Characterization of Rejuvenated Asphalt Binders Using FTIR and AFM Techniques

Rayhan Bin Ahmed and Kamal Hossain

Abstract This study investigates the chemical and morphological behavior of rejuvenated asphalt binders. A TFOT aged PG 58-28 binder was mixed with three different types of rejuvenators that include waste cooking oil/untreated used cooking oil (UT), treated used oil (TR), and Hydrolene (HL) at 3, 6, and 9% by the weight of the total binder. To understand the characteristics and the performance of these rejuvenators, three sets of characterization tests were conducted: rheological, chemical, and morphological. This paper presents a summary of the results from our chemical and morphological studies. Gas Chromatography-Mass Spectroscopy (GC-MS) was conducted to identify the chemical composition of rejuvenators, while Fourier Transformed Infrared Spectroscopy (FTIR) was conducted for obtaining chemical functional group information. Furthermore, an Atomic Force Microscopy (AFM) was employed to obtain the micro-morphological properties of rejuvenated asphalt binders. The collected data showed that rejuvenation changes the chemical composition and alters the micro-structures of binders significantly, which impacts the overall performances of binder. In fact, this experimental study showed a good correlation between chemical compositional and morphological features with the rheological performance of the binder. The research findings are expected to contribute to the performance evaluation and characterization of rejuvenated asphalt mixes.

Keywords Reclaimed asphalt pavement (RAP) · Aged binder · Rejuvenating agent · Chemical composition · Morphology

1 Introduction

Over the last few decades, the necessity for developing a sustainable method of pavement construction has led to the increase use of recycled materials. In general, reclaimed asphalt pavement (RAP) is the major source of recycled materials that can be used for pavement construction. However, RAP materials are aged, which

R. B. Ahmed (✉) · K. Hossain
Advanced Road and Transportation Engineering Lab (ARTEL), Department of Civil Engineering, Memorial University, St. John's, NF, Canada
e-mail: rbahmed@mun.ca

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may lead to pavement distress and early cracking in the pavement [1]. Therefore, it is recommended to use rejuvenators to improve the performance of the aged binder after reducing its viscosity [2]. When we use rejuvenator during recycling, one of the underlying questions is how rejuvenation helps to retrieve these properties and unfortunately the answer is still not clear. Therefore, this effort is designed to obtain an understanding of how the chemistry and microstructure of an asphalt binder changes as the rejuvenator is added with the aged binder.

FTIR is the most widely used technique to obtain an understanding of chemical properties and the functional groups of asphalt binders. Recently, in the USA, Hossain et al. [3] investigated the effect of different additives on the performance of asphalt binders using FTIR. This study reports a significant correlation between the chemical compositions of asphalt binder with its rheological properties. For asphalt microstructure analysis, researchers across the world have increasingly been using the AFM technique [4]. Many studies made significant observations on how these microstructures are associated with asphalt morphology and rheological performance [5]. Most of the studies in this area found a good correlation between the formations of microstructure (bee structure) with the modification/rejuvenation of binders. Differing observations were also reported by some studies [6]. Despite these researches, still, there is a knowledge gap on how rejuvenation affects the asphalt morphology and microstructure. Therefore, this research attempts to generate a better understanding of this topic area.

During the research project, the authors completed a comprehensive review to find out the existing literature gap on rejuvenated asphalt binders, which was reported in [7]. Based on the comprehensive review, the following objectives have been set for this study:

- To investigate the chemical characteristics of rejuvenators that affects the properties of asphalt using GC-MS and FTIR techniques
- To understand the effect of rejuvenators on the morphological features of asphalt at micro-level through AFM analysis.

2 Experimental Design

2.1 Material Collection

The PG 58-28 binder is selected for this study which is generally used in the southern region of Newfoundland and Labrador, Canada. The Thin Film Oven (TFO) test was employed to prepare the laboratory simulated aged binder as per the guideline of ASTM D1754. Rejuvenators studied in this research are used cooking oil and Hydrolene (HL). Used cooking oil has been studied in two forms: (1) collected raw oil/untreated oil (UT) and (2) chemically processed oil/treated oil (TR).

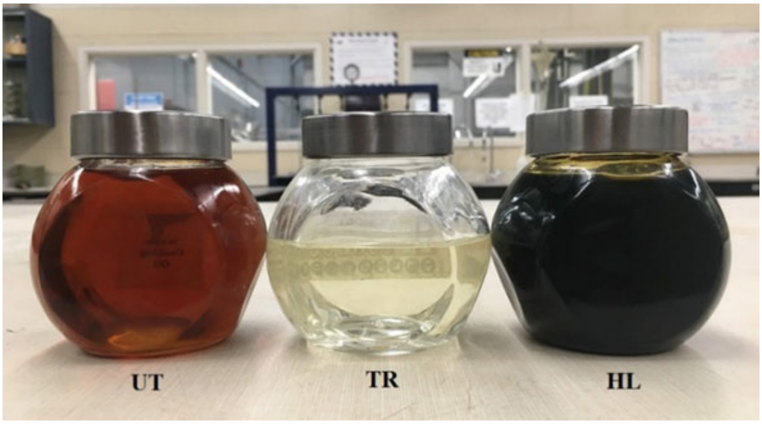

Fig. 1 Types of rejuvenators

2.2 Chemical Characterization and Modification

The chemical properties of rejuvenators are the fundamental characteristics that dominate the behavior of asphalt. HL is a commercially available material and its fundamental properties are well-known. However, UT is a used oil whose fundamental properties are still unknown, and it varies based on its source and use. One of the major properties for the used oil is the existence of free fatty acids (FFA) which weakens the adhesion with bitumen and reduces the binder adhesive properties. GC-MS is one of the widely used techniques to quantify the composition of fats and oils. This study investigates the chemical composition of UT using the methylation procedure for GC-MS analysis as per ISO 12966-2:2017. Based on the GC-MS result, the molecular components of UT contain both polar (–CH_2–) and non-polar (–COO–) ends, which denotes that molecules are hydrophilic and have a strong affinity to water. This affinity has a harmful effect on the overall moisture susceptibility of asphalt. To reduce these FFA contents, the transesterification method has been employed [8] and used to prepare the TR rejuvenator used in this project. Later, the acid value test was also conducted as per ASTM D5555 to observe the change of acid value before and after transesterification process. The test found the acid value of TR reduces to 1.95 mL/g from 5.45 mL/g for the UT sample. All types of rejuvenators, including UT, TR, and HL are shown in Fig. 1.

2.3 Blending of Rejuvenators and Asphalt Binder

A rejuvenated asphalt binder was prepared by mixing aged binder with three rejuvenators UT, TR, and HL at the concentrations of 3, 6, and 9% respectively by the weight of base asphalt. The blending process was done manually with a glass stirrer for 30 min at 100 °C.

3 Results and Discussion

3.1 *Effect of Rejuvenators on Asphalt Oxidative Potential*

The functional groups of rejuvenated asphalt binders were analyzed by IR spectrum table. For clarity, only the binder with 3 and 6% rejuvenation has been presented in Fig. 2. Out of the region specified, 1032 cm^{-1} and 1744 cm^{-1} bands correspond to sulfoxide (S=O) and carbonyl (C=O) respectively, which reflects the aging and rejuvenating degree of asphalt [9]. The intensity of C=O bond increases with the increase of UT dosages. However, this peak intensity decreased gradually for increasing dosages of HL and 9% HL shows the lowest peak. According to the literature review, this C=O bond is a saturated aliph and it is responsible for making the binder softer, which is more prone to rutting [10]. Also, this peak intensity was recorded 0.0176, 0.0171, and 0.0189 for 3, 6, and 9% TR rejuvenated sample. This result is consistent with our previous analysis, as 6% TR shows higher stiffness. Also, the peak intensity of Sulfoxide (S=O) is higher for TR samples compared to others. The presence of C=C aromatic bond was detected at 1452 cm^{-1} for all the samples which exhibit a strong bonding of the constituents. For aged asphalt, the intensity was 0.279, whereas for UT, TR and H sample, the intensity was highest for TR samples.

Another C–O alcohol peak was found at 1161.15 cm^{-1} wavelength, which was only observed for UT rejuvenated samples, not in TR and HL samples due to the chemical modification after the transesterification process. Therefore, the conclusion drawn from the FTIR spectrum analysis is that the chemical constituents of binder can be changed with different rejuvenator types and the modification of rejuvenator. Quality improvement has a notable influence on the rejuvenation property and the overall performance of the binder as well.

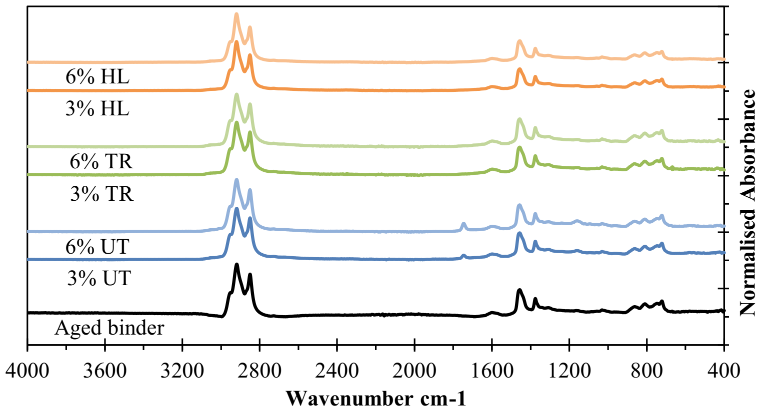

Fig. 2 Normalized FTIR spectra of aged, UT, TR, and HL rejuvenated binder

3.2 *Effect of Rejuvenators on Asphalt Morphologies*

Figure 3 shows the micrographs of 3 and 6% rejuvenated sample topography with their phase images. For the aged sample, a combination of different sized bee structure (small and large bees) was observed in the topographic image. In general, one can also easily notice that the aged specimen exhibited a fewer number of bees than specimens with rejuvenators. Also, some white spots are present in both topographic and perpetua domain of the phase image, which might be due to the aging of binder. For 3% UT sample (Fig. 3b), the size of the bee structures decreased compared to the aged binder. When the concentrations increased from 3 to 6%, the quantity of bee structure decreased but a larger sized bee structure was observed. In case of 6% UT, the phase contrast between the two phases changed significantly compared to 3% UT

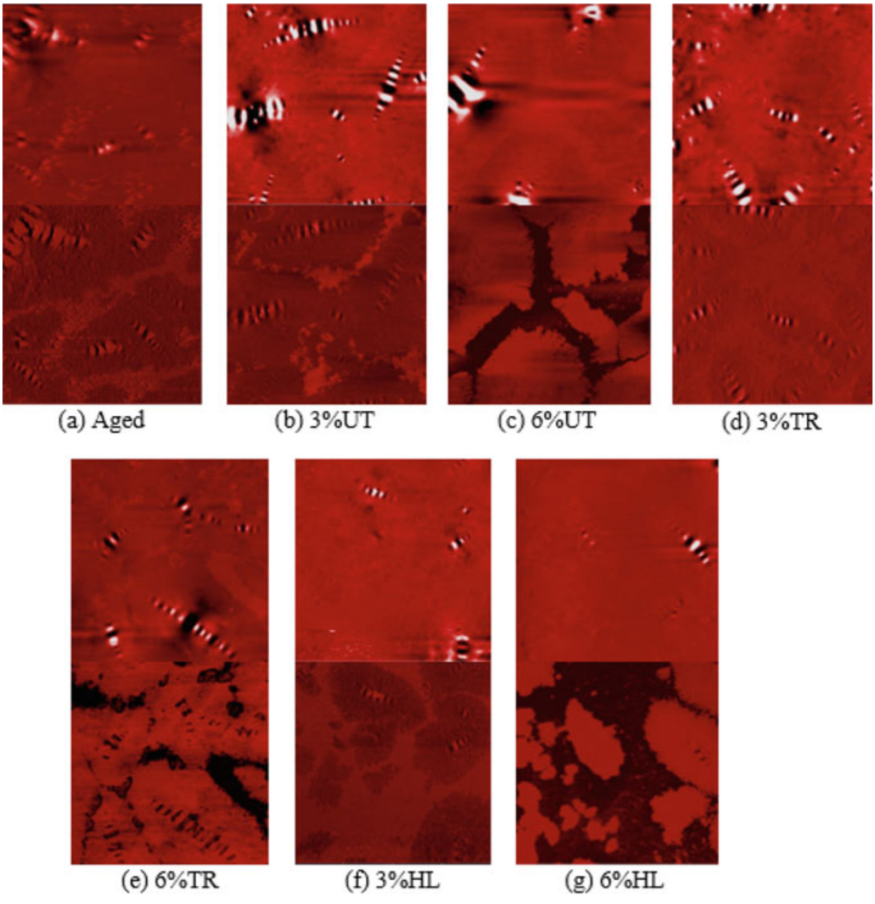

Fig. 3 Topography (top) and phase (bottom) images of different rejuvenated binders. Image dimensions are 10 μm × 10 μm; topography image scale 155.6 nm; phase image scale 34°

sample. The brighter phase represents the higher phase lag which will enhance the viscous behavior of the binder. Also, a dark region was observed for 6% UT in Fig. 3c, which might be "sal" phase mentioned by Masson et al. [11]. For the 3% TR sample (Fig. 3d), a significant increase of bee structures was observed compared to aged and UT samples, which denotes the higher stiffness of the binder. In the case of 6% TR, a reduced quantity of bee structures with reduced size was observed. However, in phase image, a clear disperse and a matrix phase was available for 3% TR samples. In topographic image, "sal" phases are visible for 6% TR which is identical to 6% UT. The HL rejuvenated samples in Fig. 3f–g exhibited the lowest bee structures. In addition, 6% HL rejuvenated asphalt shows a higher brighter phase which is responsible for the enhanced loss moduli and higher viscous property of asphalt. Based on the topographic and phase image analysis, it can be observed that the increase of rejuvenation dosage changes the microstructures and the phase contrast of the binders. This indicates a change in morphology of binders after rejuvenation.

4 Conclusions

Based on the experimental study, the following conclusions can be drawn:

- Free fatty acids (FFA) was observed in the UT rejuvenator by GC-MS analysis, which enhances hydrophilic characteristics and moisture susceptibility of asphalt binder. Therefore, it is required to reduce the FFA contents.
- The chemical modification of UT influenced the rejuvenation behavior with aged asphalt, and higher quality of UT (lower FFA) may lead to better pavement performance.
- FTIR test results exhibited a higher rate of C=O stretch at 1744 cm^{-1} for UT, which is responsible for softening the binder and inducing rutting failure. In contrast, this stretch was very negligible for other binders and therefore shows better stiffness. The result was also consistent with the stiffness trend found at the viscosity test.
- From the AFM analysis, the decreased number of bees, with the increase of bee size, was observed for the increased dosages of rejuvenation. The higher bee structure was found for TR rejuvenated sample which was consistent with the past rheological test.
- Based on the phase contrast of different samples, the higher percentages of rejuvenation show a brighter phase image which indicates the higher loss modulus. Therefore, rejuvenation of the aged binder significantly changes the morphological features.

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