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Research Article

Investigation of the Physical and Molecular Properties of Asphalt Binders Processed with Used Motor Oils

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In this work we investigated the performance aspects of addition of used motor oils (UMO) to neat and crumb rubber modified asphalts (CRMA) and related that to the change of molecular size distribution of modified asphalt's fractions; asphaltenes, saturates, naphthene aromatics, and polar aromatics. Based on the results of temperature sweep viscoelastic tests, addition of crumb rubber modifier (CRM) alone or with UMO results in the formation of internal network within the modified asphalt. Based on the results of short and long term aged asphalts, the utilization of combination of UMO and CRM enhanced the aging behavior of asphalt. Bending beam rheometer was utilized to investigate the low temperature behavior of UMO modified asphalts. Based on those tests, the utilization of the UMO and CRM enhanced the low temperature properties of asphalts. Based on the results of the asphalt separation tests and the Gel Permeation Chromatography (GPC) analysis, it was found that saturates and naphthene aromatics are the two asphalt fractions that have similar molecular size fractions as those of UMO. However, UMO only shifts the molecular sizes of saturates after interaction with asphalt. Results also show that polar aromatics pose higher molecular size structures than UMO.

1. Introduction

Asphalt is a hydrocarbon material containing about 90–95 wt% hydrogen and carbon atoms with the remaining 5–10 wt% of the atoms in the asphalt consisting of two types: (a) heteroatoms and (b) metals [1]. Hydrocarbons, heteroatoms, and metals all combine in the asphalt in a wide range of different molecules that can be grouped into three major categories: (a) aliphatics, (b) cyclics, and (c) aromatics [1]. Such molecules interact with one another through the formation of weaker types of bonding that are actually responsible for determining many of asphalt's physical properties. Three types of "weak" bonds that require relatively little energy to break and are susceptible to both heat and mechanical forces are mainly the governing bonds in asphalt; they are (a) π-π bonding, (b) hydrogen (or polar) bonding, and (c) van der Waals forces [1]. Through the aforementioned bond types, the behavior of asphalt molecules is governed by either one of the two patterns and their mutual interaction: (a) polar behavior and (b) nonpolar behavior. In the polar behavior and during service temperatures, the molecules participate in the formation of a "network" through hydrogen and π-π bonding that gives the asphalt its elastic properties, whereas the nonpolar molecular behavior is manifested by matrix in which the network is formed, thus contributing to the viscous properties of the asphalt [1]. Through such interactions between asphalt molecules, the asphalt binder structure can be categorized as being made up of asphaltenes and maltenes at the molecular level. The binders' viscosity and adhesion are attributed to the asphaltenes that are large polar compounds [2]. On the other hand, the colloidal combination of oils and resins in which the asphaltenes are dispersed is the maltenes [3, 4].

Each year, two hundred million gallons of used motor oil (UMO) are improperly disposed of [5]. Used motor oil is insoluble and persistent and can contain toxic chemicals and heavy metals.

It is slow to degrade. It sticks to everything from beach sand to bird feathers. It is a major source of oil contamination of waterways and can result in pollution of drinking water sources [6].

Addition of used motor oil (UMO) to the binder typically modifies the low molecular weight maltene structure as the role of the maltenes is to provide stability to the asphaltenes [3]. A loss of aromatics in the asphalt binder due to volatilization occurs during mixing and construction [2]. In addition, oxidation will occur on the exposed asphalt binder as the asphalt ages in service [7]. Both of the aforementioned processes lead to the conversion of maltenes into asphaltenes, yielding an overall loss of maltenes as a pavement ages [8]. A stiffer pavement that is more brittle due to a lack of cohesion inside the binder results from the loss of maltenes [2]. To properly restore the aged binder properties, maltenes must be provided to the binder to restore the binders' stability; this can be done by the utilization of UMO [9].

The average tire contains about 45% rubber with the rest being carbon black, oils waxes, fillers, antioxidants, sulfur, and curing systems. This rubber portion (45%) of the tire has different compositions passed on the source it was extracted from. The composition of crumb rubber modifier (CRM) extracted from passenger tire is about 35% natural rubber and 65% synthetic rubber, whereas, for the CRM extracted from truck tires, these values change to 65% natural rubber and 35% synthetic rubber [10]. When CRM interacts with asphalt, the behavior of its rubber components is different. The natural rubber, polyisoprene, and isobutylene isoprene rubber (IIR) tend to soften. On the other hand, styrene butadiene rubber (SBR), butadiene rubber, polychloroprene, and nitrile butadiene rubber tend to harden as a result of cross-linking [10]. This results in the ability of CRM to provide both the high and low temperature performance to a given neat asphalt. The softening polymers provide low temperature performance, while the cross-linking rubber provides high temperature performance [10].

When CRM is added to asphalt, the lighter asphalt components penetrate into the internal matrix of the rubber as they have good compatibility with the linear skeleton of the rubber [11]. Chemical composition of asphalt and its viscosity determine the CRM swell size and rate. The CRM swell rate decreases with the increase of asphalt viscosity, while the rate of asphalt penetration in CRM increases with the increase of rubber particle size [11, 12]. Molecular weight of asphalt has a major role in controlling the behavior between asphalt and CRM; lower molecular weight asphalt interacts readily with CRM, where the lighter asphalt components penetrate into the CRM; such interaction may result, however, in deterioration of the colloidal stability of asphalt leading to coagulation of asphaltenes [12]. Vulcanized rubber can be devulcanized and depolymerized in asphalt under the effect of high temperature shear; this increases when asphalt is rich in aromatics [13].

As illustrated earlier, interaction of CRM with asphalt results in the absorption of low molecular weight compounds from asphalt. This leads to having stiffer asphalt that might be prone to thermal cracking at low service temperature. UMO contribute to the low molecular weight fractions of asphalt due to the similarity between molecular structures. This in turn leads to compensation of the absorbed fractions of asphalt and thus would be beneficial for the low temperature properties of asphalt.

On the other hand, addition of UMO to asphalt in the absence of CRM would lead to the disruption of the asphalt molecular size buildup and deterioration of asphalt properties. This can be explained in terms of the factors that derive the physical properties of asphalt. Those are the weak molecular interactions such as π-π bonds, hydrogen bonds, and van der Waals bonds. Those types of bonds are the result of neighbor-neighbor interactions. Such interactions will be disrupted as a result of the addition of UMO that would add to the dispersing medium (light aromatics), while having the same dispersed interacting molecules.

2. Materials and Experimental Procedures

2.1. Processing

2.1.1. Raw Materials. In the current work, one asphalt binder was investigated in combination with one type of crumb rubber. The asphalt was a PG 64-22 based on the Superpave grading system. The CRM was a cryogenic processed CRM from a mixed source of scrap tires. The CRM particle size was smaller than mesh #30 and larger than mesh #40, according to the US standard system.

Collected used motor oils have been tested for benzene, toluene, ethyl-benzene, and xylenes (BTEX) content and it was verified that the utilized UMO in the current experiments has lower BTEX content than what is allowed by the United States Environmental Protection Agency (US-EPA) Maximum Contaminants Levels (MCLs) during leaching experiments and also from air tested samples above the interactions carried out in the lab.

2.1.2. Asphalt-CRM Interactions. Table 1 illustrates the list of interactions carried out in this research work. The interactions were conducted in 1-gallon cans, and a heating mantle connected to a bench type controller with a long temperature probe ($12''$) was used to heat the material.

A high shear mixer was used to mix the binder and crumb rubber. The amount of CRM was controlled to be either 10% or 20% of the initial asphalt binder weight in selected interactions. The UMO percentage varied from 3% to 9% of the final binder weight. Interactions were conducted for 120 minutes under one of two different temperatures (160 and 190°C) and a single mixing speed (30 Hz) for each temperature utilized. Samples were taken at 2, 30, and 120 minutes of interaction time and kept at −12°C to avoid any unwanted reactions. All interactions in this research were carried out under controlled atmosphere of nitrogen gas to prevent any oxidation.

A specific coding for the samples was adopted in the current work, starting with the asphalt type, HU-64, followed by the interaction temperature, interaction speed, interaction time, UMO percentage, and lastly CRM percentage.

2.2. Characterization

2.2.1. Extraction of Liquid Phase. It is to be noted that asphalt rubber binders consist of two components: the liquid phase and rubber particles. Both components are called the

TABLE 1: List of asphalt composites.

#	Code	Asphalt type	Inter. temp./°C	Inter. speed/Hz	CRM %	UMO %	Inter. time/min
1	UMO	NA	NA	NA	NA	100	NA
2	HU-64-NEAT	PG64-22	NA	NA	NA	NA	NA
3	HU-64-190-30-120-3% UMO	PG64-22	190	30	NA	3	120
4	HU-64-190-30-120-9% UMO	PG64-22	190	30	NA	9	120
5	HU-64-190-30-2-3% UMO-10% CRM	PG64-22	190	30	10	3	2
6	HU-64-190-30-30-3% UMO-10% CRM	PG64-22	190	30	10	3	30
7	HU-64-190-30-120-3% UMO-10% CRM	PG64-22	190	30	10	3	120
8	HU-64-190-30-2-9% UMO-20% CRM	PG64-22	190	30	20	9	2
9	HU-64-190-30-30-9% UMO-20% CRM	PG64-22	190	30	20	9	30
10	HU-64-190-30-120-9% UMO-20% CRM	PG64-22	190	30	20	9	120
11	HU-64-190-30-120-10% CRM	PG64-22	190	30	10	NA	120
12	HU-64-190-30-120-20% CRM	PG64-22	190	30	20	NA	120
13	HU-64-160-30-120-3% UMO	PG64-22	160	30	NA	3	120
14	HU-64-160-30-120-9% UMO	PG64-22	160	30	NA	9	120
15	HU-64-160-30-2-3% UMO-10% CRM	PG64-22	160	30	10	3	2
16	HU-64-160-30-30-3% UMO-10% CRM	PG64-22	160	30	10	3	30
17	HU-64-160-30-120-3% UMO-10% CRM	PG64-22	160	30	10	3	120
18	HU-64-160-30-120-9% UMO-20% CRM	PG64-22	160	30	20	9	120
19	HU-64-160-30-120-10% CRM	PG64-22	160	30	10	NA	120
20	HU-64-160-30-120-20% CRM	PG64-22	160	30	20	NA	120

binder whole matrix. In this paper, we will be utilizing the whole matrix (liquid phase and rubber particles) in the physical testing. On the other hand, the liquid phase would be employed in the fractional and molecular investigation. Earlier work dealing with physical testing of the liquid phase has been already addressed by this research group [14]. The liquid phase of CRMA was extracted by removing the nondissolved CRM particles from the CRMA matrix. In this regard, the required amount of CRMA sample was heated to 165°C and drained through mesh #200 (75 μm) in the oven at 165°C for 25 minutes. The extracted liquid phase was stored at −12°C immediately to prevent any unwanted reactions.

2.2.2. Dynamic Mechanical Analysis.
Dynamic Shear Rheometer from Bohlin Instruments CVO (Worcestershire, UK) was used for viscoelastic analysis of neat and modified asphalt samples. Single point test and temperature sweep test were performed on the whole matrix samples. The single point test was performed on all asphalt samples at 64°C and 10 radians/sec using 25 mm diameter parallel plates; two other points were employed: 58 and 70°C. The temperature sweep test was performed on the liquid phase of modified asphalt at a temperature range of 10°C to 70°C with 6°C increments. 25 mm diameter plates were used for tests conducted above 45°C, and 8 mm diameter plates were used for tests that were conducted below 45°C. The gap between plates for CRMA samples was selected to be 2 mm, which is the minimum gap size that does not affect the results due the presence of CRM particle. For samples without CRM the gap was selected to be 1 mm. For all tests that were conducted at temperatures below 45°C using the 8 mm diameter plates, the 2 mm gap size was selected, regardless of the type of the sample.

2.2.3. Short Term Aging.
Short term aging was carried out following ASTM D2872 "Standard Test Method for Effect of Heat and Air on a Moving Film of Asphalt (Rolling Thin-Film Oven Test)." Testing was done using a Coopers RTFO obtained from Cooper Technology, UK.

2.2.4. Long Term Aging.
Long term aging was carried out following ASTM D652 "Standard Practice for Accelerated Aging of Asphalt Binder Using a Pressurized Aging Vessel (PAV)." Testing was done using a PAV 9300 machine obtained from Prentex Alloy Fabrication, Inc.

2.2.5. Low Temperature Properties.
Determination of the low temperature properties of asphalt and modified asphalt was carried out following ASTM D6648 "Standard Test Method for Determining the Flexural Creep Stiffness of Asphalt Binder Using the Bending Beam Rheometer (BBR)." Testing was carried out using a bending beam rheometer machine obtained from Applied Test Systems (ATS).

2.2.6. Asphalt Separation into Four Fractions.
Separation of asphalt into four fractions, asphaltenes, saturates, naphthene aromatics, and polar aromatics, was done following the Corbett method utilizing ASTM D4124 "Standard Test Methods for Separation of Asphalt into Four Fractions." Recovery of the asphalt fractions was carried out utilizing an RV 10 basic rotary evaporator obtained from IKA.

2.2.7. Gel Permeation Chromatography (GPC).
A Gel Permeation Chromatography (GPC) system equipped with a Wyatt MiniDawn Light Scattering detector and a Wyatt ViscoStar Viscometer detector was utilized in the current research work. Samples were dissolved into THF and then filtered
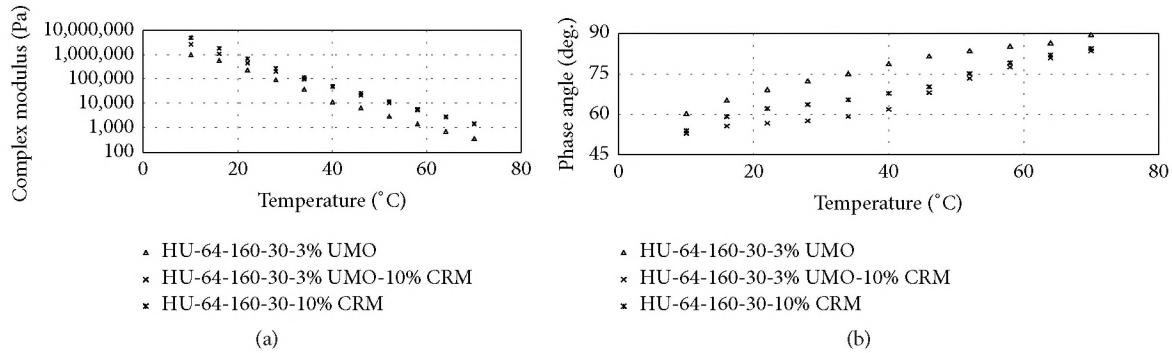
FIGURE 1: Temperature sweep viscoelastic properties for rheological properties (a) G^* and (b) δ, for the whole matrix samples interacting at 160°C, 30 Hz after 120 minutes with 3% UMO and/or 10% CRM.

through a 0.2 μm PTFE syringe filter prior to injection into the injection module. The area under the curve for a GPC chromatogram represents 100% of the samples molecules injected into the GPC system [15]. The asphalt binder constituents are generally classified into several groups [16–19]. In the current research work, the elution started at 0 minutes and finalized at 50 minutes; however molecular changes were recorded from 6 to 18 minutes. The GPC chromatogram was thus divided into three equal parts, large molecular size (LMS), medium molecular size (MMS), and small molecular size (SMS), corresponding to 6–10 minutes, 10–14 minutes, and 14–18 minutes, respectively. The LMS were only plotted and utilized to characterize the modified binder fractions' change in properties. Research has shown that the LMS components of binder had better correlations with asphalt binder properties than other components [20–22].

3. Results and Discussion

3.1. Effect of UMO and CRM on the Internal Structure of Asphalt (Internal Network Formation). Figure 1 shows the temperature sweep viscoelastic properties for rheological properties (a) G^* and (b) δ for the samples interacting at 160°C, 30 Hz after 120 minutes with 3% UMO, 10% CRM, or both modifiers after 120 minutes of interaction time, respectively.

It can be seen from Figure 1(a) that the behavior of the samples with CRM is almost similar with or without UMO addition, where the effect of CRM modification over the UMO alone modified samples is mainly manifested at higher testing temperatures; this is in agreement with other studies [23], which show that the CRM modification of asphalt mainly affects its high temperature properties and by decreasing the testing temperature the changes in physical properties reduce to a marginal level. On the other hand, a distinctive behavior for δ can be seen for the samples modified with CRM or CRM + UMO illustrated in Figure 1(b). Results in Figure 1(b) show that by addition of CRM or CRM + UMO to asphalt, a distinct plateau region appears on the phase angle graph. The appearance of the plateau region indicates that the creation of 3D entangles internal network structure in asphalt [24, 25]. It can be seen that the sample with 3% UMO + 10%

CRM shows a more distinct plateau region compared to the sample with 10% CRM interacting at the same interaction conditions. This indicates that the combination of 10% CRM + 3% UMO released components in asphalt at the utilized interaction conditions (i.e., 160°C, 30 Hz after 120 minutes) that were capable of forming 3D internal network structure in the asphalt matrix. The molecular size distribution changes of the asphalt fractions and UMO as a result of the formation of such 3D internal network structure are investigated and discussed in sections below. On the other hand, addition of UMO only to the asphalt gave no such plateau behavior, indicating that the presence of UMO modifier alone cannot initiate the formation of such 3D internal network structure.

Figure 2 shows the temperature sweep viscoelastic properties for rheological properties G^* and δ for the samples interacting at 160°C, 30 Hz after 120 minutes with 9% UMO, 20% CRM, or both modifiers after 120 minutes of interaction time, respectively.

The same behavior illustrated in Figure 1(a) can be seen in Figure 2(a), where the effect of CRM modification for samples with CRM in the presence or absence of UMO over the samples modified with UMO alone is mainly manifested at higher testing temperatures, especially for the samples with 20% CRM + 9% UMO.

Results in Figure 2(b) show that the increase in CRM or CRM + UMO percentage leads to more intensified plateau region behavior. Unlike the samples modified with 10% CRM + 3% UMO (illustrated in Figure 1(b)), the plateau behavior is more manifested for the samples with 20% CRM over those modified with 20% CRM + 9% UMO. This indicates that at the utilized interactions conditions (i.e., 160°C, 30 Hz after 120 minutes) and with the utilization of 9% UMO even in the presence of 20% CRM, the 3D internal network structure is disrupted.

As the case for asphalt modified with 3% UMO (illustrated in Figure 1), addition of 9% UMO only to the asphalt resulted in the absence of plateau behavior, indicating that the presence of UMO modifier alone cannot initiate the formation of such 3D internal network structure.

Figure 3 shows the temperature sweep viscoelastic properties for rheological properties (a) G^* and (b) δ for the samples interacting at 190°C and 30 Hz with either 3% UMO,
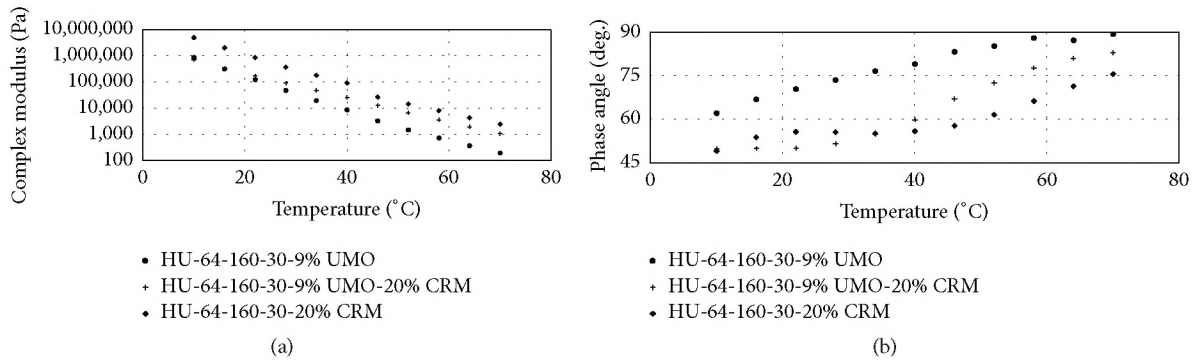
FIGURE 2: Temperature sweep viscoelastic properties for rheological properties (a) G^* and (b) δ, for the whole matrix samples interacting at 160°C, 30 Hz after 120 minutes with 9% UMO and/or 20% CRM.
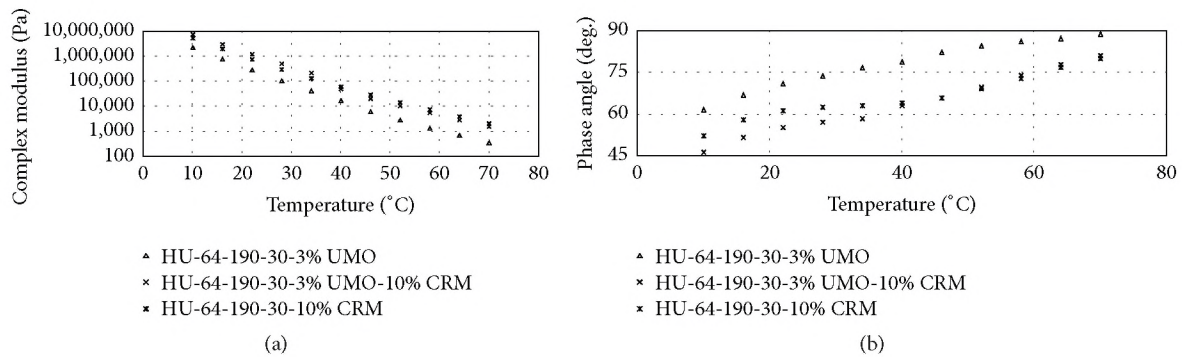

FIGURE 3: Temperature sweep viscoelastic properties for rheological properties (a) G^* and (b) δ, for the whole matrix samples interacting at 190°C, 30 Hz after 120 minutes with 3% UMO and/or 10% CRM.

10% CRM, or both modifiers after 120 minutes of interaction time, respectively.

Results in Figure 3(a) show similarity with the results of the samples interacting at 160°C and 30 Hz illustrated in Figure 1(a).

On the other hand, results in Figure 3(b) show lower values for δ at lower testing temperature, indicating better elasticity. In addition, the plateau behavior for the samples interacting with 10% CRM + 3% UMO at 190°C and 30 Hz showed a stronger trend over those interacting at 160°C and 30 Hz (illustrated in Figure 1(b)) for the same interaction time (120 minutes). This indicates that the released components of the CRM in asphalt, in the presence of UMO, at interaction conditions of 190°C and 30 Hz are more capable of forming 3D internal network structure in the asphalt matrix.

Figure 4 shows the temperature sweep viscoelastic properties for rheological properties (a) G^* and (b) δ for the samples interacting at 190°C, 30 Hz with 9% UMO, 20% CRM, or both modifiers after 120 minutes of interaction time, respectively.

Figure 4(a) indicates that the G^* values of the samples having 9% UMO are lower values, in contrast with the samples with 20% CRM or 20% CRM + 9% UMO. As can be seen from Figure 4(b), the behavior of the samples with 20% CRM + 9% UMO interacting at 190°C and 30 Hz shows a stronger plateau trend over those with the same

modifiers that are interacting at 160°C and 30 Hz (illustrated in Figure 2(b)) for the same interaction time of 120 minutes. This indicates that in the presence of both UMO and CRM the utilization of interaction conditions of 190°C and 30 Hz as compared to 160°C and 30 Hz results in better modifying of the internal structure of the asphalt as expressed in stronger plateau behavior indicating better formation for the 3D internal network structure.

3.2. Effect of UMO and CRM on the Short Term Aging Behavior of Asphalt (Rutting Susceptibility).
Starting this section and the following two sections, the investigations are done on samples interacting at 190°C and 30 Hz.

Figure 5 shows the behavior of the rutting parameter $(G^*/\sin\delta)$ for the (a) unaged and (b) Rotating Thin-Film Oven (RTFO) aged residue of unmodified PG 64-22 samples compared to samples modified with 3% UMO only, 10% CRM only, and 3% UMO + 10% CRM. In this figure all samples were interacting up to 120 minutes.

The PG grading system mandates that the rutting parameter $(G^*/\sin\delta)$ is above 1 KPa for unaged asphalt and 2.2 KPa for RTFO aged asphalt (Horizontal black lines) at temperature of 64°C for the asphalt utilized in this research work (PG 64-22). As shown in Figure 5(a) for the unaged samples, the highest values for $(G^*/\sin\delta)$ were observed for the samples mixed with 10% CRM. However, both neat asphalts and
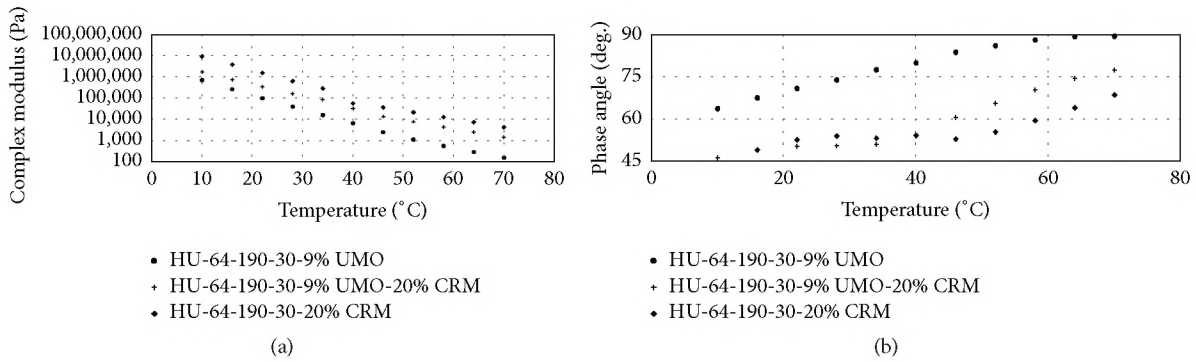
(a)   (b)

FIGURE 4: Temperature sweep viscoelastic properties for rheological properties (a) G^* and (b) δ, for the whole matrix samples interacting at 190°C, 30 Hz after 120 minutes with 9% UMO and/or 20% CRM.

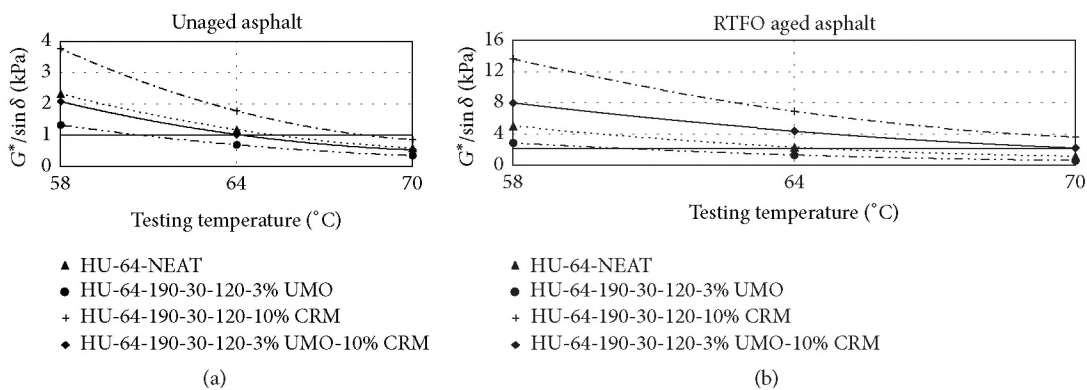(a)   (b)

FIGURE 5: Effect of UMO and/or CRM on (a) unaged and (b) short term aging behavior of whole matrix samples.

samples modified with 3% UMO + 10% CRM fulfilled the requirement. Similarly, for the RTFO aged residue samples, illustrated in Figure 5(b), the best enhancement in the rutting resistance behavior is attributable to the sample having CRM only. However, it can be seen from the figure that the sample with 10% CRM + 3% UMO was well above the 2.2 KPa PG grading requirement at 64°C testing temperature, while it was just at those values for the 70°C testing temperature. On the other hand, the sample modified with UMO only suffered deterioration of its rutting resistance parameter ($G^*/\sin\delta = 2.2$ KPa) at 64°C.

3.3. Effect of UMO and CRM on the Long Term Aging Behavior of Asphalt (Fatigue Cracking Susceptibility).

Figure 6 shows the behavior of the fatigue parameter ($G^* \cdot \sin\delta$) for the Pressure Aging Vessel (PAV) residue of PG 64-22 neat asphalt sample compared to samples modified with 3% UMO only, 10% CRM only, and 3% UMO + 10% CRM.

The samples were interacting at an interaction temperature of 190°C with 30 Hz interaction speed. In this figure all samples were interacting up to 120 minutes. The PG grading system mandates that the fatigue cracking parameter ($G^* \cdot \sin\delta$) is below 5000 KPa (Horizontal black line). As illustrated in the figure, the best enhancement in the long term aging resistance behavior is attributable to the sample having a combination of UMO + CRM. It is expected that the presence of UMO with CRM would lead to the absorption of
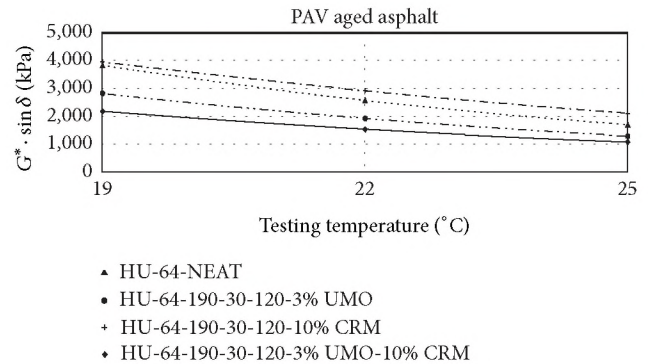

FIGURE 6: Effect of UMO and/or CRM on the long term aging behavior of whole matrix samples.

the light components from the UMO into the CRM. During long term aging and under the effect of temperature, the swelled CRM particles will continue to release components into the asphalt such as antioxidants that would resist the long term aging of asphalt. In addition, the absence of UMO would lead to the absorption of light aromatic components from the asphalt, leading to the stiffening of asphalt.

3.4. Effect of UMO and CRM on the Low Temperature Properties of Asphalt (Thermal Cracking Susceptibility).
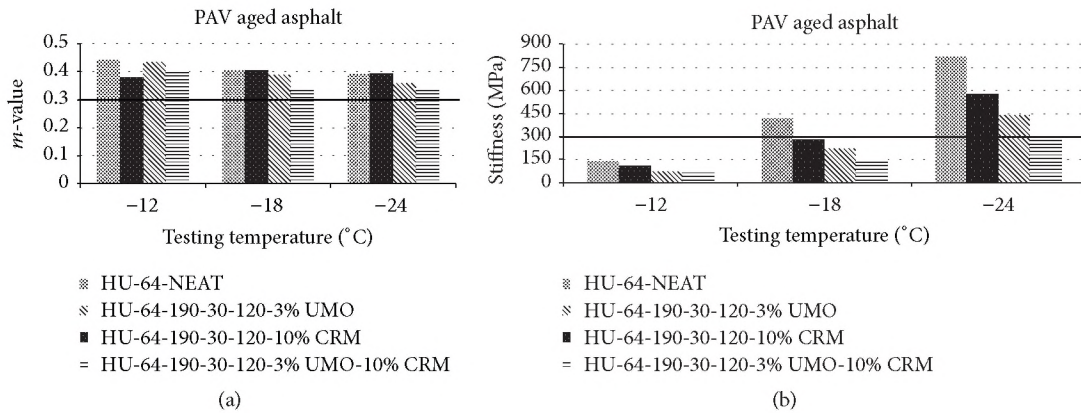
Figure 7

Figure 7: Effect of UMO and/or CRM on the low temperature parameters (a) m-value and (b) S of whole matrix.

shows the behavior of the thermal cracking parameters (a) m-value and (b) stiffness (S) for the Pressure Aging Vessel (PAV) residue of neat PG 64-22 asphalt sample compared to samples modified with 3% UMO only, 10% CRM only, and 3% UMO + 10% CRM.

The samples were interacting at an interaction temperature of 190°C with 30 Hz interaction speed. In this figure all samples were interacting up to 120 minutes. The PG grading system mandates that the m-value is higher than 0.3 and that S is lower than 300 MPa (Horizontal black lines). As illustrated in Figure 7(a), all the tested samples fulfilled the m-value requirements of PG grading system up to −34°C in service temperature. On the other hand, for the S values illustrated in Figure 7(b), the neat PG 64-22 asphalt showed deteriorated properties passed its low temperature grade (−22°C) while the asphalt modified with 10% CRM, 3% UMO, or 10% CRM and 3% UMO had acceptable S values up to −28°C in service temperature. As illustrated in the figure, the utilization of both 10% CRM and 3% UMO resulted in enhancing the low temperature resistance of the asphalt by one grade (from −22°C to −28°C).

3.5. Effect of UMO on Asphalt Fractions.
In the following section we investigated the samples interacting at 160°C with 30 Hz and 190°C with 30 Hz after 2 and 30 minutes of interaction time. Percentages of modifiers were 3% UMO with 10% CRM for the samples interacting at either 160°C or 190°C with 30 Hz and 9% UMO with 20% CRM for the samples interacting at 190°C with 30 Hz only.

Figure 8 illustrates the change in the asphalt fractions: asphaltenes, saturates, naphthene aromatics, and polar aromatics as a result of modification with UMO and CRM. Figure 8 shows that most of the components of UMO fall in the category of saturates. As illustrated in the figure also, gradual increase in the asphaltenes is associated with the addition of UMO and CRM, regardless of the interaction temperature and time. In addition, the utilization of both UMO and CRM leads to increase in saturates at low interaction temperature (160°C). On the other hand, the utilization of high UMO (9%) and CRM (20%) values at high interaction temperature
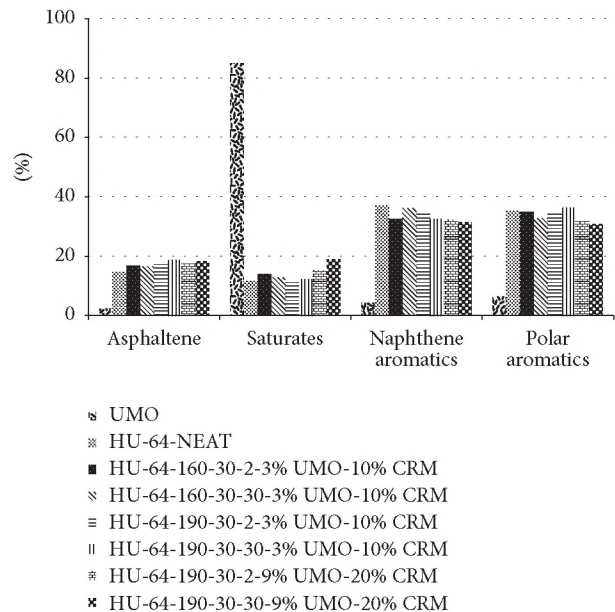

Figure 8: Effect of UMO and/or CRM on the four fractions of liquid phase samples.

(190°C) gives the same result of increasing the saturates. Continuous decrease in the naphthene aromatics is associated with the addition of UMO and CRM. Polar aromatics appear to decrease with the high percentage of UMO and CRM. To better understand the molecular size distribution of the different fractions of asphalt with the modification with UMO and CRM, GPC analysis was carried out on selected samples and results are explained in the following section.

3.6. Effect of UMO on the Molecular Size Distribution of Asphalt Fractions.
In this section we focused on the samples interacting at 190°C with 30 Hz after 2 and 30 minutes of interaction time and compared their molecular size distributions to that of neat asphalt and UMO.
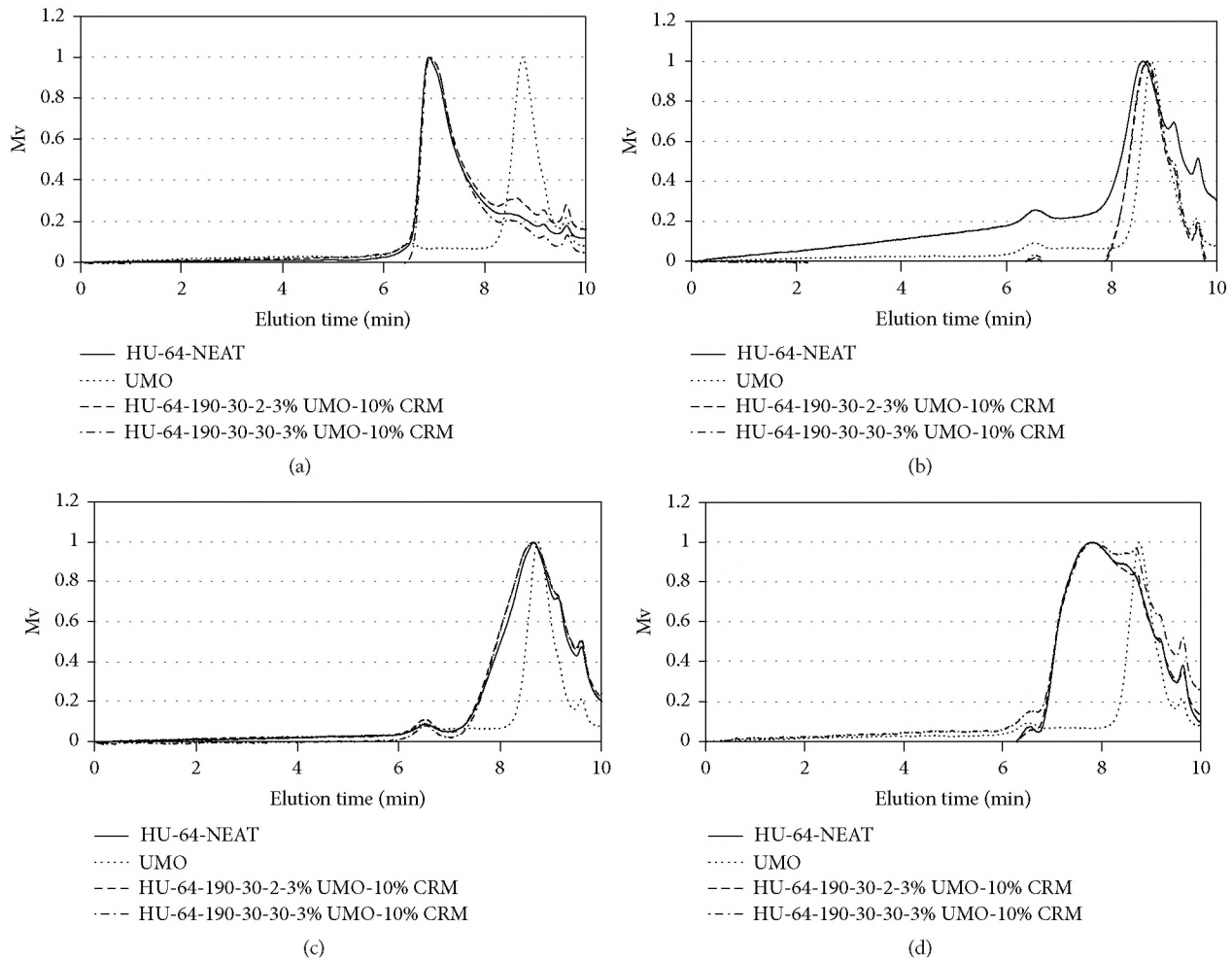
(a)

(b)

(c)

(d)

FIGURE 9: Effect of UMO and/or CRM on the GPC analysis of the liquid phase fractions (a) asphaltenes, (b) saturates, (c) naphthene aromatics, and (d) polar aromatics, in comparison with UMO.

Figure 9(a) illustrates that the asphaltenes pose the highest molecular size fractions as compared to the other fractions. In addition, the asphaltenes molecular size fractions are much higher than that of UMO.

Figure 9(b) shows that the molecular size distribution of UMO is similar to that of saturates. Another observation from Figure 9(b) is that addition of UMO and CRM leads to shift in the molecular structures of saturates.

Figure 9(c) shows that naphthene aromatics and UMO share similar molecular size fractions. However, there is no observed change in the naphthene aromatics fractions with the addition of UMO or CRM.

Figure 9(d) illustrates that polar aromatics pose higher molecular size structures than UMO. In addition, polar aromatics pose the widest range of molecular size fractions as compared to the rest of asphalt fractions.

4. Conclusions

This paper investigated the effect of utilization of UMO and CRM as modifiers for asphalt. Based on the results of temperature sweep tests, addition of crumb rubber modifier

(CRM) alone or with UMO results in the formation of internal network within the modified asphalt. Based on the results of short and long term aged asphalt, the utilization of combination of UMO and CRM enhanced the aging behavior of asphalt. Based on low temperature testing investigation, the utilization of the UMO and CRM enhanced the low temperature properties of asphalt. GPC analysis proved that saturates and naphthene aromatics are the two asphalt fractions that have similar molecular size fractions as those of UMO. During the modification of asphalt with UMO, the UMO shifts the behavior of saturates only. This indicates that the utilization of UMO with CRM as modifiers for asphalt would produce a more balanced asphalt matrix structure as a result of the compensation of the UMO to the fractions absorbed by CRM and also because UMO would further enhance the associations between CRM and asphalt leading to better internal network structure buildup for the modified asphalt.

Disclaimer

Any opinions, findings, and conclusions or recommendations expressed in this material are those of the writer(s) and

References

[1] D. R. Jones, "An asphalt primer: understanding how the origin and composition of paving-grade asphalt cements affect their performance," Technical Memorandum 4, SHRP Asphalt Research Program, National Research Council, Washington, DC, USA, 1992.

[2] C. D. DeDene and Z.-P. You, "The performance of aged asphalt materials rejuvenated with waste engine oil," International Journal of Pavement Research and Technology, vol. 7, no. 2, pp. 145–152, 2014.

[3] N. M. Katamine, "Physical and mechanical properties of bituminous mixtures containing oil shales," Journal of Transportation Engineering, vol. 126, no. 2, pp. 178–184, 2000.

[4] M. S. Mamlouk and J. P. Zaniewski, Materials for Civil and Construction Engineers, Addison-Wesley, Reading, Mass, USA, 1999.

[5] H. Liu, Z. Chen, W. Wang, H. Wang, and P. Hao, "Investigation of the rheological modification mechanism of crumb rubber modified asphalt (CRMA) containing TOR additive," Construction and Building Materials, vol. 67, part B, pp. 225–233, 2014.

[6] E. P. Agency, Used Oil Management Program, http://www.epa.gov/solidwaste/conserve/materials/usedoil/index.htm.

[7] R. B. McGennis, S. Shuler, and H. U. Bahia, Background of Superpave Asphalt Binder Test Methods, Federal Highway Administration, Office of Technology Applications, 1994.

[8] F. L. Roberts, P. S. Kandhal, E. R. Brown, D. Y. Lee, and T. W. Kennedy, Hot Mix Asphalt Materials, Mixture Design and Construction, 2nd edition, 1996.

[9] M. N. Borhan, F. Suja, and A. Bin Ismail, "The effects of used cylinder oil on asphalt mixes," European Journal of Scientific Research, vol. 28, no. 3, p. 22, 2009.

[10] A. Usmani, Asphalt Science and Technology, CRC Press, 1997.

[11] I. Gawel, R. Stepkowski, and F. Czechowski, "Molecular interactions between rubber and asphalt," Industrial & Engineering Chemistry Research, vol. 45, no. 9, pp. 3044–3049, 2006.

[12] M. Stroup-Gardiner, D. E. Newcomb, and B. Tanquist, "Asphalt-rubber interactions," Transportation Research Record, no. 1417, pp. 99–108, 1993.

[13] T. C. Billiter, J. S. Chun, R. R. Davison, C. J. Glover, and J. A. Bullin, "Investigation of the curing variables of asphalt-rubber binder," Petroleum Science and Technology, vol. 15, no. 5-6, pp. 445–469, 1997.

[14] M. Abdelrahman, M. Ragab, and D. Bergerson, "Effect of used motor oil on the macro and micromechanical properties of crumb rubber modified asphalt," International Journal of Waste Resources, vol. 5, no. 3, article 180, 2015.

[15] K.-W. Kim, Y.-S. Doh, and S. N. Amerkhanian, "Evaluation of aging characteristics of selected PMA using HP-GPC," Journal of the Korean Society of Road Engineers, vol. 6, no. 2, pp. 15–24, 2004.

[16] P. Jennings, P. W. Pribanic, W. Campbell, K. Dawson, S. Shane, and R. Taylor, High Pressure Liquid Chromatography As a Method of Measuring Asphalt Composition, The Dept, 1980.

[17] P. Jennings and J. Prinbanic, "The expanded montana asphalt quality study using high pressure liquid chromatography," Final Report, 1985.

[18] K. W. Kim, J. L. Burati Jr., and J.-S. Park, "Methodology for defining LMS portion in asphalt chromatogram," Journal of Materials in Civil Engineering, vol. 7, no. 1, pp. 31–40, 1995.

[19] A. S. Noureldin and L. E. Wood, "Variations in molecular size distribution of virgin and recycled asphalt binders associated with aging," Transportation Research Record, vol. 1228, pp. 191–197, 1989.

[20] H. I. Al-Abdul Wahhab, I. M. Asi, F. M. Ali, and I. A. Al-Dubabi, "Prediction of asphalt rheological properties using HP-GPC," Journal of Materials in Civil Engineering, vol. 11, no. 1, pp. 6–14, 1999.

[21] K. W. Kim and J. L. Burati Jr., "Use of GPC chromatograms to characterize aged asphalt cements," Journal of Materials in Civil Engineering, vol. 5, no. 1, pp. 41–52, 1993.

[22] K. W. Kim, K. Kim, Y. S. Doh, and S. N. Amirkhanian, "Estimation of RAP's binder viscosity using GPC without binder recovery," Journal of Materials in Civil Engineering, vol. 18, no. 4, pp. 561–567, 2006.

[23] M. Heitzman, "State of the practice: design and construction of asphalt paving materials with crumb-rubber modifier," Final Report, Office of Engineering, Federal Highway Administration, Washington, DC, USA, 1992.

[24] X. Lu and U. Isacsson, "Modification of road bitumens with thermoplastic polymers," Polymer Testing, vol. 20, no. 1, pp. 77–86, 2000.

[25] G. D. Airey, "Rheological properties of styrene butadiene styrene polymer modified road bitumens," Fuel, vol. 82, no. 14, pp. 1709–1719, 2003.