Characterization of Industrial Wastes as Raw Materials for the Formulation of Emulsified Modified Bitumen (EMB)

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Abstract. This study was conducted to characterize industrial wastes for the formulation of emulsified modified bitumen (EMB), in relation to their physical characteristics and elemental compositions. The aim was to determine which raw materials from industrial wastes could be used for EMB formulation. Bitumen is produced from crude oil extracted from the ground, which categorizes crude oil as one of the non-renewable fossil fuels. Various environmental issues that have risen in Malaysia are caused by the excessive manufacturing activities and the miss-management of industrial wastes. In an effort to mitigate these issues, industrial wastes are being used in various EMB formulations. Industrial wastes, such as polystyrene, polyethylene, and used automotive oil can be used as alternatives to formulate bitumen. Normally, a suitable emulsifier is needed to produce the final product, which is EMB. The emulsifier will yield a charge, depending on its properties, to bind the oily bitumen with water. In this current study, physical characteristic studies were performed using thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), flash point test, density test, and moisture content test. Fourier Transform Infrared Spectroscopy (FTIR) analysis was also performed to determine the material's molecular composition and structure.

Key word: *Emulsified Modified Bitumen (EMB); Non-renewable; Polyethylene; Polystyrene; Used Automotive Oil; Emulsifier*

1. Introduction

Bitumen is used mainly in road paving, roofing application, road construction, waterproofing products, building materials, and industrial coatings. It is estimated that the current world consumption of bitumen is 102 million tonnes per year, where 85% of bitumen are used as binder for pavements, 10% for roofing application, and the rest are used for various purposes (Asphalt Institute and Eurobitume, 2011). In Malaysia, the need to solve environmental issues is getting crucial. Significantly, industrial wastes, such as crumb rubber, polystyrene, plastics, and used oil have contributed to these problems. These wastes can be formulated into modified bitumen and with the help of a suitable emulsifier, it can become emulsified in the form of modified bitumen (EMB).

Bitumen is considered as a non-renewable product because it is produced from crude oil. To prevent this non-renewable source from being drained from the earth, as well as to use wastes produced by the industry, EMB can be formulated using crumb rubber, polystyrene, plastics, and used

oil to replace bitumen from crude oil. The formulated EMB will solve human dependency on the natural resources as well as the environmental problems that resulted from the overuse of natural resources. The formulated EMB will be used as insulation and coating in buildings. Additionally, most EMB formulations have shown better performances compared to unmodified bitumen (Carrera et al., 2015).

The increasing quantity of industrial wastes in Malaysia has led to numerous environmental problems. The solid waste in Malaysia had increased from 16,200 tonnes/day in 2001 to 19,100 tonnes/day in 2005, or at an average of 0.8 kilogram per capita/day (Tarmudi et al., 2009). In 2014, the Environmental Protection Expenditure (EPE) was reported at a total of RM2.244 billion, with the manufacturing sector as the highest contributor, at RM1.619 billion (Department of Statistics Malaysia, 2016). The industrial solid wastes have exceeded the maximum amount, which are usually disposed in landfills because the current waste management is poorly implemented. This method is not sustainable and needs to be improved because otherwise, it would affect our environment, social life, and it could lead to economic losses (Sin et al., 2012). Moreover, the growing demand for crude oil, at 4.5% annually from 2000-2005 to 6.2% per annum from 2006-2010 (Rahim & Liwan, 2012) has consequently decreases the percentage of natural resources in Malaysia. Thus, the development of modified bituminous emulsions from industrial wastes is one of the alternative ways to reduce these threats.

The EMB will be formulated using a recycling technology, thus, many industrial aspects that could lead to serious effects can be decreased, such as energy consumption, high level of CO_2 emission to the environment during construction, maintenance operation, and workers' health (Yaacob et al., 2013). In addition, bitumen emulsion has lower viscosity as it is diluted with water and can be applied at lower temperatures, as low as 80 °C. In this study, physical characteristic studies were performed using thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), flash point test, density test, and moisture content test. Fourier Transform Infrared Spectroscopy (FTIR) analysis was also performed to determine the EMB's molecular composition and structure. A suitable raw material for the formulation of emulsified modified bitumen was chosen based on the six analyses conducted in this study.

2. Methodology

2.1. Thermogravimetric Analysis (TGA)

TGA was performed to determine the decompose temperature and composition of the EMB sample. This analysis measured the percentage of weight loss of the test sample while it was being heated at 10 °C/min to approximately 900 °C under inert air. First, 2.5 mg of EMB was weighed and placed in an aluminium pan. The pan was placed on a constantan disc on a platform in the TGA cell and it was hung off a hook, which was connected by a microgram arm to a tare pan. The loss in weight over specific temperature ranges provided an indication of the composition of the sample.

2.2. Differential Scanning Calorimetry (DSC)

This analysis was performed to determine the melting temperature (Tm) of the sample. Approximately 2.5 mg of EMB was weighed and placed in an aluminium pan. Then, the pan was placed upon a constantan disc on a platform in the DSC cell with a chromel wafer immediately underneath. A chromel-alumel thermocouple under the constantan disc measured the sample temperature. An empty reference pan sat on a symmetric platform with its own underlying chromel wafer and chromel-alumel thermocouple. Heat flow was measured by comparing the difference in temperature across the sample and the reference chromel wafers. The sample was left to melt for about 33 minutes by specifying the final temperature of the sample at 350 °C.

2.3. Fourier-transform infrared spectroscopy (FTIR)

FTIR analysis was conducted to determine the material's molecular composition and structure. FTIR measures the range of wavelengths in the infrared region that are absorbed by a material. This is accomplished through the application of infrared radiation (IR) to samples of a material. The sample will absorb the infrared light's energy at various wavelengths. The first step in this study was to collect

a background spectrum to subtract from the test spectra, to ensure that the actual sample was all that was being analysed. A simple device called an interferometer was used to identify the EMB sample. It produced an optical signal with all the IR frequencies encoded into it. Then, the signal was decoded by applying a mathematical technique, known as Fourier transformation, which generates the absorbance spectra showing the unique chemical bonds and the molecular structure of the sample.

2.4. Flash Point Test

A flash point test was performed. Approximately 70 mL of EMB sample was placed in a test cup. The temperature of the sample was rapidly increased at first and then, at a slower constant rate as the flash point was approached. At specified intervals, a test flame was passed across the cup. The flash point is the lowest liquid temperature at which application of the test flame causes vapours from the test specimen to ignite. To determine the fire point of the sample in this study, the test was continued until the application of the test flame caused it to ignite and sustain being burned for a minimum of 5 s.

2.5. Density Test

A density test was performed using a gas pycnometer to determine the density of each sample. To conduct this test, the liquid sample was filled in a steel cup and placed in the device. The gas pycnometer works by employing Archimedes' principle of fluid displacement, and Boyle's law of gas expansion. A sealed sample chamber of known volume was pressurized to a target pressure with the displacement gas. Once stabilized, this pressure was recorded. Then, a valve was opened to allow the gas to expand into a reference chamber, whose volume was also known. Once stabilized, this second pressure was recorded. The pressure drop ratio was then compared to the behaviour of the system when a known volume standard underwent the same process.

2.6. Moisture Content Test

Moisture content analysis was performed to determine moisture content in each sample. Approximately 2 g of the sample was evenly filled in a pan and placed on the platform. The drying temperature was set to the standard drying temperature, which was 105 °C and then, the lid was closed.

3. Results and Discussions

3.1. Thermogravimetric Analysis (TGA)

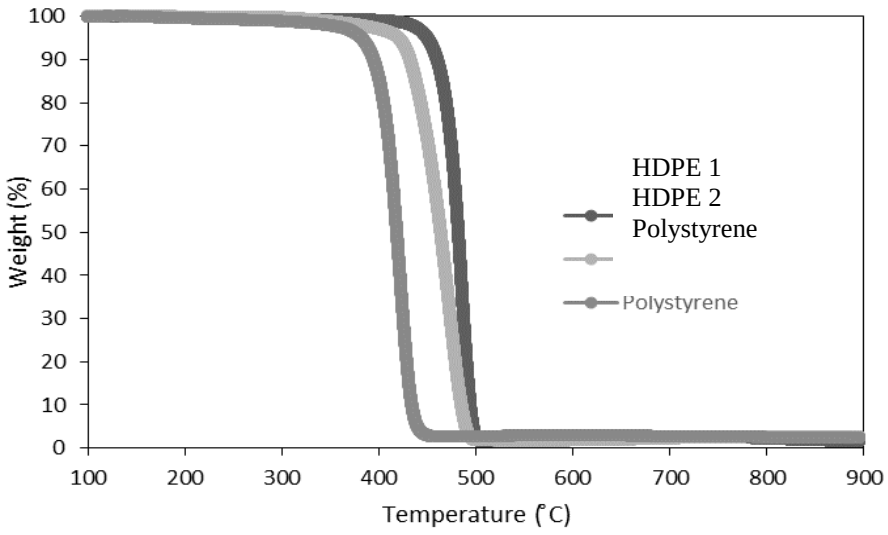

Figure 1. Graph of Weight Loss (%) against Temperature (°C)

Based on Figure 1, the curves showed continuous mass loss steps relating to the loss of volatile components, such as moisture and additives, the decomposition temperature of the polymers, and the combustion of final residues, such as ash and fillers (Turi, 1997). According to Joseph (2009), the multicomponent materials in one polymer, which are low-molecular mass compounds, polymeric materials, and inorganic additives can be divided by temperature. Thus, each composition and degradation temperature can be known.

Based on the figure, all samples showed the same degradation temperature, but different weight losses, namely, polystyrene sample, with 0.4476% of its components degraded at lower than 200 °C, 97.16% at 402.9 °C, and 2.355% at 900 °C. Meanwhile, the high density polyethylene 2 (HDPE 2) had 0.0852% of its components degraded at lower than 200 °C, 97.33% at 402.9 °C, and 2.606% at 900 °C. Lastly, the high density polyethylene 1 (HDPE 1) was 0.3235% degraded at lower than 200 °C, 98.17% at 402.9 °C, and 1.510% at 900 °C. These results showed that these samples had consisted of low-molecular-mass components, such as water and additives because they completely lost their mass at a low temperature. Furthermore, the major weight loss of approximately 80% of each sample had occurred at 402.9 °C. At 350-500 °C, all carbon-carbon bonds were typically ruptured by undergoing three possible mechanisms; random scission, depolymerisation, and side group elimination (Crompton, 2012). In addition, the residues, which were about 3% of the samples at the end of analysis, can be classified as additives or fillers because inorganic additives are usually stable in an inert atmosphere up to 900 °C or higher. The residues that remain at higher than 600 °C are normally associated with inorganic compounds, such as silica particles, glass fibres, and calcium carbonate (Joseph, 2009).

Therefore, based on these results, it was concluded that HDPE 1 was the best sample that would be able to tolerate the bitumen formulation because it contained the least amount of filler and the highest purity of polymer, with 98.17% of its total weight was the hydrocarbon component.

3.2. Differential Scanning Calorimetry (DSC)

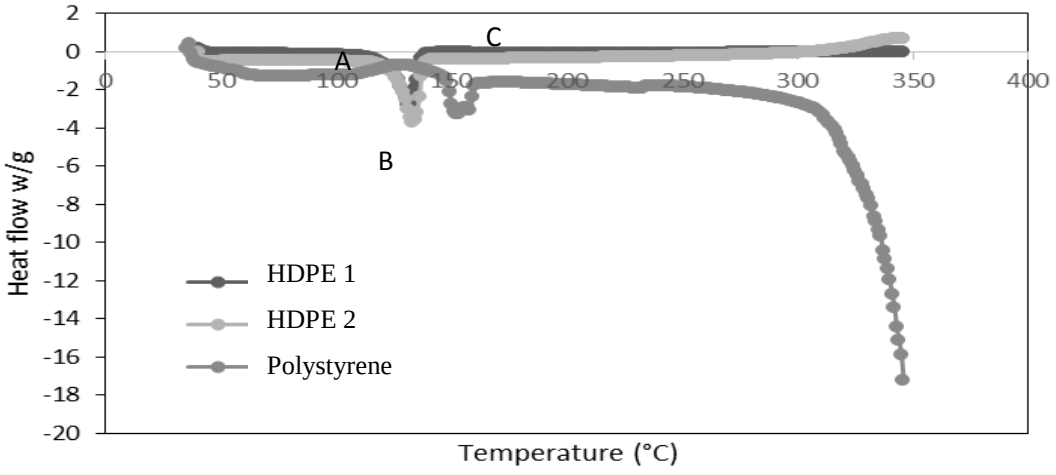

Figure 2. Graph of Heat flow (w/g) against Temperature (°C)

From Figure 2, samples of HDPE 1 and 2 showed approximately the same trend, which deviated from the polystyrene sample. This was because both samples came from the same group of polymer. The DSC graph showed three different melting values for each material, which were denoted as A, B, and C. At point A, the materials began to melt. Point B depicted the peak melting temperature, where it indicated the maximum rate of melting. Lastly, the real melting point was at point C, when the curves reached steady-state before they continued down the endotherm (Joseph, 2009). Therefore, to formulate bitumen, the melting point of each sample was determined in order to develope a method for this study, which could ensure all materials used were melted according to their melting temperature.

3.3. Fourier Transform Infrared Spectroscopy (FTIR)

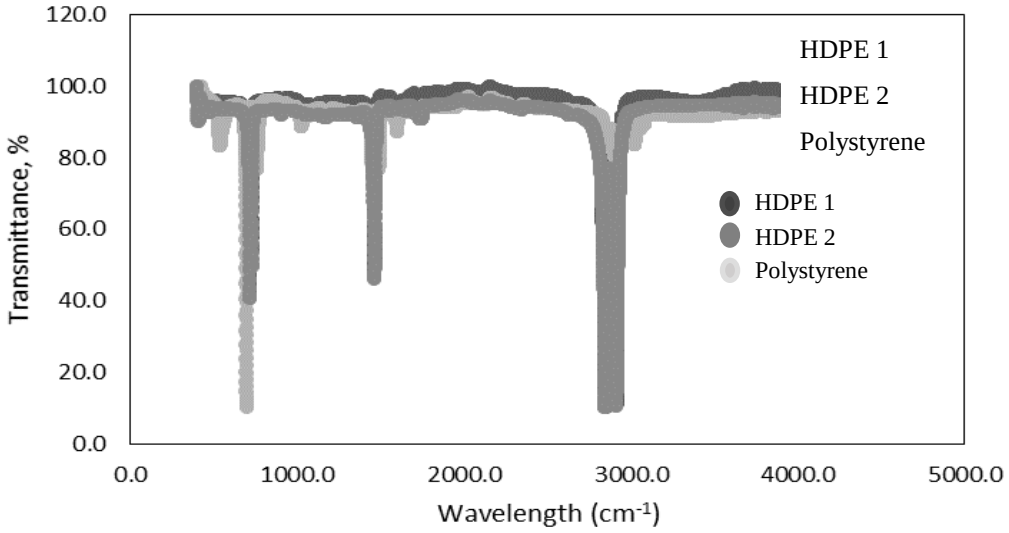

Figure 3. Graph of Transmittance (%) against Wavelength (cm^{-1})

Figure 3 shows the spectra of the three types of polymer used in this study, namely, HDPE 1, HDPE 2, and polystyrene. FTIR is a technique based on the vibrations of the atoms of a molecule. An IR spectrum is commonly obtained by passing IR radiation through a sample and determining what fraction of the incident radiation is absorbed at a particular energy. This energy is determined at any peak in an absorption spectrum that appears to correspond to the frequency of the vibration of a part of a sample molecule. This test was conducted to determine the actual group of the three samples, especially the HDPE 1 and 2 samples, as they were used for the same application, which was as detergent bottles. From the figure, it was noted that all samples had presented the same absorption, varying only in terms of intensity, which can be attributed to their degree of branching, i.e., the number and size of ramifications. The samples of HDPE 1 and HDPE 2 showed the exact same trend because they both came from the same group. For the HDPE or LDPE group, significant bands can be seen in the regions of 3000–2800, 1550–1400, and 750–650 cm^{-1} (Gulmine, 2002) because they have nearly similar spectra. When the HDPE-LDPE spectra were compared, no noticeable difference was observed. The only exception would be the inclusion of additional thickness or length of the peaks due to additional branching in some samples (Petrovich, 2015). FTIR also allows the determination if any water molecule that exists in a sample. If the sample has water molecules, the spectrum will resonate around the 3450 cm^{-1} region. Amongst the three samples, none of them showed significant resonances around 3450 cm^{-1}. It can be said that the water contents in all these samples were negligeable. Thus, moisture content analysis was performed to determine the exact amount of moisture content in a sample.

3.4. Flash Point (ASTM D93-08)

Table 1. Flash Point Temperature for liquid samples

Sample Name	Flash Point Temperature (°C)
Base oil 1	132.5
Base oil 2	20.0
Base oil 3	65.0
Sludge	145.5

Table 1 shows the flash point temperatures for four different samples that mainly contained different blends of oil, which were collected from different sources. Flash point is defined as the

lowest temperature of a liquid at which its vapors will form a combustible mixture with air (Gharagheizi, 2008). Generally, the more viscous and higher additive content in the oil, the higher the flash point. From the table , base oil 1 has the highest flash point at 132.5°C, while base oil 2 has the lowest flash point at 20 °C. Physically, base oil 2 was more watery-like compared to the other samples. This could be the effect of the addition of other components that diluted the oil. In order to formulate modified bitumen, the oil needs to have a high flash point since this experiment was conducted at the maximum temperature of 180 °C, and the oil was used as the medium for the polymer to melt.

3.5. Density

Table 2. Density for liquid samples

Sample Name	Density (kg/m^3)
Base oil 1	0.9304
Base oil 2	0.8070
Base oil 3	0.8720
Sludge	1.1831

Table 2 shows the density results for four different oil samples that mainly contained different blends of oil. This test was conducted to determine the physical behavior of the oils. Generally, in order to mix different materials into one mixture, the density of all materials involved must be closed enough to homogeneously mix the mixture. In a comparison of the density of the oil samples, base oil 1 showed the highest density of 0.9304 kg/m^3, whereas the lowest density belonged to base oil 2 at 0.8070 kg/m^3. In this case, base oil 3 was chosen because the supplier for base oil 1 no longer produce it and base oil 3 has a higher density compared to base oil 2.

3.6. Moisture Content

Table 3. Moisture content for all solid and liquid samples

Sample Name	Moisture Content (%)
Base oil 1	1.019
Base oil 2	0.504
Base oil 3	0.311
Sludge	14.479
HDPE 1	0.266
HDPE 2	0.389
Polystyrene	0.757

Table 3 shows the moisture content of all raw materials, which consisted of oil and polymer. A moisture content analyser was run to determine any moisture that could exist in the samples because a standard for moisture content in raw materials needs to be developed in order to control the quality of the final products. Amongst the three polymeric materials, HDPE 1 sample has the least moisture content at 0.266%, followed by HDPE 2 sample at 0.389%, and polystyrene sample at 0.757%. Meanwhile, for the base oil samples, base oil 1 has the highest moisture content at 1.02% and the lowest moisture content was for base oil 3 at 0.311%. The formulated bitumen was then emulsified using a suitable emulsifier to dilute the bitumen into liquid form. Therefore, the bitumen sample would not necessarily have the exact same performance as the original pavement bitumen, which is more viscous compared to the formulated bitumen in this study.

Table 4. Summary and result of all the test conducted

Sample Test	HDPE 1	HDPE 2	Polystyrene	Base oil 1	Base oil 2	Base oil 3	Sludge
TGA (℃)	468.68	439.54	402.90	-	-	-	-
			Solid sample only				
DSC (℃)	131.24	133.19	151.90	-	-	-	-
			Solid sample only				
Flash Point (℃)	-	-	-	20	132.5	65	145.5
			Liquid sample only				
Density (kg/m^3)	-	-	-	0.807	0.9304	0.872	1.1831
			Liquid sample only				
Moisture Content (%)	0.266	0.389	0.757	0.504	1.019	0.311	14.48

Table 4 summarizes the results for each test. TGA and DSC had only allowed solid samples to be tested, while the flash point and density testing had only allowed liquid samples. On the other hand, moisture content analysis had allowed both liquid and solid samples to be tested using the analyzer. TGA measured the decomposition temperature and composition one of each sample, so the exact amount of filler can be determined from this analysis. Furthermore, DSC was applied to determine the melting point of each sample because it is an important parameter for establishing a method for bitumen formulation. In addition, it is also important that the oil used in this formulation has a high flash point.

4. Conclusion

HDPE 1 was chosen over the other polymer because it contains lesser amount of fillers. It can easily undergo the depolymerisation process while being heated and mixed with the bitumen. Second, the melting temperature of the material was determined from the DSC analysis because it must be homogenously mixed into the formulation. Third, automotive oil was used as the medium for the polymer to melt because an oil with a high flash point was necessary for this experiment. Only two suppliers can supply base oils for a long term, which were suppliers for base oil 2 and base oil 3. Hence, base oil 3 was selected since it has a higher flash point compared to base oil 2. In addition, base oil 3 was also chosen for its higher density because it would be able to tolerate the polymer in the mixture better compared to the other samples.

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References

Asphalt Institute and Eurobitume (2011). *The Bitumen Industry – A Global Perspective: Production, Chemistry, Use, Specification and Occupational Exposure*, 2nd Edition. Lexington, Kentucky, USA.

Crompton, T.R. Thermal Stability of Polymer. Smithers Lapra Technology Ltd. United Kingdom

Department of Statistics Malaysia. (2016). Department of Statistics Malaysia Press Release Report on Survey of Manufacturing Industries 2015, (June), 2–6.

Gharagheizi, F., & Alamdari, R. F. (2008). Prediction of Flash Point Temperature of Pure Components Using a Quantitative Structure–Property Relationship Model. *QSAR & Combinatorial Science*, ***27***(6), 679–683.

Gulmine, J.,Janissek P.R.(2002). Polyethylene Characterization by FTIR, ***21***:557-563.

Joseph, W. (2009). Characterization and analysis of polymers. John Wiley & sons. Hoboken, NewJersey.

Petrovich, J. (2015). FTIR and DSC of polymers films used for packaging: LLDPE, PP, PVDC. SHAPE American High School.

Rahim, K. A., & Liwan, A. (2012). Oil and gas trends and implications in Malaysia. *Energy Policy*, ***50*:**262–271.

Sin, T. J., Chen, G. K., Long, K. S., Goh, I., & Hwang, H. (2012). Current practice of waste management system in Malaysia : Towards sustainable waste management Current Practices for Malaysia.

Tarmudi, Z., Abdullah, M., & Tap, A. M. (2009). an Overview of Municipal Solid Wastes Generation in Malaysia. *Jurnal Teknologi*, *51 (F)*(November 2016), 1–15.

Turi, A. (1997). Thermal Characterization of Polymeric Materials. 1st Edition.

Yaacob, H., Hainin, M. R., Aziz, M. M. A., Warid, M. N. M., Chang, F. L., Ismail, C. R., & Hassan, N. A. (2013). Bitumen emulsion in malaysia-a conspectus. *Jurnal Teknologi (Sciences and Engineering)*, ***65***(3), 97–104.