Characterization of industrial wastes as raw materials for Emulsified Modified Bitumen (EMB) formulation

Mohd Najib Razali, Syarifah Nur Ezatie Mohd Isa, Noor Adilah Md Salehan, Musafikri Musa, Mohd Aizuddin Abd Aziz, Abdurahman Hamid Nour and Rosli Mohd Yunus

Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang, Malaysia.

Email: najibrazali@ump.edu.my

Abstract. This study was conducted to characterize industrial wastes for formulation of emulsified modified bitumen (EMB) in relation to their physical characteristic and elemental composition. This analysis will give information either raw materials from industrial wastes can be used for EMB formulation. Bitumen is produced from crude oil that is extracted from the ground which categorizes the crude oil as one of the non-renewable form of product. A vast environmental problem issues arises in Malaysia cause by the excessive manufacturing activity that lead to a miss-management of industrial waste has leads to the used of industrial waste in the EMB formulation. Industrial waste such as polystyrene, polyethylene and used automotive oil can be used as alternative to formulate bitumen. Then a suitable emulsifier needs to be added to produce the final product which is EMB. The emulsifier will yield a charge depends on its properties to bind the oily bitumen with water. Physical characteristic studies were performed by thermogravimetric Analysis (TGA), differential scanning calorimetry (DSC), flash point test, density rest and moisture content test. Fourier Transform Infrared Spectroscopy (FTIR) analysis was measured to determine the material’s molecular composition and structure.

1. Introduction
Bitumen is used mainly in road paving, roofing application, roads construction, waterproofing products, building materials and industrial coatings [1]. It is estimated that the current world consumption of bitumen is 102 million tonnes per year which 85% from it is used as binder for pavements, 10% for roofing application and the rest is used for other variety kind of purposes [2]. In Malaysia, the urge to solve environmental issue is getting crucial. Significantly, the industrial waste such as crumb rubber, polystyrene, plastics and used oil has been contributed to this problem. These wastes can be formulate to become modified bitumen and essentially with the help of suitable emulsifier, it can become emulsified modification bitumen (EMB).

Bitumen is considered as one of the non-renewable product when it is produced from crude oil. In order to prevent this renewable source replenished from earth as well as to maximize the use of waste produce by the industry, EMB can be formulated from industrial waste by using crumb rubber, polystyrene, plastics and used oil to replace the existed bitumen from crude oil. The EMB formulated will solve the dependency to the natural resources as well as the vast environmental problem that
consequently happen because of the overused of natural resources. The EMB formulated will be used for insulation and coating of building. Not only that, most EMB shows a better performance than unmodified one [3].

The increasing quantities of industrial waste in Malaysia have led to many serious environmental problems which require a better solution to handle it. The solid waste in Malaysia increased from 16,200 tonnes/day in 2001 to 19,100 tonnes/day in 2005 or an average of 0.8 kilogram per capita/ day [4]. In 2014, the Environmental Protection Expenditure (EPE) was reported at a total of RM2.244 billion where the manufacturing sector was the highest contributor to this EPE at RM1.619 billion [5] and since the solid wastes generated are exceeding the maximum amount, these generated wastes are finally disposed in landfills as the current implemented waste management is poorly managed. This method is not sustainable and need to be improved or else it would affect our environment, social and lead to economic lose [6]. Moreover, with the growing demand of crude oil at a rate of 4.5% annually during 2000-2005 to 6.2% per annum during 2006-2010 [7], it is consequently decrease the rate of natural resources in Malaysia. Thus, the development of emulsified modification bitumen from industrial waste is one of the alternative ways to reduce this problem.

As the EMB will be formulated through recycling technology, many environmental aspects that will lead to serious effect can be decreased such as energy consumption, high level of CO$_2$ emission to the environment during work construction, maintenance operation and worker’s health [8]. Besides, bitumen emulsion presents much lower viscosity as it is diluted with water and can be applied at lower temperature as low as 80°C. Conventional binders are sprayed at 160-200°C so there is much more additional risk of fire and explosion [1]. Physical characteristic studies were performed by thermogravimetric Analysis (TGA), differential scanning calorimetry (DSC), flash point test, density rest and moisture content test. Fourier Transform Infrared Spectroscopy (FTIR) analysis was measured to determine the material’s molecular composition and structure. The suitable raw material for formulation of emulsified modified bitumen will be choose based on six analysis conducted.

2. Materials and Methods

2.1. Materials
The raw materials used for this research are bitumen grade 80/100 from Kemaman Bitumen Company (KBC), high density polyethylene and polystyrene from landfill. Three type of recycled base oil collected from Kemaman, Banting and Kuantan. Lastly, the waste sludge is from Kemaman.

2.2. Thermogravimetric Analysis (TGA)
TGA was performed to determine the decompose temperature and the composition in a sample. This analysis measures the percent weight loss of a test sample while it is heated at 10°C/min until approximately 900 °C under inert air. Firstly, 2.5 mg pf test specimen is weight and placed in an aluminium pan and sits upon a constantan disc on a platform in the TGA cell and it is hangs off a hook which is connected by a microgram arm to a tare pan. The loss in weight over specific temperature ranges provides an indication of the composition of the sample.

2.3. Differential Scanning Calorimetry (DSC)
This analysis was done to determine its melting temperature (Tm). Approximately 2.5 mg of test specimen is weight and placed in a aluminium pan and sits 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 measures the sample temperature. An empty reference pan sits on a symmetric platform with its own underlying chromel wafer and chromel-alumel thermocouple. Heat flow is measured by comparing the difference in temperature across the sample and the reference chromel wafers. The sample was running for about 33 minute by specifying the final temperature of the sample at 350°C.
2.4. Fourier-transform infrared spectroscopy (FTIR)

FTIR analysis was measured to determine the material’s molecular composition and structure. It 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’s absorbance of the infrared light’s energy at various wavelengths. The first step is to collect a background spectra to subtract from the test spectra to ensure the actual sample is all that is analyzed. A simple device called an interferometer is used to identify samples by producing an optical signal with all the IR frequencies encoded into it. Then, the signal is 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 material.

2.5. Flash Point Test

A flash point test was performed. Approximately 70 ml test specimen is placed into a test cup. The temperature of the test specimen is increased rapidly 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 the vapors of the test specimen to ignite. To determine the fire point, the test is continued until the application of the test flame causes the test specimen to ignite and sustain burning for a minimum of 5s.

2.6. Density Test

Density test was performed by using gas pycnometer device to determine the density of each samples. To conduct the testing, the liquid sample is filled in a steel cup and then 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 is pressurized to a target pressure with the displacement gas. Once stabilized, this pressure is recorded. A valve is then opened allowing the gas to expand into a reference chamber whose volume is also known. Once stabilized, this second pressure is recorded. This pressure drop ratio is then compared to the behavior of the system when a known volume standard underwent the same process.

2.7. Moisture Content Test

Moisture content analysis was performed to check on any moisture in each samples. About 2g of the sample is filled in its pan evenly and placed on the platform. The drying temperature was set to standard drying temperature which is 105 °C and the lid was closed.

3. Results and Discussions

3.1. Thermogravimetric Analysis (TGA)

Based on figure 1, the curve shows a continuous mass loss steps relating to the loss of volatile components such as moisture and additives, decomposition temperature of the polymer and combustion of final residue such as ash and filler [9]. According to [10], the multicomponent material in one polymer which are low-molecular mass compounds, polymeric material and inorganic additives can be divided by temperature. Thus, each composition and degradation temperature can be known.

By referring to figure 1, all of the sample shows the same degradation temperature but different weight loss for three existing component which for polystyrene sample, 0.4476% of its component degrade at temperature below 200°C, 97.16% at 402.9°C and 2.355% at 900°C while for high density polyethylene 2 (HDPE 2), 0.0852% of its component degrade at temperature below 200°C, 97.33% at 402.9°C, 2.606% at 900°C and lastly for high density polyethylene 1 (HDPE 1), 0.3235% degrade at temperature below 200°C, 98.17°C at 402.9°C, 1.510% at 900°C. These results show that all of the sample consist of low-molecular-mass components such as water and additives as it completely loses its mass at low temperature. Furthermore, the major weight loss which is approximately 80% of each samples occur at 402.9°C. At temperature around 350-500°C, all carbon-carbon bonds is typically rupture by undergoing three possible mechanism; random scission, depolymerisation and side group
elimination (Crompton, 2012). Besides that, the residue left which 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 residue that remain above 600°C are normally associated with inorganic compounds such as silica particles, glass fibers or calcium carbonate [10].

Consequently, based on the result above, HDPE 1 sample should be able to tolerate with the bitumen formulation the most as it contains the least amount of filler and the highest purity of polymer with 98.17\% of the total weight is the hydrocarbon component.

![Figure 1. Graph of Weight Loss (%) against Temperature (°C).](image)

**3.2. Differential Scanning Calorimetry (DSC)**

From figure 2, the HDPE 1 and 2 sample shows approximately the same trend which deviate from the polystyrene sample. This is because both sample is come from the same group of polymer. Graph form DSC will provide 3 different value of melting for each material which from the graph, it is denotes as A, B and C. At point A, it is the point where the material starts to melt. Point B depicts the peak temperature of melting where it indicates the maximum rate of melting. Lastly, the real melting point value is at point C when the graph reach steady state before it is going down the endotherm [10]. Therefore, in order to formulate a bitumen, the melting point of each sample need to determine so that the method developed for this research will ensure all of the material use is melted accordingly based on the temperature. In semicrystalline polymers such as polyethylene, the degree of crystallinity (\% crystallinity) influences the degree of stiffness, hardness and heat resistance. The ratio of melting heat of the samples and the melting heat of the completely crystallized polyethylene was used to calculate the degree of crystallization. From table 2, it is clearly shown that polystyrene sample exhibit much deviate value from HDPE sample at 101.97\% of crystallinity. This is because polystyrene is an amorphous polymer while HDPE is a type of semicrystalline polymer. Semi-crystalline polymers exhibit organized and tightly packed molecular chains also consist of at least some disorganized region whereas the polymer chains for amorphous plastics are more disorganized. When heat is applied on semicrystalline polymer, weaker bonds in polymer chains which is in disorganized areas break at Glass Transition Temperature. However, the bonds at organized areas do not break until the Melting Temperature. At this point the material changes from a solid-like to a liquid-like state [11].
Figure 2. Graph of Heat Flow (w/g) against Temperature (°C).

Table 1. Degree of Crystallinity of Polymer Sample.

| Sample       | Melt Peak Temperature (°C) | Enthalpy (J/g) | Degree of Crystallinity (%) |
|--------------|---------------------------|----------------|----------------------------|
| HDPE1        | 125.72                    | 172.2          | 58.65                      |
| HDPE2        | 123.75                    | 166.4          | 56.67                      |
| Polystyrene  | 147.79                    | 98.69          | 101.97                     |

3.3. **Fourier Transform Infrared Spectroscopy (FTIR)**

Figure 3 shows the spectra of three types of polymer which are HDPE 1, HDPE 2 and polystyrene. FTIR is a technique based on the vibrations of 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. The energy at which any peak in an absorption spectrum appears corresponds to the frequency of a vibration of a part of a sample molecule. This test was conducted to know the actual group of the three samples especially HDPE 1 and 2 sample as they were used as the same application which is as detergent bottle. From figure 3, it is noted that all present the same absorptions, varying only in terms of intensity which can be attributed to their degree of branching, that is, number and size of ramifications. Farm fresh bottle and dynamo bottle sample shows the exact same trend as both of it comes from the same group. For HDPE or LDPE group, the significant band are in the regions of 3000–2800, 1550–1400 and 750–650 cm\(^{-1}\) [12] because they have the nearly same spectra. When one compares the HDPE-LDPE spectra, it lacks any noticeable difference in structure. The only exception would be the inclusion of additional thickness or length to peaks due to additional branching in some sample [13]. FTIR also allow the determination if any water molecule exist in a sample. If the sample is having water molecule, it will resonate around 3450 cm\(^{-1}\) region. Amongst the three samples, none of them shows significant resonance around 3450 cm\(^{-1}\) so it can be said that the water content in all of the sample are so small. So, the moisture content analysis need to be done in order to know the exact amount of moisture content in a sample.
3.4. Flash Point (ASTM D93-08)
Table 2 shows the flash point temperature result for four different samples mainly contain different blend 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 [14]. Generally, the more viscous and more contained of additives in the oil, the higher the flash point. From table 1, base oil 1 have the highest flash point with 132.5°C while base oil 2 is having the lowest flash point with 20°C. Physically, the base oil 2 is much more watery-like compare to others. This might be affected by the addition of other component that has diluted the oil. In order to formulate a bitumen, the oil needs to have a high flash point as this experiment is conducted at maximum temperature of 180°C and the oil was used as the medium of the polymer to melt.

Table 2. 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                        |

3.5. Density
Table 3 shows the density result for four different sources of oil sample mainly contain different blend of oil. This test was conducted to check on the physical behavior of the oils. Generally, in order to mix a different material in one mixture, the density of all the materials involved need to be closed enough to each other to make the mixture homogeneously mixed. To compare the density amongst the oil, base oil 1 has the highest density which is 0.9304 kg/m³ whereas the lowest density is base oil 2 with a density of 0.8070 kg/m³. In this case, base oil 3 was chosen because the supplier for base oil 1 have no more production of base oil to supply and base oil 3 has the higher density compare to base oil 2.

Table 3. Density for liquid samples.

| Sample Name | Density (kg/m³) |
|-------------|-----------------|
| Base oil 1  | 0.9304          |
| Base oil 2  | 0.8070          |
| Base oil 3  | 0.8720          |
| Sludge      | 1.1831          |
3.6. Moisture Content

Table 4 shows the moisture content result for all raw material which consist of oil and polymer. Moisture content analyzer test was run to check on any moisture existed in the sample because one standard of moisture content in raw material need to develop in order to control the quality of the final products. Amongst three polymeric material, HDPE 1 sample has the least moisture content of 0.266% followed by HDPE 2 sample at 0.389% and polystyrene sample at 0.757%. Whereas for the base oil samples, base oil 1 has the highest moisture content at 1.02% and the lowest content is base oil 3 which at 0.311%. Since the formulated bitumen was then being emulsified by using a suitable emulsifier by means, to dilute the bitumen into liquid form, so the bitumen sample that was formulated is not necessarily has the exact same performance as the original pavement bitumen which is more viscous compare to the bitumen formulated in this research.

Table 4. 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 5 summarize all the results for all the testing that already conducted. TGA and DSC only allow solid sample, flash point and density testing only allow liquid sample whereas moisture content analysis allow both liquid and solid sample to be run on the analyzer. From all of these analysis, TGA measures the decomposition temperature and composition in one sample so the exact amount of filler content can be known throughout this analysis. Furthermore, DSC determine the melting point of each samples as it is an important parameter we need to know before establish a method for bitumen formulation. In addition, it is important for the oil that used in this formulation to have a high flash point.

Table 5. 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 (°C)    | 468.68  | 439.54  | 402.90      | -         | -         | -         | -     |
| DSC (°C)    | 131.24  | 133.19  | 151.90      | -         | -         | -         | -     |
| Flash Point (°C) | -       | -       | -           | 20        | 132.5     | 65        | 145.5 |
| Density (kg/m³) | -       | -       | -           | 0.807     | 0.93      | 0.872     | 1.1831 |
| Moisture Content (%) | 0.266   | 0.389   | 0.757       | 0.504     | 1.019     | 0.311     | 14.48 |
4. Conclusion
HDPE 1 is chose above other polymer as it contain less amount of filler so it is easier to undergo depolymerisation process while being heated and mix with the bitumen. Secondly, it is important to know the melting temperature of the material through DSC analysis as the material need to be melt to mix it in the formulation homogenously. Thirdly, automotive oil is used as the medium of the polymer to melt so an oil that having a high flash point is necessary for this experiment. Thus by comparing all type of base oil, there are two supplier that can supply the base oil for long term which are supplier for base oil 2 and base oil 3. Hence, base oil 3 is selected since it has higher flash point compared to base oil 2. Also, to compare in term of density, the higher density which is base oil 3 is chosen as it will tolerate with the polymer in the mixture the most.

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