Journal of Engineering and Technological Sciences

Research Paper

Physicothermal and Topography Analysis of Polyurethane Modified Bitumen with Rediset for WMA Application

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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. Penetration, softening point, viscosity, and ductility tests were employed for consistency testing, while the differential scanning calorimetry was used for thermal characterization. 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 to 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; Rediset; thermal behavior; topography; warm mix asphalt.*

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, which can cause various types of road degradation, such as cracking, fatigue and rutting [1-3]. Despite the significance of bitumen, all components contribute to determining the performance of the asphalt mixture [4]. Biomass is most useful when converted to 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 world's growing energy needs [5]. One example of biomass is palm kernel shell (PKS), where the kernel is utilized as charcoal in the boiler system and the ashes are used as fertilizer 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 known bio-binder could replace the petroleum-based bitumen for road construction because of its higher resistance to flow and similar thermal susceptibility to conventional bitumen. Khairuddin *et al.* [8] investigated the viability of utilizing 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

ISSN: 2337-5779
J. Eng. Technol. Sci. Vol. 55, No. 1, 2023, 31-39
DOI: 10.5614/j.eng.technol.sci.2023.55.1.4

low mixing temperature range of 100 to 140 °C in WMA technologies reduces carbon emissions [11]. WMA technologies use chemical, foamed, or organic additives. The additives lower the mixture's viscosity thus making it easier to work the bitumen, facilitate the compaction process, and improve the adhesion quality [12]. Cecabase RT 945, for example, decreases bitumen mix production and paving temperatures by 20 to 40°C while retaining the same mechanical qualities as conventional HMA [13], and Rediset LQ-1106, which reduces the mixing and paving temperatures and impedes the built-in anti-stripping effect [14].

The present 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 a green paving material towards achieving sustainable development goals in the pavement industry.

Materials and Sample Preparation

This research utilized a 60/70 penetration grade bitumen (BB), PU, and the WMA chemical additive, Rediset LQ1106. We employed the pre-polymerisation method to produce 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 2,000 rotations per minute at 110 °C [15]. The physical properties of the BB are 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 are listed in Table 1. The physical tests are the conventionally used tests for evaluating the initial hardness, softness, fluidity, flow resistivity, and tensile properties of the modified bitumen. The findings for each test are 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 the 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.

Morphology Test

The morphological analysis was carried out using an 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 the 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.

DOI: 10.5614/j.eng.technol.sci.2023.55.1.4

Figure 1 The Shimadzu DSC-50 device used for the thermal analysis.

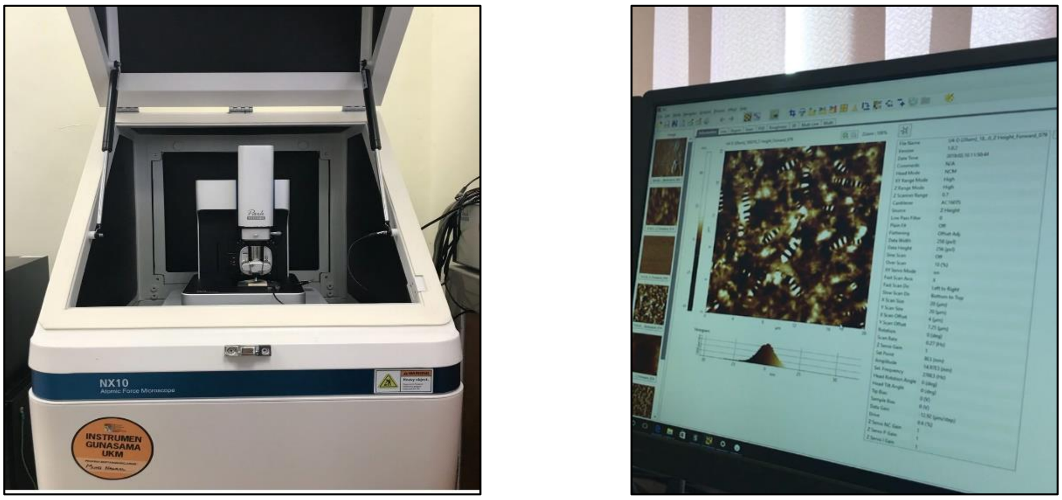


Figure 2 The atomic force microscopy device used for the morphology analysis.

Topography

This study used the original non-contact AFM mode to evaluate the bitumen's surface topography and the 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 1 Hz.

Surface Roughness

The surface roughness (Ra) of the 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.

$$\frac{SRR=(SR\ wet-SR\ dry)}{SR\ dry} \tag{1}$$

Results and Discussion

Physical Properties

Table 2 compares the modified and unmodified bitumen 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 was stiffer than the BB. According to Airey et al. [17], the modified bitumen's lower penetration value increases its temperature susceptibility. The viscosity values at 135 °C 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 viscosity allows for 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 had 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}), crystallization (T_c), glass transition (T_g), melting point (T_m) and the T_g, also known as the brittle point, is one of the primary thermodynamic parameter changes that characterize the liquid-to-solid transition [20]. T_m is the temperature at which a substance melts and transforms from a solid to a 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 °C and 31.63 °C, respectively. PUMB had the lowest T_g value and is thus more resistant to low-temperature cracking [21].

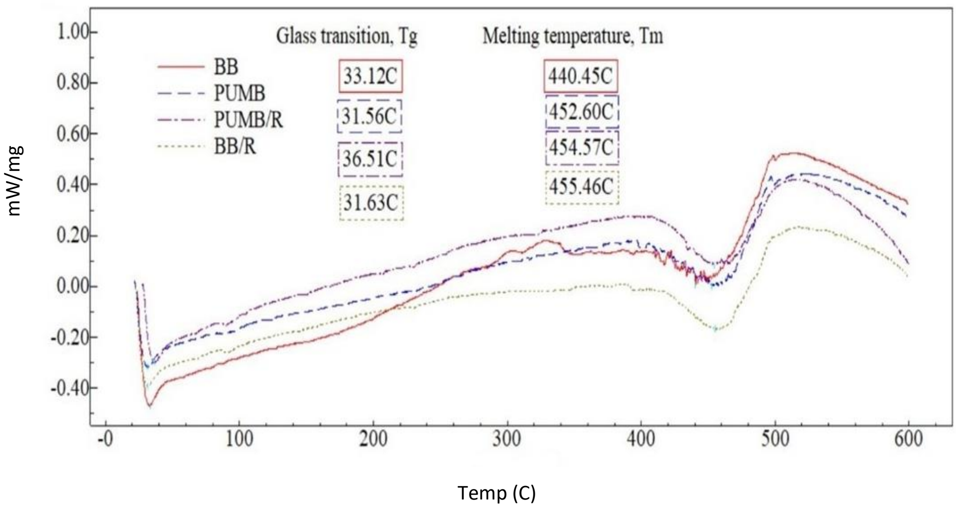


Figure 3 DSC thermogram for the unmodified and modified bitumen.

The T_m for BB, PUMB, PUMB/R, and BB/R was detected at 440.45, 452.60, 454.57, and 455.46 °C, respectively; the values show that the BB incorporated with Rediset had the highest melting temperature. The temperature

DOI: 10.5614/j.eng.technol.sci.2023.55.1.4

at which the wax completely melts is substantially higher than the temperature at which it initially crystallizes. The thermal history prior to scanning influences the form of the DCS curve. The endothermic peaks for BB, PUMB, PUMB/R, and BB/R were 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 were similar.

Morphological Properties

Surface Topography

The bitumen surface topography had a bee structure representing the asphaltenes in the bitumen [22]. There are three phases in bitumen's topography, namely the peri, para and catana phases, as shown in Figure 4 [23]. Figures 5 (a-d) and 6 (a-d) show 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's bee structure.

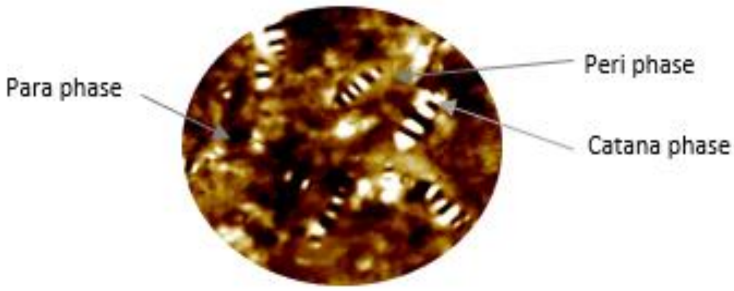
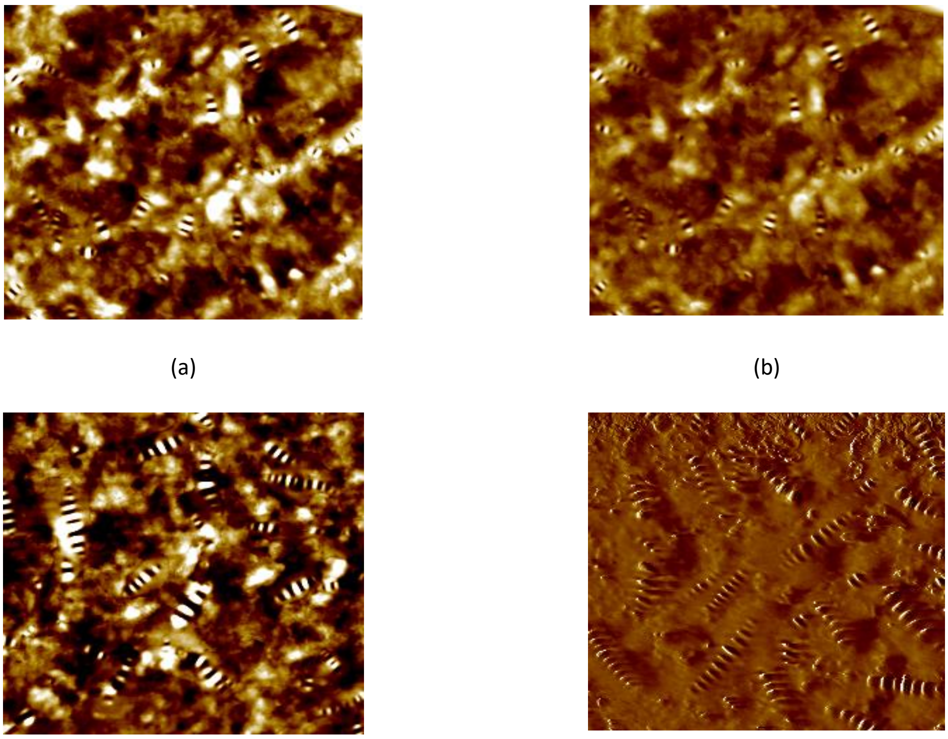


Figure 4 Three phases in bitumen topography.

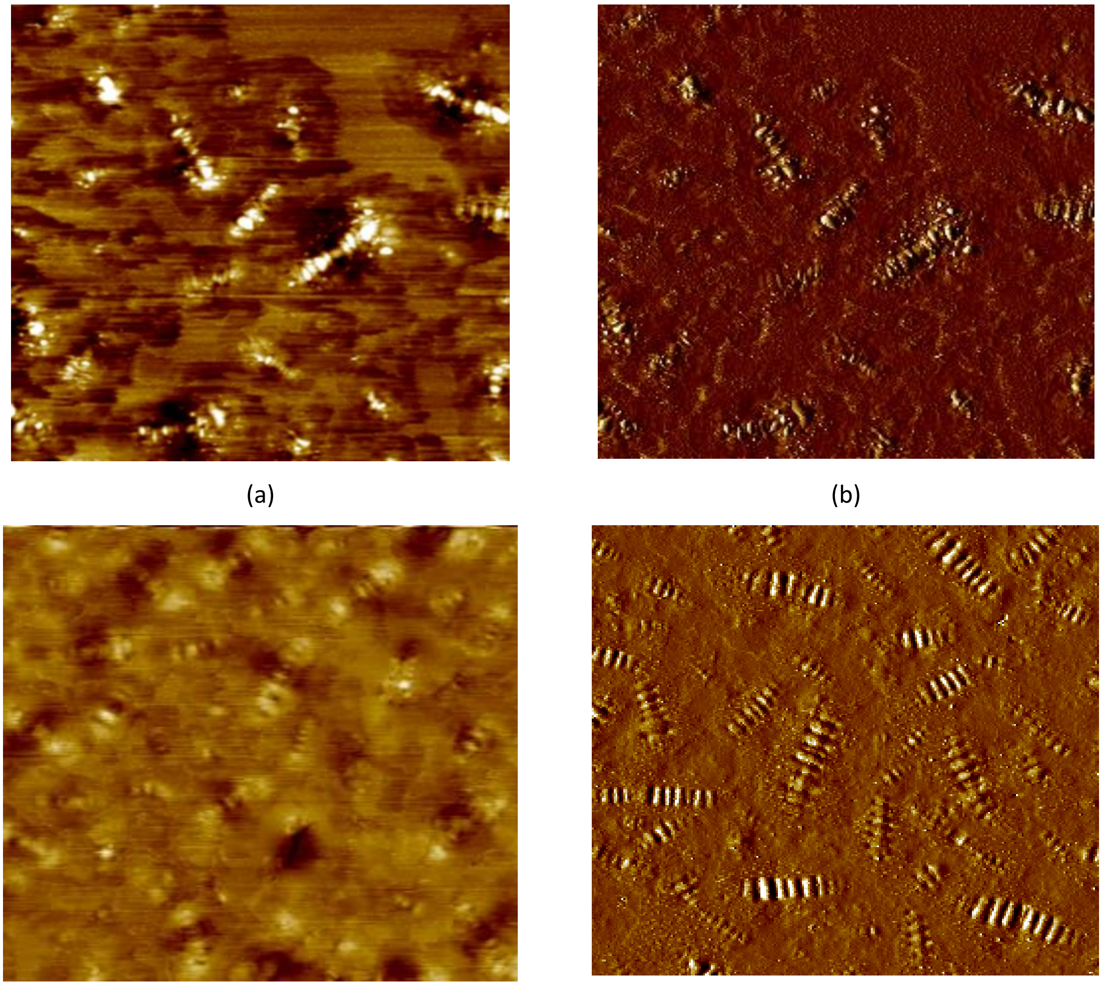


(a) (b)

(c) (d)

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 was 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 alters 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, a method that can be further explored [26].



(a) (b) (c) (d)

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

Surface Roughness

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

DOI: 10.5614/j.eng.technol.sci.2023.55.1.4

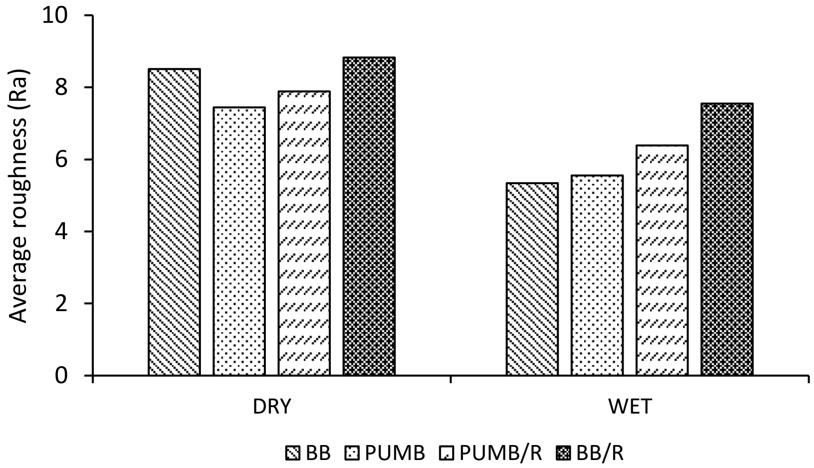


Figure 7 Surface roughness of the unmodified and modified bitumen in dry and wet conditions.

Surface Roughness Ratio

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

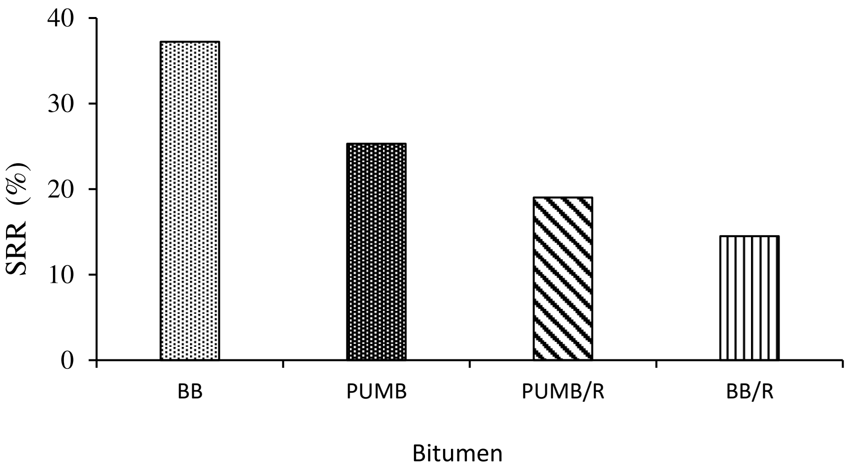


Figure 8 SRR for the unmodified and modified bitumen.

Conclusion

This study 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 behavior of the 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 had lower wax contents in moisture condition, which reduced the catana and para phases. The lower SRR value of the modified bitumen showed that the sample was less susceptible to moisture damage.

Acknowledgement

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

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Manuscript Received: 4 October 2022
Revised Manuscript Received: 8 December 2022
Accepted Manuscript: 2 January 2023