Balancing the Performance and Environmental Concerns of Used Motor Oil as Rejuvenator in Asphalt Mixes

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Abstract: Road deterioration inspires researchers to enhance the properties of asphalt binder for better performing mixes. Recycled tire rubber, or crumb rubber modifier (CRM), and used motor oil (UMO) are two modifiers that enhance asphalt binder performance through two different mechanisms. CRM affects high-temperature properties while UMO modifies low-temperature properties. Potential environmental concerns arising from the use of UMO have been raised in the literature. In this paper, the two recycled materials were investigated for their ability to complement each other. Both performance benefits of using both materials and the environmental concerns of using UMO were studied. Four CRM asphalt binders were investigated: two with UMO and two without UMO. Environmental impacts were evaluated using gas chromatography to check air emissions for benzene, toluene, ethyl-benzene, and xylenes (BTEX). The potential for toxic leaching of elements from modified hot mix asphalt (HMA) were checked using the US Environmental Protection Agency (EPA) Toxicity Characteristic Leaching Protocol (TCLP). For asphalt binders modified by CRM-UMO combinations, CRM decreased the amounts of released BTEX components, presumably by absorbing UMO and slowing the release of BTEX. Leaching results concluded that UMO mixtures showed a notable percentage of sulfur (S) as compared to non-UMO mixes. All these leachate components were under EPA limits.

Keywords: UMO; modified asphalt; Rejuvenator; CRM; BTEX; TCLP; EPA; MSCR Test; Master curve; Cole-Cole diagram

1. Introduction

Pavement aging and oxidation accumulates with years due to loss of aromatics and low molecular weight components, leading to an increase in stiffness and a reduction in both durability and the rate of stress relaxation. Therefore, researchers have been interested in the restoration of asphalt binder to original constituents and behavior. Rejuvenators, in combination with other types of modifiers, have been key in addressing this issue. Additionally, the increased softening of asphalt binder due to the high saturates fractionation percentage in rejuvenators is essential, especially at low temperatures. Used motor oil (UMO) is one of the best-known potential rejuvenators due to its unique components, availability, and low cost. Nevertheless, limited work has been done in implementing UMO-modified asphalt due to environmental concerns.
Abdelrahman et al. [1] investigated the effect of adding UMO on the macro (|G*| and δ) and micromechanical properties (hardness and elastic modulus) of neat and crumb rubber modified asphalt (CRMA) binders. It was found that using UMO deteriorated the properties of the neat asphalt binders [1,2]. Furthermore, it was noticed that asphalt binders modified with crumb rubber (CRM) only enhanced rutting resistance, increasing the value of (|G*|/sinδ). The best enhancement in fatigue cracking resistance, the |G*|sinδ parameter, was achieved using asphalt binder modified with both UMO and CRM when compared with samples modified by UMO or CRM only [2]. The same research group [2] investigated the effect of mixing UMO on asphalt binder’s fractions: asphaltenes, saturates, naphthene aromatics, and polar aromatics. It was found that for UMO, most components are located in the category of saturates. Moreover, it was observed that asphaltene fraction increased with the addition of CRM and UMO regardless of the interaction time or temperature. For an intermediate interaction temperature of 190 °C, it was noted that adding CRM and UMO slightly increased the saturates fraction [2]. A bending beam rheometer (BBR) was utilized to observe the effect of using both CRM and UMO on the modification of asphalt binder to resist low-temperature (thermal) cracking. It was noted that the best resistance to thermal cracking was achieved by using asphalt binder modified by both UMO and CRM [2]. Gel permeation chromatography was used to evaluate the molecular size distribution in the asphalt binder’s fractions as a result of their interaction with CRM and UMO. UMO was determined to have a similar molecular size distribution of saturates and naphthene aromatics [2]. Both CRM and UMO played an essential role in the modification of asphalt binders’ properties since both enhanced the resistance to aging and the performance grade (PG) low temperature by approximately one grade from −22 to −28 °C [1,2].

A low slope of the G* curve can be achieved using asphalt binder modified with both CRM and UMO, which reflects low susceptibility to temperature changes. Moreover, the unique property of UMO is that it is able to, in combination with other polymers, increase stiffness at high temperature and reduce it at low temperature, a requisite at low temperature to avoid thermal cracking problems [3–6]. PG low temperature decreased from −26 to −30 °C for asphalt binder oxidized for 3.5 h (air blown), as the percentage of lubricating oil increased from 0 to 10%; this result indicates using UMO will increase the softening of asphalt binder [3]. The excessive softening of UMO-modified asphalt binder is not required since it would in turn increase rutting depth [7–9]. Consequently, using UMO only up to a certain percentage is recommended, with a suggestion of less than 3% by weight of asphalt binder [1,2].

Recycled engine oil bottoms (REOB), obtained from the distillation of used motor oils, have been used to modify the low-temperature properties of asphalt binder to enhance cracking resistance [10,11]. It was reported that using a modest amount of REOB (6 to 8%) with asphalt binder or polymer-modified asphalt binder increased grade span of asphalt binder or, in some cases, caused it to remain constant. Also, double-edged notched tension (DENT) was used to measure essential work of failure (we) and crack tip opening displacement (CTOD). It was found that adding 8% REOB to 7% styrene butadiene styrene (SBS)-modified asphalt decreased both we and CTOD by 70% and 50% respectively, which indicated reduced cracking performance [10].

Fernandes et al. [12] investigated the effect of adding UMO to SBS-modified asphalt. It was found that UMO enhanced durability since mixtures became less sensitive to moisture and had increased resistance to both rutting and fatigue cracking. For reclaimed asphalt pavement (RAP) modified with UMO, it was found that UMO offset the aging of the mixture [13] since it compensated the loss of low molecular weight components that volatilized due to short-term and long-term aging. This paper focuses on the effectiveness of using UMO as a rejuvenator in crumb rubber modified asphalt (CRMA) in terms of both the performance of modified mixes and also environmental concerns arising from using UMO. These concerns are due to the potential presence of polynuclear aromatic hydrocarbons (PAH) that accumulate in motor oil during engine operation and potential high levels of heavy metals such as lead (Pb), zinc (Zn), copper (Cu), chromium (Cr), nickel (Ni) and cadmium (Cd). The PAH content of UMO can be 670 times greater than the new motor oil [14].
Bergerson et al. [15] evaluated the rheological properties and BTEX components in air for PG 64-22 modified asphalt binder with 9% UMO and with or without 20% CRM. Table 1 illustrates asphalt binder’s list of interactions.

<table>
<thead>
<tr>
<th>Asphalt Binder</th>
<th>CRM %</th>
<th>UMO %</th>
<th>Interaction Temperature (°C)</th>
<th>Interaction Speed (Hz)</th>
<th>Testing</th>
</tr>
</thead>
<tbody>
<tr>
<td>PG 64-22</td>
<td>20</td>
<td>9</td>
<td>190</td>
<td>30</td>
<td>√</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0</td>
<td></td>
<td></td>
<td>√</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>9</td>
<td></td>
<td></td>
<td>√</td>
</tr>
</tbody>
</table>

Although UMO has a beneficial impact on CRMA, the challenge is to avoid the release of potentially toxic compounds or elements without removing such undesired material through re-refining or distillation. In this study, different interaction parameters were evaluated for two different types of asphalt binders. The release of BTEX during the process of modifying the binder was determined, as was the different rheological properties for modified asphalt binder and the rutting distress’s resistance. Finally, rutting resistance for and leaching from modified asphalt mixtures were measured.

2. Results and Discussion

2.1. Material Properties

2.1.1. Neat and Modified Asphalt Binders’ PG Determination

The PG of neat and modified asphalt binder samples are shown in Table 2. For asphalt binder PG 52-28, using 15% CRM plus 2.5% UMO resulted in a PG high temperature between the PG of the neat and that of the 15% CRM modified asphalt binder, a value of 64 °C, which leads to stiff asphalt binder with softening properties since the PG low temperature decreased one grade from −28 to −34. The same trend was obtained for asphalt binder PG 64-22; using 10% CRM plus 2.5% UMO achieved a PG high temperature between the PG of the neat and that of the 10% CRM modified asphalt binder, a value of 70 °C. The PG low temperature was the same for neat and modified PG 64-22 asphalt binders; however, the stiffness value was enhanced for the modified asphalt binders. The best enhancement in PG 64-22 asphalt binder’s stiffness value was achieved by using both modifiers, 10% CRM plus 2.5% UMO.
Table 2. PG values for neat and modified asphalt binders.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>PG 52-28</th>
<th>PG 64-22</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature (°C)</td>
<td>1G*/sinδ (Pa)</td>
</tr>
<tr>
<td>Neat asphalt binder, unaged</td>
<td>52</td>
<td>2023</td>
</tr>
<tr>
<td></td>
<td>58</td>
<td>912</td>
</tr>
<tr>
<td>Neat asphalt binder, RTFO aged</td>
<td>52</td>
<td>4601</td>
</tr>
<tr>
<td></td>
<td>58</td>
<td>2017</td>
</tr>
<tr>
<td>Asphalt binder modified by CRM, unaged</td>
<td>70</td>
<td>1518</td>
</tr>
<tr>
<td></td>
<td>76</td>
<td>806</td>
</tr>
<tr>
<td>Asphalt binder modified by CRM, RTFO aged</td>
<td>70</td>
<td>3215</td>
</tr>
<tr>
<td></td>
<td>76</td>
<td>1891</td>
</tr>
<tr>
<td>Asphalt binder modified by CRM and UMO, unaged</td>
<td>64</td>
<td>1393</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>802</td>
</tr>
<tr>
<td>Asphalt binder modified by CRM and UMO, RTFO aged</td>
<td>64</td>
<td>4317</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>2540</td>
</tr>
</tbody>
</table>

PG Low Temperature Results Using BBR (PAV-aged Samples)

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>PG 52-28</th>
<th>PG 64-22</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature (°C)</td>
<td>Stiffness (MPa)</td>
</tr>
<tr>
<td>Neat asphalt binder</td>
<td>−12</td>
<td>81.71</td>
</tr>
<tr>
<td></td>
<td>−18</td>
<td>198.11</td>
</tr>
<tr>
<td></td>
<td>−24</td>
<td>367.53</td>
</tr>
<tr>
<td>Asphalt binder modified by CRM</td>
<td>−12</td>
<td>50.33</td>
</tr>
<tr>
<td></td>
<td>−18</td>
<td>103.66</td>
</tr>
<tr>
<td></td>
<td>−24</td>
<td>208.55</td>
</tr>
<tr>
<td>Asphalt binder modified by CRM and UMO</td>
<td>−18</td>
<td>73.55</td>
</tr>
<tr>
<td></td>
<td>−24</td>
<td>163.05</td>
</tr>
<tr>
<td></td>
<td>−30</td>
<td>319.59</td>
</tr>
</tbody>
</table>

PG High and Low Temperature Results

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>PG 52-28</th>
<th>PG 64-22</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat asphalt binder</td>
<td>52-28</td>
<td>64-22</td>
</tr>
<tr>
<td>Asphalt binder modified by CRM</td>
<td>70-28</td>
<td>76-22</td>
</tr>
<tr>
<td>Asphalt binder modified by CRM and UMO</td>
<td>64-34</td>
<td>70-22</td>
</tr>
</tbody>
</table>

Stiffness and m-value are measured at 60 sec.

2.1.2. Evaluation of Neat and Modified Asphalt Binders’ Rheological Properties at High, Intermediate and Low Temperatures

Figure 1 presents the effect of using PG 64-22 modified with 9% UMO, 20% CRM, or 9% UMO plus 20% CRM on the complex modulus and phase angle values. Tests were conducted at 64 °C and 10 rad/sec using a 25 mm diameter for parallel plates and 2 mm gap width for samples containing CRM or 1 mm gap width for neat asphalt binder samples and samples without CRM. Using asphalt binder modified with 9% UMO resulted in worsening for G* and δ values. The G* value decreased and δ value increased. However, using asphalt binder modified with 20% CRM enhanced both G* and δ values, presumably due to the absorbance of the low molecular weight components in asphalt binder by CRM particles. Using asphalt binder modified with 20% CRM plus 9% UMO resulted in G* and δ values between what obtained for samples modified by 20% CRM only and 9% UMO only. The impact on mechanical properties of adding UMO and CRM has been shown to be due to UMO...
supplying asphalt binder with low molecular weight fractions that are depleted by sorption by CRM particles [15].

Figure 1. Rheological properties for PG 64-22 asphalt binder modified with CRM and UMO interacted at 190 °C—30 Hz and measured at different interaction times: (a) $G^*$; (b) $\delta$ [15].

Figure 2 illustrates the rheological properties for neat and modified PG 52-28 asphalt binder samples interacted at 170 °C, 50 Hz, for 75 min (unaged, RTFO-aged and PAV-aged) and tested at different temperatures. Figure 2a shows the values of $|G^*|/\sin\delta$ for unaged and RTFO aged tested at different temperatures. The value of this parameter increased by adding modifiers, but the best improvement was obtained by adding 15% CRM to neat samples. Moreover, the sample containing 15% CRM had the best improvement in the rutting parameter for RTFO aged samples. The sample containing 15% CRM and 2.5% UMO showed good resistance to rutting as compared to the neat asphalt binder, which indicated that a rejuvenator like UMO has the ability to provide a balance between stiffness and softening of asphalt binder; both properties are required for good performance at high and low temperatures. Figure 2b shows the values of $|G^*| \cdot \sin\delta$, obtained from the DSR test after long-term aging of samples (PAV), which represents fatigue cracking. The $|G^*| \cdot \sin\delta$ parameter decreased for the two samples modified with 15% CRM and 15% CRM plus 2.5% UMO. The largest decrease in this value was for the sample modified with 15% CRM and 2.5% UMO, giving a value of 3.78 MPa at 10 °C, which agrees with other reports [2]. This decrease in the fatigue cracking parameter indicates softening due to adding UMO to the CRMA. This increase in the asphalt binder softness is most likely due to the ability of the rejuvenator to compensate asphalt binder with low molecular weight components lost by absorption into CRM particles.
Figure 2 illustrates the rheological properties for neat and modified PG 52-28 asphalt binder samples interacted at 170 °C, 50 Hz, for 75 min (unaged, RTFO-aged and PAV-aged) and tested at different temperatures. Figure 2a shows the values of $|G^*|/\sin \delta$ for unaged and RTFO aged tested at different temperatures. The value of this parameter increased by adding modifiers, but the best improvement was obtained by adding 15% CRM to neat samples. Moreover, the sample containing 15% CRM had the best improvement in the rutting parameter for RTFO aged samples. The sample containing 15% CRM and 2.5% UMO showed good resistance to rutting as compared to the neat asphalt binder, which indicated that a rejuvenator like UMO has the ability to provide a balance between stiffness and softening of asphalt binder; both properties are required for good performance at high and low temperatures. Figure 2b shows the values of $|G^*|.\sin \delta$, obtained from the DSR test after long-term aging of samples (PAV), which represents fatigue cracking. The $|G^*|.\sin \delta$ parameter decreased for the two samples modified with 15% CRM and 15% CRM plus 2.5% UMO. The largest decrease in this value was for the sample modified with 15% CRM and 2.5% UMO, giving a value of 3.78 MPa at 10 °C, which agrees with other reports [2]. This decrease in the fatigue cracking parameter indicates softening due to adding UMO to the CRMA. This increase in the asphalt binder softness is most likely due to the ability of the rejuvenator to compensate asphalt binder with low molecular weight components lost by absorption into CRM particles.

Figure 2. Rheological properties for PG 52-28 neat and modified asphalt binders based on: (a) DSR for unaged and RTFO-aged; (b) DSR for PAV-aged, interacted at 170 °C—50 Hz—75 min.

Figure 3 illustrates the rheological properties for neat and modified PG 64-22 asphalt binder samples interacted at 190 °C, 50 Hz, for 62 min (unaged, RTFO-aged and PAV-aged) and tested at different temperatures. Figure 3a shows the values of $|G^*|/\sin \delta$ for unaged and RTFO aged at different temperatures. It reflects the same trend shown in Figure 2a. The value of the rutting parameter increased by adding modifiers, with the best improvement obtained by adding 10% CRM for neat asphalt binder samples. Figure 3b shows the values of $|G^*|.\sin \delta$; this parameter decreased for the two modified samples, 10% CRM and 10% CRM plus 2.5% UMO. The largest decrease in this value was for the sample modified with 10% CRM and 2.5% UMO, achieving a value of 4.37 MPa at 16 °C.
Figure 3 illustrates the rheological properties for neat and modified PG 64-22 asphalt binder samples interacted at 190 °C, 50 Hz, for 62 min (unaged, RTFO-aged and PAV-aged) and tested at different temperatures. Figure 3a shows the values of \( |G^*|/\sin \delta \) for unaged and RTFO aged at different temperatures. It reflects the same trend shown in Figure 2a. The value of the rutting parameter increased by adding modifiers, with the best improvement obtained by adding 10% CRM for neat asphalt binder samples. Figure 3b shows the values of \( |G^*| \cdot \sin \delta \); this parameter decreased for the two modified samples, 10% CRM and 10% CRM plus 2.5% UMO. The largest decrease in this value was for the sample modified with 10% CRM and 2.5% UMO, achieving a value of 4.37 MPa at 16 °C.

**Figure 3.** Rheological properties for PG 64-22 neat and modified asphalt binders based on: (a) DSR for unaged and RTFO-aged; (b) DSR for PAV-aged, interacted at 190 °C—50 Hz—62 min.

BBR results for PG 52-28 neat and modified asphalt binders are shown in Figure 4. The stiffness values in MPa are presented in Figure 4a, while Figure 4b shows the m-value. According to these data, asphalt binder samples modified by 15% CRM plus 2.5% UMO demonstrated more resistance to low temperature cracking since they gave the lowest stiffness, 163.05 MPa, the highest m-value, 0.309, measured at −24 °C, and had the PG low temperature changed to −34 °C. The rejuvenator succeeded as a modifier in enhancing both low- and high-temperature properties by introducing a balance between stiffness and softness of the asphalt binder. On the other hand, the low PG temperature for the CRM asphalt binder was unchanged from that of neat asphalt binder, −28 °C. Asphalt binder modified with CRM showed more enhancement in the stiffness value, which decreased from 198.11 MPa for the neat asphalt binder to 103.66 MPa at −18 °C BBR temperature, while the m-value remained essentially constant. This can be explained if CRM released polymeric or high molecular weight components to the liquid phase of the asphalt binder that decreased its stiffness.
Figure 4. BBR test results: (a) BBR stiffness; (b) BBR m-value, measured for PG 52-28 neat and modified asphalt binder samples interacted at 170 °C—50 Hz—75 min.

Figure 5 shows the BBR test results for PG 64-22 neat and modified asphalt binders. The values of stiffness at low-temperatures are shown in Figure 5a. The best enhancement in the stiffness values was achieved by using asphalt binder modified with 10% CRM plus 2.5% UMO, presumably due to the CRM’s release of polymeric components in the asphalt binder’s liquid phase and the ability of the rejuvenator to soften the asphalt binder. However, the m-value presented in Figure 5b shows a decrease compared to neat for both modified asphalt binders. Overall, the enhancement in the performance of the asphalt binder at low temperatures did not only depend on rejuvenator but also on other factors: asphalt binder type, CRM particle sizes, and interaction conditions.

Figure 6 shows the rotational viscometer test results for PG 52-28 and PG 64-22 neat and modified asphalt binders. PG 52-28 was modified with 15% CRM both with and without 2.5% UMO, interacted at 170 °C, 50 Hz, for 75 min. PG 64-22 was modified with 10% CRM both with or without 2.5% UMO, interacted at 190 °C, 50 Hz, for 62 min. Error bars indicate variability in the results; the mean and variance were estimated from triplicate testing for each sample. It can be concluded that all the
samples had a viscosity, measured at 135 °C, below the 3 Pa s (3000 cP) maximum specification limit. The sample modified with CRM had the highest viscosity and the neat asphalt binder had the lowest viscosity. The asphalt binder modified with CRM-UMO had a viscosity between the neat binder’s viscosity and the CRMA binder’s viscosity; UMO is expected to act as a lubricant between the CRM particles, which causes reduction in the viscosity. Furthermore, the viscosity values of the modified PG 64-22 asphalt binders were higher than the viscosity for the modified PG 52-28 asphalt binders; however, PG 64-22 was modified with only 10% CRM. This can be explained due to the existence of a higher percentage of asphaltene component in the asphalt binder PG 64-22, which increased its stiffness and resistance to flow as compared to PG 52-28 asphalt binder.

![Figure 6. Viscosity of neat and modified asphalt binder samples at different interaction conditions.](image)

**2.1.3. Frequency Sweep Test**

Frequency sweep test results for the neat and modified asphalt binders were used to draw master curves. Figure 7 presents the master curve for PG 52-28 neat and modified asphalt binders interacted at 170 °C, 50 Hz, for 75 min, which illustrates the relation between reduced frequency (Hz) and loss (G'') or storage (G') modulus measured at 60 °C. Loss modulus reflects the viscous behavior of asphalt binder and storage modulus depicts the asphalt binder’s elastic behavior. For asphalt binders modified by 15% CRM or 15% CRM plus 2.5% UMO, both G' and G'' values increased; however, the increase in storage modulus was higher than the increase in the loss modulus due to the elastic property of the CRM particles and their polymeric components released in the asphalt binder. The best enhancement in G' and G'' values was observed for asphalt binders modified only with 15% CRM.

Figure 8 illustrates the master curve for PG 64-22 neat and modified asphalt binders interacted at 190 °C, 50Hz, for 62 min, measured at 60 °C. The same trend shown in Figure 7 was observed, in that samples modified with 10% CRM had the highest loss and storage moduli values. Nevertheless, the difference between the loss or storage modulus values for samples modified with 10% CRM and 10% CRM plus 2.5% UMO was smaller than difference in values achieved in Figure 7. Furthermore, most of the loss and storage moduli values were around (1–10,000) Pa and (1–100,000) Pa for PG 52-28 and PG 64-22 modified asphalt binders respectively. This could be due to many factors: the differences in the interaction conditions, the used asphalt binder’s type, and the particle sizes of the CRM. Overall, neat asphalt binders had the lowest storage and loss moduli values, neat asphalt binders modified by CRM only had the highest moduli values, and neat asphalt binders modified by CRM-UMO had moduli values between those for neat and neat modified by CRM.
Frequency sweep test results obtained through a wide range of temperatures and frequencies can be used to draw Cole-Cole plots [16], measured at a reference temperature 60 °C. The Cole-Cole plot presents the relation between $G'$ and $G''$. This plot can be used to understand the overall change in the

![Graph](image-url)

**Figure 7.** Master curve for PG 52-28 neat and modified asphalt binders interacted at 170 °C—50 Hz—75 min, measured at 60 °C as a reference temperature.

![Graph](image-url)

**Figure 8.** Master curve for PG 64-22 neat and modified asphalt binders interacted at 190 °C—50 Hz—62 min, measured at 60 °C as a reference temperature.
shear complex modulus $|G^*|$ based on the changes in $G'$ and $G''$ values [17,18]. Additionally, it is used to verify the results obtained from the master curve [19].

Figure 9 shows the Cole-Cole plot for PG 52-28 neat and modified asphalt binders interacted at 170 °C, 50 Hz, for 75 min. A shift towards the storage modulus axis can be observed, which illustrates enhancement in the elastic behavior of the modified samples. This enhancement likely happened due to the release of the CRM’s polymeric components in the liquid phase of the asphalt binder. Moreover, the best enhancement in the elastic behavior was achieved for samples modified by 15% CRM. This agrees with the results obtained from master curve in Figure 7.

![Figure 9](image_url)

**Figure 9.** Cole-Cole diagram for PG 52-28 neat and modified asphalt binders interacted at 170 °C—50 Hz—75 min, measured at a reference temperature 60 °C.

Figure 10 shows the Cole-Cole plot for PG 64-22 neat and modified asphalt binders interacted at 190 °C, 50 Hz, for 62 min. A shift towards the storage modulus axis can be observed, which illustrates enhancement in the elastic behavior of the modified samples. This enhancement is also likely due to the release of the CRM’s polymeric components in the liquid phase of the asphalt binder. Both modified asphalt binders had approximately the same storage modulus for the same loss modulus; however, a slight increase for both loss and storage moduli values were observed for samples modified with CRM. For instance, storage range values were (0.1–3432) Pa, (0.51–14891) Pa, and (0.8–21131) Pa for neat asphalt binder, neat asphalt binder modified by CRM-UMO, and neat asphalt binder modified with CRM, respectively. This agrees with the results obtained from the master curve in Figure 8 since neat asphalt binder modified by CRM had the best enhancement in $G'$ and $G''$ moduli values followed by neat asphalt binder modified by CRM-UMO.

A black diagram illustrates the relation between the complex shear modulus $|G^*|$ and phase angle $\delta$. Figure 11 shows the black diagram for PG 52-28 neat and modified asphalt binders interacted at 170 °C, 50 Hz, for 75 min, measures at a reference temperature 60 °C. The shift towards the $|G^*|$ axis in the curves for the modified asphalt binders happened due to the increase in the $|G^*|$ values (more stiff) and decrease in the phase angle $\delta$ values (more elastic). This shifting happened to all modified asphalt binder samples, with the maximum shift for CRM asphalt binders. This agrees with the results shown in Figure 7.
Recycling 2019, 4, 11 presented better performance at high, intermediate, and low temperatures as compared to the neat asphalt binder. Modified PG 52-28 asphalt binders had a better enhancement of rheological properties as compared to modified PG 64-22 asphalt binders for many reasons: the differences in asphalt binder type, CRM particle sizes, interaction conditions, and mixing procedures. This suggests that any variation in the aforementioned factors will lead to different results.

**Figure 10.** Cole-Cole diagram for PG 64-22 neat and modified asphalt binders interacted at 190 °C—50 Hz—62 min, measured at a reference temperature 60 °C.

![Cole-Cole diagram for PG 64-22](image)

- Neat asphalt binder
- Neat asphalt binder modified by 10% CRM and 2.5% UMO
- Neat asphalt binder modified by 10% CRM

**Figure 11.** Black diagram for PG 52-28 neat and modified asphalt binders interacted at 170 °C—50 Hz—75 min, measured at a reference temperature 60 °C.

![Black diagram for PG 52-28](image)

- Neat asphalt binder
- Neat asphalt binder modified by 15% CRM and 2.5% UMO
- Neat asphalt binder modified by 15% CRM

Figure 12 presents the black diagram for PG 64-22 neat and modified asphalt binders interacted at 190 °C, 50 Hz, for 62 min. The same findings were noted as in Figure 8; samples modified by 10% CRM had lower phase angle values as compared to samples modified with 10% CRM plus 2.5% UMO. However, no significant difference was found between samples modified by CRM and CRM-UMO. These findings support the results obtained in Table 2 since the modified asphalt binders presented better performance at high, intermediate, and low temperatures as compared to the neat asphalt binder. Modified PG 52-28 asphalt binders had a better enhancement of rheological properties as compared to modified PG 64-22 asphalt binders for many reasons: the differences in asphalt binder type, CRM particle sizes, interaction conditions, and mixing procedures. This suggests that any variation in the aforementioned factors will lead to different results.
for N = 11 to 20 (1)

10% CRM plus 2.5% UMO achieved resistance to rutting distresses higher than neat asphalt binder.

15% CRM plus 2.5% UMO decreased the shear strain values. The lowest shear strain values were observed as at the lower shear stress; using modified asphalt binders decreased the shear strain values. The lowest shear strain values were obtained for samples modified with 15% CRM. That agrees with the results obtained from the rutting parameter since \( |G^*|/\sin \delta \) was higher for asphalt binder modified by 15% CRM at 70 °C as compared to asphalt binder modified by 15% CRM plus 2.5% UMO at the same temperature. Figure 13b shows the strain values for neat and modified asphalt binders at 3.2 KPa shear stress. The same results were observed as at the lower shear stress; using modified asphalt binders decreased the shear strain values. Figure 14 illustrates MSCR test results for PG 64-22 neat and modified asphalt binder samples interacted at 190 °C, 50 Hz, for 62 min, also tested at 60 °C. As with PG 52-28, samples modified with 10% CRM plus 2.5% UMO achieved resistance to rutting distresses higher than neat asphalt binder and lower than sample modified only with 10% CRM.

Elastic recovery (%R) and non-recoverable creep compliance (Jnr) can be calculated using MSCR test results. Figure 15a illustrates elastic recovery percentage for neat and modified samples at 0.1 and 3.2 KPa shear stress. The %R at 0.1 KPa (R0.1) can be calculated from Equation (1), and Equation (2) for R3.2. It can be noted that R0.1 and R3.2 were 3.15 and zero, respectively, for PG 52-28 neat asphalt binder. The %R was enhanced for modified asphalt binders. The best enhancement for PG 52-28 asphalt binder was by 15% CRM, which is in agreement with the values of rutting parameter measured at 70 °C. Similar results were observed for PG 64-22 neat and modified asphalt binders. It appears that rubber’s polymeric components released in the liquid phase of the asphalt binder enhanced its ability to resist deformation since asphalt binder almost returns to its initial shape with low permeant deformation.

\[
R0.1 = \frac{\text{SUM}(\varepsilon_t(0.1,N))}{10} \quad \text{for } N = 11 \text{ to } 20
\]

in which

\[
\varepsilon_t(0.1,N) = \frac{(\varepsilon_{1} - \varepsilon_{10}) \times 100}{\varepsilon_{1}};
\]
$\varepsilon_1$: the adjusted strain value at the end of the creep portion (after 1 sec.) of each cycle; 
$\varepsilon_1 = \varepsilon_c - \varepsilon_0$;

$\varepsilon_0$: initial strain value at the beginning of the creep portion of each cycle;

$\varepsilon_c$: strain value at the end of the creep portion (after 1 sec.) of each cycle;

If $\varepsilon_r (0.1, N) < 0$ then record $\varepsilon_r (0.1, N)$ as zero;

$\varepsilon_{10}$: the adjusted strain value at the end of the recovery portion (after 10 sec.) of each cycle;

$\varepsilon_{10} = \varepsilon_r - \varepsilon_0$; and

$\varepsilon_r$: strain value at the end of the recovery portion (after 10 sec.) of each cycle.

$$R3.2 = \sum_{N=1}^{10} \frac{\epsilon_r(3.2, N)}{10} \text{ for } N = 1 \text{ to } 10 \quad (2)$$

in which

$\epsilon_r (3.2, N) = \frac{(\varepsilon_1 - \varepsilon_{10}) \times 100}{\varepsilon_1}$;

$\varepsilon_1$ and $\varepsilon_{10}$ are the same laws for 0.1 KPa but they are calculated at 3.2 KPa shear stress; and

If $\epsilon_r (3.2, N) < 0$ then record $\epsilon_r (3.2, N)$ as zero.

Figure 13. MSCR results for PG 52-28 neat and modified binders interacted at 170 °C—50 Hz—75 min, tested at 60 °C: (a) 0.1 KPa; (b) 3.2 KPa shear stress.
Figure 14. MSCR results for PG 64-22 neat and modified binders interacted at 190 °C—50 Hz—62 min, tested at 60 °C: (a) 0.1 KPa; (b) 3.2 KPa shear stress.

Figure 15b shows Jnr at 0.1 and 3.2 KPa shear stress; Jnr values were calculated using Equation (3) for Jnr0.1 and Equation (4) for Jnr3.2. The non-recoverable creep compliance decreased for all modified samples. The lowest values of Jnr were obtained for PG 52-28 asphalt binder modified with 15% CRM. This is in agreement with the results shown in Figure 2a; this sample had the highest percentage of recovery compared to the neat asphalt binder or the asphalt binder modified by 15% CRM plus 2.5% UMO. Similar results were obtained for PG 64-22 neat and modified asphalt binders. It was found that PG 64-22 neat asphalt binder had a higher percentage of recovery and lower non-recoverable creep compliance than PG 52-28 neat asphalt binder due to its high stiffness, related to PG 64-22 having a high asphaltene content and low molecular weight fractions.

\[
J_{nr0.1} = \frac{\text{SUM} \left( J_{nr}(0.1, N) \right)}{10} \quad \text{for} \quad N = 11 \text{ to } 20
\]  

in which

\[
J_{nr} (0.1, N) = \frac{\varepsilon_{10}}{\varepsilon_{TT}}; \quad \text{and}
\]

If \( \varepsilon_r (0.1, N) < 0 \) then \( J_{nr} (0.1, N) = \frac{\varepsilon_{r1}}{\varepsilon_{TT}}. \)

\[
J_{nr3.2} = \frac{\text{SUM} \left( J_{nr}(3.2, N) \right)}{10} \quad \text{for} \quad N = 1 \text{ to } 10
\]
in which
\[ J_{n(r)}(3.2, N) = \frac{j_0(3.2)}{j_2}; \] and
If \( \varepsilon_r(3.2, N) < 0 \) then \( J_{n(r)}(3.2,N) = \frac{j_1(3.2)}{j_2}. \)

Figure 15. Effect of using CRM and UMO on: (a) elastic recovery (b) non-recoverable creep compliance for PG 52-28 and PG 64-22 neat and modified asphalt binders.

2.1.5. HMA Rutting Evaluation Using APA

The results of APA testing at 60 °C, measured for PG 52-28 neat and modified asphalt binders, are presented in Figure 16. APA results indicate that the mixture modified with 15% CRM had the lowest rutting depth, 3.9 mm after 8000 cycles, in agreement with other research [2]. Also, this in agreement with DSR results since asphalt binder modified by 15% CRM had the highest \( |G^*|/\sin\delta \) values, percentage of elastic recovery (\%R), and the lowest non-recoverable creep compliance (Jnr). On the other hand, the lowest resistance to rutting was obtained for mixtures containing neat asphalt binder, with a 7.33 mm rutting depth after 8000 cycles. The asphaltic mixture modified by 15% CRM plus 2.5% UMO showed a 5.7 mm rutting depth after 8000 cycles. This agrees with rheological properties since asphalt binder modified by 15% CRM plus 2.5% UMO had a high PG temperature of 64 °C, between the 52 °C and 70 °C for neat and asphalt binder modified by 15% CRM, respectively. Consequently, UMO enhanced rutting resistance and at the same time enhanced fatigue and low-temperature cracking.
resistance. Accordingly, the role of a rejuvenator appeared here to create stability of asphalt enhanced properties since it did not improve one property and worsen the other.

2.2. Environmental Results

Two aspects of potential environmental impact were examined. The first was estimating BTEX in air emissions during the interaction between asphalt binder and modifiers. The second was measuring toxics leaching from HMA samples using the TCLP method.

2.2.1. Portable Gas Chromatography Results

Figure 17 shows the concentration of BTEX components in air measured above PG 64-22 modified asphalt binder with 9% UMO or with 9% UMO plus 20% CRM. The general trend in this Figure is that as the interaction time increased, the amount of BTEX released into the air decreased. It can be noted that samples modified with CRM had higher percentage of benzene than sample modified without CRM. Furthermore, after 120 min interaction time, the release of benzene was negligible from modified samples. Xylenes were present at the highest concentration of the four BTEX components [15].
Portable gas chromatography test results for PG 52-28 neat and modified asphalt binders with 15% CRM and with or without 2.5% UMO are presented in Figure 18. These samples were interacted at 170 °C at 50Hz interaction speed with measurement during the interaction time. Emissions measured above neat and modified asphalt binder by 15% CRM are illustrated in Figure 18a,b respectively, whereas Figure 18c shows the emissions resulting from asphalt binder modified by 15% CRM plus 2.5% UMO. It can be noted that neat asphalt binder samples had significantly lower BTEX concentrations and that these amounts decreased with time. The lowest BTEX concentrations were observed at the end of the 62-min interaction time. The sample modified with 15% CRM (full gradation) had higher concentrations of BTEX, especially toluene, and these concentrations declined with time. However, the concentration of m- and p-xylene fluctuated, with the highest values noted at 22 min and 62 min interaction times. Including UMO increased BTEX; the 15% CRM plus 2.5% UMO sample had higher amounts of BTEX after 2 min interaction time than did the sample modified with 15% CRM and no oil. At 62 min of interaction time, ethylbenzene and o-xylene released from asphalt binder modified by 15% CRM plus 2.5% UMO and asphalt binder modified by 15% CRM were approximately equal. Nevertheless, the sum of benzene, toluene, and m- and p-xylene concentrations were generally higher with UMO than without. Interestingly, a lower increase in BTEX concentrations was noted for samples modified with CRM-UMO than only CRM. This illustrates the ability of the CRM to absorb UMO and release its BTEX components slowly; this is in agreement with another study that reported samples modified by CRM-UMO had lower BTEX concentrations than samples modified with UMO only [15].

It can be inferred that toluene had the highest concentrations in both modified asphalt binders, while o-xylene had the lowest concentrations. Finally, the total sum of the BTEX concentrations measured at seven times during interaction (2–62 min at 10 min intervals) were 0.79, 20.61, and 30.62 ppb for neat, 15% CRM modified, and 15% CRM plus 2.5% UMO modified asphalt binders, respectively. The net emissions increased by adding crumb rubber, and increased slightly more by adding oil.

Figure 19 shows BTEX results for PG 64-22. BTEX components were higher for this neat binder as compared to what measured for PG 52-28 neat asphalt binder, Figure 19a. The interaction temperature for PG 64-22 was higher by 20 °C, which would increase the vapor pressure of these volatile organics. However, the total of BTEX concentrations for PG 64-22 neat asphalt binder summed over seven interaction times (2–62 min at 10 min intervals) was 8% higher than for PG 52-28 modified by 15% CRM, indicating the PG 64-22 neat binder had significantly higher amounts of BTEX than PG 52-28 modified with 15% CRM. The highest concentration of BTEX components released by PG 64-22 neat asphalt binder was m-, p-xylene and o-xylene components, and the lowest concentrations were those of toluene and benzene. BTEX concentrations decreased with interaction time.

Figure 19b shows BTEX measure in air above PG 64-22 asphalt binder modified with 10% CRM. Adding 10% CRM (30–40) apparently slowed or inhibited the release of BTEX, with observable values lower than 0.5 ppb. It was noted that the m-, p-xylene component increased after the measurement at 2 min. The coarse CRM particles with size (30–40) are expected to have absorbed the oils and low molecular weight fractions from the asphalt binder and released them slowly over the interaction time; this explains the BTEX results, 11.5% lower with CRM than for neat asphalt binder. This was different from what was obtained for PG 52-28 (Figure 18b) which had different CRM particle sizes and interaction temperature as well as a different asphalt binder. Figure 19c shows the impact of adding UMO, with slightly increased BTEX concentrations after 12 min of interaction time, although the m-, p-xylene component significantly increased for all interaction times, as was also seen for PG 52-28 asphalt binder. The total sum of BTEX concentrations for the PG 64-22 modified with CRM-UMO measured was 1.8% higher than that measured for the neat asphalt binder.

Overall, using CRM appears to regulate the release of BTEX from asphalt binder. Rubber will absorb low molecular weight organics and then release these organics as they are lost by the liquid phase. The release of BTEX components depend not only on the asphalt binder’s type but also on other factors: interaction temperature, interaction time, and modifier’s particle size.
Figure 18. BTEX in air above PG 52-28 neat and modified asphalt binder samples interacted at 170 °C—50 Hz and different interaction times; these samples were (a) neat asphalt binder (AC); (b) AC + 15% CRM; (c) AC + 15% CRM + 2.5% UMO.
Figure 19. BTEX in air above PG 64-22 neat and modified asphalt binder samples interacted at 190 °C—50 Hz and different interaction times; these samples were (a) neat asphalt binder (AC); (b) AC + 10% CRM; (c) AC + 10% CRM + 2.5% UMO.

2.2.2. TCLP Test Results

Figure 20 presents TCLP testing results including elements which were detected as leaching from PG 52-28 neat and modified asphalt mixtures. The neat mixture did leach some elements, most notably sulfur and copper. For arsenic and cadmium, no detectable amount was found for the neat HMA,
HMA modified by 15% CRM, and HMA modified by 15% CRM plus 2.5% UMO. Chromium was detected at 0.052 mg/L for each asphalt mix, significantly lower than the 5 mg/L EPA maximum (the value above which a waste is considered hazardous). For lead, 0.149 mg/L was detected for each asphalt mix, which also does not reach the 5 mg/L value set by the EPA. For sulfur, a concentration of approximately 3.5 mg/L was detected for the asphalt mix modified with 15% CRM plus 2.5% UMO. In addition, close to 1 mg/L of S was found in the neat mix and 0.5 mg/L in the HMA modified by 15% CRM. This was not as surprising, as sulfur compounds are present in all Saturate, Aromatic, Resin and AsphaltenODE (SARA) fractions with different mass distribution and molecular composition [20]. The lowest concentration of sulfur was observed for samples modified by 15% CRM only, probably of CRM absorbance of asphalt's light molecular weight components. Iron was only detected as leaching from the neat mix. Lastly, copper was present in leachate at concentrations under 0.5 mg/L for the neat mix, HMA modified by 15% CRM, and HMA modified by 15% CRM and 2.5% UMO. From these results, it can be concluded that UMO can be used with modified asphalt mixture without leaching of elements at levels above EPA standards. Hence, UMO is an effective rejuvenator that can be used in combination with other modifiers to enhance the properties of asphalt without significant environmental concerns.

3. Materials and Experimental Procedures

3.1. Raw Materials

It has been recommended that UMO percentage should be less than 3% in combination with at least 10% CRM [1,2], with mixing at 190 °C at 30 Hz for 120 min interaction time; these interaction conditions were able to form an internal 3D network structure and a plateau region in temperature sweep viscoelastic curves was found [1,2]. Both macro and micromechanical properties were enhanced [1]. Therefore, 2.5% UMO and 10 or 15% CRM percentages were selected in this work to be added to asphalt binder. Two asphalt binders were used in combination with one type of CRM. Asphalt types were PG 52-28 and PG 64-22 obtained from Philips 66 Company (Granite, IL, USA). The CRM was a cryogenically processed crumb rubber obtained from Liberty Tire Recycling Company (Montgomery, IL, USA), a blend of truck and passenger car tires. Cryogenic grinding is considered better than ambient since little or no heat is used, which results in negligible degradation of particles [21]. The gradation of CRM as determined by weight fractions from sieve analysis is shown in Figure 21. The full CRM gradation was used with asphalt binder PG 52-28. CRM (30–40), particles
passed from sieve #30 and retained on sieve #40, was used with asphalt binder PG 64-22. UMO with a viscosity of 5.5 centipoise (cP) was mixed with CRMA binders. The UMO was not re-refined, and was obtained from a local auto repair shop. Aggregate, sand and mineral filler (MF) were used in asphalt pavement analyzer (APA) specimens with the gradation presented in Figure 22, which also shows the combined gradation of the mix. Properties and proportions of the aggregate that was used in the mixtures are illustrated in Table 3.

![Figure 21. Gradation of crumb rubber modifier.](image)

![Figure 22. Gradation of aggregate, sand, MF and combined mix.](image)

### Table 3. Properties of the aggregate.

<table>
<thead>
<tr>
<th>Material</th>
<th>9/16”</th>
<th>3/8”</th>
<th>Screenings</th>
<th>ManSand *</th>
<th>MF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proportions (%wt)</td>
<td>29</td>
<td>29</td>
<td>15</td>
<td>25</td>
<td>2</td>
</tr>
<tr>
<td>Bulk Specific Gravity (Gsb)</td>
<td>2.735</td>
<td>2.681</td>
<td>2.664</td>
<td>2.383</td>
<td></td>
</tr>
<tr>
<td>Apparent Specific Gravity (Gsa)</td>
<td>2.810</td>
<td>2.801</td>
<td>2.813</td>
<td>2.658</td>
<td></td>
</tr>
<tr>
<td>Absorption (%)</td>
<td>1.0</td>
<td>1.6</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Crushed Meramec River gravel.
3.2. CRMA-UMO Interactions

In this research, 1600 g of PG 52-28 asphalt binder was added to a 1-gallon can, heated to 170 °C in an oven, and transferred to a hot plate under a fume hood. Then 240 g of CRM, 15% CRM of asphalt binder weight, was added at time zero. Asphalt binder with CRM was mixed at high speed (50 Hz) using a drill for 75 min. For the sample modified by UMO, 40 g UMO or 2.5% UMO by weight of asphalt binder was added after 2 min of interaction between CRM and asphalt binder, then mixing continued to the end of 75 min. The same procedures were followed for PG 64-22 asphalt binder; however, the CRM percentage was 10% by asphalt binder weight and the CRM particles’ size was (30–40)—passing from sieve #30 and being retained on sieve #40. The interaction temperature was 190 °C as controlled using DIGI-SENSE probe type J attached to temperature controller DIGI-SENSE TC 9100 which in turn controlled a Glas-Col heating mantle obtained from Cole-Parmer Co. (Vernon Hills, IL, USA). The interaction speed was 50 Hz, monitored using LCI-t (CHARLES ROSS & SON COMPANY, Hauppauge, NY, USA) high shear mixer; the interaction time was 62 min, and the same UMO percentage, 2.5% by weight of the asphalt binder, was used. Table 4 illustrates the modifiers’ percentages and the interaction conditions. Both CRM and UMO percentages were selected based on previous research [1,2].

<table>
<thead>
<tr>
<th>Table 4. Interaction conditions for the modified asphalt binders.</th>
</tr>
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<tbody>
<tr>
<td><strong>Asphalt Binder</strong></td>
</tr>
<tr>
<td>---------------------</td>
</tr>
<tr>
<td>PG 52-28</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>PG 64-22</td>
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</table>

3.3. Experimental Design

The experimental design is presented in Figure 23. Neat asphalt, neat asphalt modified by CRM, and neat asphalt modified by CRM-UMO binders and mixtures were investigated in this research. Specifically, the mixtures were evaluated by using (a) neat PG 52-28 asphalt binder, (b) neat PG 52-28 asphalt binder modified by 15% CRM, and (c) neat PG 52-28 asphalt binder modified by 15% CRM and 2.5% UMO. The properties of the unaged, short-term aged using a rolling thin film oven (RTFO), and long-term aged using a pressure aging vessel (PAV) asphalt binders were evaluated through dynamic shear rheometer (DSR), bending beam rheometer (BBR), and rotational viscometer (RV). The properties of the mixtures were assessed through measuring rutting depth by using APA. Potential environmental problems such as air emissions were evaluated using a portable gas chromatograph (GC) to measure BTEX, at different interaction times (2, 12, 22, 32, 42, 52, and 62 min) for the neat and modified asphalt binder samples. The leaching of the neat and modified asphaltic mixtures was evaluated to determine the toxic components that leached and concentrations in (mg/L) by EPA’s Toxicity Characteristic Leaching Protocol (TCLP) with the leachate measured using an ion coupled plasma—optical emission spectrometer (ICP-OES, Waltham, MA, USA).
used to perform a frequency sweep test for unaged neat and modified asphalt binders at 58, 64 and 70 °C from 0.1 to 100 rad/sec using 25 mm parallel plate geometry and a 1 mm gap since the measuring temperatures were above 40 °C. Additionally, master curve, Cole-Cole diagram, and black diagram were plotted by analyzing the frequency sweep tests’ results. A multiple stress creep recovery (MSCR) test was used to evaluate the resistance of neat and modified asphalt binder samples to rutting distress and to validate the results of rutting parameter $|G^*|/\sin \delta$; this test was implemented according to ASTM D7405 at 60 °C temperature.

### 3.3.2. Viscosity of Asphalt Binder

Viscosity was measured using a Rotational Viscometer (RV) and following ASTM 4402. The rotational viscometer model was RVDVII+ obtained from Brookfield Engineering Laboratories, INC, Middleborough, MA, USA.
3.3.3. Short-Term Aging (RTFO)

Short-term aging was carried out following ASTM D2872. Testing was implemented using a CS 325-B model obtained from James Cox & Sons INC, Colfax, CA, USA.

3.3.4. Long-Term Aging (PAV)

Long-term aging was carried out following ASTM D652. Testing was done using a PAV 9300 machine obtained from Prentex Alloy Fabrication, INC, Dallas, TX, USA.

3.3.5. Bending Beam Rheometer

Low-temperature properties of neat and modified asphalt binders were carried out following ASTM D6648. Testing was implemented using a bending beam rheometer machine obtained from Applied Test Systems (ATS), INC, Butler, PA, USA.

3.3.6. Performance of Hot Mix Asphalt (HMA) at High Temperature Degrees

Rutting resistance of HMA was deduced using APA following AASHTO T340. This test was performed on PG 52-28 neat and modified mixtures and the APA was obtained from Pavement Technology, INC, Covington, GA, USA.

3.3.7. Gas Chromatography

To measure volatile emissions from the two types of asphalt binders modified with CRM and UMO, different samples were evaluated: neat asphalt binders, asphalt binders modified by CRM, and asphalt binders modified by CRM-UMO. A NovaTest™ P100 Portable Gas Chromatography Photoionization Detector (GC-PID, Columbia, MO, USA) from Nanova Environmental, Inc. was used. The GC-PID consists of an automatic sampling/preconcentrator and a 6 m long, 0.25 mm i.d. Rtx-VMS™ capillary GC column (Restek Corp, Bellefonte, PA, USA) with an at-column heater configuration. An air sample was pulled by vacuum and passed through the preconcentrator at 10 mL/min for 1 min. After sampling, the flow direction through the preconcentrator was reversed and the collected sample was thermally desorbed directly into the column. The GC separation of a six-component BTEX mixture was completed in less than 2 min when the column was heated from 50 to 80 °C at 15 °C/min with 10 mL/min helium carrier gas flow. The GC could not separate m and p-xylenes, so they are reported together.

The portable GC-PID was calibrated with BTEX standards prepared by injecting BTEX stock solution into 5 L Tedlar® bags filled with high-purity nitrogen gas. Peak area was used to establish calibration curves and the variation in peak area was less than 6% RSD. Good linearity (R² > 0.99) was obtained for all the calibration curves.

HMA was produced using the neat and modified asphalt binders, and BTEX compounds in fumes were monitored real time during the processing of two types of neat and modified asphalt binders containing CRM with or without UMO at 170 °C and 190 °C, respectively. A two-foot-long Teflon tube connected to the sampling port of the GC-PID was placed over the vessel containing the binder sample. The emission from the asphalt binders was sampled at 10 min intervals after mixing.

3.3.8. Measuring Toxicity Leaching Characteristics

This test was performed following EPA TCLP SW 846 Method 1311, which was performed on PG 52-28 HMA neat and modified samples in order to determine the potential mobility of primarily inorganic analytes present in the samples. This procedure was focused on whether recycled materials such as CRM and UMO might include leachable materials.

A loose 100-gram HMA sample was placed in a given volume of leachant solution, acetic acid with an acetate buffer, (L/S liquid per solid ration is equal to 20 L/kg) for a set period of time (18 h) with agitation on a shaker at 30 rpm. At the end of the leaching period, the liquid was removed and analyzed,
the final pH measured, and the mixture filtered using a glass fiber filter. The filtrate was analyzed using an Avio 200 Inductively Coupled Plasma (ICP) optical emission spectrometer, PerkinElmer Co. (Waltham, MA, USA), for constituents such as arsenic, cadmium, chromium, lead, sulfur, iron, and copper. If these constituent concentrations equal or exceed the concentrations described in 40 Code of Federal Regulations (CFR) 261, then a waste is characteristically hazardous for toxicity.

4. Conclusions

There are both engineering and environmental concerns relevant to the use of used motor oil (UMO) as a rejuvenator in asphalt applications. Engineering concerns are focused on the ability of UMO to control the stiffness of asphalt binders and mixes, for example the case of using recycled tires as crumb rubber modifier (CRM). Combining both additives balances both low and high temperature properties of asphalt binders and mixes. Depending on the percentage of each additive and the interaction conditions, balanced modifications at low temperature and high-temperature can be achieved. Environmental concerns are potential air emissions and leaching into surface or ground water, especially if UMO contains toxic components that emit and/or leach out when used.

Engineering concerns were evaluated in this study through rheological testing to confirm the ability of UMO as a rejuvenator to regulate the properties of CRM binders at different temperatures. CRM-UMO combinations interacted with two types of asphalt binders enhanced rutting resistance, fatigue cracking resistance, and low-temperature cracking resistance in comparison with the neat samples. Results show that CRM-UMO enhanced rutting performance by increasing the PG binder high-temperature grade between one and two grades, increased the percentage of elastic recovery by around 600%, and decreased the rutting depth of asphalt mixtures by 22.5% after 8000 cycles using the APA mix tester. CRM-UMO decreased the PG binder intermediate temperature grade between two and three grades which illustrates higher resistance to fatigue cracking. CRM-UMO decreased the low-temperature binder stiffness between 35% and 56% indicating enhanced resistance to thermal cracking.

Environmental concerns were evaluated through gas chromatography to monitor the concentration of BTEX components during mix construction and leaching test (TCLP) to determine field performance. Results indicated a decrease of BTEX in air over interaction time. The concentrations of benzene and \( m-, p-\)Xylene increased with the addition of CRM to the neat asphalt binders. Samples modified with CRM-UMO combinations showed delays in releasing BTEX components, as expected due to absorption then the slow release of UMO by CRM particles. Batch leaching test results showed that the neat asphalt mixture had other leachate components such as chromium, lead, sulfur, iron and copper. Furthermore, both neat and CRM mixtures had approximately the same leachate composition while asphalt mixtures modified with CRM-UMO combinations had higher percentages of sulfur present. It is remarkable that all the metals were below EPA maximum standards.

This study confirms that engineered CRM-UMO combinations can regulate the rheological properties of asphalt binders without causing harm to the environment. It is recommended that UMO percentage be less than 3%, and that UMO should be used only after testing random samples collected from different sources to ensure that air emissions and leachate are within applicable regulations.


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Conflicts of Interest: The authors declare no conflict of interest.
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