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# PHYSICAL AND MORPHOLOGICAL PROPERTIES OF POLYURETHANE MODIFIED BITUMEN UNDER AGEING CONDITIONS

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**ABSTRACT:** The aim of this research is to evaluate the effects of ageing on 60/70 penetration grade bitumen modified with polyurethane (PU). Effects of ageing were evaluated by performing consistency test through ageing index and morphology evaluation. The results of these tests show that adding 3 wt% of PU stiffens the bitumen in comparison to base bitumen. A very high increase in viscosity was observed due to the hardening effect of PU. The computed ageing index shows that this alternative material reduces ageing effects on the physical properties of the bitumen, as indicated by the lower ageing index value of physical testing subsequent to ageing. Therefore, the addition of PU results in improved bitumen resistance to oxidative ageing. Optical microscopy shows the sample was homogeneously blended. Atomic Force Microscopy (AFM) was conducted to evaluate the catana phase, peri phase, and para phase topography images of PU modified bitumen. Topography image from AFM test indicates that the inclusion of PU and ageing conditions has decreased the bee-like structures of the bitumen, showing larger dispersion in the sample.

*Keywords: Polyurethane Modified Bitumen, Ageing, Atomic Force Microscopy, Morphology, Topography*

## 1. INTRODUCTION

The past several decades has witnessed hot mix asphalt (HMA) being used as the primary material in the paving industry, where bitumen is used as a coating for aggregates. Bitumen is a sticky, dark brown or black, semisolid material and is highly viscous at ambient temperature [1,2]. A strong bond between bitumen and aggregate is required to accommodate traffic loading. This is to ensure that pavements are strong and durable and provide a smooth surface for road users.

However, the increase in traffic volume, pressure and load in recent years had an adverse impact on pavement performance. In order to deal with these problems, the quality of existing pavements have to be improved. Additions of modifier or replacement to bitumens are done to improve its resistance to rutting, fatigue, and temperature susceptibility [3]. Recent research has shown that bio-binders can be used as modifiers (<10% bitumen replacement), extenders (25% to 75% bitumen replacement), or 100% replacement for bitumen [4].

One study investigated the effects of using waste cooking oil and spent coffee ground as a modifier on the physical and chemical properties of bio-binders. Results showed that longer oxidation time improved the viscoelasticity of the waste oil [5]. A study conducted by Al-Omari et al. [6] used waste vegetable oil as a modifier; the researchers observed improvement in temperature susceptibility, penetration, ductility, flash and fire points, fluidity, and m-value, along with a decrease in the bitumen's softening point, rotational viscosity, and creep stiffness. A research using bio-oil generated from waste wood source found that the bio-binders lower the mixing temperature of bituminous mixtures and improved the performance of the bitumen. Khairuddin et al. [7] conducted a study on bitumen modification using polyurethane (PU). The outcomes of this study show that the addition of PU at intermediate and higher temperatures has stiffened the bitumen properties and increased resistance to fatigue and rutting. According to the previous study, PU was used for road flood damage control showing that the strength of subgrade soil from the inundation effect can be increased or maintained by using a PU layer [8].

Besides investigating the physical and chemical properties of the modified bitumen, the interrelationship of structure-property is important to obtain the bitumen optimum performance by interpretation the morphology using microscopic method. Surface morphology using Atomic Force Microscopy (AFM) is widely used by researchers to study the topography, roughness, adhesion, and local mechanical properties of the bitumen [4-9]. As bitumen consist of 'bumble bees' structures, it is important to investigate the effect of modifier in term of dispersion and matrix domains [10].

One of the causes of road pavement deterioration is bitumen oxidation [11]. Short-term ageing (STA) occurs during the mixing and compacting of mixtures, where higher temperatures results in higher oxidation rate. Long-term ageing (LTA) occurs during the service life of a pavement. Oxidation occurs when bitumen reacts with oxygen diffused in the air voids on aggregate surface [12]. The higher viscosity caused by oxidation process increase the stiffness of pavements, which then causes cracking [13]. As ageing occurs, the physical and chemical properties of bitumen alter the behavior of bitumen significantly. Ageing affects the physical properties of bitumen, such as penetration, viscosity, ductility and stiffness [11]. Therefore, investigation of ageing process and its effect on modified bitumen is very important in real application.

This study seeks to evaluate the physical, morphological, and ageing effect of a new material, palm kernel oil polyol (PKO-p) and 2,4-diphenylmethane diisocyanate (MDI) under STA and LTA conditions. The addition of these two materials will form PU. The morphology of the modified bitumen was observed to evaluate the homogeneity, separation, and dispersion of bee-like structure in the bitumen with the inclusion of the new material. The following section will present a comprehensive discussion of the tests and their results.

## 2. METHODOLOGY

### 2.1 Material

In this study, a 60/70 penetration grade bitumen was used as the control sample. The physical characteristics of the control sample is given in Table 1. The sample was modified by adding PU to the bitumen. In order to produce PU, pre-polymerization method of PKO-p from palm kernel oil were done at first stage. Next, polymerization will occur during mixing process of PKO-p with MDI that will produce PU.

Table 1 Physical properties of control sample

| Physical test | Bitumen Grade 60/70 | |
|---|---|---|
| | Value | Specification |
| Penetration (0.1 mm) at 25 °C | 66 | 60-70 (ASTM D5) |
| Softening point (°C) | 49 | 47-52 (ASTM D36) |
| Ductility (cm) at 25 °C | 100 | 100 (ASTM D113) |
| Viscosity (mPa.s) at 135 °C | 550 | - (ASTM D4402) |
| Specific gravity (g/cm$^3$) at 25 °C | 1.03 | 1.0-1.06 (ASTM D70 |

### 2.2 Sample Preparation

Modification of the bitumen was carried out by heating the base bitumen (B-B) at 145°C for about 30 minutes until it turned liquid. PU in the amount of 3% by weight of bitumen was used to produce the polyurethane modified bitumen (B-PU) [7,14]. This optimum percentage of 3 wt% PU was predetermined by Design Expert Software using Response Surface Method. PKO-p and MDI were then added at a ratio of 1:0.6 by weight of PU. The PKO-p and bitumen were blended for 15 minutes at 110°C and 2000 revolutions per minute using shear mechanical mixer; MDI was then added and blended using the same parameter. Prior to obtain a homogeneous blend, penetration and softening point results were monitored until consistent results were obtained and taken as indicators of a well-blended mix.

### 2.3 Laboratory Testing

*2.3.1 Penetration Test*

The penetration test was conducted in compliance with ASTM D5. The value of penetration is dependent upon the hardness or softness of a bitumen. Higher value of penetration measured in tenths of millimetre indicates a bitumen with softer characteristic.

*2.3.2 Softening point and storage stability*

The softening point test was carried out to measure the temperature at which the bitumen starts to flow. It was carried out in compliance with ASTM 36. For bitumen with a given penetration (determined at 25 °C), higher softening point indicates lower temperature sensitivity. Storage stability test was conducted to evaluate the homogeneity of a blend as well the stability during storage. This test was conducted in compliance with ASTM-D5976 (2000).

*2.3.3 Viscosity test at 135°C*

Evaluation of bitumen's viscosity at high temperature is important to determine the optimal temperature for the mixing and compacting of bituminous mixture at site. It indicates the extent to which the bitumen can be pumped through bitumen plant. This test was conducted in compliance with ASTM D4402.

*2.3.4 Ageing of bitumen*

To simulate STA, the samples were prepared using the Rolling Thin Film Oven procedure in accordance with ASTM D2782. STA of a bitumen occurs during the production of bituminous mix at the plant. Simulation of LTA were carried out using the Pressure Aging Vessel method in accordance with ASTM D6521. LTA is an indication of the service life of a pavement.

*2.3.5 Ageing Index*

The effects of ageing on B-PU were measured using the penetration, softening point, and rotational viscosity tests, and the results were compared with the B-B. The ageing index (AI) for each test was computed using Eq. (1) below to evaluate the ageing susceptibility.

$$AI = \frac{T\ aged}{T\ unaged} \quad (1)$$

where $T_{aged}$ is the penetration/softening point/viscosity test value of the aged sample and $T_{unaged}$ is the penetration/softening point/viscosity test value of the unaged sample.

*2.3.6 Microscopic DINO-LITE*

The morphological property of B-B and B-PU were observed using the optical microscope DINO-LITE Pro Digital, 500X. The sample was heated at 145°C until it turned viscous. Then, the sample was dropped on a glass slide to form an even surface and leave for 30 minutes before being viewed under a microscope. The DINO-LITE is capable to capture high image resolution and good image quality of a sample.

*2.3.7 Atomic Force Microscopy*

To further investigate the morphology characteristics of B-B and B-PU sample, AFM test was conducted using the XE-10 AFM from Park Systems Corporation. To evaluate the surface and bee characteristics of the bitumen, heat cast method was applied where sample were heat until it turned liquid and dropped on a glass slide. For this study, 20 x 20 µm area at 1 Hz scan rate was selected. The sample was tested using a silicon cantilever tip sized < 10 nm tip radius by non-contact mode method, at 0.2 N/m constant force for the quantifications of sample surface.

## 3. RESULT AND DISCUSSION

### 3.1 Physical Testing

*3.1.1 Penetration test*

Penetration test was used to evaluate the fluidity of bitumen before and after modification with PU under unaged (UA), STA, and LTA conditions. Figure 1 shows the results of the penetration tests for B-B and B-PU. The addition of 3% of PU to bitumen decreased the penetration value by 7.3% for UA, 10.7% for STA, and 10.3% for LTA. This shows that the samples become stiffer subsequent to modification and ageing. This is consistent with the previous findings made by another researcher that the addition of PU had a hardening effect on the bitumen.

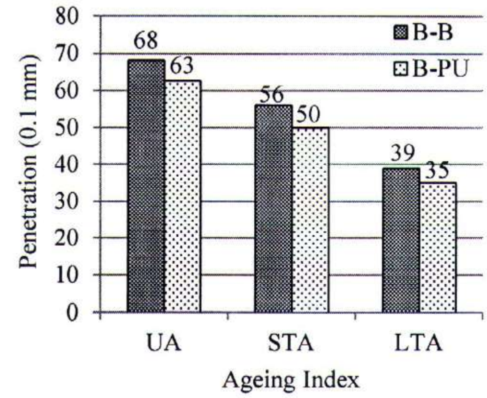



Fig. 1 Penetration values for UA, STA and LTA

*3.1.2 Softening point and storage stability test*

Figure 2 shows the softening point values for B-B and B-PU under UA, STA, and LTA conditions. The general trend shows that adding PU to bitumen improves softening point by 10% for UA, 8.5% for STA, and 7.6% for LTA. This indicates the extent to which the bitumen hardened after modification and ageing. The increase in softening point is due to the change in the structural molecules in the bitumen's content of fraction during the ageing process [15].

In addition, storage stability test conducted shows the differences between the top and bottom section for softening point value of B-PU is 0.50 °C which is less than 2.2 °C. This result indicates that there is no separation occurred between the top and bottom section and the B-PU sample are homogeneously, storage stable blended [16].

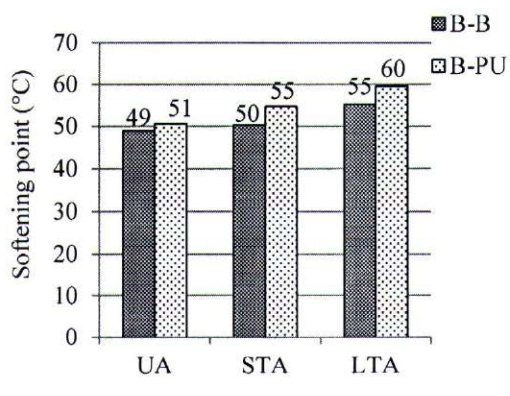



Fig. 2 Softening point values for UA, STA and LTA

*3.1.3 Viscosity test*

Figure 3 shows the experimental value for viscosity at 135 °C, which is the average mixing and compaction temperatures for bituminous mixture. The addition of PU markedly increased viscosity by 64% for UA, 22% for STA, and 12% for LTA. This increase is still within specification permitted by the Strategic Highway Research Program which states that the increase in viscosity should not exceed 3000 mPa.s [12]. The increase in viscosity occurred due to the increase in bitumen stiffness which limited molecule movement during the test. The addition of PU is the contribution of higher viscosity value [16].

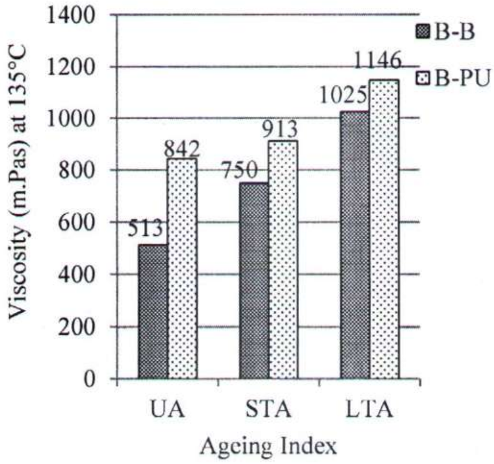



Fig. 3 Viscosity value for UA, STA and LTA

*3.1.4 Ageing Index*

Table 2 shows the penetration aging index (PAI) computed using AI equation. The table shows that the value of PAI decreased after STA and LTA, which indicate that B-PU has a higher ageing resistance in comparison to B-B. The softening point ageing index (SPAI) is listed in Table 3 showing an increased value due to the change in the structural molecules in the bitumen's content of fraction during the ageing process. Thus, the addition of PU improved the bitumen's resistance to oxidative ageing [17]. Table 4 presents the viscosity aging index (VAI). It shows that VAI decreased with the addition of PU, thus reduce the ageing sensitivity.

Table 2 PAI for B-B and B-PU

| Bitumen | STA | LTA |
|---|---|---|
| B-B | 0.83 | 0.57 |
| B-PU | 0.81 | 0.57 |

Table 3 SPAI for B-B and B-PU

| Bitumen | STA | LTA |
|---|---|---|
| B-B | 1.09 | 1.20 |
| B-PU | 1.08 | 1.18 |

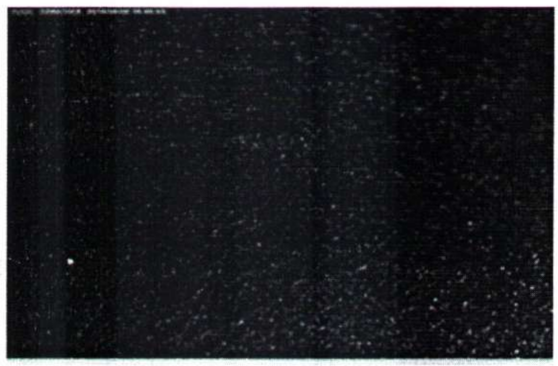
Table 4 VAI for B-B and B-PU

| Bitumen | STA | LTA |
|---|---|---|
| B-B | 1.46 | 1.99 |
| B-PU | 1.08 | 1.36 |

**3.2 Morphological properties of Bitumen**

*3.2.1 Optical microscopic test*

Figures 4(a) and (b) show the image of B-B and B-PU used in this research. No separation was observed in the microscopy images. (Fig. 4.b) shows clearly the image of a homogeneous blend of the B-PU, which indicate that the PU has been uniformly dispersed and evenly spread during the mixing process. There are no lumps observed after mixing 3 wt% PU with bitumen at selected parameters showing analogous mix was formed. This is in agreement with the result of storage stability test.



(a)

(b)

Fig. 4 Optical Microscopic for (a) B-B, (b) B-PU

*3.2.2 Atomic Force Microscopy test*

The typical bee structure was clearly found in both unmodified and modified sample with reduction off bee lines with ageing condition. As stated by Lyne et al. [9] there are three phases observed in bitumen namely the catana phase, the peri phase and the para phase respectively as shown in Figure 5(a). The catana phase represents the black line like a bee structure that indicate the high and low of the topography image, the peri phase that is outerpart to the catana phase while the para phase is alongside the peri phase. In bitumen, the bee structure occurred because of the crystallization of the wax composition as well dispersion of the molecule [18]. The existence of various nonpolar alkane chains together with the wax are the contribution factors to the 'bee-like structures' appearance in bitumen [10].

Figures 6(a)-(f) and Figures 7(a)-(f) represent the 2D and 3D topography images of B-B and B-PU before and after ageing, respectively, obtained from AFM test. The presence of bee-like structures or catana phase for UA sample can be clearly seen in accordance with (Fig. 6.a) and (Fig. 7.a). This indicates that the addition of PU did not affect the bitumen bee-like structures. The dispersion in the aged samples, however, decreases remarkably, particularly for both B-B and B-PU samples after ageing. This showed that during STA and LTA there was a great interaction of the distributed domains in bitumen. It can be clarified that oxidation leads to the reduction of the difference in chemical properties between the distributed domains and the matrix during STA and LTA. The domains can spread in the matrix gradually before ageing, but not after ageing [19].

The topographic image in (Fig. 7.c) and (Fig. 7.e) shows that after STA and LTA for the B-PU sample, the dimension and quantity of bee-like structures are significantly reduced. The bee-like structures seem to float much and obviously spread throughout as seen in (Fig. 7.e). In addition, with the inclusion of PU, at certain points in STA and LTA, it is noted that the dimension of bee-like structures is reduced compared to the B-B sample in (Fig. 6.c). This shows that the addition of PU and the hardening of bitumen from ageing have led to the substantial decrease in the bee-like structure as well as the absence of the boundary.

This outcome is comparable to the research performed by Zhang et al. [20] using AFM to perform morphology analysis on unmodified and modified organo-montmorillonite bitumen. The findings showed that bitumen showed a 'bee-like' structure and, with the introduction of the organo-montmorillonite, the dimension of the 'bee-like' structures was reduced to some degree. Due to the increased solubility of microcrystalline waxes (>C40) and waxy molecules in bitumen during ageing, which can impede their crystallization, the dimension and quantity of 'bee-like' structures have been reduced after ageing.

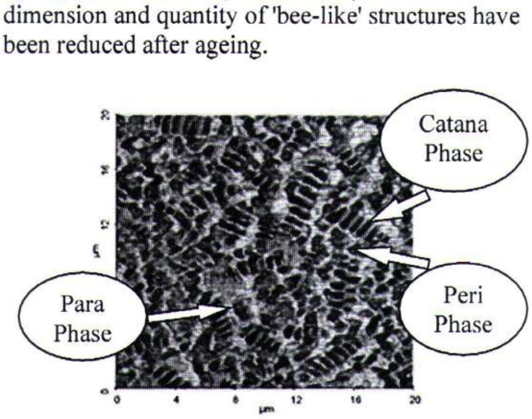



Fig. 5 Sample showing the catana phase, peri phase and para phase in bitumen structure

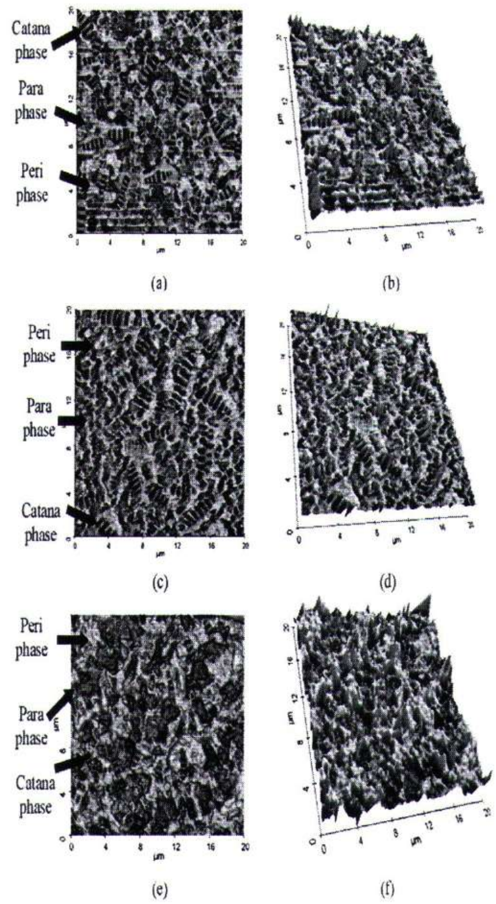



Fig. 6 2D & 3D topography image of B-B for (a)-(b) UA, (c) STA and (e)-(f) LTA

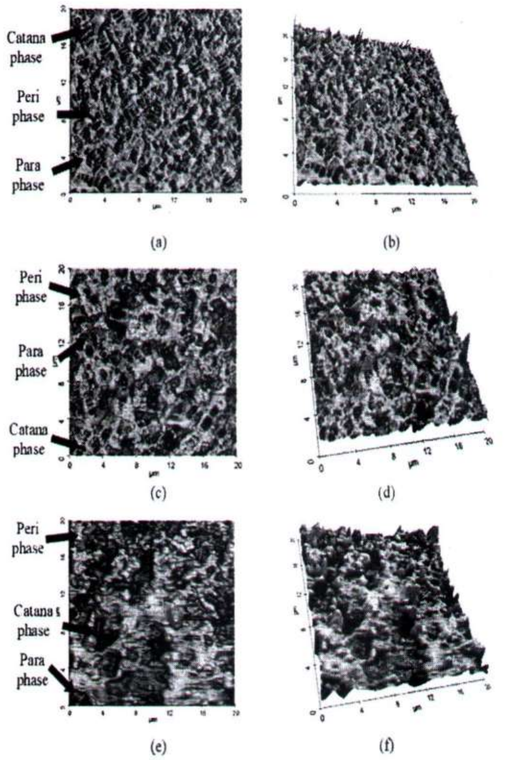



Fig. 7 2D & 3D topography image of B-PU for (a)-(b) UA, (c)-(d) STA and (e)-(f) LTA

## 4. CONCLUSION

The present study evaluates the effect of ageing on the physical and morphological properties of B-PU and compares the results with those of conventional bitumen. Result reveals that the addition of PU to B-B decreased the penetration value, which shows that harder bitumen has been formed while softening point value increased with the addition of PU. This is consistent with the results of the penetration test, where stiffer bitumen increases the melting point of the bitumen. The AI for both penetration and softening point indicate that the B-PUs have higher ageing resistance in comparison to B-B. Besides, viscosity test shows that the addition of PU significantly increased viscosity value at 135 °C; the lower VAI shows that addition of PU reduced the ageing sensitivity of the bitumen.

Image analysis from optical microscopic test shows that no separation occurred in the B-PU sample. This shows that the sample has been homogeneously blended and uniformly dispersed during the mixing process. The topography images from AFM test indicate that the inclusion of PU and ageing conditions has decreased the bee-like structures of the bitumen, showing larger dispersion in the sample.

## 5. ACKNOWLEDGEMENT

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