Physical, Chemical and Thermal Properties of Palm Oil Boiler Ash/Rediset-Modified Asphalt Binder

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Abstract: The growth of the palm oil industry has resulted in an increase in the production of solid waste, created from the extraction of fresh fruit bunches, which can take the form of palm oil boiler ash (POBA). POBA can be used to modify asphalt binder and asphalt mixtures to reduce the harmful effect of this waste on the environment. The objective of each modification is to increase the strength, stiffness, durability, workability and constructability of asphalt mixtures while reducing the environmental effects. This study examines the physical and chemical properties of 60/70 penetration-grade asphalt binder, modified using POBA and warm mix asphalt (WMA) additive. Ranges of modified binder were prepared by adding 2% of the warm additive Rediset with different POBA contents (3%, 5%, 7% and 9%) throughout the wet mixing process. Physical properties of modified binder were obtained from penetration, softening point, ductility and rotational viscosity tests. Molecular components and structures of the modified binder were identified using Fourier transform infrared (FTIR) and scanning electron microscopy (SEM). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to determine the thermal properties of modified asphalt binder. The addition of 7% POBA in WMA binder showed the best characteristics in the tested consistency of its physical properties. As a modifier, POBA showed no chemical interaction with the molecules and structures of the asphalt binder and did not significantly change the physicochemical transitions. From the results, it can be concluded that using POBA in WMA binder for pavement construction is a viable option.

Keywords: physical properties; chemical properties; palm oil boiler ash; modified asphalt binder; warm mix asphalt

1. Introduction

In the palm oil industry, fresh fruit bunches (FFB) are required to create palm kernel oil (PKO), crude palm oil (CPO) and other biomass [1]. Through palm oil milling activities, these FFB produce several wastes, including liquid and solid waste. These solid wastes are harmful if not properly regulated and monitored, which can result in soil contamination, air and water pollution, and the release of greenhouse gases [2]. The use of these plant-derived
materials can ease the load on landfill in the region; one such use is their utilization in the modification of asphalt binders [3].

Various studies by different researchers and organizations have been conducted to utilize POBA in asphalt pavement as filler, fine aggregate or combination modifier, especially in hot mix asphalt. The utilization of 25% waste CPO ash as a filler in hot rolled sheet–wearing course mixture led to increased stability [4]. Agusmaniza [5] found that the use of combined palm oil shell ash (POSA) as filler and plastic substitution in asphalt concrete–wearing course mixtures can increase the value of stability and the Marshall quotient, with a 6.7% plastic and 5.8% POSA combination.

Ritonga et al. [6] modified asphalt mixtures with cyclic natural rubber (CNR) and palm oil shell ash as filler material, and found that the asphalt stability values increased with 80 g CNR additions and with an optimum asphalt binder content of 6% in the asphalt mixtures. Rizal et al. [7] investigated whether POBA can be used as reinforcement or filler in epoxy polymers, and they tested it as an alternative to silica-based inorganic fillers, used in order to improve the physical, mechanical and thermal characteristics.

In other industries, POBA can also substitute black carbon as a filler in the production of natural rubber compounds [8]. Besides that, POBA can be utilized as sand and cement replacement in concrete: it was found that an increase in the POBA replacement level in a cement mixture will linearly reduce the compressive strength of the concrete mixer [9]. POBA can also be used as an admixture in soil stabilization by mixing the variation of 6% POBA and 2% MATOS: this combination changes the California bearing ratio (CBR) value behavior; therefore, it is a viable soil stabilization solution [10].

POBA is a solid waste generated by the palm oil industry and it is an environmental issue. After CPO extraction, a massive amount of solid biomass waste is produced, primarily consisting of empty fruit bunches (EFB), palm-pressed fiber (PPF), and palm kernel shells (PKS). Approximately 1.77 tons of solid biomass waste is created for every ton of CPO production [11]. Based on the average palm oil mill’s capacity (10–60 tons FFB/h), an estimated 6–12 tons of solid biomass waste or 65–394 kg of ash is produced every hour [12].

If it is not handled correctly, then this enormous volume of solid waste poses a severe threat to the environment. The studies of Rusbintardjo et al. [13] and Babalghaith [14] showed that POBA is a solid waste that has a high silica (SiO$_2$) content, which has the potential to pollute the ground. Natural radioactive radiation can have harmful health consequences, such as genetic abnormalities and cancer, that will cause damage to generations to come—POBA is categorized as hazardous waste due to its carcinogenic properties for humans, where the level of natural radioactivity potassium $^{40}$K is higher than the standard average range [15].

POBA has been used as a geopolymer composite material [16], as a heavy metal absorbent in treating wastewater [17], as an absorbent of solvent-dispersed dyes [18], as a source of nutrients for fertilizer production [19], and as a coarse aggregate replacement in high-strength lightweight concrete [20]. POBA was shown to be able to eliminate 98% of carotenoids, thus producing refined oil colors equivalent to those generated by traditional bleaching earths [21]. Furthermore, the stiffness of POBA geopolymer brick was improved to a maximum strength of 16.1 MPa, making it a medium-weight, non-loading brick type [16]. Additionally, POBA’s high organic carbon content was shown to boost nutrient-absorption efficiency, resulting in higher crop quality [22]. These efforts, however, are not sufficient to make the palm oil industry waste-free. This is because wastes are still disposed of or left to degrade into the ground. This situation urges new inventions and in-depth research to turn POBA into a useful final product—especially in road construction industry applications—in order to reduce solid waste from the palm oil industry, lowering its negative environmental impact.

WMA additive has been developed to enable the production of asphalt mixtures at temperatures lower than conventional hot mix asphalt, thus leading to reductions in fuel consumption and emissions of pollutants and greenhouse gases. Previous researchers have found that WMA additives can enhance asphalt mixture characteristics, such as ageing,
viscosity and adhesion, in addition to lowering the mixing temperature. The objectives of this study were to investigate the physical and chemical properties of a 60/70 penetration-grade asphalt binder, modified with 2% of Rediset containing various percentages of POBA, and to determine the optimum percentage of POBA in the modified asphalt binder.

The unmodified asphalt binder (without POBA) was selected as the control mixture. The physical tests selected in this research included the test of the penetration, softening temperature, ductility and viscosity of the mixtures, while the chemical tests included FTIR to identify the chemical compounds, SEM to identify the elemental composition of POBA, TGA to calculate the kinematic parameters for thermal degradation, and DSC to evaluate the changes of physicochemical transition in the modified asphalt binder.

2. Materials and Methods

2.1. Asphalt Binder

A 60/70 penetration-grade asphalt binder was utilized in the study, which was supplied by Sunway Quarry Industries Sdn. Bhd. (Semenyih) in Selangor, Malaysia. The properties of the asphalt binder used in this research are shown in Table 1.

| Asphalt Binder Properties | Standard Test | Result | Specification |
|---------------------------|---------------|--------|---------------|
| Penetration (0.1 mm) at 25 °C | ASTM D5 | 67.00 | 60–70 |
| Softening point (°C) | ASTM D36 | 48.40 | min 47 |
| Ductility (mm) at 25 °C | ASTM D113 | >150 | min 100 |
| Flash point (°C) | ASTM D92 | 309.00 | min 250 |
| Penetration after thin film oven (0.1 mm) | ASTM D1754 | 66.00 | min 52 |
| Loss on heating (%), mass loss | ASTM D6 | <0.1 | max 0.2 |
| Solubility in trichloroethylene (%) | ASTM D2042 | 99.99 | min 99.0 |

2.2. Rediset

The additive used in this study was a liquid chemical warm additive, namely Rediset LQ-1200 (hereafter referred to as Rediset), produced by AkzoNobel Company. Rediset is known to improve performance, especially the tensile strength [23], the resistance to moisture damage [24], the anti-rutting properties [25], the stability [26], and the fatigue lifespan [27]. Rediset was added at the optimum content of 2% of the weight of the asphalt binder [28–31]. The physical properties of Rediset are presented in Table 2.

| Additive Properties | Index |
|---------------------|-------|
| Appearance at 25 °C | Liquid |
| Pour point (°C) | < −20 |
| Color | Dark brown |
| Odor | Slight |
| Solubility in water | Partly soluble |
| Boiling point (°C) | 215 |
| Flash point (°C) | 230 |
| Viscosity at 40 °C (mPa.s) | 135 |
| Density at 40 °C (g/cc) | 0.962 |

2.3. POBA

POBA was used in this research as the modifier material of the asphalt binder. POBA was obtained from Sedenak Palm Oil Mill in Johor, Malaysia. POBA consists of large particles, which include unburned kernels, nutshells, and fibers. POBA was obtained as a powder and sieved using a 0.15 mm (#100) sieve size.

Figure 1 shows the surface morphology of POBA. The formation showed a good distribution in the pore structure of silica sand (Electron Image 1) with 1000 times magnification.
With a 1500 times magnification, Electron Image 2 and 3 revealed an uneven surface with porous structure and flaky shape, demonstrating a highly absorbent surface. The sieving process altered the characteristics of POBA. The elemental composition of POBA, evaluated by scanning electron microscopy, is shown in Table 3. It was also seen that the carbon content in the POBA was closer to the carbon content in the petroleum-based asphalt binder. That could indicate the compatibility of POBA with asphalt binder and its behavior could be similar to the asphalt. On the other hand, the oxygen content in POBA was much higher compared with the asphalt, which is expected, because the POBA material is derived from biomass resources as an organic material. However, compared with most of the biomass materials that contain oxygen content between 15% and 45%, the average oxygen content of 14% in POBA is considered below the normal range of oxygen in most biomass materials that have been used as modifiers for asphalt binder. Therefore, POBA-modified asphalt is expected to have an adequate aging resistance.

![Figure 1](image1.png)

**Figure 1.** Scanning electron microscopy images of POBA.

| Elements         | Weight (%) |
|------------------|------------|
| Carbon (C)       | 76–84      |
| Oxygen (O)       | 11–16      |
| Silicon (Si)     | 0.3–3.0    |
| Potassium (K)    | 0.8–2.1    |
| Calcium (Ca)     | 0.8–2.4    |
| Magnesium (Mg)   | 0.4–1.1    |
| Phosphorus (P)   | 0.2–0.5    |
| Iron (Fe)        | 0.2–0.7    |
| Chlorine (Cl)    | 0.2        |
| Sulphur (S)      | 0.1–0.3    |
| Aluminum (Al)    | 0.1–0.3    |

2.4. Sample Preparation

For preparation of the modifier for this project, POBA was heated at 70 °C for 20 h (according to ASTM C70—20) in the oven and sieved through a 0.15 mm (#100) sieve size. During the preparations of the blending, asphalt binder was transferred into a 500 mL tin can then heated 155 °C for about 10 min to avoid hardening during the blending procedure and testing. Based on the specification of the product, the blending would be applied
beforehand, by adding Rediset into asphalt binder at 170 °C and mixing at 5000 rpm for 2 h to reach the homogeneity of the binder blending. The blending of the asphalt binder with POBA and Rediset was completed using a shear mixer and stirrer.

The blending procedure started with a small tin can, then, the preheated asphalt binder weight was measured before 10 g of Rediset and varied weights of POBA were added. The percentages of POBA in each binder investigated in this research was 0%, 3%, 5%, 7% and 9%. The mixing temperature of warm mix additive specification according to the literature is between 16 and 33 °C less than the temperature of hot mix asphalt. Even though WMA binder is produced in a temperature range of 100–140 °C, these temperatures are only applicable to virgin binder. As for modified binder, the mixing temperature can be higher than 140 °C [32,33]. In addition, trial-and-error procedures have been conducted to control the storage stability of the blends and to ensure the homogeneity of the blends containing POBA and Rediset.

2.5. Storage Stability

The modified asphalt binder’s stability when stored at high temperatures was determined using a storage stability test. The heated modified asphalt binder was put into a 25 mm diameter aluminum tube with a length of 140 mm, and then heated for 48 h at 163 °C. After cooling, the aluminum tube was sliced into three pieces. A softening point test was used to determine the asphalt binder portions from the tube’s top and bottom. Based on ASTM D36, the difference between softening points must be less than or equal to 2.5 °C to pass the test.

2.6. Physical Test

Consistency tests were carried out to determine the physical parameters of the mixtures, in order to discover whether POBA can be utilized to improve or maintain the asphalt binder’s characteristics. Physical tests, such as penetration, softening point and ductility, were carried out in accordance with ASTM D5-13, ASTM D36-14 and ASTM D113-07, respectively.

2.7. Viscosity

In this study, the viscosity test was conducted according to ASTM D4402-15. Temperatures ranging from 100 to 200 °C were used. For each round of the test, around 10 ± 1 g of binder were required. A sample chamber was filled with a hot asphalt binder, which was then kept in a thermos container at the correct test temperature (38–260 °C). The test was performed by spinning the spindle at 20 rpm.

2.8. Dimensional Analysis

Dimensional analysis is a technique for reducing the number of relevant variables in a physical issue by utilizing dimensional homogeneity [34]. In other words, it is an analysis of the connections between various physical quantities based on identification of their base quantities and their units of measurement. In this analysis, POBA—as the modifier binder—was the variable.

The viscosities of four asphalt binders, containing varying quantities of POBA, were evaluated in order to assess the efficiency of modifier in the asphalt binder system. The impact of POBA was assessed using rotational viscosity and viscosity-reduction efficiency (\(\nabla)\). \(\nabla\) was defined as the contribution of the POBA percentage (3%, 5%, 7% and 9%) to the viscosity-reduction rate; that is, the higher the viscosity-reduction efficiency, the greater the cost effectiveness of the mixture.

A non-dimensional viscosity index was also utilized to evaluate and describe the changing rate of the asphalt binder’s rheological properties with POBA and Rediset against the asphalt 60/70 with Rediset. The viscosity was formulated by Equations (1) and (2), as follows:
\[\eta_R = \frac{\nu}{\nu_c}\]  

(1)

and

\[\nabla \eta_R = \left(\frac{\delta \eta_R}{\delta R}\right) = \left(\frac{\Delta \eta_R}{\Delta R}\right) = \frac{\eta_R - \eta_c}{R}\]  

(2)

where \(\eta_R\)—the mixings relative viscosity; \(\nu\)—the binder mix viscosity; \(\nu_c\)—asphalt 60/70 plus Rediset viscosity; \(\nabla\eta\)—the non-dimensional viscosity index.

The activation energy \((E_a)\) of the flow was determined by the value of the asphalt binder viscosity over a predetermined temperature range.

In this research, the temperature range was set from 130 °C to 180 °C, with 10 °C increments. In addition, the activation energy of the flow was another index used to measure the temperature susceptibility of the asphalt binders. The calculation was based on Arrhenius equation, as per Equation (3):

\[\eta = Ae^{\frac{E_a}{RT}}\]  

(3)

By introducing the ln factor to both sides of the equation, Equation (3) becomes:

\[\ln \eta = \ln A + \ln e \times \left(\frac{E_a}{RT}\right)\]  

(4)

Since \(\ln e = 1\), Equation (4) can be arranged into:

\[\ln \eta = \left(\frac{E_a}{R}\right) \frac{1}{T} + \ln A\]  

(5)

In linear plot, the slope \((m)\) represents \(\left(\frac{E_a}{R}\right)\). Since \(R\) is a constant, \(E_a\) can be calculated straight away. A higher value of \(E_a\) means more energy is needed to make the material flow. For all types of asphalt binders, two dependent (\([\ln (V)]\)) and independent variables (\([\frac{1}{T}\] in \([K])\) were plotted. \(E_a\) values were obtained from the slope parameter multiplied by the constant \((A)\). The calculation of the change in the \(E_a\) of the asphalt 60/70 and Rediset–POBA blends is presented in Equation (6).

\[\text{Change in } E_{aT} = E_{a_{60/70}} - E_{a_{3\%5\%,7\%,\%}}\]  

(6)

The flow resistance of the asphalt binder decreased at lower \(E_a\). When the asphalt binder is less sensitive to temperature changes, it has lower \(E_a\), whereas a higher sensitivity to temperature changes indicates higher \(E_a\). A linear relationship between temperature and viscosity, referred to as the “\(A-VTS\)” relationship, is a transformation from the nonlinear relationship between the two parameters. The relationship is shown mathematically in Equation (7), as follows:

\[\log \log \eta = \begin{cases} 
A + VTS \log(T_R) & T_R > T_{\text{critical}} \\
1.095 & T_R \leq T_{\text{critical}}
\end{cases}\]  

(7)

where \(\eta\)—viscosity (mPas); \(A\)—intercept of temperature susceptibility relationship; \(VTS\)—slope of temperature susceptibility; \(T_R\)—temperature in Rankine; \(T_{\text{critical}}\)—temperature in Rankine at which the viscosity was equal to 0.27 mPas.

With reference to Equation (7), the slope of the curve represents the VTS and the intercept is \(A\). Flatter slope means a lower VTS, implying a reduced viscosity–temperature susceptibility of the asphalt binder to rutting distresses and thermal cracking.
2.9. Fourier Transform Infrared Test

The FTIR test is used to determine unknown materials, assess sample quality and investigate the individual elements in a mixture [35]. Some of the infrared (IR) light passing through an asphalt binder sample was absorbed by the asphalt binder components. Then, a series of absorption bands at a specific wave number were recorded as transmittance or absorbance against the wave number. The spectra depicts molecule absorption and transmission, resulting in a molecular fingerprint of the asphalt binder’s constituents [36]. The resulting wave number or wavelength indicates the existence of different functional groups. Wave numbers ranging from 4000 to 400 cm\(^{-1}\) were used to record the whole spectrum of the asphalt binder’s functional groups.

2.10. Thermogravimetric Analysis

TGA is an analytical technique for determining the physicochemical properties, thermal stability and volatile components fractions of materials by measuring the weight changes while a sample is heated at a constant rate; another definition of TGA is as a thermal analysis technique for measuring the mass of a sample over time, as the temperature changes [37].

TGA is applied on a device known as a thermogravimetric analyzer. This instrument can function at maximum 600 °C, for which, mass, temperature and time are considered as the three basic measurements. The analysis was conducted by utilizing thermogravimetric analyzer in a nitrogen protective environment, with heating and cooling speeds ranging from 0.001 K/min to 50 K/min. To begin the analysis, the asphalt binders’ sample was maintained at room temperature and kept in an aluminum cell. The sample was then heated from ambient temperature to 600 °C. A microbalance was used to track their weight reduction.

2.11. Differential Scanning Calorimetry

DSC analysis is a thermal analysis technique for determining the direct absorption of thermal energy in a sample during a controlled temperature increase or decrease, in which the heat flow into or out of a sample is monitored as a function of temperature or time [38]. Calorimetric analysis is a general approach for examining such a process, since chemical processes and many physical transitions are connected to the creation or consumption of heat.

It is the primary approach for measuring the thermal characteristics of materials in order to create a link between temperature and particular physical properties of materials, and it is the sole method of determining the enthalpy associated with the desired process directly [39]. When the sample was heated, the changes in the heat capacity of the asphalt binder were recorded as changes in the heat flow. The changes in structure (physicochemical processes), such as glass transition, melting, crystallization and oxidation phase changes, were identified.

2.12. Statistical Analysis

In this study, the results of the tests were computed using analysis of variance (ANOVA). ANOVA is a statistical test for finding differences in group means, when there is one parametric dependent variable and one or more independent variables. The one-way ANOVA technique was chosen for comparing the averages of two or more groups of samples, while also determining whether there is a correlation between them [40].

The results—statistically analyzed using the data analysis tools in Microsoft Excel, ANOVA, \(t\)-test, correlations and coefficient of variance—were included in testing the hypotheses in this study. ANOVA and \(t\)-test were used to study whether a group of data was different from the other groups. To run these analyses, three assumptions had been made. First, the independence assumption, stating that the elements of one group were not related to the other group of samples. The second was a normality assumption, of which the samples were randomly picked from the sample population’s normal distribution with
unknown population means. The equal variance assumption assumes that the variances of the two group’s populations are equal. If not, the means are no longer valid to measure the central tendency, and thus test will not be valid either. Figure 2 shows the experimental flowchart of this study.

Figure 2. The flowchart of experimental design.

3. Results and Discussion

3.1. Storage Stability

The results of the storage stability test of the modified asphalt binders, displayed in Table 4, show that the difference ratios were in the range 0.7–2.3, demonstrating the heat stability of the binders modified by POBA and Rediset. The modified asphalt binders passed the softening point criteria (the temperature differential between the bottom and top sections of test tube should be less than 2.5 °C), in accordance with ASTM-D7173—14.

Table 4. Storage stability results test of all binders.

| Sample | Top | Bottom | Difference |
|--------|-----|--------|------------|
| 0%     | 48.7| 51.1   | 2.4        |
| 3%     | 47.1| 46.3   | 0.8        |
| 5%     | 46.7| 48.7   | 2.0        |
| 7%     | 47.3| 46.6   | 0.7        |
| 9%     | 48.4| 46.1   | 2.3        |
3.2. Physical Tests

Table 5 describes the penetration value, which increased when asphalt 60/70 was blended with 2% of Rediset (without POBA added), indicating that the hardness of the binder increased when Rediset was added. The penetration value decreased when blended with 3% weight of POBA but increased when 5% of POBA added. While the decrement in the penetration value of 7% is not very much compared with 5%, the other blending with 9% showed a significant difference, with 72.48 dmm. This result means that adding between 5% and 9% of POBA to the asphalt binder could maintain the penetration value specifications for base asphalt specified by the Malaysian Public Works Department (PWD). The softening point value of the modified asphalt binder was slightly lower when incorporated with Rediset, decreasing from 48.40 to 48.00 °C.

Table 5. Summary of all physical tests on all binders.

| Experimental Test       | PWD Specifications | 0%   | 3%   | 5%   | 7%   | 9%   |
|-------------------------|-------------------|------|------|------|------|------|
| Penetration             | 60–70             | 75.28| 53.44| 68.16| 62.94| 72.48|
| Softening Point         | >47               | 48.00| 51.25| 45.20| 48.95| 48.10|
| Penetration Index       | −3–7              | −0.72| −0.74| −1.78| −0.93| −0.80|
| Ductility               | min 100           | >150 | 97.0 | 129.5| 110.5| 84.1 |

However, the softening point value increased when blended with 3% weight of POBA, then decreased slightly for 5%, but showed a consistent increment when higher weights of POBA (7% and 9%) were added. Nonetheless, the softening points were found to increase compared with the base binders; although the decrement of the softening point value of 5% was not significant compared with those at 0%, 7% and 9%, these results prove that the incorporation of POBA and Rediset into the asphalt binder would increase the softening temperature values.

The ductility value of the binder samples was not constant. However, generally, the ductility decreased with the addition of POBA, with the 3% and 9% having the smallest values. The control asphalt binder (0%) sample had the same ductility value as the base asphalt binder, more than 150 cm, and the samples with 5% and 7% had values above 100 cm. Meanwhile, the 3% and 9% samples both had a ductility value below the minimum of 100 cm. The lower ductility indicated that the modified binder became brittle and stiffer after modification. However, both 5% and 7%, in comparison, may have had better low-temperature performances.

The hypothesis was evaluated using a 0.05 level of significance (p-value) where there was no statistically significant change in the average value between the asphalt 60/70 with POBA and Rediset addition. Table 6 shows that, because the (p) was less than 0.05, the null hypothesis for the assumption of variance homogeneity was rejected, indicating that the difference between the asphalt binders was statistically significant, as established by the one-way ANOVA for all tests. This proves that the incorporation of POBA and Rediset into asphalt binder significantly altered its physical properties, and the tested combinations produced different results.
Table 6. ANOVA for the physical properties results.

| Source of Variation          | SS        | df  | MS        | F          | p-Value      | F crit  |
|-----------------------------|-----------|-----|-----------|------------|--------------|---------|
| Penetration                 |           |     |           |            |              |         |
| Between groups              | 1581.5697 | 5.00| 316.3139  | 182.7524   | $2.76277 \times 10^{-18}$ | 2.6207  |
| Within groups               | 41.5400   | 24.00| 1.7308    |            |              |         |
| Total                       | 1623.1097 | 29.00|           |            |              |         |
| Softening point             |           |     |           |            |              |         |
| Between groups              | 56.6200   | 5.00| 11.3240   | 388.2514   | $7.82198 \times 10^{-13}$ | 3.1059  |
| Within groups               | 0.3500    | 12.00| 0.0292    |            |              |         |
| Total                       | 56.9700   | 17.00|           |            |              |         |
| Ductility                   |           |     |           |            |              |         |
| Between groups              | 11,401.5444 | 5.00| 2280.3089 | 69.5346    | $1.93628 \times 10^{-8}$ | 3.1059  |
| Within groups               | 393.5267  | 12.00| 32.7939   |            |              |         |
| Total                       | 11,795.0711 | 17.00|           |            |              |         |

3.3. Viscosity Test

The temperature test began at 100 °C and ended at 200 °C, when the results were relatively constant, respectively. The viscosity value ranged from 100 °C to 130 °C, and the viscosity reading started to become constant when the temperature reached 180 °C. The rotational viscosity values for mixing and compaction temperatures were taken at 135 and 165 °C. Table 7 shows the rotational viscosity values of the control and modified binders. It can be seen that the viscosity of the modified binders increased up to 3% POBA, and then declined at the high POBA contents. Such a tendency of the viscosity to decline could be attributed to the reduction in the average amount of bitumen surrounding the added POBA. It may also be a result of the formation of a new structure of asphalt binder due to the occurrence of chemical reactions and physical dispersion phenomena. Another justification could be the clumping in the POBA, or the settlement of the filler materials in the binder blend at the high contents. Viscosity analysis by two-way ANOVA, presented in Table 8, found that with $p$-value < 0.05, the difference between groups was significant.

Table 7. Rotational viscosity tests on all binders.

| Viscosity Analysis                  | Temp | 0%   | 3%   | 5%   | 7%   | 9%   |
|-------------------------------------|------|------|------|------|------|------|
| Rotational viscosity (mPas)         |      |      |      |      |      |      |
| 135 °C                              | 752.33 | 770.83 | 734.33 | 718.17 | 711.67 |
| 165 °C                              | 295.17 | 338.00 | 313.17 | 270.17 | 254.50 |
| Penetration–viscosity number—PVN    | -    | 0.38 | 0.02 | 0.23 | 0.10 | 0.25 |
| Activation energy—$E_a$             | -    | 40.16 | 40.01 | 40.25 | 41.73 | 44.17 |
| Viscosity–temp. susceptibility—VTS  | -    | 1.8661 | 1.8562 | 1.8777 | 1.9515 | 2.0811 |

Table 8. Two-way ANOVA analysis for viscosity test.

| Source of Variation | SS            | df  | MS            | F              | p-Value       | F crit  |
|---------------------|---------------|-----|---------------|----------------|---------------|---------|
| Viscosity           | 1,473,640.0333 | 1.00| 1,473,640.0333 | 1,804,457.1837 | $4.92932 \times 10^{-51}$ | 4.3512  |
| Temperature         | 18,936.1667   | 4.00| 4734.0417     | 5796.7857      | $2.48391 \times 10^{-30}$ | 2.3683  |
| POBA                | 1509.1333     | 4.00| 377.2833      | 461.9796       | $2.15708 \times 10^{-19}$ | 2.8661  |
| Interaction         | 16.3333       | 20.00| 0.8167        |                |               |         |
| Total               | 1,494,101.6667 | 29.00|              |                |               |         |
3.3.1. Dimension Analysis

In dimension analysis, the impact of POBA was assessed using rotational viscosity and viscosity-reduction efficiency ($\nabla)$). $\nabla$ is defined as the contribution of the percentage of POBA (3%, 5%, 7% and 9%) to the viscosity-reduction rate. POBA is the variable, as the modifier binder; the viscosities of the four asphalt binder mixtures, containing varying quantities of POBA, were tested in order to evaluate the efficiency of the modifier in the asphalt binder system. The higher the viscosity-reduction efficiency, the greater the cost effectiveness.

Figure 3 and Table 9 show the connections between $\nabla$ and temperature for each sample. The non-dimensional viscosity indexes for 3%, 5%, 7% and 9% of POBA compositions varied for each sample. For instance, at 140 °C, the $\nabla$ values for 3%, 5%, 7% and 9% POBA were 1.65%, −1.02%, −1.34% and −1.24%, respectively. This indicated that by adding POBA and Rediset into asphalt binder, the viscosity decreased regardless of the quantity.

At temperatures of 170 and 180 °C, only 5% and 7% POBA showed an increase in viscosity value (3.83 and −0.68, respectively) while other samples decreased. Other showed decreasing viscosity at other temperatures. In conclusion, the change in performance (observed by the value of $\nabla$) was caused by adding several different weight percentages of POBA at the same test temperature.

Table 9. The relationship between $\nabla$ and temperature for each binder.

| Temp (°C) | Viscosity (mPas) | 0% | 3% | 5% | 7% | 9% |
|-----------|------------------|----|----|----|----|----|
| 130       | 777.00           | 777.00 | 778.00 | 777.00 | 777.00 |
| 140       | 722.67           | 763.67 | 690.67 | 659.33 | 646.33 |
| 150       | 448.33           | 583.00 | 555.67 | 557.33 | 533.00 |
| 160       | 339.67           | 414.00 | 327.67 | 295.33 | 275.33 |
| 170       | 250.67           | 262.00 | 298.67 | 245.00 | 233.67 |
| 180       | 245.67           | 248.67 | 223.00 | 234.00 | 213.67 |

| Temp (°C) | Relative Viscosity | 0% | 3% | 5% | 7% | 9% |
|-----------|--------------------|----|----|----|----|----|
| 130       | 1                  | 1.00 | 1.00 | 1.00 | 1.00 |
| 140       | 1                  | 1.05 | 0.95 | 0.91 | 0.89 |
| 150       | 1                  | 1.30 | 1.24 | 1.24 | 1.19 |
| 160       | 1                  | 1.22 | 0.96 | 0.87 | 0.81 |
| 170       | 1                  | 1.05 | 1.19 | 0.98 | 0.93 |
| 180       | 1                  | 1.01 | 0.91 | 1.95 | 0.87 |

| Temp (°C) | Difference in Relative Viscosity of POBA | 0% | 3% | 5% | 7% | 9% |
|-----------|------------------------------------------|----|----|----|----|----|
| 130       | NA                                       | 0.04 | 0.03 | 0.00 | 0.00 |
| 140       | NA                                       | 1.65 | −1.02 | −1.34 | −1.24 |
| 150       | NA                                       | 10.01 | 4.79 | 3.47 | 2.10 |
| 160       | NA                                       | 7.29 | −0.71 | −1.86 | −2.10 |
| 170       | NA                                       | 1.51 | 3.83 | −0.32 | −0.75 |
| 180       | NA                                       | 0.41 | −1.85 | −0.68 | −1.45 |
3.3.2. Activation Energy—$E_a$

The calculated $E_a$ for a 60/70 penetration-grade asphalt binder was 40.16 KJ/mol, and the $E_a$ values for the rest of the 4 binder samples were 40.01, 40.25, 41.73 and 44.17 KJ/mol, as shown in Table 7. Omar et al. [41] reported that, for 60/70 penetration-grade asphalt binder, with temperature ranges between 135 and 165 °C of viscosity, the $E_a$ values were found to be 75–90 kJ/mol; meanwhile, adding the (2–4% halloysite nano-tube) modifier binder, the measured $E_a$ was between 79 and 85 kJ/mol.

In Figure 4, the analyses show that the activation energy for asphalt binders with POBA was higher than the control sample (0%), except for 3% POBA. $E_a$ values for 5%, 7% and 9% POBA increased incrementally. The 60/70 penetration-grade asphalt binder with Rediset consumed less energy, and the presence of POBA caused the mixture to consume more energy.
3.3.3. Viscosity–Temperature Susceptibility

Figure 5 shows the linear curve of the relationship between the binder viscosities and temperatures. Thus, the viscosity–temperature susceptibility of all samples can be understood.

Table 10 shows the list of A, VTS, $R^2$ and $T_{critical}$ values obtained from the analyses. The numbers indicate that the viscosity–temperature susceptibility increased with increasing POBA content.

| Parameters | 0%   | 3%   | 5%   | 7%   | 9%   |
|------------|------|------|------|------|------|
| A          | 5.8038 | 5.7819 | 5.8396 | 6.0489 | 6.4197 |
| VTS        | 1.8661 | 1.8562 | 1.8777 | 1.9515 | 2.0811 |
| $R^2$      | 0.9541 | 0.9366 | 0.9600 | 0.9311 | 0.9395 |
| $T_{critical}$ (°C) | 242.00 | 244.00 | 242.00 | 235.00 | 228.00 |

3.3.4. Indices Relationship

If two variables yield a correlation coefficient of +0.95, then they are closely related; if the coefficient is near zero, then they are unrelated [42]. Figure 6 shows the connections between the VTS index and POBA content. It was found that the value $R^2$, which represents the strength of the connections between the two variables, was 0.7773.
The value falls between 0.3 and 0.7, which is generally considered significant in terms of having a weak or low effect size, while a value above 0.7 is almost always considered to be a significant or strong effect size. A positive correlation (direct connection) describes the movement of two variables in the same direction—either up or down. On the other hand, a negative correlation (inverse connection) occurs when two variables move in opposite directions. The regression line formula is $y = mx + b$, where $m$ is the slope of the line and $b$ is the $y$-intercept. The value on the $y$-axis where the line crosses is called the $y$-intercept. For example, in Figure 6, the regression formula is $y = 0.0525x + 1.7689$, meaning that the regression line crosses the $y$-axis at the value VTS index at 1.7689, where the POBA content is 0.00.

For the relationship between activation energy and penetration index, the value of $R^2$ is found to be in the range above 0.5, which can also be considered a strong or high effect size, as shown in Figure 7a.

![Figure 6](image)

**Figure 6.** The relationship between the VTS index and the POBA content.

However, compared with the $R^2$ value for the relationship between the VTS index and the POBA content, the value was at a higher range, with 0.9093. Lastly, the $R^2$ value for the relationship between the activation energy and the VTS index was found to be 0.9987, with reference to Figure 7b. In conclusion, compared with the $R^2$ value, for the relationship between activation energy and penetration index, the value was in a higher range.

![Figure 7](image)

(a) (b)

**Figure 7.** (a) The relationship between $E_a$ and PI. (b) The relationship between $E_a$ and VTS Index.
3.3.5. Statistical Analysis

ANOVA was used to check whether the difference between averages for viscosity–temperature susceptibility (VTS), activation energy of flow ($E_a$) and penetration index (PI) was significant or simply due to random noise within each group. The null hypothesis in this study consisted of individual properties between VTS, $E_a$, and PI being equal. Table 11 lists the ANOVA for the VTS index, $E_a$, PI, and viscosity (135 °C) of the asphalt binder with POBA and Rediset, individually.

Table 11. ANOVA for VTS, $E_a$, PI and viscosity of the asphalt binder.

| Source of Variation | SS     | df  | MS          | F          | p-Value       | F crit       |
|---------------------|--------|-----|-------------|------------|---------------|--------------|
| VTS                 | 8.8221 | 1.00| 8.8221      | 1747.9076  | $1.18033 \times 10^{-10}$ | 5.3177       |
| POBA%               |        |     |             |            |               |              |
| Within groups       | 0.0404 | 8.00| 0.0050      |            |               |              |
| Total               | 8.8625 | 9.00|             |            |               |              |
| Activation energy   | 4246.8993 | 1.00| 4246.8993   | 2717.5333  | $2.03199 \times 10^{-11}$ | 5.3177       |
| POBA%               |        |     |             |            |               |              |
| Within groups       | 12.5022 | 8.00| 1.5628      |            |               |              |
| Total               | 4259.4015 | 9.00|             |            |               |              |
| Penetration index   | 11.7676 | 1.00| 11.7676     | 33.3119    | 0.000418495   | 5.3177       |
| POBA%               |        |     |             |            |               |              |
| Within groups       | 2.8260 | 8.00| 0.3533      |            |               |              |
| Total               | 14.5936 | 9.00|             |            |               |              |
| Binder’s viscosity  | 1,359,463.2668 | 1.00| 1,359,463.26| 4566.3558   | 2.55978 $\times 10^{-12}$ | 5.3177       |
| POBA%               |        |     |             |            |               |              |
| Within groups       | 2381.7036 | 8.00| 297.7130    |            |               |              |
| Total               | 1,361,844.9704 | 9.00|             |            |               |              |
| Viscosity properties| 1,970,189.3014 | 3.00| 656,729.7671| 4383.5816   | 1.58652 $\times 10^{-23}$ | 3.2389       |
| Groups (between)    | 2397.0527 | 16.00| 149.8158    |            |               |              |
| Error (within groups)| 1,972,586.3542 | 19.00|             |            |               |              |

The values show that for each mechanical property, the effect of the POBA percentage was significant for VTS, $E_a$, PI and viscosity, where all the $p$-values were more than 0.05, respectively. Table 12 lists the ANOVA for VTS, $E_a$, PI and viscosity (135 °C) of the modified asphalt binders as a whole. The F-statistics represents the difference in variance between groups and within groups. Unlike other statistical tests, the smaller the F-statistics, the more likely the averages are to be the same. The test F-statistics value was 4383.5816, which is not in the 95% critical value accepted range: [$-\infty: 3.2389$].

Table 12. Mean comparison of each index variations by using Tukey test.

| Treatment Pair | Difference | Critical Mean | * Significant |
|----------------|------------|---------------|---------------|
| %–VTS         | 1.8785     | 1.779376      | Yes           |
| %–$E_a$       | 41.2160    | 1.779376      | Yes           |
| %–PI          | 2.1696     | 1.779376      | Yes           |
| VTS–$E_a$     | 39.3375    | 1.779376      | Yes           |
| VTS–PI        | 4.0481     | 1.779376      | Yes           |
| $E_a$–PI      | 43.3856    | 1.779376      | Yes           |

* Significant if difference > critical mean.

This study had a high F value, which means that the chance that not all the groups’ means were equal is greater. Moreover, the smaller $p$-value obtained in this study was in agreement with the previous conclusion of the F value, increasing the likelihood that not all of the groups’ averages were equal. The $p$-value equals $1.58652 \times 10^{-23}$, and since the
p-value was less than 0.05, $H_0$ was not accepted ($H_1$ was accepted). This means that the difference between the indices was big enough to be statistically significant.

To compare the means with an alpha level of 0.05, Tukey’s test was used. Tukey’s test is statistical test that uses a single-step multiple comparison technique to find means that are significantly different from each other. It compares the means of every group to the means of every other group (% VTS, $E_a$ and PI), applying all pair-wise comparisons to the groups simultaneously, and identifies any differences between any two means that is greater than the expected standard error. The test goal was to compare the means with an alpha level of 0.05.

Table 12 shows the results, which suggest a significant difference between the percentage of POBA, $E_a$ and PI, between the VTS index, $E_a$ and PI, as well as between $E_a$ and PI. The value of the difference is more than that of the critical mean values, meaning that the addition of POBA and Rediset to the asphalt binder mixtures had a significant effect on VTS, $E_a$ and PI.

3.4. Chemical Analysis
3.4.1. FTIR Analysis

Asphalt binder is a complex mixture of organic molecules that vary greatly in the compositions of the hydrocarbon material, consisting primarily of single bond of carbon–carbon (C–C) and carbon–hydrogen (C–H) and other elements (heteroatoms), such as oxygen (O), sulphur (S), and nitrogen (N), which construct the main functional groups [43]. A functional group is a group of atoms present in an organic molecule which gives certain chemical properties to the molecule. An FTIR test was conducted to identify the possible chemical changes in the asphalt binders after modification. The presence of different functional group bonds is a good indication of the chemical linkages between 60/70 penetration-grade asphalt binder, POBA and Rediset, as shown in Table 13.

Table 13. FTIR transmittance of functional groups on tested asphalt binders.

| Functional Group        | Bond      | Wavenumber, cm$^{-1}$ |
|-------------------------|-----------|-----------------------|
|                         | Range     | Strong | Moderate | Weak |
| Alcohol, phenols        | 0-H, H-   | 3500–3200 |     |     |     |
| Amines, amides          | N-H, C-N  | 3400–3250 |     |     |     |
| Alkynes                 | C≡C-H     | 3300     |     |     |     |
| Alkenes                 | C-H, C-H2 | 2850–2950 |     |     |     |
| Alkynes                 | C≡C       | 2260–2100 |     |     |     |
| Carbonyls               | C=O       | 1740–1700 |     |     |     |
| Alkene, amines          | C=C, N-H  | 1650–1580 |     |     |     |
| Aromatic, alkane        | C-C, C-H  | 1440–1350 |     |     |     |
| Nitro compounds         | N-0       | 1360–1290 |     |     |     |
| Aromatics amines        | C-N       | 1335–1250 |     |     |     |
| Alcohol, carboxylic acid| C-O       | 1320–1000 |     |     |     |
| Aliphatic amines        | C-N       | 1250–1020 |     |     |     |
| Amines                  | N-H       | 910–665   |     |     |     |
| Alkene                  | C-H       | 900–675   |     |     |     |
| Alkyl halides           | C-Cl      | 850–550   |     |     |     |

Any change in the asphalt binder’s major functional groups, as indicated by the IR spectrum, is connected to the molecular structures of various molecular groups. Table 14 shows the functional groups for every peak position on the spectrum. The IR absorption spectrum is a graphic representation of the energy measurement as a function of the wavelength of the radiation.
Table 14. Observed peak of FTIR spectrum.

| Samples | Wave Number, cm\(^{-1}\) |
|---------|-------------------------|
| 0%      | 2924 2853 1463 1377     |
| 3%      | 2924 2853 1463 1377     |
| 5%      | 2924 2853 1463 1377     |
| 7%      | 2924 2853 1463 1377     |
| 9%      | 2924 2853 1463 1377     |

| Type of peak | -CH | -CH\(_2\) | C-C | C-H |
|--------------|-----|-----------|-----|-----|
| Functional group | alkenes | Alkenes | aromatic | alkenes |

The utilization of IR defined the use of the wave number (as opposed to the wavelength, which is proportional to the frequency of the radiation) and the percentage of transmission (T\%) or absorbance (A), which is connected to the energy of the radiation. In the FTIR spectrum, the Y-axis indicates the degree of atomic movements with the help of the wave number position; the number of IR peaks and intensity absorption bands indicate the structural characteristics of the molecule, and thus can be used to identify the structural composition of unknown objects or their chemical groups [44].

A comparable spectrum was produced for all the tested asphalt binders, before and after addition of POBA, with identical peaks and valleys, indicating that the addition of POBA did not give any additional functionality. Figure 8 shows the FTIR spectra of all samples, showing that the asphalt binder comprised mainly alkenes (alkyl), aliphatic and aromatic compounds, and a byproduct, heteroatoms. The variation in peak height arose from the different materials of each composite, which generated different strengths for each peak value.

![Figure 8. The FTIR spectrogram of POBA material and all asphalt binders.](image)

Therefore, it was essential to further analyze and process the spectrum. It can be observed that there were insignificant differences in the functional peaks in the spectrum of the samples. Some differences between the samples can be seen in the intensities of peaks;
however, there were variations of difference, observed at the fingerprint part (wave number 1500–500 cm$^{-1}$). This demonstrates that the contents of some of the functional groups changed with the addition of POBA. From the spectrum, high-intensity peaks—2924, 2853, 1463 and 1377 cm$^{-1}$—can be observed in this study. However, the magnitudes of the peaks of each binder mixture were different. Small dense peaks after 3250 cm$^{-1}$ and from 2300 to 2000 cm$^{-1}$ can be neglected because these can be an indicator of mishandling of the cells in the FTIR test. A peak occurring at around 2900 cm$^{-1}$ belongs to the C-H stretch; more specifically, two intense peak points were detected in the 2924–2853 cm$^{-1}$ array, which could be allocated to the C-H group that forms alkenes chains.

The spectrum matches that in a study by Ren et al. [45], which found strong absorption peaks at wave numbers around 2924 cm$^{-1}$ and 2853 cm$^{-1}$, which were associated with the methylene of the C–H stretch; meanwhile, weak absorption peak appeared near the wave number at 1700 cm$^{-1}$, which represents the stretching vibration of the C=O stretch. This means that the weak peaks at 1650 and 1700 cm$^{-1}$ belong to the C=O carbonyl. A moderately intensive sharp peak was found at 1463 cm$^{-1}$ due to spreading vibrations of the C-H of the methyl C-CH$_3$ plane, and strain vibrations at the C-H of the -CH$_2$-plane. Likewise, a smaller sharp peak occurred at the wave number of 1377 cm$^{-1}$, due to the asymmetrical and symmetrical (angle) of the CH$_3$ vibration.

A wave number below 1500 cm$^{-1}$ describes the fingerprint region. The moderate absorption peak at 1050 cm$^{-1}$ was caused by the strain vibration of C-N aliphatic amines. The moderate transmittance peak between 900 cm$^{-1}$ and 700 cm$^{-1}$ indicates a wagging vibration of the C-H plane on the benzene alkenes ring. The FTIR spectrum shows that the asphalt binder mainly consists of alkenes, aliphatic and aromatic compounds, and derivative heteroatoms. Since there is no significant shift in the peak position or any new peaks at the functional group part, it can be concluded that there was no chemical bonding between the asphalt binder and the POBA.

By comparing the results of the unmodified asphalt binder (0%) and the modified WMA binder blends, it can be seen that the position of the peaks that appear in the modified asphalt binder sample matched the peaks in the unmodified asphalt binder, and no shift in the position was observed. The outcomes show that the unmodified binder, even when POBA was added at different percentage weights, indicated that a change in the blending is purely a physical (mixing) process.

Even though it can be seen that there are some uneven different spikes in all the samples tested, these can be due to impurities in the samples. With the analysis of the spectrum peaks and the wave numbers observed for the modified asphalt binder, it was found that there was no indication of chemical bonding between the asphalt binder and the POBA–Rediset. The three substances have about the same chemical structure.

### 3.4.2. Thermogravimetric Analysis

A thermogram analysis curve consists of thermogravimetric analysis (TGA) and difference thermogravimetric analysis (DTG). A thermogravimetric curve describes mass loss as a function of temperature, which provides information regarding thermal stability and composition of the initial sample, whereas a DTG curve is the measurement of the weight loss ratio at heating interpretation over time (T). Thermogram of samples 0%, 3%, 5%, 7% and 9% are shown in Figure 9. In the TGA curve, all binder samples show a single step of degradation. The thermogram showed that the curve has three horizontal regions.
“brittle points”—that are used to describe the transition from a liquid to a solid state [38], and its temperature is always lower than $T_c$.

3.4.3. Differential Scanning Calorimetry

The physicochemical transitions that can be observed from the DSC thermogram are the oxidation phase ($T_{ox}$), crystallization ($T_c$), melting point ($T_m$) and glass transition ($T_g$). $T_g$ is one of the initial thermodynamic parameter changes—which are also called “brittle points”—that are used to describe the transition from a liquid to a solid state [38], and its temperature is always lower than $T_m$. $T_m$ is the melting-point temperature of the substance at which it transitions from solid to liquid. The freezing-point/crystallization-
point temperature, or \( T_c \), is the temperature at which the inverse transition from liquid to solid occurs [46].

Furthermore, \( T_{ox} \) refers to a temperature that marks the transition of a chemical reaction involving a metallic substance and atmospheric oxygen that produces corrosion at elevated heat [47]. The output test of the DSC thermogram is shown in Figure 10a–e. In the DSC curve, all the binder samples showed a single step of these physicochemical processes, starting between 30 °C and 400 °C, respectively. The initial zone, up to 100 °C, shows the loss of the asphalt binder sample volatiles with the increment of the heat flow. Followed by the second zone, the glass transition region, the control sample (0%) detected a slight glass transition (\( T_g \)) at 302.6 °C, 3% POBA at 100.3 °C, 5% POBA at 263 °C, 7% POBA at 76.1 °C, and 9% POBA at 134.8 °C. The values of \( T_g \) and the peak were determined using Netzsch Proteus Analysis Software, and the \( T_g \) values were obtained from the inflection point of the step function. Lower \( T_g \) values indicate better low-temperature performances; therefore, the 7% POBA-modified binder showed more resistance to low-temperature cracking. The exothermic peak of \( T_g \) for all binders occurred at the same point, 35 °C. These peaks were identified as wax crystallization. From the thermograms, all tested samples had a melting point (\( T_m \)) above 400 °C, except for 3% POBA, which showed its melting point at 389.4 °C, and 7% POBA, which showed its melting point at 103 °C—considerably higher than the temperatures for initial crystallization. The \( T_c \) and \( T_{ox} \) values of the samples were not detected in the ranges of the tested temperatures. In conclusion, by comparing the DSC curve of the control sample, it can be shown that the incorporation of POBA and Rediset into the 60/70 penetration-grade asphalt binder did not significantly change the physicochemical transitions in terms of thermal properties.

Figure 10. Cont.
Figure 10. Cont.
4. Conclusions and Future Research

Based on the results and discussion in this study, the following conclusions were made:

1. The physical properties of the tested POBA-modified warm mix asphalt binders showed good consistency with certain compositions of POBA weight incorporated, especially in the sample with the addition of 7% POBA weight, which showed an average of 16.3% improvement compared with the control in the penetration-grade asphalt binder.

2. The addition of POBA enhanced the penetration values, the softening point temperatures and the ductility characteristics up to 7% added POBA, then the consistency reduced at 9% added POBA, with maintained consistency values better than the control binder sample.
3. PI showed a decrement with 3% and 5% added POBA, and an increment pattern with 7% and 9% added POBA, which reflects the enhancement of the temperature susceptibility resistance of modified binders with high contents of POBA.

4. The rotational viscosity of each combination decreased with the increment of temperature, even though the trend was not significantly constant. The highest viscosity was found at 3% POBA, with an average improvement of 8.5% compared with the control binder.

5. From the ANOVA results, the difference between the averages for viscosity–temperature susceptibility (VT S), activation energy of flow ($E_a$) and penetration index (PI) had a high $F$ (ratio of two variances) value, which means that the chance that not all the groups’ means would be equal was greater. Moreover, the results of the $p$-value were smaller, which indicates that not all of the groups’ averages were equal. From this study, we can highlight that the difference between the indices was big enough to be statistically significant within each group—not simply due to random noise.

6. Based on the FTIR analysis, it was found that the POBA-modified warm mix asphalt binders had comparable functional groups to the control asphalt binder, which indicated the suitability of POBA as an asphalt binder. Meanwhile, the intensity of some of the functional groups changed with the addition of POBA, which indicated no chemical interactions of POBA within the asphalt matrix.

7. The chemical properties obtained from TGA and DSC thermogram showed that the percentage of the weight loss of the POBA-modified binders was lower compared with the highest loss found for the control asphalt, with 84.6%. The 5% added POBA showed the lowest value of 77.6%. This indicated that the thermal stability of the POBA-modified binders went beyond its mixing and compaction temperature.

8. Based on the results obtained from the DSC, it can be stated that the incorporation of POBA and Rediset into the base asphalt binder did not significantly alter the physicochemical transitions in terms of thermal properties.

Further analysis of the effect of POBA and the warm mix additive Rediset on binder properties should involve following intentions:

- To enhance the properties of POBA-modified binders; furthermore, surface chemistry studies, such as those of surface energy and physical adhesion characteristics, will be determined using a goniometer (contact angles) and a boiling water test.
- Extensive study of the topography of POBA-modified binders at a micro scale will be conducted via atomic force microscopy (AFM) to find related forces.
- A tank leaching study will be conducted to observe the pollution potential; furthermore, this will simulate the effect of a submerged pavement in various flood conditions.

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