, the compatibility between CR and binder will determine the quality of morphology and also mechanical performance of the modified binder. Previous studies showed that increasing on content of crumb rubber particles on the modified binder has increased the ductility and tensile strength of asphalt binder although it exhibited poor compatibility of mixture.[27, 28]

SEM analyses were conducted for various contents of CR (5%, 10% and 20%) that used to produce rubberized asphalt, the SEM images of modified asphalt with various CR contents are depicted in Figure 7, it can be observed that the morphology of asphalt was affected by CR additives which absorbs the maltene into asphalt, so some CR particles are clearly separated in binder’s bulk as swelling clusters. this can be ascribed to incomplete distribution of CR modifiers in the asphalt binder which decrease the homogeneity of the mixture.

Moreover, size of crumb rubber particle plays a main role in determination of the rheological and morphological behaviour of the modified binder. It is worth mentioning that ideal rheological behaviour of modified asphalt can be obtained from compatible system of asphalt with modifier.



(a)



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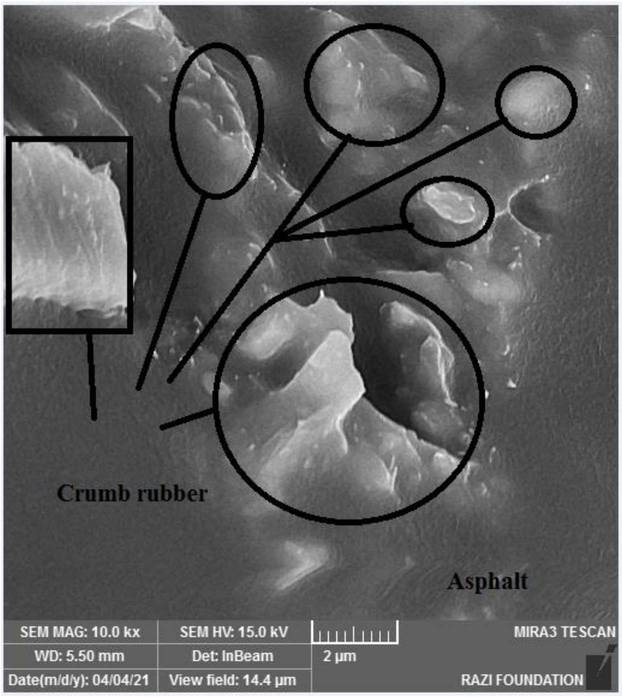

(c)

Figure 7: SEM images for asphalt with CR: (a) 5% CR, (b) 10% CR and (c) 20% CR.

It is possible to obtain CR modified asphalt where the CR is more dispersed into the binder via finely ground of CR, it can be recommended using 40, 80 or 100 mesh of CR as modifier for binder instead of 20 mesh in order to enhance the performance and characteristics of the asphalt mixtures.

4. Conclusions

Based on obtained results in this study, it can be concluded that the addition of CR increases the values of the softening point and decrease the values of penetration and ductility, this current study attempts to enhance the performance of asphalt through modification process. The CR modifiers were added to unmodified asphalt in the range of 3-20% by weight of the asphalt. A comparative study indicated that incorporation 20% of CR into base asphalt was helpful to improve the rheological properties of asphalt via reduce in penetration values and increase in the temperatures of softening point, besides that slight reduce in the ductility values compared to the unmodified asphalt binder. Moreover,a deeper insight into the chemical structure of asphalt used has been made. It is clear that combination TLC technique and ^{1}H NMR spectroscopy is an integral approach to identify the main chemical components in asphalt especially after separation of binder into the asphaltene and maltene fractions. ^{1}H NMR spectra confirmed the chemical structure of asphaltene and maltenes that extracted from asphalt, asphaltene content into asphalt plays a crucial role indetermination of the performance of the binder with modifiers. Furthermore,SEM images of CR modified asphalt showed that the morphology of the binder was affected by CR modifier (20 mesh) to produce less homogeneous mixture which effects on rheological behaviour of the asphalt. This can be attributed to swelling of CR in asphalt as clusters.It can be recommended to use 40 to 100 mesh of CR modifier to obtain more homogenous modified asphalt. Obviously, size of CR particle, content and shape play a significant role on most of the rheological and morphological properties of a modifier asphalt binder. Further investigations into CR modified binder by Marshall Stability test are currently underway.

Conflicts of interest.

The author declare that this is no conflict of intrest.

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