Thermal, chemical and imaging analysis of Polyurethane/ Cecabase modified bitumen

F H Khairuddin1,2, N I Md Yusof2, K Badri3, H Ceylan4 and S N Mohd Tawil5

1 Smart and Sustainable Township Research Centre (SUTRA), Universiti Kebangsaan Malaysia, Selangor, Malaysia
2 Department of Civil Engineering, Universiti Pertahanan Nasional Malaysia, Kuala Lumpur, Malaysia
3 School of Chemical Science & Food Technology, Universiti Kebangsaan Malaysia, Selangor, Malaysia
4 Department of Civil, Construction and Environmental Engineering, IOWA State University, USA
5 Department of Electrical & Electronic Engineering, Universiti Pertahanan Nasional Malaysia, Kuala Lumpur, Malaysia

E-mail: arename1004@gmail.com

Abstract. In this study, a 60/70 penetration grade bitumen was modified with polyurethane (PU) added with a Warm Mix Asphalt (WMA) additive, i.e. Cecabase, in the amount of 0.5 wt % with respect to bitumen. The thermal characterization was done using the Differential Scanning Calorimetry (DSC) while the chemical analysis was done using Fourier Transform Infrared (FTIR). Raman Spectroscopy was used to characterize the asphaltic materials in the bitumen, namely the D (Defect) and G (Graphite) bands. Test results showed that adding PU and Cecabase to the bitumen slightly shifted the Tg and Tm peaks of the thermal behaviour. The result of FTIR showed that there was no shift in the carbonyl and sulfoxide peaks, which indicate that no chemical interaction occurred in the unmodified and modified bitumen. Furthermore, the Raman Spectroscopy investigation revealed that PU and Cecabase reduced the wax content and decreased the bee-structure of the bitumen samples. However, the order structures of unmodified and modified bitumen were still within the boundary limit of the D and G bands of the Raman spectra. In conclusion, the use of PU and Cecabase as bitumen modifier are promising for alternative source for bitumen.

1. Introduction
In recent years, researchers have been making more attempts to modify bitumen with bio oils. Modification of bitumen is an alternative method to improve pavement performance in the attempt to deal with excessive traffic load and changes in the environmental conditions. Recent research were conducted utilizing various sources of bio-oils, such as waste cooking oil, swine waste, and waste wood as bio binder [1–3]. Sun et al. [1] reported the addition of waste cooking oil decreased the complex modulus and creep stiffness of the modified bitumen while at the same time increasing the m-value and phase angle of the modified bitumen. Julian et al. [2] investigated the feasibility of adding swine waste to base bitumen and observed a reduction in the viscosity of unaged, short-term aged, and long term-aged modified bitumen. Furthermore, the results of rheological testing have shown that modified bitumen have lower complex moduli and phase angles in comparison to the base
bitumen while the results of bending beam rheometer test indicated that the addition of swine waste have a potential to improve the thermal cracking performance of base bitumen by reducing creep stiffness and increasing m-value. Bitumen modified with bio-oil generated from waste wood sources requires lower mixing temperature and improve the performance of the bitumen [3]. Therefore, it can be concluded that bio-oil has a promising potential for use as a bitumen modifier.

The environmental problems brought about by the high temperature required for the manufacture of bitumen and road paving have prompted research to discover eco-friendly and sustainable materials. As a result, the Warm Mix Asphalt (WMA) technology was introduced and it has been widely utilised in the paving industry due to its ability to reduce the mixing and compacting temperatures by 30-50°C in comparison to Hot Mix Asphalt (HMA) [4,5]. Among the advantages of utilizing WMA are enhanced economic value, improved resistance and durability, less environmental pollution, and ease of construction. WMA reduces production temperatures and odour emission at the plant, extends paving seasons, allows for a longer hauling distance, allows for earlier traffic opening, reduces binder aging, reduces cracking, and minimises oxidative hardening since the mixtures are produced closer to operating temperatures. The example of WMA chemical additives are Evotherm, Rediset WMX and Cecabase RT. Rediset WMX and Cecabase RT are made of adhesion agents and surfactant that will improve the wetting condition of aggregates as well the adhesion behaviour without changing the actual bitumen performance [6,7]. Besides that, the mixing production temperature of asphalt mix Cecabase RT 945 reduced by 20 to 40°C and the mechanical properties are same as HMA [8,9].

Since the utilization of bio-oil and warm mix asphalt in the pavement industry are promising, this study is conducted to evaluate the feasibility of using polyurethane (PU) and WMA additive, i.e. Cecabase RT 975, as a modifier for base bitumen. The effects of this modifier were investigated through thermal, chemical, and image analysis and the modified bitumens were then compared with the base bitumen.

2. Experimental designs
2.1. Materials
This study used 60/70 penetration grade bitumen as the control sample. The physical properties of unmodified bitumen are presented in Table 1. A modifier, PU was produced through prepolymerisation process from palm kernel oil based polyol (PKO-p) and 2,4-diphenylmethane diisocyanate (MDI). A WMA chemical additive, Cecabase RT 975, was added to bitumen at a dosage rate of 0.5% by weight of bitumen, as recommended by supplier, in the attempt to achieve lower production and compaction temperatures of asphalt mixtures.

| Table 1. Physical properties of 60/70 Penetration Grade Bitumen |
|---------------------------------|---------------|---------------|----|
| Properties                       | Standard      | Specification | Value |
| Penetration (dmm)                | ASTM D5       | 60 - 70       | 66  |
| Softening point (°C)             | ASTM D36      | 47 - 52       | 49  |
| Viscosity at 135°C (mPa.s)       | ASTM D113     | -             | 550 |
| Ductility (cm)                   | ASTM D4402    | > 100         | 100 |
| Specific gravity                 | ASTM D70      | 1.0 – 1.06    | 1.03|

2.2. Sample preparation
Three modified bitumen samples were prepared and coded as bitumen-PU (B-PU), bitumen-PU-Cecabase (B-PU-C), and bitumen-Cecabase (B-C). The base bitumen (B-B) was heated at 145°C until it turns into liquid. PKO-p was then added to the bitumen at 110°C and blended at 2000 revolutions per minute for 15 minutes using a mechanical shear mixer. MDI was then added and blended using the same mixing parameter. For the B-PU-C sample, Cecabase was added and blended for 10 minutes after the B-PU has been homogeneously blended.
3. Laboratory Testing
The effects of adding PU and Cecabase to bitumen were evaluated with regard to thermal condition by using the Differential Scanning Calorimetry (DSC) test. Shimadzu DSC-50 was used under Nitrogen atmosphere at flow rate of 10ml/min and heating rate of 10˚C/min from room temperature to 600˚C. The chemical characterization was done using Perkin Elmer-1650 thermogravimetric with wavenumbers ranging from 600 cm\(^{-1}\) to 4000 cm\(^{-1}\). The topography of the bee-structures of unmodified and modified samples were determined using the inVia Confocal Raman equipped with a 532 nm solid state laser with a 20 \(\mu\)m x 20 \(\mu\)m area in-view laser beam size. The Raman spectra showed the structure of the D (Defect) and G (Graphite) bands of the bitumen.

4. Results and Discussion

4.1. Differential Scanning Calorimetry (DSC)
DSC tests were conducted to understand the thermal transitions as well as the initial wax crystallisation and melting temperatures of the unmodified and modified bitumen. Figure 1 shows the DSC curve for the transition glass temperature (\(T_g\)), melting temperature (\(T_m\)), and segregation temperature of the bitumen samples. It shows that the \(T_g\), \(T_m\), and segregation temperature of B-B are lower than those of the modified bitumen. The effects of low temperature on bitumen properties are typically indicated by the glass transition temperature (\(T_g\)). An exothermic peak was observed at a temperature of about 33°C for B-B, 31°C for B-PU, 33°C for B-PU-C and 30°C for B-C and this was interpreted as wax crystallisation or oxidation reaction \[10\]. The temperature required for melting transition, \(T_m\) to occur for B-B, B-PU, B-PU-C and B-C are 88°C, 97°C, 100°C and 90°C respectively. The temperature at which all wax completely melt is considerably higher than the temperature for initial crystallization. The DSC curve shows that the shape of the curve is very dependent on thermal history prior to recording the scans. B-C had the lowest \(T_g\) value, which makes it more resistance to low temperature cracking, while B-PU-C has the highest \(T_m\) value in comparison to B-B and B-PU. Segregation occurred at 447°C for B-B, 457°C for B-PU, 461°C for B-PU-C and 451°C for B-C. The endothermic peak was observed at 505°C, 513°C, 519°C and 520°C for B-B, B-PU, B-PU-C and B-C respectively.

Figure 1 shows that the addition of PU or Cecabase did not affect the \(T_g\). B-B containing natural wax had a lower glass transition temperature and this can be attributed to the stiffening effect of natural wax when measurement of penetration was made at 25°C. At this temperature, natural wax, which is partly crystalline, stiffens the bitumen. Therefore, bitumen with a lower penetration grade is more likely to have a higher \(T_g\)\[11,12\]. These results indicate that the trends for \(T_g\) and \(T_m\) peaks are almost similar for the unmodified and modified bitumen.
4.2. Fourier Transform Infrared (FTIR)
The chemical changes in modified bitumen were measured through FTIR analysis. The FTIR spectrum for unmodified and modified bitumen in figure 2 shows the peak position for possible functional group. The major peaks typically occur at similar wavenumber for all samples tested. The first major bond is the CH stretching vibrations of hydrocarbon at 2918-2850 cm$^{-1}$ for B-B, 2918-2849 cm$^{-1}$ for B-PU and B-PU-C and 2917-2850 cm$^{-1}$ for B-C; this indicates that the possible peak position for this functional group is between 3055-2730 cm$^{-1}$. The next absorption peaks, which is due to C=O bond in the aromatic hydroxyl, was observed at similar wavenumber, i.e. 1653 cm$^{-1}$, 1655 cm$^{-1}$, 1664 cm$^{-1}$, and 1652 cm$^{-1}$ for B-B, B-PU, B-PU-C and B-C respectively. The absorption peak at 1597cm$^{-1}$ is due to C=C stretching bond, which was also observed at 1596cm$^{-1}$ for B-B, 1598 cm$^{-1}$ for B-PU, 1595 cm$^{-1}$ for B-PU-C and 1597cm$^{-1}$ for B-C.

The stretching vibrations of the sulfoxide bond S=O were observed at 1026cm$^{-1}$ for B-B and B-PU, 1030 cm$^{-1}$ for B-PU-C and 1028 cm$^{-1}$ for B-C. Based on the IR spectra results, it can be concluded that the addition of PU and Cecabase did not cause any significant shift in the peaks of the modified bitumen [13,14]. Therefore, there was no chemical interaction between the unmodified bitumen and the modifier [15].
4.3. Raman Spectroscopy

4.3.1. Topography of the Bee-Structures. Bitumen is composed of several organic and inorganic compounds which have a complex microstructure. Loeber et al. [16] reported that bitumen structures are composed of wax and show a ‘bee-like structure’ or catana phase. Bitumen with wax content exhibits a more distinct bee-structure. Figures 3 (a-d) show the bee-structures of the unmodified and modified bitumen. However the number of bee-structures in B-PU and B-C are less than those in B-B and B-PU-C. This indicates that the addition of only PU or Cecabase to unmodified bitumen reduced the bitumen’s wax content. The loss of wax could caused an increase in the temperature of the laser, which then caused the wax crystals to melt into the matrix phases of the bitumen. The size and shape of the structures decrease uniformly as a result of the melting process which begin outside the structures and move inwards [17].
4.3.2. Raman Spectra. Figures 4 (a-d) show the Raman peaks for unmodified and modified bitumen. Two types of band were analysed, the D band at a frequency of 1350 cm\(^{-1}\) and the G band at 1580 cm\(^{-1}\). The D and G bands refer to the in-plane breathing vibration made possible by the defect in the ideal graphitic structure [18].

For B-B, the D band occurred at 1355 cm\(^{-1}\) and the G band at 1584 cm\(^{-1}\). The addition of PU shifted both bands and the D band occurred at 1373 cm\(^{-1}\) while the G band at 1589 cm\(^{-1}\). This is because the PU structure has a strong carbonyl compound. For B-PU-C and B-C, the D peaks occurred at 1352 cm\(^{-1}\) and 1372 cm\(^{-1}\) and the G peaks at 1582 cm\(^{-1}\) and 1586 cm\(^{-1}\), respectively. These peaks show that the addition of Cecabase to B-PU slightly shifted both peaks. Hence, it can be concluded that the ordered structures for all modified bitumen are still within the boundary limits of the defect and graphite bands, which is consistent with the result obtained in previous study [19,20].
5. Conclusion
The thermal behaviour of unmodified and modified bitumen were investigated using DSC. Results show similar trends for the tested bitumen, with B-B having the lowest $T_g$ and $T_m$ value. This indicates that addition of PU and Cecabase had little effect on the thermal transition of the B-B. Changes in chemical composition were determined through FTIR and result showed that there was no chemical interaction between the unmodified and modified bitumen since the carbonyl and sulfoxide bond remained almost unchanged. The morphology of the bee-structure from the Raman Spectroscopy revealed that there was a decrease in the wax content of B-PU and B-C, which reduced the catana phase, in comparison to B-B and B-PU-C. The ordered structures for all tested bitumen were still within the boundary limits of both the D and G bands. In conclusion, the use of PU and Cecabase as bitumen modifier are promising for alternative source for bitumen. It is recommended that the rheological and ageing conditions of PU/Cecabase modified bitumen to be conducted for further understanding of this new materials.

6. References
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