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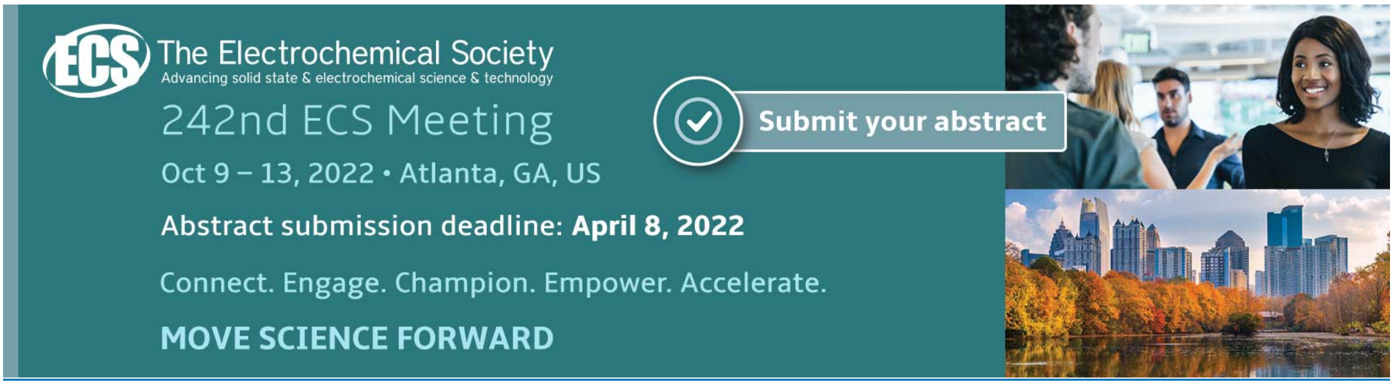

Characterisation of bitumen, refined waste oil, and emulsifiers for coating and insulation purposes

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Abstract The current study aims to characterise bitumen, refined waste oil, and emulsifiers to formulate emulsified modified bitumen for coating and insulation purposes. These raw materials were characterised in terms of their physical properties and elemental composition. This analysis provides significant information for setting the formulation parameters and determining the coating application conditions. Bitumen is a non-renewable petroleum substance; thus, the utilisation of refined waste oil in bitumen modification will reduce the dependency on neat bitumen and solve the increasing environmental problems in Malaysia. The physical characterisation was carried out using the tests of viscosity, flash point, density, penetration, softening point, moisture content, and X-ray diffraction. Fourier transform infrared analysis was conducted to determine the molecular composition and structure of the materials. In conclusion, the characterised materials showed the potential properties to formulate a highly adhesive, stable, and homogeneous emulsion.

1. Introduction

Bitumen is a hydrocarbon derivative produced during the refining process by extracting the lighter fractions of petroleum from crude oil [1]. Historically, bitumen was used for the embalming of mummies, remedy for various illnesses (e.g., eczema, asthma), as a disinfectant or an insecticide, and as the road pavement material in the early 19th century due to its adhesive and waterproofing properties [2]. Bitumen exhibits low instability and very high viscosity at ambient temperature, where its viscosity decreases as temperature increases [3].

The world's current bitumen consumption is estimated to be over 102 million tons annually, where 85% is used as a pavement binder, 10% for roofing and industrial coating applications, and the rest is used for other purposes [4]. The increasing demand of crude oil consumption, the accelerated pressure imposed by the depletion of scarce raw materials, and the urgent environmental protection requirements are influencing the change of the dependency on bitumen in the coating industry, and the academia community's research has made an effort towards the development of low emission and eco-friendly coating substances that can significantly reduce mixing and compaction temperatures, as well as the consumption of virgin raw materials [5].

Several materials (modifiers) have been introduced to overcome the dependence on neat bitumen, reinforce its properties, and utilise bitumen more efficiently [6]. Many studies showed that modified bitumen emulsions performed better than non-modified emulsions, and the modification of bitumen with refined waste oil could reduce the use of neat bitumen and the environmental pollution caused by the manufacturing industry [7].

Bitumen emulsions modified with solid modifiers, such as crumb rubber, polyethylene, styrene-butadiene-styrene (SBS), styrene-butadiene rubber (SBR), and waste plastic are suitable for paving applications rather than coating and insulation purposes. These modifiers lead to a heterogeneous emulsion and require high temperatures of more than 150 °C in the emulsification process, which results in an unstable emulsion. Hence, liquid modifiers with low viscosity are often used to prepare a stable and low mixing temperature emulsion with the aid of a suitable emulsifier [8].

Bitumen possesses complex chemical and physical properties. Bitumen contains hydrocarbon chains with a small volume of heterocyclic structurally similar compounds and different functional groups. Its physicochemical properties and elemental composition widely depend on the source of the crude oil, the geographical location, and the distillation process [9]. To formulate a potential coating emulsion, the identification of the physicochemical properties, the chemical structure of bitumen, the emulsifying agent, and the modifiers is very significant [10]. Therefore, raw material characterisation is fundamental to assure the quality of the materials and their composition, which will determine the concentration of the ingredients and formulation parameters [11].

In this study, physical characterisation was carried out using the tests of viscosity, flash point, density, penetration, softening point, moisture content, and X-ray diffraction (XRD). Fourier transform infrared (FTIR) analysis was conducted to determine the molecular composition and structure of the materials.

2. Experimental Methodology

2.1. Materials

The materials utilised for this study are 60/70 grade bitumen supplied by Kemaman Bitumen Company (KBC) and refined waste oil obtained from Pentas Flora. Two emulsifying agents (2-bromostearic acid tech. of analytical grade and didodecyldimethylammonium bromide (DDAB) of analytical grade) were purchased from Sigma-Aldrich. 2-bromostearic acid and DDAB are selected due to their lower cost and the ability to formulate a stable emulsion.

2.2. Physical Analysis

2.2.1Penetration Test. The penetration test was performed using the American Standard Testing Methods (ASTM) D5. The penetration value is the vertical separation navigated or entered into the bituminous specimen by the point of a standard needle under different load, time, and operating temperature. This measurement is estimated in one-tenth of a millimetre. The quality of bitumen was assessed through its penetration test value. The instruments used in the study were a water bath, a sample container, a penetrometer with a needle and a clock, and a thermometer. The dissolved sample was filled into the sample jar, which was allowed to cool in the air for 45 min to 1.5 h. The sample was placed at the appropriate temperature in the water bath and put in the container for 45 min to 2 h. The needle was in place and simply hit the outer layer of the sample surface. Then, for the same time (5 s), the needle holders were released, and the instrument was calibrated to measure the distance in millimetres. The penetration allows the needle to pervade but without much resistance, and it is measured accurately to achieve the results of one-tenth of a millimetre [12].

2.2.2. Softening Point Test. The bitumen softening point was calculated by following ASTM D36. The instruments used in this experiment were a shouldered ring, a ball centering guide, a ring carrier and assembly, a bath (beaker), an electrical heater, and a thermometer. The warmed sample was poured into two shouldered rings with a small excess and allowed to cool at least 30 min at room temperature. As the specimen cooled, the excess bitumen was removed with a slightly hot knife. The bath appliance was equipped with circles, ball centering guides, and a thermometer. The ball was put in every guide for ball centering. After that, the bath was heated from below at a controlled rate using a heater. The softening point is where the temperature implies that two disks soften sufficiently to enable each ball envelope to drop at 250 mm/1 inch [12].

2.2.3. Flash Point Test. In this study, the characterisation of the material's flash point was determined according to ASTM D93. The flash point is the minimum temperature where the material evaporates quickly and forms a flammable mixture with air, such that the mixture is ignited in the presence of flames for a moment (i.e., a minimum of 5 s). Hence, the oil melting point is a crucial parameter in deciding the substance's operating range. This physical property is an indicator for determining a substance's flammability and volatility.

2.2.4. Viscosity Test. The viscosity of the materials was measured using a rotational viscometer. The viscometer was equipped with a plate geometry of 1 mm (Malvern Instruments) and set up with a rotational speed of 50 rpm. The average viscosity was calculated from the overall 10 points taken [13].

2.2.5. Moisture Content Test. The moisture content test for the materials was performed through the conventional oven-dry method. Approximately 3 g of each sample was held in an aluminium box. The initial weight of the aluminium boxes with the samples was recorded and left in an oven for 15 min at 105 °C. The weight of the oven-dried samples was recorded. Finally, the moisture content of the samples was calculated.

2.2.6. Density Test. The density test for bitumen and refined waste oil was carried out using ASTM D70. The devices used in this experiment include a pycnometer, an oven, a balance, a refrigerator bath, and a thermometer. First, the sample was loaded in a calibrated pycnometer at about 3/4 of the volume. Then, the pycnometer and the sample were weighed. After that, the remaining volume was filled with water. Next, the filled pycnometer was brought to the test temperature using a refrigerator bath. The filled pycnometer was then weighed after at least 30 min in the bath. The density of the sample in the filled pycnometer was measured based on the mass of water displaced by the sample.

2.3. Chemical Analysis

2.3.1. X-Ray Diffraction. XRD analysis was utilised to evaluate the crystal structure of the materials through continuous scanning. The XRD analyser was radiated with Cu-Kα (k = 0.15418 nm). The voltage acceleration and the current applied were 45 kV and 40 mA, respectively. In the phase scanning mode, the XRD pattern start and end positions were 3.0064 and 59.9904, respectively, with the step size of 0.0170, and the reading was registered.

2.3.2. Fourier Transform Infrared Spectroscopy. An FTIR spectrometer was utilised to record the spectra of bitumen, refined waste oil, 2-bromostearic acid, and DDAB. The spectrometer measures the variety of wavelengths absorbed by a substance in the infrared region. All spectra were recorded in the wavenumber ranging from 4000 to 500 cm^{-1}.

3. Results and Discussion

3.1. Physical Analysis

3.1.1. Flash Point, Moisture Content, Density, Penetration, and Softening Point Tests. Table 1 shows the results of flash point, moisture content, density, penetration, and softening point tests of bitumen and refined waste oil. The flash points of bitumen and refined waste oil were 260 °C and 114.5 °C, respectively. A higher flash point of a sample indicates higher viscosity and more additives are present in the sample. As the bitumen modification experiment is performed at a maximum temperature of higher than 160 °C, the oil needs to have a high flash point. Bitumen and refined waste oil have less moisture content. However, bitumen is denser than refined waste oil.

The penetration test is used as an indicator of bitumen quality. Its behaviour in an application can be predicted. For cold environments, bitumen with a high penetration value of 160/220 grade (named "soft") is utilised, whereas bitumen with a relatively low penetration value of 80/100 or below (named "hard") is often used in warm climates [14], where the lower the penetration grade, the harder the bitumen [15]. According to the outcome of the penetration test shown in Table 1, the penetration value of bitumen was found to be 68.3 mm, which is suitable to be used in high atmospheric temperature regions like Malaysia. Bitumen with a lower penetration grade can prevent deformation during performance at high temperatures.

The material softening point can be defined as the temperature at which the material reaches a degree of viscosity that it can no longer be considered a solid. Bitumen with a higher softening point is favourable as a binder in a warmer climate. Based on the softening point test result shown in Table 1, the average softening point of the sample was 44.1 °C, which is suitable for Malaysian climate.

Table 1. Flash point, moisture content, density, penetration, and softening point tests of bitumen and refined waste oil.

Test	Unit	Bitumen	Refined Waste Oil
Flash Point	°C	260	114.5
Moisture Content	%	0.18	0.32
Density	kg/m^3	1.203	0.883
Penetration	mm	68.3	-
Softening Point	°C	44.1	-

3.1.2. Viscosity Test. Bitumen viscosity is its internal flow resistance or the measurement of its resistance to deformation by either shear stress or tensile stress. The deformation characteristics differ not only with the load but also with the load application time rate and the temperature. It is neither elastic in behaviour nor viscous. It exhibits elastic behaviour at low temperatures and viscous behaviour at high temperatures [12]. The obtained result in Figure 1 shows that bitumen has higher viscosity (500 cP) than the refined waste oil (69 cP). The curves provide important information about storage stability and pumping conditions.

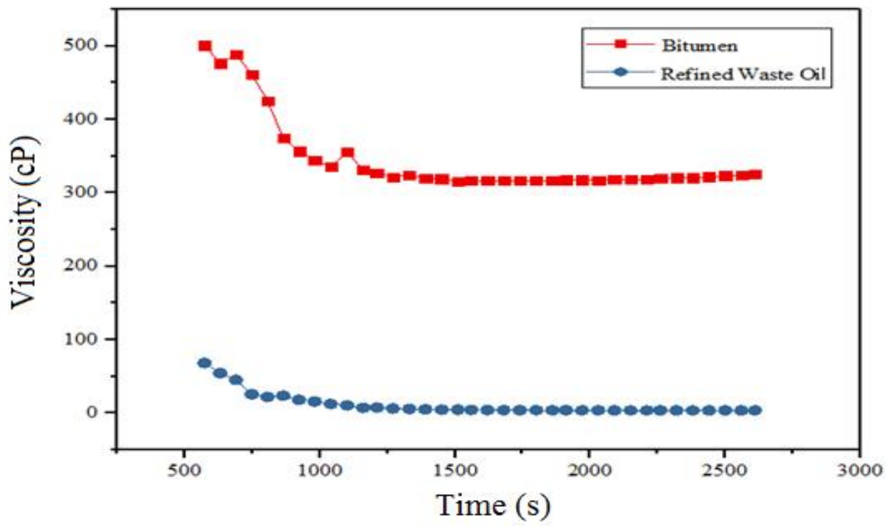

Figure 1. Viscosity of bitumen and refined waste oil at 120 °C.

3.2. *Chemical Analysis*

3.2.1. X-Ray Diffraction. The powder XRD pattern is treated as nothing more than a one-dimensional image, and a deep coevolutionary neural network (CNN) is used and trained to learn the underlying features from many XRD patterns. Any logic that is used with a conventional approach can hardly grasp the underlying characteristics. Deep learning technologies have achieved a valued role in the research community for materials and may make it possible to achieve a dream protocol that would allow samples of unknown mixtures to be detected instantaneously in phases [16]. From Figure 2, the main peaks of 2-bromostearic acid are (5.0124), (7.4264), and (23.5254), whereas the main peaks of DDAB are (3.0744), (4.5874), (9.1774), (13.8014), and (21.9444). According to XRD patterns, the shape of the molecules looks like a "nail" consisting of the "nail-head" (four methyl groups linked to a nitrogen atom) and "nail-body" (long alkyl chain) [17]. It is identified that both emulsifiers have a crystalline structure [18]. Although a crystalline emulsifier enhances the texture of coating materials, it needs more energy to dissolve. Therefore, the end formulation needs to be amorphous to reduce energy consumption.

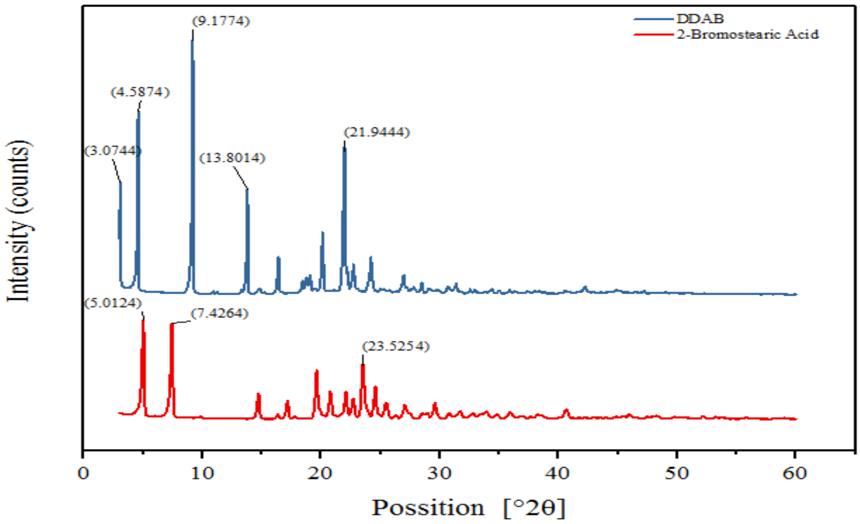

Figure 2. XRD patterns of 2-bromostearic acid and DDAB.

3.2.2. Fourier Transform Infrared Spectroscopy. This test was performed to determine the actual groups of the raw materials. According to the transmittance spectra in Figure 3, the bitumen sample contained aliphatic primary amines and aliphatic hydrocarbons, whereas the bands for refined waste oil indicated the presence of aliphatic acetate esters and aliphatic hydrocarbons. Meanwhile, the DDAB bands indicated the presence of aliphatic hydrocarbons and tertiary aliphatic alcohols, and the 2-bromostearic acid bands contained aliphatic carboxylic acids and aliphatic hydrocarbons.

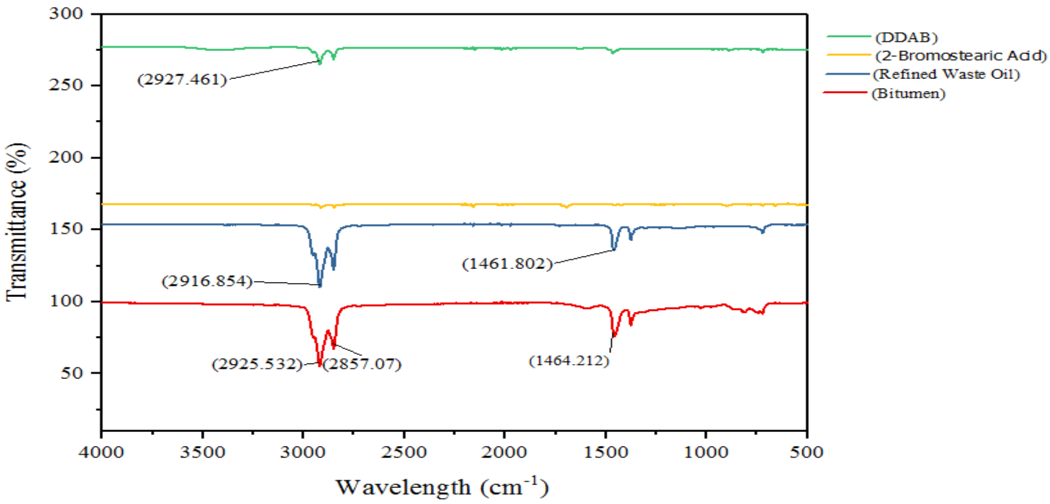

Figure 3. FTIR spectra of bitumen, refined waste oil, 2-bromostearic acid, and DDAB.

4. Conclusion

Based on the results of this study, bitumen is of high quality and suitable to be used in warm regions. Both bitumen and refined waste oil have high flash points of 260 °C and 114.5 °C, respectively, which is a significant parameter in bitumen modification. Although bitumen and refined waste oil have different viscosities, their chemical compositions are relatively similar. The XRD analysis of the emulsifiers showed the presence of a crystalline structure.

In summary, the characterised materials showed the potential properties to formulate a highly adhesive, stable, and homogeneous emulsion.

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Conflict of interest
No conflict of interest.