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Aging Influence on Chemical Properties of Palm Oil Mill Sludge Modified Asphalt Binder

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Abstract: The usage of asphalt binder as a primary component of the surface course required a high cost although used in a lower percentage besides it is a non-renewable substance. The present binder materials, on the other hand, have a problem with bitumen ageing. As a result, a lot of research is focusing on changing the asphalt binder to reduce the reliance on this non-renewable substance and its effect to the chemical composition of the asphalt binder changes owing to oxidation. This study presents the physical properties of unmodified and modified asphalt binder follows with quantify the effect of aging on chemical properties of palm oil mill sludge (POMS) modified asphalt binder. The PEN 60/70 was used in this study as a control sample while percentage of POMS varies from 0% to 5%. Three tests were conducted to investigate the properties of unmodified and modified asphalt binder, these include penetration, softening point and Fourier Transform Infrared Spectroscopy (FTIR) test. The findings showed that the POMS modified asphalt binder is soften throughout the addition of percent. It indicates that the POMS modified asphalt binder has a high temperature susceptibility. The effect of aging also has proved to be delayed throughout the addition of 4% of POMS modified asphalt binder. Future study on the rheological characteristic can be made in determining the performance of asphalt binder under certain range temperature.

Keywords: Aging, Chemical Composition, POMS Modified Asphalt Binder

1. Introduction

Malaysia has been one of the main producers and exporters of palm oil products in recent decades [1]. Every year, the number of palm oil mills (POM) expands, resulting in an increase in the volume of effluent discharge and POM waste into the environment. The palm oil mill sludge (POMS) is a highly polluting material that contributes significantly to environmental contamination in Malaysia as a result of the oil extraction process [2]. Before being released into the wild, the POMS must undergo a successful and efficient treatment. Unfortunately, because a large amount of palm oil sludge is produced

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at a time, treatment of this wastewater is expensive and difficult to manage [3]. The present binder materials, on the other hand, have a problem with bitumen ageing. The impact of ageing is that it diminishes the pavement's performance and durability while also affecting its cracking resistance [4]. Due to changes in the viscoelastic behavior of the materials over time, the problem of asphalt binder ageing will also have a significant impact on stiffness and brittleness [5]. The asphalt pavement will suffer as a result of this.

Recycling's economic and environmental benefits have led to an increase in the use of recycled materials in asphalt binders. The majority of research into the use of biomass, such as palm oil, has improved its low-temperature performance as well as its resistance to deformation at high temperatures [6]. Because the modifier softens the asphalt binder, palm oil mill sludge (POMS) as a biomass or bio-waste material is thought to improve moisture susceptibility and cracking resistance to a degree of temperature. According to [6], earlier study on the rheological properties of bio-asphalt binder has indicated that the composite adjustment improves low and high temperature performance. Previous investigations of asphalt binder modification using palm oil waste which is POFA have shown that it improves the performance of the asphalt binder over its service life [7]. The proportion employed in the alteration will also have an effect on its performance. According to the findings of the tests, adding POFA to the binder improves the binder's resistance to oxidative ageing.

POMS modified binder is a superior approach for POMS treatment since it can be used as a raw material to make value products. POMS make it an excellent raw material for bioconversion employing a variety of biotechnology methods. As a result, POMS is a substance that can be employed as a recycling binder in an asphalt binder modification to address ageing, deformation, cost, and environmental concerns in asphalt pavement construction [6]. The POMS modified asphalt binder is thought to increase asphalt pavement performance while also helping to solve the environmental challenge. The addition of POMS as a modifier changed the chemical structure of the asphalt binder, which was supposed to soften it and results in improvement on its aging process[6].

The aim of this study is to compare the physical properties of unmodified and POMS modified asphalt binder as well as to observed the effect on chemical properties in short term aging. This study will investigate the suitability of POMS as a modifier to asphalt binders and in which percent gives the best results to suit and perform well as asphalt pavement. This study is focused on the laboratory investigations on the properties of unmodified and POMS modified asphalt binder and its effectiveness to improve its properties and performance throughout the addition percentage of POMS into asphalt binder. The POMS used to modify the asphalt binder are in 0% to 5% while asphalt binder PEN 60/70 is used as a control binder. The laboratory testing was conducted includes penetration, softening and FTIR test to evaluate its properties and investigate its behavior throughout the addition percentage of POMS.

2. Materials and Methods

The study was conducted to investigate the effects of modification of asphalt binder with POMS on the properties of this modified asphalt binder. This section discussed the specifics of the materials utilized, sample preparation, and experimental methods employed to achieve the study's principal goals. The material was chosen in accordance with current Malaysian practice. The laboratory testing specification and technique are based on the American Society for Testing and Materials (ASTM) and Malaysian Standard (MS)

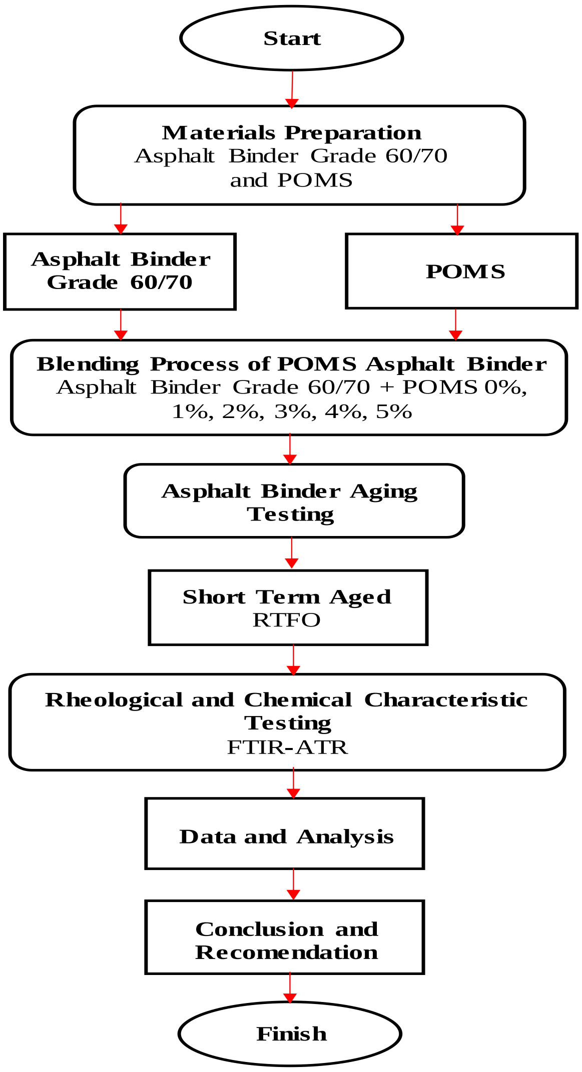

Figure 1: Flow process of the experiments

2.1 Materials

In this investigation, there were two main materials employed. Asphalt binder with a penetration grade of 60/70, as well as palm oil mill sludge (POMS) as a modifier, were used. Asphalt binder with penetration grade of 60/70 used in this study was supplied by Kemaman Bitumen Company (KBC). In an asphalt binder, POMS with different proportions of POMS (0%, 1%, 2%, 3%, 4% and 5%) by total weight of the asphalt binder were used for this study.

2.2 Methods

The modified asphalt binder was created first by blending different POMS (0%, 1%, 2%, 3%, 4% and 5%) with an asphalt binder penetration grade of 60/70 using a Silverson mixer. The modified asphalt binder was combined in a Silverson mixer with a hot plate at 160°C mixing temperature, 30 minutes mixing time, and 800 rpm mixing steering speed [8]. The asphalt binder was left heated until it reached 160 °C then the POMS were added gradually. The mixture was let until well blended for 30 minutes.

The further testing on its properties were conducted after all six different proportion of POMS modified asphalt binder were made. The physical properties of unmodified and modified asphalt binder were tested by performing a penetration and softening point test. The penetration testing followed the American Society for Testing and Materials (ASTM) D5 procedure (American Society for Testing

Materials, 2013a). Before testing, the asphalt binder sample was melted in a water bath for 1 to 1.5 hours and chilled under regulated conditions. The penetration was carried out using a specific needle under standard temperature, time, and loading parameters of 25°C, 5 seconds, and 100 g, respectively. In tenths of a millimeter (deci-millimeter, dmm), the penetration was measured. The penetration needle firstly is positioned at the tip of the surface and the loading is released to observe it penetration value. Three determination was made on the surface of samples at least 10 mm from the container's side and at least 10 mm apart.

The Ring and Ball test is another name for the softening point test was carried out in accordance with ASTM D36 (American Society for Testing Materials, 2014) guidelines. The asphalt binder was heated in the oven at 100°C for not more than 30 minutes until it became suitably pourable. The bitumen then be poured into the rings and left to cool for at least 30 minutes. The top of the specimen was cut off after cooling, and it was then set on a flat smooth brass plate with ball centering guides and a thermometer in place. After all were set in place, the beaker was filled with distilled water to a depth of not less than 102 mm and not more than 108 mm and held at 5°C for 15 minutes. Heat was applied until the temperature was gradually increased 5℃ per minute until the ball could penetrate through the asphalt and sag downward at a distance of 25 mm at which temperature point was recorded as the softening point.

The short-term ageing of POMS modified asphalt binder in this study was simulated by rolling thin-film oven (RTFO). The oxidative ageing time chosen for the rolling thin-film oven (RTFO) test is 75 minutes at a temperature of 163 ℃ to bring the asphalt binder into a short-term-aging state [9]. An open cylindrical glass bottle with a diameter of 64 mm and a height of 140 mm was filled with 35 grams of asphalt samples. The samples are then promptly introduced into the RTFO, which has been preheated to 163 ℃ and then rotated at 15 revolutions per minute. At the same time, 4000 mL/minute of hot air was continuously blasted in [10].

The chemical functional and structural changes in a medium were determined using Fourier Transform Infrared Spectroscopy (FTIR) [11]. The chemical research of unmodified and POMS modified binder under unaged and short-term aged conditions was conducted using FTIR-ATR (Attenuated Total Reflectance). Before each measurement, a background scan was carried out. The acquisition parameters were adjusted to 32 scans [9] a resolution of 4 cm^{-1}, and a wavenumber range of 600 to 4000 cm^{-1} for the reflective mode of test [10]. A 20g asphalt binder was preheat for not more than 10 minutes at 163 ℃ in a sealed container [9]. The aging asphalt was directly sampled in the flowing state at the end of the aging simulation experiment to avoid from reheating and prevent any further change in chemical composition of the binder. The optics first need to be cleaned with an organic solvent to remove any leftover binder is followed by sweeping any remaining solvents with acetone. The preheat binder was applied directly to the FTIR optics in a tiny bulk using a spatula. To evaluate the change in chemical composition caused by simulated oxidative ageing, all spectra were analyzed. Changes in the carbonyl and sulfoxide groups are taken into account.

3. Results and Discussion

This results from laboratory testing were observe in order to relates to the aim of this study. The results explained the data and evaluation of physical properties of unmodified and POMS modified asphalt binder as well as chemical properties and its effect to the aging. For easier comparison and comprehension, the results were displayed in graphs and tables.

3.1 Penetration Test

Figure 2 shows the penetration value of unmodified and POMS modified asphalt binder. The penetration test value was observed increases with the addition of POMS to the asphalt binder, rising from 67.7mm in the unmodified to 87.8mm in the 5% of POMS addition. The higher value of penetration has described that the hardness of the asphalt binder is lowering. The modified asphalt binder become softer as more percentage of POMS is blended with the asphalt binder. This results is supported by previous researcher where it is found that the addition of bio-oil into asphalt binder will increased the penetration value [12]. The penetration grade started at 4% POMS also was observed to change from PEN60/70 to PEN80/100 in which the value lies within range of 80 to 100 according to MS124.

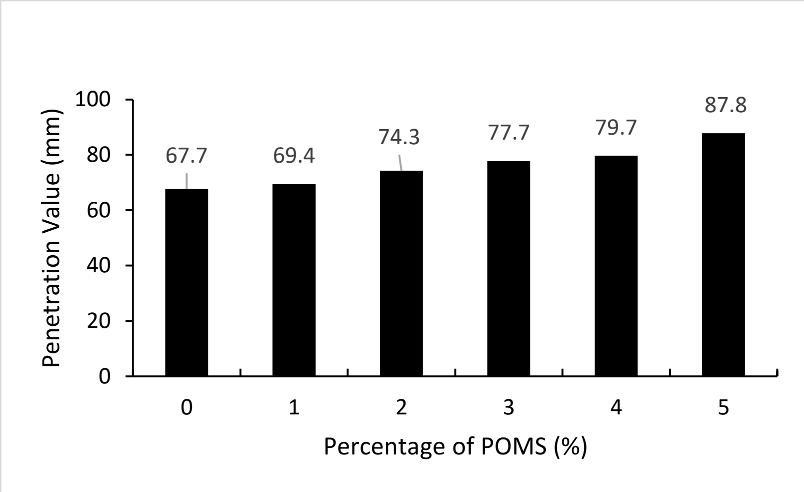

Figure 2: Penetration value of unmodified and POMS modified asphalt binder.

3.3 Softening Point

The softening point of unmodified and POMS modified asphalt binder has shown that it decreasing throughout the addition of POMS percent into asphalt binder as illustrates in Figure 3. The temperature in which asphalt binder to change its physical state to flowing under weight of steel ball were recorded as its softening point. As shown in the Figure 3, the average softening point value of unmodified asphalt binder is 55.5 °C in which it is in range as MS specification for asphalt binder PEN 60/70. The softening point were gradually decreasing until 51.6°C at 5% addition of POMS. This study showed that the addition of POMS to asphalt binder is suitable for a lower temperature condition, since it has a high temperature susceptibility, which will improve the deformation when temperatures are high.

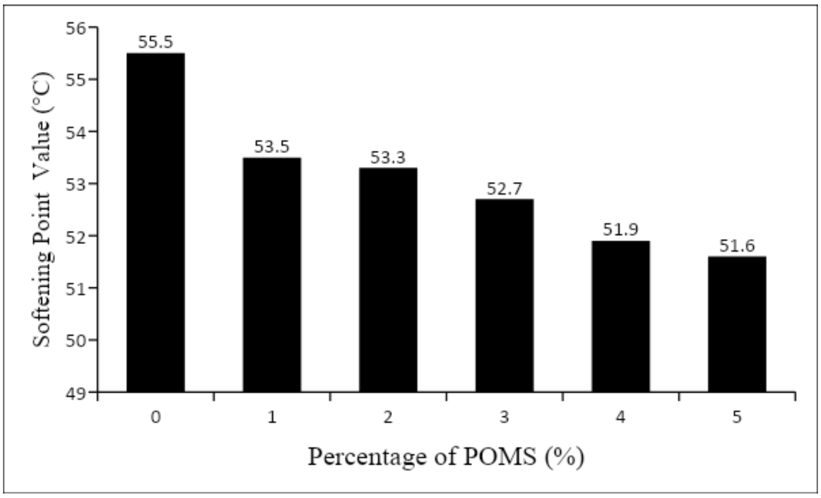

Figure 3: Softening point of unmodified and POMS modified asphalt binder

3.4 Chemical Properties

The structural alterations and chemical functions of carbonyl (C=O) and sulfoxide (S=O) groups are studied using infrared vibration modes [13]. Figure 4 and Figure 5 shows the FTIR absorbance spectra for carbonyl and sulfoxide group for unmodified and POMS modified asphalt binder under unaged and short-term age respectively. The chemical bonding for the POMS modified asphalt binder in varied percentages under simulation of unaged and STA has no significant variation, according to the findings. Most of the chemical bonds that were present at peak in the original asphalt binder are also present in the modified asphalt binder, although their absorbance is slightly altered. The chemical bond group presence at peak in the original and modified asphalt binder under unaged and STA condition are hydrocarbon CH (stretching vibration) 2851 – 2921 cm^{-1}, carbonyl group C=O (stretching vibrations) 1598 – 1600 cm^{-1}, Alkene C=C (stretching vibrations) 1598 – 1600 cm^{-1}, hydrocarbon (bending vibration) 1455 – 1458 cm^{-1}, Ether C-O-C, alcohols C-OH (stretching vibration) 1032 – 1057 cm^{-1}. At wavenumbers of 1030 cm^{-1} and 1700 cm^{-1}, the absorbance spectra of unaged and STA treated asphalt binder. In comparison to the carbonyl group, both unaged and STA treated asphalt binder gained a high amount in the sulfoxide group, as seen in the spectra. It is because the high content of sulfur in asphalt binder [5].

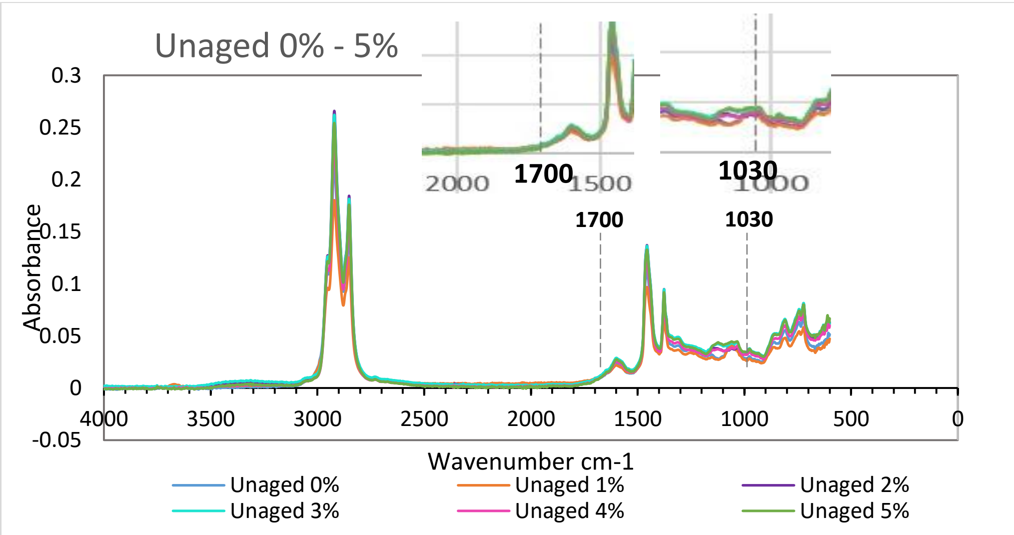

Figure 4: FTIR absorbance spectra for carbonyl and sulfoxide group for unmodified and POMS modified asphalt binder (unaged)

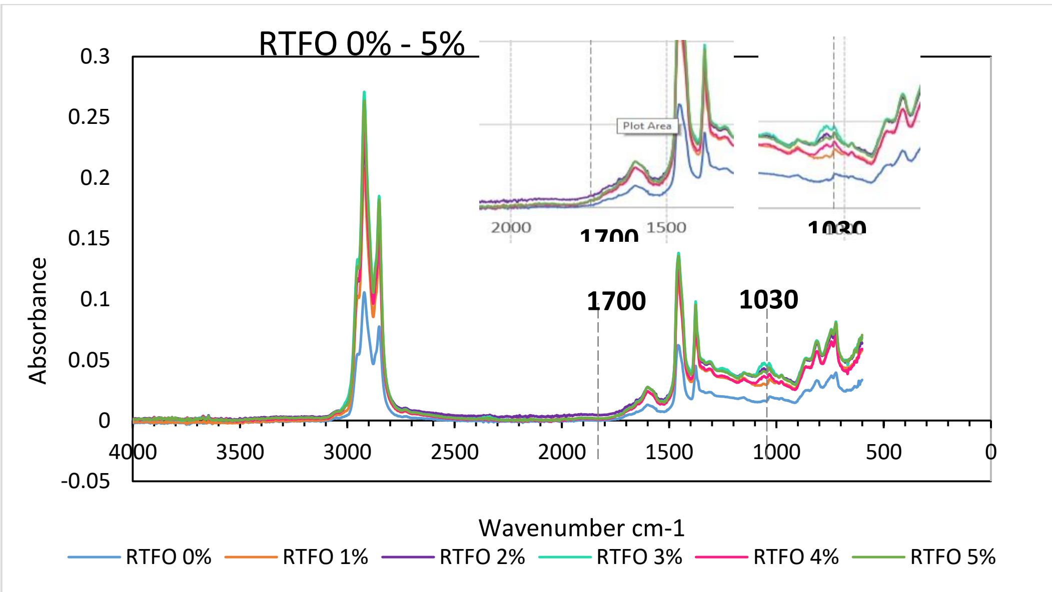

Figure 5: FTIR absorbance spectra for carbonyl and sulfoxide group for unmodified and POMS modified asphalt binder (unaged)

The presence of C=O absorption at 1700 cm^{-1} indicates the presence of the carbonyl group, while the presence of S=O absorption at 1030 cm^{-1} indicates the presence of the sulfoxide group. This region is investigated to determine the carbonyl and sulfoxide groups as indicators of asphalt ageing performance before and after the ageing process. The carbonyl function group is used to determine the degree of oxidation during the ageing of a binder [13]. The value of absorbance for sulfoxide and carbonyl group for unaged and STA condition is shown respectively in Table 1 and Table 2. As shown in Table 1, the detection of carbonyl group in un-aged asphalt binder is consistently decreasing except at 3% POMS, whereas in short-term aged asphalt binder, it is spotted to be increasing until 2% POMS, decreasing through addition percent of POMS, and increasing back at 5% addition of POMS as in Table 2.

Table 1: Carbonyl and sulfoxide absorbance value for unmodified and POMS modified asphalt binder (unaged)

POMS percentage	**0%**	**1%**	**2%**	**3%**	**4%**	**5%**
Carbonyl Absorbance	0.0175	0.0093	0.0085	0.0093	0.0084	0.0073
Sulfoxide Absorbance	0.0372	0.0362	0.0385	0.0398	0.0464	0.0394

Table 2: Carbonyl and sulfoxide absorbance value for unmodified and POMS modified asphalt binder (STA)

POMS percentage	**0%**	**1%**	**2%**	**3%**	**4%**	**5%**
Carbonyl Absorbance	0.0079	0.0114	0.012	0.0108	0.0100	0.0108
Sulfoxide Absorbance	0.0287	0.0349	0.0438	0.0497	0.0482	0.0505

A clear comparison graph illustrates as in Figure 6 and Figure 7. The absorbance amount of carbonyl and sulfoxide group in unmodified and various percentage of POMS modified asphalt binder were compared between unaged and STA condition. According to the graph in Figure 6, the sulfoxide group was observed had a steady absorbance value throughout the addition of POMS, with the exception of 4%, which increased somewhat for un-aged. Except for the POMS at 4%, the sulfoxide group in STA is growing. Figure 7 shows that the carbonyl group in the un-aged condition decreases as POMS is added, whereas the carbonyl group in the STA condition increases until POMS is added at 2% and then decreases. The addition of POMS to asphalt binder has been found to have an impact on chemical structures.

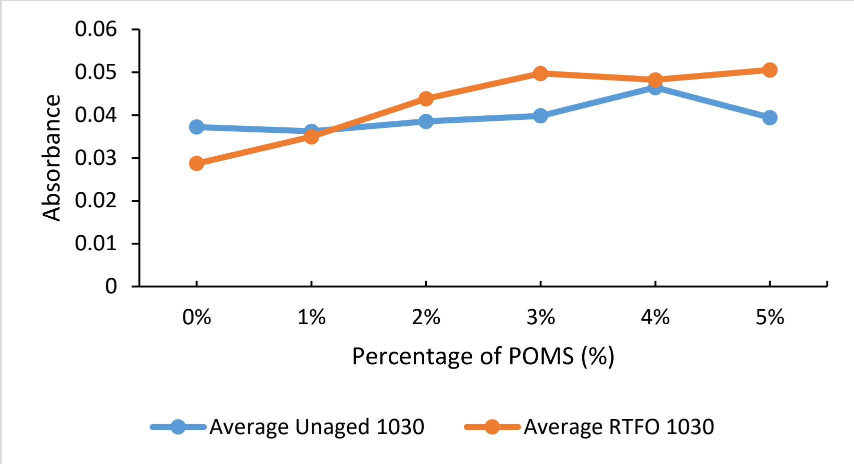

Figure 6: Comparison of sulfoxide absorbance for unaged and STA POMS modified asphalt binder

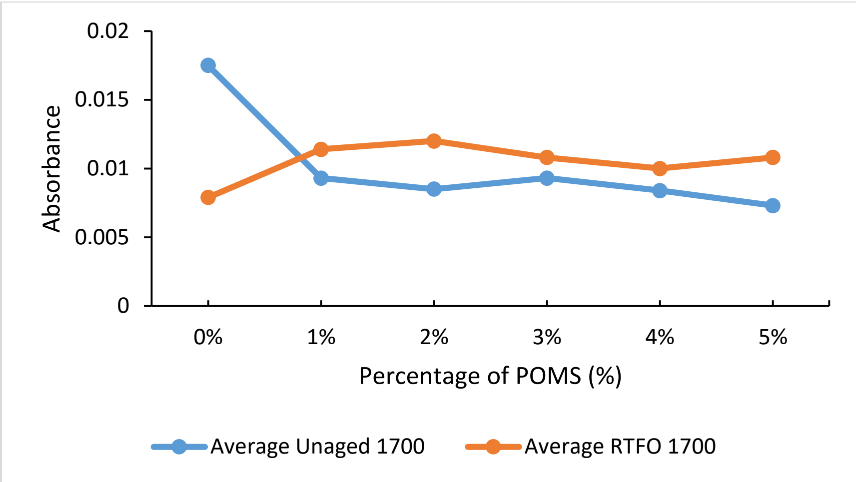

Figure 7: Comparison of carbonyl absorbance for unaged and STA POMS modified asphalt binder

Carbonyl absorbance increases as the ageing process progresses, as shown in both graphs. This indicates that the POMS modified asphalt binder undergoes an oxidation reaction during the manufacturing process. The oxidation process is detected in this study after the simulation under STA conditions utilizing the RTFO method. Because of the decreased carbonyl absorbance, adding a fraction of POMS additive to asphalt binder modifies its chemical composition, reducing the ageing process of the changed asphalt binder. It was discovered that adding the POMS additive to the asphalt binder changed the absorbance spectra and softened the asphalt binder.

4. Conclusion

Conclusions were drawn based on the overall findings of this research. With the addition of POMS, the penetration value and softening point of POMS modified asphalt binder changes. The penetration value increased progressively with the addition of POMS, but the softening point decreased as the amounts of POMS in the asphalt binder increased. The modified asphalt binder softened with the addition of the POMS ingredient and had a high temperature susceptibility, indicating that it is not suited for use in high-temperature conditions. The effect of adding POMS on the chemical characteristics of modified asphalt binder was examined. The addition of POMS to modified asphalt binder slows the ageing process, according to the findings.

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