

Physicothermal and topography analysis of Polyurethane Modified Bitumen with Rediset for WMA application

Faridah Hanim Khairuddin^{1*}, Siti Zubaidah Mohd Asri¹, Noor Aina Misnon¹, Nur Izzi Md Yusoff², Auni Diyana Fadzil², Ku Zarina Ku Ahmad³

¹Department of Civil Engineering, Universiti Pertahanan Nasional Malaysia, 57000 Kuala Lumpur, Malaysia

²Department of Civil Engineering, Universiti Kebangsaan Malaysia, 43600 Bangi, Malaysia

³Department of Mechanical Engineering, Universiti Pertahanan Nasional Malaysia, 57000 Kuala Lumpur, Malaysia

Email: hanim@upnm.edu.my

Abstract. The effects of modifying a 60/70 penetration grade bitumen with 3 wt% polyurethane (PU) and a Warm Mix Asphalt (WMA) additive namely Rediset, were explored in this research. The penetration, softening point, viscosity, and ductility tests were employed for consistency testing, while the Differential Scanning Calorimetry was used for thermal characterisation. The topography and surface roughness of the modified bitumen were evaluated using Atomic Force Microscopy. Adding PU and Rediset to the base bitumen (BB) stiffens the BB slightly, giving it a lower penetration and higher viscosity values, which improves the rutting resistance. The thermal transition of the glass temperature and melting temperature are similar to the BB. Furthermore, the addition of PU and Rediset into BB shows a clear bee structure topography in dry condition indicating better dispersion while in wet condition, the bee structure is mostly affected in the catana and para phase that reveals a reduced in the the wax content of the BB. The bitumen modified with PU and Rediset has a lower surface roughness than BB, making it less susceptible to moisture damage.

Keywords: *polyurethane, warm mix asphalt, Rediset, thermal behavior, topography.*

Introduction

The quality of the materials and accurate design and construction determine the performance of asphalt pavement. The construction materials are the source of the pavement's mechanical properties, which determine its durability over its service life due to environmental effects, such as heat, oxygen, or ultraviolet (UV) radiation, causes various road degradation, such as cracking, fatigue and rutting [1], [2], [3]. Despite the significance of bitumen, all components contribute to determining the performance of the asphalt mixture [4]. Biomass is most useful when converted into renewable fuels to replace the finite supplies of fossil fuels. Biomass waste is among the most potential sources of renewable energy, and it could contribute to fulfilling the growing energy needs [5]. One example of biomass is palm kernel shell (PKS), where the kernel is utilised as charcoal in the boiler system and the ashes are used as fertiliser and landfill filler [6]. Alamawi et al. [7] introduced palm kernel oil polyol (PKO-p) extracted from PKS as a partial substitute for bitumen. The new bio-binder could replace the petroleum-based bitumen for road construction because of its higher resistance to flow and similar thermal susceptibility to the conventional bitumen. Khairuddin *et al.* [8] investigated the viability of utilising polyurethane (PU) as a modifier in paving bitumen and found, that adding PU to bitumen reduces the temperature susceptibility, making the PU modified bitumen a viable paving material.

Since Warm Mix Asphalt (WMA) technologies have lower mixing and compacting temperatures than conventional Hot Mix Asphalt (HMA), environmental awareness of volatile emissions during pavement construction promotes the use of these techniques to produce green and sustainable pavements [9], [10]. The low mixing temperature range of 100 to 140 °C in WMA technology reduces carbon emissions [11]. The WMA technologies use chemical, foamed, or organic additives. The additives lower the mixture's viscosity and thus make it easier to work the bitumen, facilitate the compaction process, and improve the adhesion quality [12]. The Cecabase RT 945, for example, decreases bitumen mix production and paving temperatures by 20 to 40 °C while preserving the same mechanical qualities as conventional HMA [13], and Rediset LQ-1106, which reduces the mixing and paving temperatures and imparts the built-in anti-stripping effect [14].

This research aimed to investigate the viability of utilizing PU and a WMA chemical additive, Rediset LQ1106, a new novel material to modify the base bitumen (BB) and determined the effects of incorporating this modifier on BB by conducting physical, thermal, and morphological tests in wet and dry conditions. This alternative material has the potential to be used as green paving material towards achieving the sustainable development goals in pavement industry.

Materials and Sample Preparation

This research utilized a 60/70 penetration grade bitumen (BB), PU, and WMA chemical additive, Rediset LQ1106. The study employed the pre-polymerisation method to produce the PU by mixing PKO-p and 2,4-diphenylmethane diisocyanate (MDI). The BB was altered with 3 %wt of PU (designated PUMB), 3 %wt of PU and 0.6 wt% of Rediset (designated PUMB/R), and 0.6 %wt Rediset (designated BB/R). The mixtures were mixed for 15 minutes at 2000 rotations per minute at 110 °C [15]. The physical properties of the BB is shown in Table 1.

Table 1 Physical characteristics of BB

Testing	Unit	Value	Requirement	Standard
Penetration	dmm	69	60-70	ASTM D5
Softening point	°C	49	47-52	ASTM D36
Viscosity at 135 °C	mPa.s	550	-	ASTM D113
Viscosity at 165 °C	mPa.s	150	-	ASTM D113
Ductility	cm	120	min 100	ASTM D4402
Specific gravity	g/cm ³	1.03	1.00-1.06	ASTM D70

Laboratory Tests

Physical Test

The physical tests and specification carried out in this study is listed in Table 1. These physical tests are the conventional tests for evaluating the initial hardness, softness, fluidity, flow resistivity, and tensile properties of the modified bitumen. The findings for each test is the average of three duplicate samples.

Thermal Test

The Differential Scanning Calorimetry (DSC) test was used in this research to assess the thermal condition of the unmodified and modified bitumen. The experiment was carried out in a nitrogen gas ambiance using a Shimadzu DSC-50 calorimeter as shown in Figure 1 at a heating rate of 10 C/min with

a flow rate of 10 ml/min. The sample was heated starting at room temperature to 600 °C. Then, the thermal changes for the glass transition (T_g) and melting temperature (T_m) were determined.

Morphological test

The morphological analysis was carried out using the Atomic Force Microscopy (AFM) instrument, which is seen in Figure 2, to quantify possible changes based on the distance of the two atoms. The Park System Corporation XE-10 AFM model was employed in this research, and XEI software was used for data analysis and processing. The data analysis used a tip with a radius of 10 nm for the non-contact mode data gathering method. The XEI software converted the data into surface topography parameters before processing it.

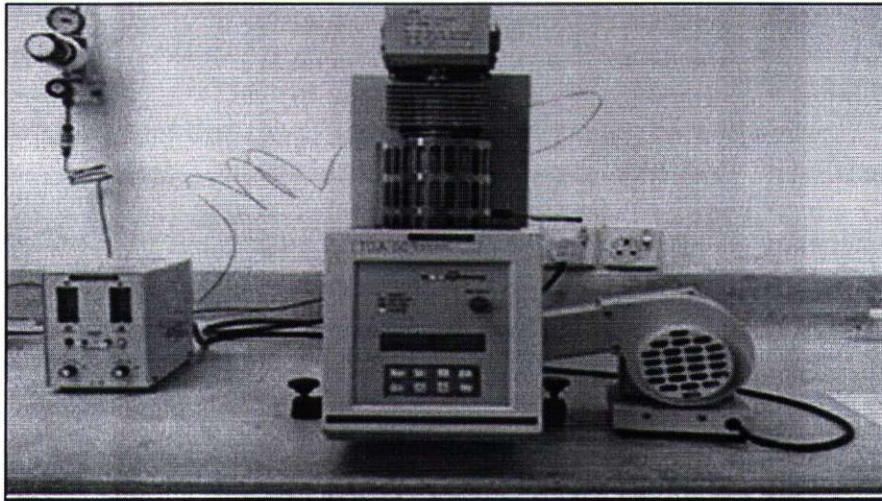


Figure 1 The Shimadzu DSC-50 device for thermal analysis

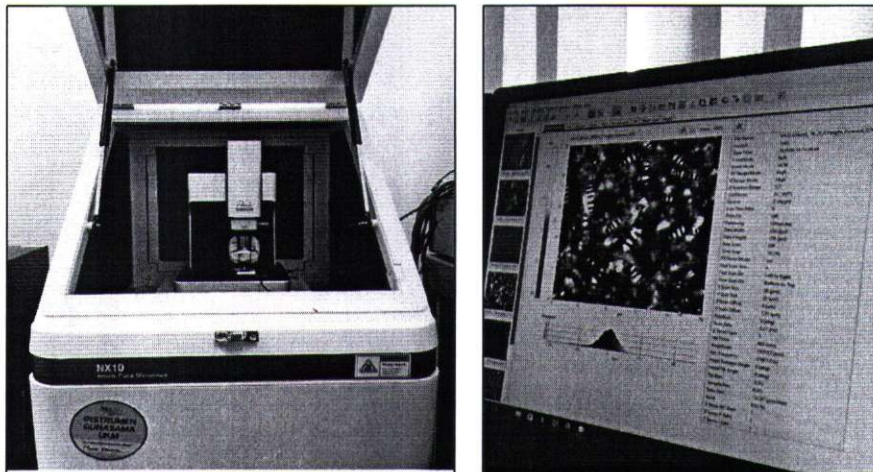


Figure 2 The Atomic Force Microscopy device used for the morphology analysis

Topography

This study used the original non-contact AFM mode to evaluate the bitumen's surface topography and bee characteristics in dry and wet conditions. The wet sample was submerged in 25 °C water for 24 hours before the test. The AFM scanned the 20 x 20 µm samples at a scan rate of 1Hz.

Surface Roughness

The surface roughness (Ra) of bitumen was measured in both dry and wet conditions. This study used the Surface Roughness Ratio (SRR) given in Eq. 1 to determine the moisture effect on the unmodified and modified samples.

$$SRR = \frac{SR_{wet} - SR_{dry}}{SR_{dry}} \quad (1)$$

Result and Discussion

Physical Properties

Table 2 compares the modified and unmodified bitumens in terms of penetration, softening point, viscosity, and ductility. The reduced penetration and greater softening point value of the BB mixed with PU and Rediset suggest that the hardening impact of PU is related to the increased bitumen hardness [16]. All modified bitumen is stiffer than the BB. According to Airey et al. [17], the modified bitumen's lower penetration value increases its temperature susceptibility. The viscosity at 135 and 165 °C show that the incorporation of PU increased the bitumen's flow resistance by 292 and 175 mPa.s respectively. However, incorporating Rediset into BB and PUMB reduced the viscosity value, consistent with the study by Yero and Hainin [18], which found that adding a WMA chemical additive reduced bitumen viscosity. Bitumen with lower viscosities allows a more efficient aggregate coating and improves workability during the mixing process [19]. The result shows that the bitumen viscosity decreased with increasing temperatures. All modified bitumen has an acceptable ductility value of greater than 10 cm.

Table 2 Physical properties of the unmodified and modified bitumen

Bitumen	Penetration (dmm)	Softening Point (°C)	Viscosity at 135 °C	Viscosity at 165 °C	Ductility (cm)
BB	69	49	550	150	120
PUMB	63	51	842	325	113
PUMB/R	63	50	327	105	116
BB/R	66	48	225	101	102

Thermal Property

The DSC thermogram reveals the thermal transitions including the oxidation phase (T_{ox}), crystallisation (T_c), glass transition (T_g), melting point (T_m) and the T_b , also known as the brittle point, is one of the primary thermodynamic parameter changes that characterises the liquid-to-solid transition [20]. T_m is the temperature at which a substance melts and transforms from solid to liquid. Figure 3 depicts the DSC thermogram result shows that adding PU or Rediset changed the T_g . The exothermic peak of T_g for PUMB/R increased to 36.51 °C, while the value for PUMB and BB/R decreased to 31.56 and 31.63 °C, respectively. PUMB has the lowest T_g value and thus is more resistant to low temperature cracking [21].

The T_m for BB, PUMB, PUMB/R, and BB/R is detected at 440.45, 452.60, 454.57, and 455.46 °C, respectively; the values show that the BB incorporated with Rediset has the highest melting temperature. The temperature at which the wax completely melts is substantially greater than the temperature at which it initially crystallises. The thermal history prior to scanning influences the form of the DCS curve. The endothermic peaks for BB, PUMB, PUMB/R, and BB/R are 514.55°C, 517.65°C, 513.67°C, and 516.71°C, respectively, showing that the trends for T_g and T_m peaks for the unmodified and modified bitumen are similar.

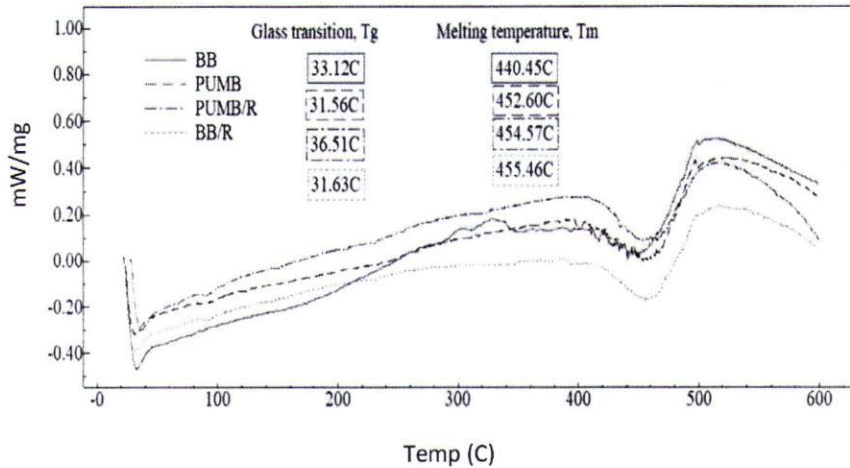


Figure 3 DSC thermogram for the unmodified and modified bitumen

Morphological properties

Surface topography

The bitumen surface topography shows a bee structures representing the asphaltenes in the bitumen [22]. There are three phases in bitumen topography, namely the peri, para and catana phases as shown in Figure 4 [23]. Figures 5 (a-d) and 6 (a-d) show the topographical images of BB, PUMB, PUMB/R, and BB/R in dry and wet conditions. The BB incorporated with PU and Rediset shows a clear bee structure (catana phase) in dry conditions, as shown in Figure 5 (b-d), indicating that PU and Rediset did not affect the bitumen bee structure.

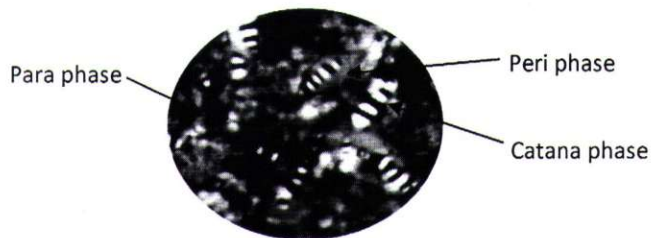


Figure 4 Three phases in bitumen topography

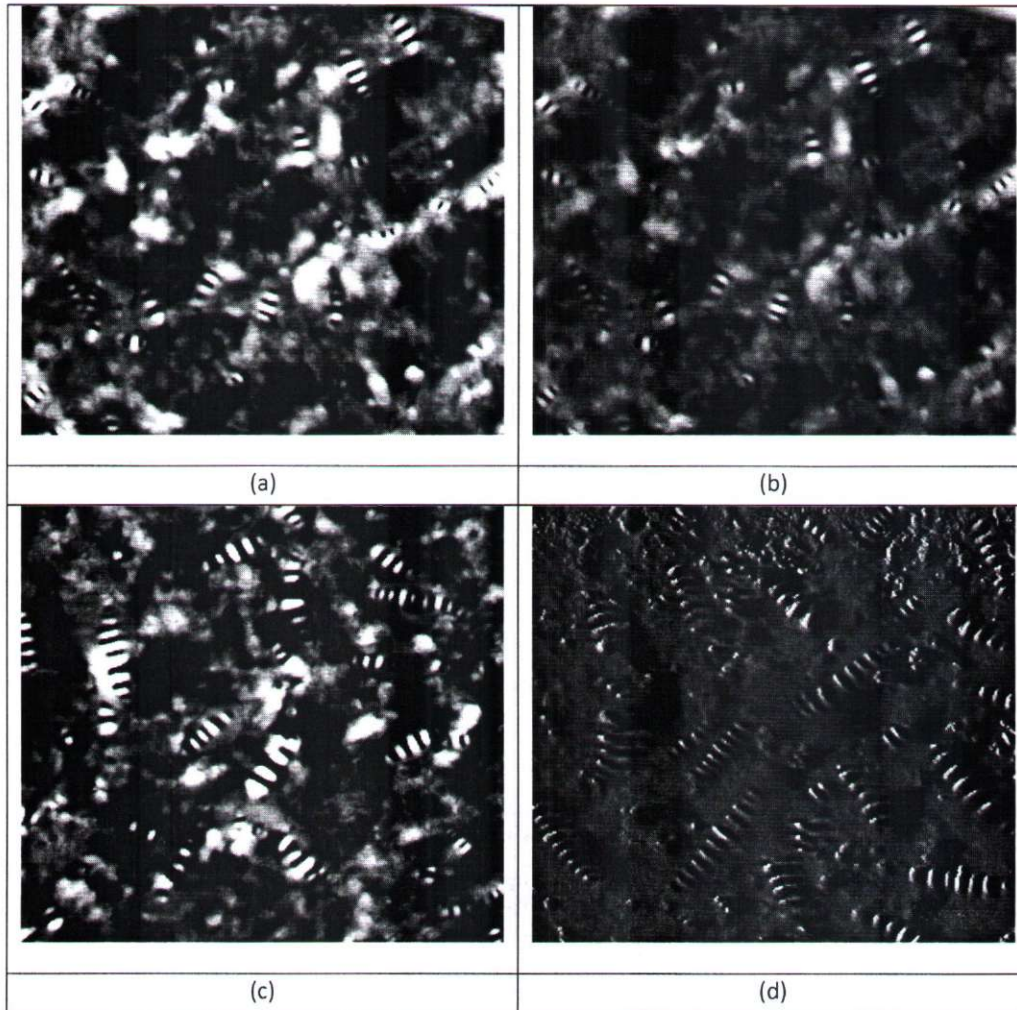


Figure 5 (a)-(d) Surface topography of the unmodified and modified bitumen in dry condition (Scale: 20x20 μm)

Figure 6 (a-d) shows that moisture affected the bee structure. The para phase region is the most affected which is consistent with the findings of Santos et al. [24]. The water intrusion reduced the prominence of the bee structure. According to Zeheng Yao et al. [25], the interaction between moisture and bitumen altered the bitumen surface topography. This result indicates that the PU and Rediset caused the bee structure to disappear after immersion in water. A recent study used LC-amplified optofluidic resonators to detect ultrasensitive real-time bio-molecular interactions, which this method can be further explored in this study [26].

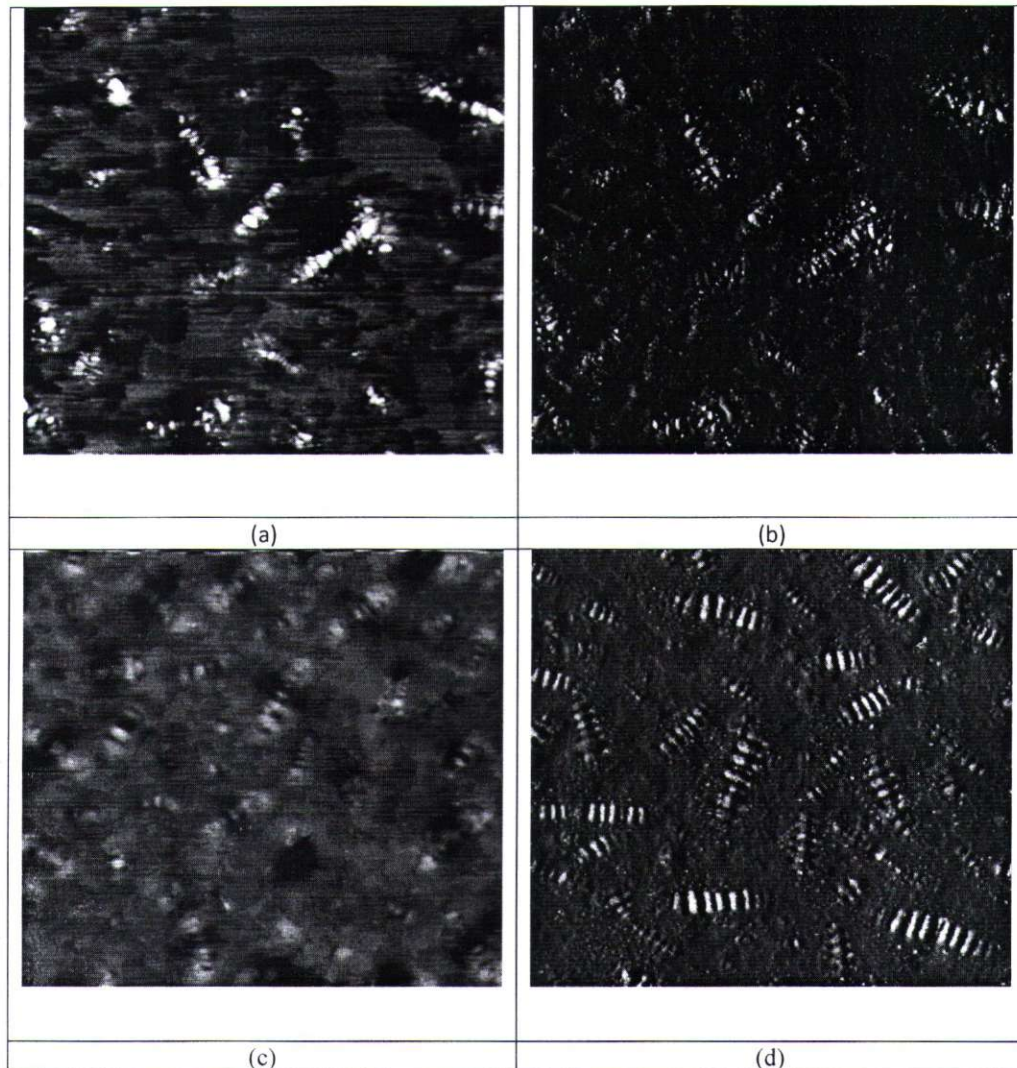


Figure 6 (a)-(d) Surface topography of the unmodified and modified bitumen in wet condition (Scale: 20x20 μm)

Surface Roughness

This study used the R_a obtained from the XEI in the quantitative investigation of the bitumen morphology. Figure 7 shows the R_a for the BB, PUMB, PUMB/R, and BB/R in dry and wet conditions. Adding PU reduced the R_a , while Rediset increased the R_a . The moisture altered the R_a of all tested samples and showed a declining pattern. However, PU and Rediset shoot up compared to BB. This finding is similar with a research done by Liu et al. in [27].

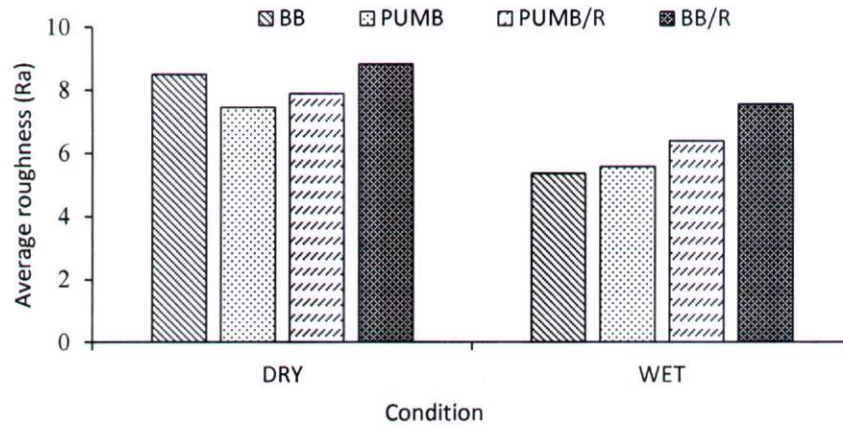


Figure 7 Surface roughness of the unmodified and modified bitumen in under dry and wet conditions

Surface Roughness ratio

Figure 8 shows that the SRR for BB, PUMB, PUMB/R, and BB/R is lower than the SRR of the modified bitumen. The highest SRR value of the BB could be due to moisture infiltration. This concludes that the modified bitumen improved the moisture damage.

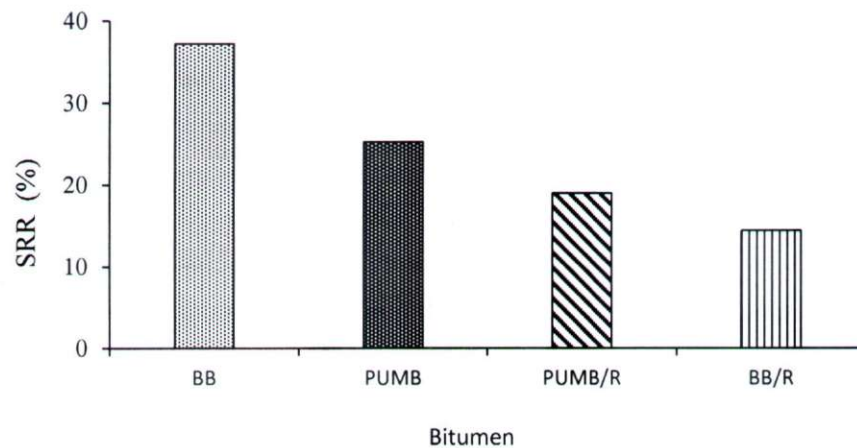


Figure 8 SRR for the unmodified and modified bitumen

Conclusion

This study has investigated the physical, thermal, and morphological characteristics of BB modified with PU and Rediset. The physical tests revealed that the modification of the BB with PU and Rediset stiffened the bitumen. The DSC evaluation of the thermal behaviour of unmodified and modified bitumen showed similar T_g and T_m values, indicating that the modification with PU and Rediset did not significantly affect the thermal transition. The bee-structure morphology from the AFM analysis showed that the modified bitumen have lower wax contents in moisture condition, which reduced the catana and para phase. The lower SRR value of the modified bitumen showed that the sample is less susceptible to moisture damage.

Acknowledgement

The authors would like to acknowledge Ministry of Higher Education Malaysia and Universiti Pertahanan Nasional Malaysia for the financial support (FRGS/1/2020/TK0/UPNM/03/4) and materials used in this research.

References

- [1] Feng, Z., Cai, F., Yao, D. & Li, X., *Aging Properties of Ultraviolet Absorber/SBS Modified Bitumen Based on FTIR Analysis*, *Construction Building Material*, **273**, pp. 121713, 2021.
- [2] Al-Sabaei, A. M., Mustofa, B. A., Sutanto, M. H., Sunarjono, S., Bala, N., *Aging and Rheological Properties of Latex and Crumb Rubber Modified Bitumen Using Dynamic Shear Rheometer*, *Journal of Engineering and Technology Science*, **52**, pp. 385-398, 2020.
- [3] Haryanto, I., Takahashi, O., *Crack Initiation Assessment of Wearing Course Asphalt Mixtures Using Aggregate Gradation Characteristic*, *Journal of Engineering and Technology Science*, **39**, pp. 28-42, 2007.
- [4] Gaudenzi, E., Canestrari, F., Lu, X. & Cardone, F., *Performance Assessment of Asphalt Mixture Produced with A Bio-Based Binder*, *Materials (Basel)*, **14**, pp. 1–13, 2021.
- [5] Yaro, N. S. A., Napiah, M., Sutanto, M. H., Usman, A., Mizwar, I. K., Umar, A. M., *Engineering Properties of Palm Oil Clinker Fine-Modified Asphaltic Concrete Mixtures*, *Journal of Engineering and Technology Science*, **54**, pp. 220205, 2022.
- [6] Nurhayati, C., Susilawati, N., Susanto, T., Marthalia, W., Nugroho, A. K., Pane, A. P., *The Effect of Linear Low-Density Polyethylene and Palm Kernel Shell Ash Mixture on the Physical, Mechanical and Degradation Properties of Paving Blocks*, *Journal of Engineering and Technology Science*, **54**, pp. 220307, 2022.
- [7] Alamawi, M. Y., Khairuddin, F. H., Yusoff, N. I., Badri, K. & Ceylan, H., *Investigation Of Engineering Properties of Bio-Based Binder Derived From Palm Oil as A Replacement For Bituminous Binder*, *Connecting Asia with Better Roads, 2nd IRF Asia Regional Congress & Exhibition*, 2016.
- [8] Khairuddin, F. H., Alamawi, M. Y., Md Yusoff, N. I., Badri, Ceylan, K. H. & Mohd Tawil, S. N., *Physicochemical and Thermal Analyses of Polyurethane Modified Bitumen Incorporated with Cecabase and Rediset: Optimization Using Response Surface Methodology*, *Fuel*, **254**, pp. 115662, 2019.

- [9] Rubio, M. C., Martínez, Baena, G. L. & Moreno, F., *Warm Mix Asphalt: An overview*, Journal Cleaner Production, **24**, pp. 76–84, 2012.
- [10] Zaumanis, M., *Warm Mix Asphalt Investigation*. Master Thesis, Riga Technical University, 2010.
- [11] Yao, H., You, Z., Li, L., Goh, S. W., Lee C. H., & Yap, Y. K., Shi, X., *Rheological Properties and Chemical Analysis of Nanoclay and Carbon Microfiber Modified Asphalt with Fourier Transform Infrared Spectroscopy*, Construction Building Material, **38**, pp. 327–337, 2013.
- [12] Asmael, N. M. & Waheed, M. Q., *Performance of Chemical WMA Mixtures – A review*, International Journal Advance Scientific Research Engineering, **06(01)**, pp. 120–126, 2020.
- [13] Goh, S. W., Hasan, M. R. M. & You, Z., *Performances Evaluation of Cecabase® RT in Warm Mix Asphalt Technology*, in Procedia - Social and Behavioral Sciences, pp. 2782–2790, 2013.
- [14] Hamzah, M. O., Gungat, L., Md Yusoff, N. I. & Valentin, J., *Recycled Asphalt Pavement with Warm Mix Additive for Sustainable Road Construction*, International Journal Civil, Environmental Structural Construction Architectural Engineering., **10(3)**, pp. 313–316, 2016.
- [15] Khairuddin, F. H., Mohd Yusoff, N. I., Badri, K. H. & Ceylan, H. *Thermal , Chemical and Imaging Analysis of Polyurethane / Cecabase Modified Bitumen*, Material Science Engineering, **512**, pp. 012032, 2019.
- [16] Awazhar, N. A., Khairuddin, F. H., Rahmad, S., Fadzil, S. M., Omar, H. A., Md. Yusoff, N. I. & Badri, K. H., *Engineering and Leaching Properties of Asphalt Binders Modified with Polyurethane and Cecabase Additives For Warm-Mix Asphalt Application*, Construction Building Material, **238**, pp. 117699, 2020.
- [17] Airey, G. D., *Rheological Evaluation of Ethylene Vinyl Acetate Polymer Modified Bitumens*, Construction Building Material, **16**, pp. 473–487, 2002.
- [18] Yero, S., & Hainin, M., *Evaluation of Bitumen Properties Modified With Additive*, International Journal Recent Research and Applied Study, **13**, pp. 93–97, 2012.
- [19] Vaitkus, A., Čygas, D., Laurinavičius, A., & Perveneckas, Z., *Analysis and Evaluation of Possibilities for the Use of Warm mix Asphalt in Lithuania*, Baltic Journal Road and Bridge Engineering, **4(2)**, pp. 80–86, 2009.
- [20] Gill, P., Moghadam, T. T. & Ranjbar, B., *Differential Scanning Calorimetry Techniques: Applications in Biology and Nanoscience*, Journal of Biomolecular Techniques, pp. 167–193,

- 2010.
- [21] Rosyidi, S. A. P., Idiajir, B., Akhir, N. M., Rahmad, S. & Lestari, N. P., *Physical , Chemical and Thermal Properties of Palm Oil Boiler Ash / Rediset- sustainability Physical , Chemical and Thermal Properties of Palm Oil Boiler Ash / Rediset-Modified Asphalt Binder*, Sustainability, **14**, pp. 3016, 2022.
- [22] Rahmad, S., Hussain, S., Atmaja, S. & Rosyidi, P., *Assessment of Metal Leaching from Rediset-Polymer Modified Asphalt Binder on Groundwater and Soil Contamination Case Studies in Construction Materials Assessment of metal leaching from rediset-polymer modified asphalt binder on groundwater and soil contam*, Case Study Construction Material, **16**, pp. e01108, 2022.
- [23] Lyne, Å. L., Wallqvist, V. & Birgisson, B., *Adhesive Surface Characteristics of Bitumen Binders Investigated by Atomic Force Microscopy*, Fuel, **113**, pp. 248–256, 2013.
- [24] Santos, S., Partl, M. N. & Poulikakos, L. D., *Newly Observed Effects of Water on The Microstructures of Bitumen Surface*, Construction Building Material, **71**, pp. 618–627, 2014.
- [25] Yao, Z., Zhu, H., Gong, Yang, M. J., Xu, G. & Zhong, Y. *Characterization Of Asphalt Materials ' Moisture Susceptibility using Multiple Methods*, Construction Building Material, **155**, pp. 286–295, 2017.
- [26] Wang, Z., Liu, Y., Gong, C., Yuan, Z., Shen, L., Chang, P., Liu, K., Xu, T., Jiang, J., Chen, Yu-C., & Liu, T., *Liquid Crystal-Amplified Optofluidic Biosensor For Ultra-Highly Sensitive and Stable Protein Assay*, Photonix, **2**(1), pp. 1–16, 2021,
- [27] Liu, S., Zhou, S., & Peng, A., *Analysis of Moisture Susceptibility of Foamed Warm Mix Asphalt Based on Cohesion , Adhesion , Bond Strength , and Morphology*, Journal Cleaner Production, **277**, pp. 123334, 2020.
-