

Influence of palm oil fuel ash as a modifier on bitumen to improve aging resistance

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ABSTRACT

The abundance and increase of waste from palm oil mills in recent years has led to environmental pollution. This problem can be addressed by recycling and reusing such waste materials. In this study, palm oil fuel ash (POFA), a by-product of palm oil mills, was used as a bitumen modifier under normal conditions and subjected to aging. The properties of the modified bitumen were investigated in terms of penetration, softening point, penetration index, penetration-viscosity number, and viscosity tests. Two laboratory simulation aging methods were conducted in this study: the standard rolling thin film oven test and the pressure aging vessel test. Experimental results show an increase in the softening point and a decrease in the penetration of the bitumen mixed with POFA. The addition of POFA, especially in large amounts, increased the temperature susceptibility of the bitumen. The use of POFA as a bitumen modifier generally reduces the aging effect on the physical and rheological properties of bitumen, as indicated by the reduced aging index of viscosity.

Keywords: POFA; waste material; modified bitumen; aging; viscosity.

INTRODUCTION

Road structures have deteriorated more rapidly in recent years because of the increase in traffic volume, loading, and poor maintenance. To minimize such deterioration and increase the long-term durability of a flexible pavement, bituminous layers must be improved. Specifically, performance properties, such as resistance to permanent deformation, fatigue, wear, stripping, and aging, must be enhanced (Navarro *et al.*, 2009). One approach to increasing the quality of a flexible material layer is the use of high-quality materials, particularly, modified bitumen. Modified bitumen with additives, which strengthen the properties of the bitumen, has been used in various forms for more than 150 years. The behavior of modified bitumen has recently drawn renewed interest (Simon & Hesp, 2007). Mashaan *et al.* (2012) indicated that the use of waste materials to modify bitumen has significantly improved several properties of bitumen, such as viscosity, penetration, and softening point. Palm oil fuel ash (POFA) has been reported to enhance the properties of asphalt mixture. For instance, Ahmad *et al.* (2012) investigated the practical use of POFA at different percentages as a filler in asphalt pavement. They found that the addition of 3% POFA can increase the stability and resilient modulus of asphalt pavement. Despite a number of studies on POFA, no research on the use of POFA as a bitumen modifier has been published and explored (Hurley & Prowell, 2005). Hadavand (2010) used bitumen modification with polysulphide polymer (PSP) prepared from heavy end waste and found that the incorporation of PSP can increase the softening point but decrease the penetration of bitumen. Binders resistant to aging or changes in physical properties during long-term services are described as durable (Lu & Isacsson, 2002). In service, pavement layers are exposed to the atmospheric air, allowing the binder to react with oxygen. This reaction changes the composition of bitumen and renders it susceptible to wear and moisture damage. The effect of the compositional change in the binder is reflected in the increased hardening of the binder, which also indicates increases in stiffness and viscosity. Several methods have been proposed to replicate the effects of aging, with the rolling thin-film oven test (RTFOT) and the pressure aging vessel (PAV) test as the most commonly used techniques (Chen & Huang, 2000; Gawel & Baqinska, 2004; Yu *et al.*, 2009). RTFOT is used to simulate aging during mixing and placement, whereas PAV is used to simulate aging during service life. Therefore, asphalt binder tests on mix and placement properties, such as the dynamic shear rheometer (DSR) test, are conducted on RTFOT-aged samples, whereas asphalt binder tests concerned with in-service performance, such as tests using DSRs, bending beam rheometers, and direct tension testers (DTT), are performed on samples that are first aged in RTFOT and then in PAV (Šušteršić *et al.*, 2013). The current study aims to investigate the effects of the common waste material POFA on conventional bitumen under various aging conditions.

MATERIALS AND EXPERIMENTAL

Materials

The conventional Pen Bitumen 80/100 that was used as the virgin asphalt binder in this study was obtained from Malaysia. The asphalt exhibits the following physical properties: penetration, 84 PEN at 25 °C (ASTM D5, 2006); softening point, 43°C (ASTM D36, 2012); relative density, 1.02; and ductility, 120 cm at 25 °C. POFA produced by Kahang Palm Oil Mill, Malaysia is described as a modifier or an asphalt flow improver. POFA is a waste product obtained in the form of ash on a burning palm oil husk or fiber and palm kernel shell as fuel in a palm oil mill boiler. The POFA initially collected from the mill was dried in an oven at 110 ± 5 °C for 24 h. Ashes were then grounded and sieved to obtain the particle size that can pass through a 75 im sieve. The chemical composition of the POFA is as follows: 8.30%, CaO; 53.50%, SiO₂; 1.90%, Al₂O₃; 1.10%, Fe₂O₃; 4.10%, MgO; and 2.40%, SO₃. The POFA mainly consists of SiO₂ and exhibits the following physical properties: fineness, 519 m²/kg; soundness, 1 mm; and specific gravity, 2.22.

Preparation of POFA-Modified Bitumen

The modified bitumen was prepared using a high-shear mixer. The bitumen was first heated until it became a well-melting fluid at approximately 160 °C in an iron container. The POFA was then added into the bitumen at 2.5%, 5%, 7.5%, and 10% of the total weight of the bitumen content. The mixture was finally blended at 800 rpm for 60 min to ensure the uniform dispersion of the POFA. The neat bitumen was used as the controlled samples.

Aging Procedure

RTFOT and PAV were used to age the bitumen. RTFOT was used for short-term aging. The standard aging procedure of 75 min, 163 °C, and air flow at 4 L/min for the RTFOT was applied according to ASTM D2872-04 (ASTM, 2004). After the RTFOT, all specimens were further aged using PAV. The PAV apparatus consisted of a pressure aging vessel and a temperature chamber. In the PAV, binders were aged for 20 h at 100 °C under 2.1 MPa of air as described in the ASTM D6521-08 (ASTM, 2008).

Test Methods

The POFA-modified bitumen was subjected to the following conventional binder tests: The penetration test was conducted with 100 g load for 5 s at 25 °C

as specified by ASTM D5-06 (ASTM, 2006). The softening point test was conducted with ring and ball following ASTM D36-12 (ASTM, 2012) specifications. A Brookfield viscometer was used to conduct the viscosity test according to ASTM D2170-10 (ASTM, 2010). The viscosity test temperature ranged from 60 °C to 170 °C.

RESULTS AND DISCUSSION

Penetration

Figure 1 shows the effects of mixing POFA into aged bitumen on the penetration value. The results indicated that for the un-aged bitumen, POFA mix with 2.5, 5.0, 7.5, and 10% replacement bitumen obtained penetration values of 41.7, 37.4, 37.3, and 36.7 PEN, respectively. Meanwhile, 0% POFA mix with 0% replacement obtained 44.7 PEN. The addition of POFA into the bitumen directly reduces bitumen penetration. Therefore, a 0.5% increase in POFA content can cause a decrease of 4.72% in bitumen penetration. These results indicate that the penetration of the bitumen binder dramatically decreases with increasing POFA content. Increasing the percentage of POFA tends to increase the hardness of the bitumen, thereby reducing bitumen penetration. Meanwhile, all modified specimens subjected to short-term aging showed a decrease in penetration. The control or 0% POFA mix exhibited the highest penetration, whereas the 10% POFA mix exhibited the lowest penetration. For example, the penetration values were 19.8 and 15.3 PEN at 2.5% and 5.0% POFA, respectively, whereas the corresponding penetrations were 12.6 and 12.2 PEN at 7.5% and 10% POFA, respectively. These results suggest that the penetration of the bitumen-POFA binder changes after short-term aging, which can be attributed to the aging effect on the network structure of the POFA-modified bitumen. Aging damages the bitumen-polymer network structure, degrades the modifiers, and changes the properties of the modified bitumen (Yadollahi & Mollahosseini, 2011). The present study also shows that short-term aging significantly affected the penetration of the binder. In addition, the penetration of the bitumen containing POFA decreased under long-term aging. The penetration value decreased from 8.6 PEN to 5.7 PEN when the POFA content was increased from 0% to 10%, as shown in Figure 1. This result suggests that all samples incorporated with POFA exhibited less penetration than did the un-aged samples and the specimens that underwent short-term aging. Therefore, the penetration aging value decreases with increasing POFA content, thereby reducing the degree of aging of the POFA-bitumen binder. Moreover, the addition of POFA improves the resistance of the binder to oxidative aging. Thus, POFA can improve the performance properties of the bitumen.

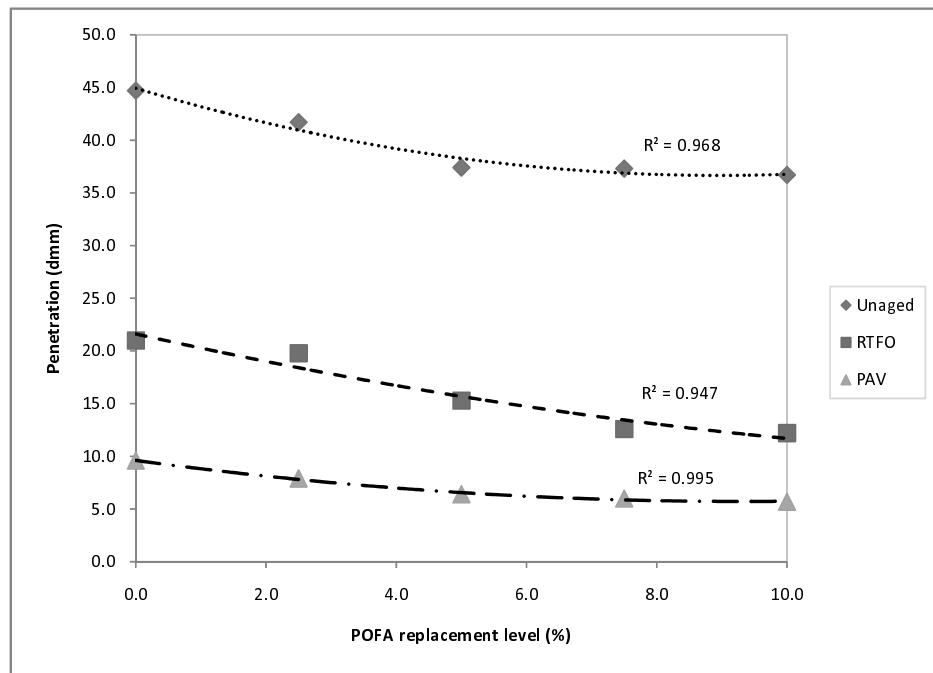


Fig. 1. Effects of POFA concentration on the penetration at different aging conditions

Retained Penetration

The original and the RTFO penetration values were used to calculate the magnitude of aging for each test binder. In the current study, the amount of aging was referred to as the percent retained penetration and calculated as follows:

$$\% \text{ Retained Penetration} = \frac{\text{Penetration of RTFO}}{\text{Penetration of unaged}} \times 100 \quad (\text{Equation 1})$$

Aging influences the percent retained penetration values of the POFA-bitumen, as presented in Table 1. As shown in the table, the incorporation of POFA in higher quantities decreased the retained penetration. For instance, the retained penetration was 47.48% at 2.5% POFA content. However, the retained penetration decreased to 33.24% when the POFA content increased to 10%. The tendency to age-harden decreases with increased retained penetration. Thus, the bitumen containing POFA exhibits higher aging resistance than does the controlled samples, indicating that the addition of POFA in bitumen can reduce the retained penetration of the bitumen during oxidative aging. This result can be attributed to the obstruction of POFA to the hardening process of

the bitumen. The results also show that the addition of POFA to the bitumen can reduce aging tendencies, as determined by the penetration test.

Table 1.Table 1: Results of retained penetration (%) under RTFO

POFA replacement level (%)	Aging test		
	Pen Before RTFO	Pen After RTFO	Retained Pen (%)
0.0	44.7	22.2	49.66
2.5	41.7	19.8	47.48
5.0	37.4	15.3	40.91
7.5	37.3	12.6	33.78
10	36.7	12.2	33.24

Penetration Index (PI)

The penetration index (PI) is used to classify bitumen. PI values can also measure the temperature susceptibility of bitumen. Hadavand (2010) defines temperature susceptibility as the change in the consistency of bitumen as a function of temperature. PI can also identify a particular type of bituminous material to a limited extent (Lu & Isacsson, 2002). Table 2 lists the PI values for mixtures prepared at varying POFA contents and exposed to different degrees of aging. As indicated in the table, the incorporation of POFA content into the bitumen reduced the temperature susceptibility of the binder. Lower PI values indicate higher temperature susceptibility. Higher PI values indicate higher resistance to low-temperature cracking and permanent deformation (Durrieu *et al.*, 2004). The PI decreased from -1.75 to -2.01 when the amount of POFA incorporated into the bitumen was increased. However, a less negative PI value after the addition of POFA suggests improved PI, as shown in Table 2. For instance, the lowest PI values of -1.76, -1.48, and -1.95 were obtained at 2.5% POFA content for the un-aged, RTFO, and PAV aging, respectively. Meanwhile, the incorporation of 5.0%, 7.5%, and 10% POFA into the bitumen decreased the PI to -1.69, -1.71, and -2.24, respectively, for short-term aging and to -1.95, -2.10, and -2.55, respectively, for long-term aging. A decrease in PI toward the negative zone thus indicates that the bitumen becomes more brittle even when subjected to different aging conditions.

Table 2. Table 2: Results of penetration index before and after aged

POFA level (%)	Aging test		
	Un-aged	RTFO	PAV
0.0	-1.69	-2.22	-2.20
2.5	-1.76	-1.48	-1.73
5.0	-1.97	-1.69	-1.95
7.5	-1.98	-1.71	-2.10
10	-2.01	-2.24	-2.55

Softening Point

The ring and ball softening point test was included in the accelerated aging analysis to determine if laboratory aging processes significantly increase the solid-to-liquid transition temperature of the bitumen. Figure 2 shows the effect of POFA on the softening point of the bitumen after RTFO and PAV aging. Notably, the softening point of the bitumen containing POFA increased after the two different aging processes, indicating an inherent hardening process of the material during aging. However, the variations in the softening point values were uniform with increasing POFA content. For instance, at 2.5% POFA, the softening point value increased from 49 °C to 61.8 °C as the aging test changed from un-aged to PAV. This result represents an increase in the softening point in the order of 15.21% and 25.35% for RTFO and PAV aging, respectively. In addition, a significant increase in the softening point temperature of the POFA-bitumen was observed at 7.5% POFA content. Thus, the increased softening point temperature indicates an increase in the hardness of the bitumen. Moreover, the incorporation of POFA improves the aging resistance of bitumen.

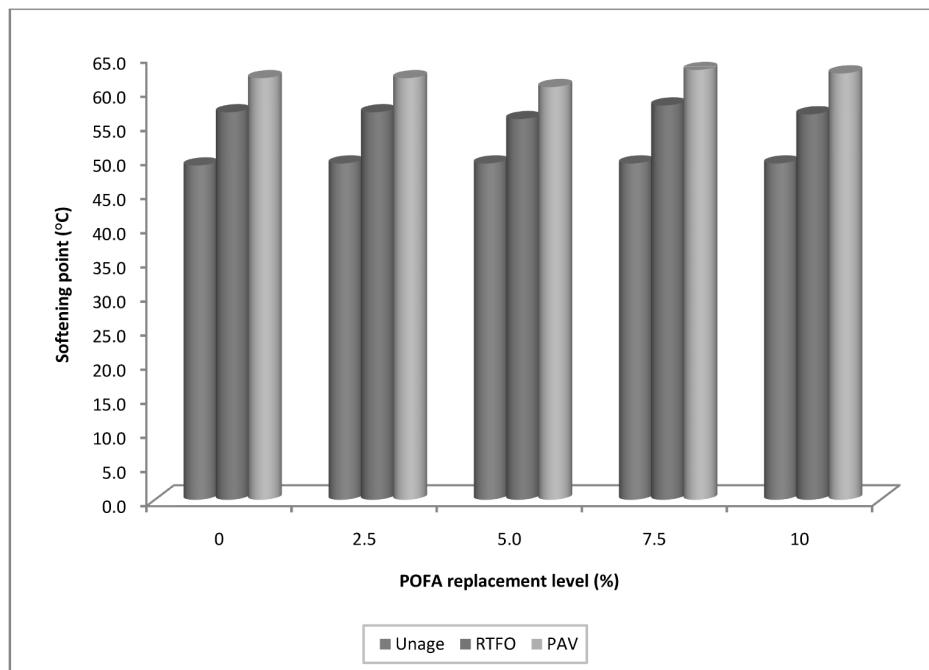


Fig. 2. Effects of POFA concentration on the softening point at different aging conditions

Viscosity

Figures 3 to 5 show the effects of aging on viscosity with temperature on the bitumen containing POFA. Viscosity significantly increased with the addition of POFA into the bitumen before and after aging. The increased viscosity of the POFA-bitumen can be attributed to the oxidation effect under the influence of heat and oxygen (Zhang *et al.*, 2012), which contributes to the formation of oxygen-containing functional groups in the bitumen molecules, i.e., carbonyl groups and sulfoxides (Durrieu *et al.*, 2007). Aging changes the viscosity of the POFA-bitumen, as shown in Figures 4 and 5. However, this waste material exerts no substantial effect on the bitumen for all percentage levels. Furthermore, the viscosities of POFA were markedly higher than those of the controlled samples at high temperatures, suggesting that the introduction of POFA can improve the susceptibility of the bitumen to temperature. Another important observation is that POFA markedly affects the bitumen at high temperature, indicating that the resulting POFA-bitumen is resistant to permanent deformation at high temperatures.

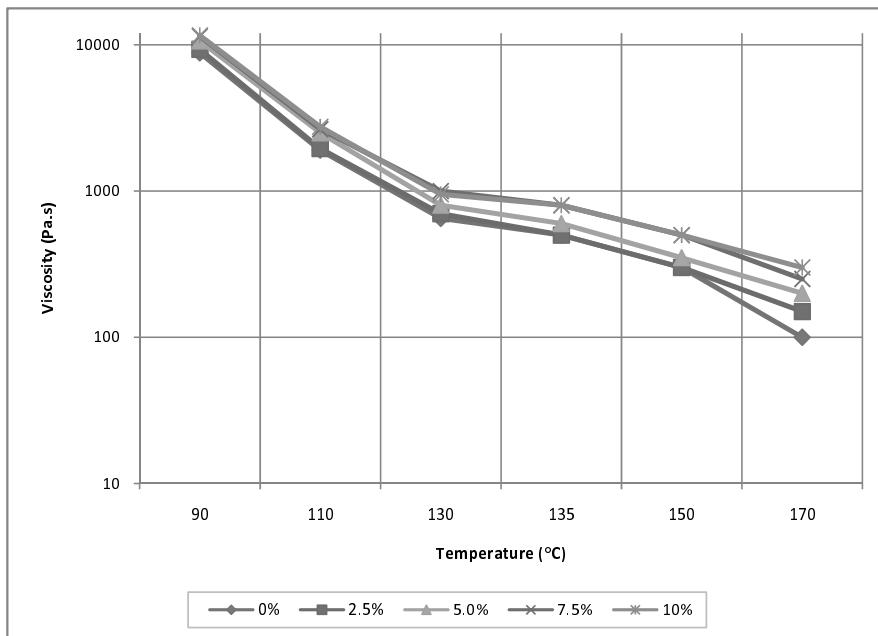


Fig. 3 Effects of POFA concentration on the viscosity-temperature before aging

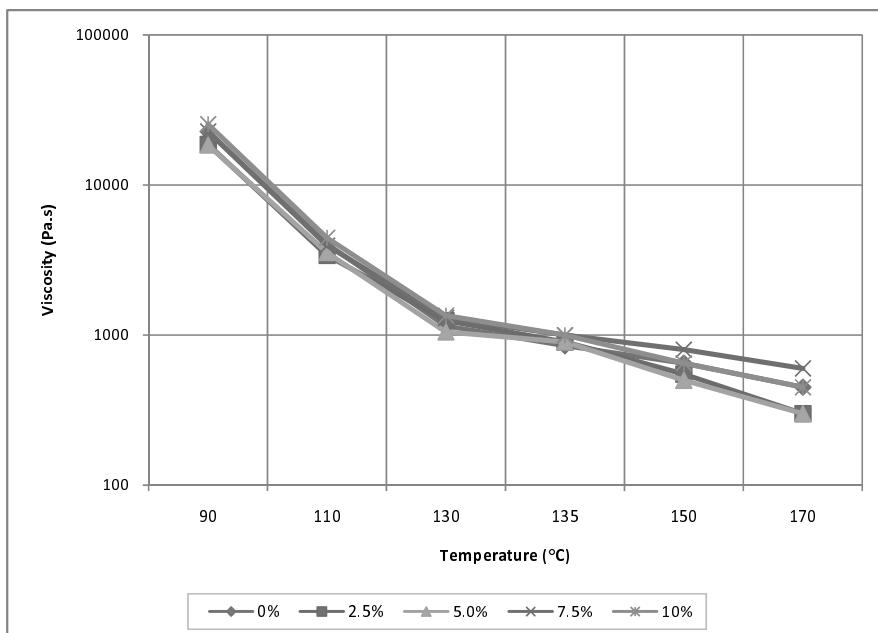


Fig. 4. Effects of POFA concentration on the viscosity-temperature (RTFO)

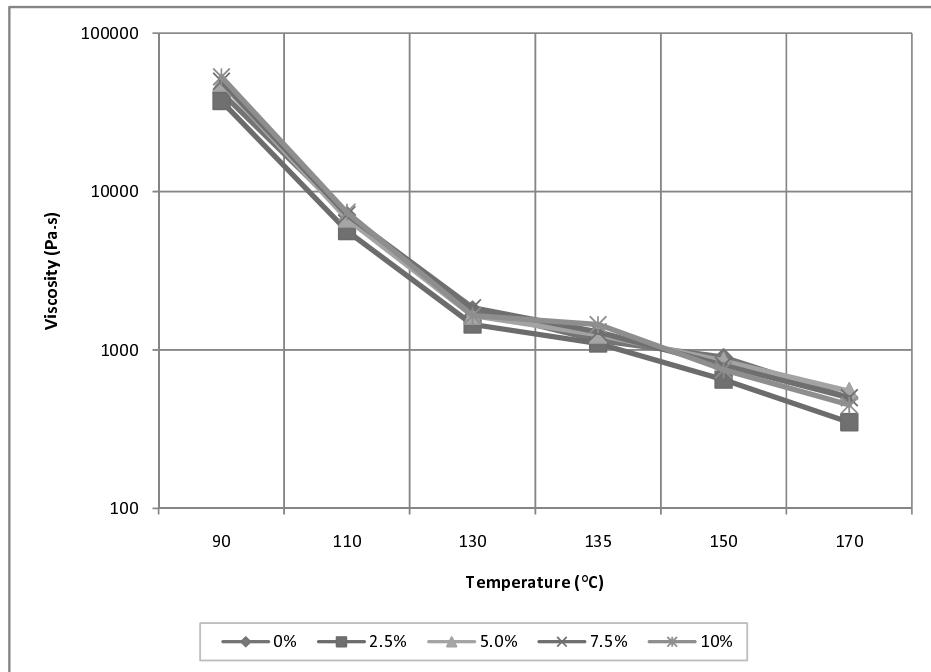


Fig. 5. Effects of POFA concentration on the viscosity-temperature (PAV)

Penetration-Viscosity Number (PVN)

The PVN is based on penetration at 25 °C and viscosity at either 60 °C or 135 °C, which are standard specifications for paving asphalt. According to Roberts *et al.* (1991) and Saleh (2006), the PVN can be expressed as follows:

$$PVN = \frac{L - X}{L - M} (-1.5) \quad (Equation\ 2)$$

Where: X is the logarithm of viscosity in centistokes measured at 135 °C; L is the logarithm of viscosity at 135 °C for a PVN of 0.0; M is the logarithm of viscosity at 135 °C for a PVN of -1.5.

The values of L and M can be determined using the equation (3) and (4) (best on the least square fits).

$$L = \log(Vis.\@135C) = 4.258 - 0.7967 * \log(Pen5^oC) \quad (Equation\ 3)$$

$$M = \log(Vis.\@135C) = 3.46289 - 0.61094 * \log(Penat\ 25^oC) \quad (Equation\ 4)$$

Table 3 shows the PVN values of the bitumen containing POFA for un-aged, RTFOT, and PAV aging. The results show that increasing POFA content from 0% to 10% increases the PVN. For instance, for un-aged, the PVN values increased from -0.85 to -0.35 when the POFA content was increased from 0% to 10%. This effect suggests that the addition of POFA can significantly improve the temperature susceptibility of bitumen in the range of 25 °C to 135 °C. The PVN values are more characteristic of the temperature susceptibility of the bitumen within high temperature ranges. The results also indicate that the introduction of POFA into the bitumen can improve the rutting resistance of the bitumen at temperatures ranging from 25 °C to 135 °C. Meanwhile, the PVN of the POFA-bitumen increased after RTFO and PAV aging, as shown in Table 3. The POFA of the modified bitumen before aging was lower than that under the RTFO aging. Nevertheless, the PVN values of the bitumen containing POFA further increased under PAV aging. The increased PVN of the bitumen subjected to aging can be attributed to the oxidation effect caused by heat and oxygen.

Table 3. Table 3: Results of PVN before and after aged

POFA replacement level (%)	Penetration-viscosity number		
	Un-aged	RTFO	PAV
0.0	-0.85	-1.20	-1.31
2.5	-0.79	-1.00	-1.24
5.0	-0.72	-0.85	-1.20
7.5	-0.36	-0.77	-1.18
10	-0.35	-0.76	-0.88

CONCLUSIONS

- The addition of POFA can markedly increase the PI of bitumen even when subjected to aging, indicating that POFA-modified binders are less susceptible to temperature, especially at high content.
- The softening point value of the bitumen containing POFA increased under two different aging conditions, indicating an inherent hardening process of the material during aging.
- From the point of viscosity-temperature susceptibility, the addition of POFA can increase the temperature susceptibility of the bitumen in the range of 60 °C to 135 °C, especially at high POFA content.
- According to the PVN, the addition of POFA can lower the temperature susceptibility of the bitumen, thereby increasing the rutting resistance at in-service pavement temperatures.

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DECLARATIONS OF INTEREST

The Author(s) declare that they have no competing interests.

REFERENCES

- Ahmad, J., Mohd Yunus, K.Z., Mohd Kamaruddin, N.H. & Zainorabidin, A. 2012.** The practical use of palm oil fuel ash as a filler in asphalt pavement. Proceedings of the 1st International Conference on Civil and Environmental Engineering Sustainability (IConCEES2012), Johor Bahru, Malaysia, Pp. 1-7.
- ASTM D2170-10,** Standard Test Method for Kinematic Viscosity of Asphalts, American Society for Testing and Materials, 2010, 1-10.
- ASTM D2872-04,** Standard Test Method for Effect of Heat and Air on a Moving Film of Asphalt (Rolling Thin-Film Oven Test), American Society for Testing and Materials, 2004, 1-6.
- ASTM D36-12,** Standard Test Method for Softening Point of Bitumen (Ring-and-Ball Apparatus), American Society for Testing and Materials, 2012, 1-4.
- ASTM D5-06,** Standard Test Method for Penetration of Bituminous Materials, American Society for Testing and Materials, 2006, 1-4.
- ASTM D6521-08,** Standard Practice for Accelerated Aging of Asphalt Binder Using a Pressurized Aging Vessel (PAV), American Society for Testing and Materials, 2008, 1-6.
- Chen, J.S. & Huang, L.S. 2000.** Developing an aging model to evaluate engineering properties of asphalt paving binders. *Materials and Structures* **33(9)**: 559-565.
- Durrieu, F., Farcaas, F. & Mouillet, V. 2007.** The influence of UV aging of a styrene/butadiene/styrene modified bitumen: comparison between laboratory and on site aging. *Fuel* **86(10-11)**: 1446-1451.
- Durrieu, F., Lamontagne, J., Mouillet, V. & Planche, J.P. 2004.** Differentiated chemical evolutions of phases in polymer modified bitumen during aging: an infrared microspectrometric study. Proceedings of the 3rd Eurasphalt & Eurobitume Congress. Vienna, Austria, **2(2004)**: 1251-1260.
- Gawel, I. & Baqinska, K. 2004.** Effect of chemical nature on the susceptibility of asphalt to aging. *Petroleum Science and Technology* **22(9)**: 1261-1271.
- Hadavand, B. S. 2010.** Bitumen modification with polysulphide polymer prepared from heavy end waste. *Iranian Polymer Journal* **19(5)**: 363-373
- Hurley, G. & Prowell, B. 2005.** Evaluation of Sasobit for use in warm mix asphalt. National Center for Asphalt Technology Report 05-06, Auburn, AL, USA.
- Lu, X.H. & Isacsson, U. 2002.** Effect of ageing on bitumen chemistry and rheology. *Construction and Building Materials* **16(1)**: 15-22.
- Mashaan, N.S., Ali, A.H., Karim, M.R. & Mahrez, A. 2012.** An overview of crumb rubber modified asphalt. *International Journal of Physical Sciences* **7(2)**: 166-170.
- Navarro, F.J., Partal, P., Garcia-Morales, M., Martin-Alfonso, M.J., Martinez-Boza, F., Gallegos, C., Bordado, J.C.M. & Diogo, A.C. 2009.** Bitumen modification with reactive and non-reactive

- (virgin and recycled) polymers: a comparative analysis. *Journal of Industrial and Engineering Chemistry* **15(4)**: 458-464.
- Saleh, M.F. 2006.** Experimental investigation of bitumen physical properties on foamability and mechanical properties of foam bitumen stabilized mixes. *Proceedings of 3rd Gulf Conference on Roads (TGCR06)*, Muscat, Oman, Pp. 92-98.
- Simon, A. & Hesp, M. 2007.** Reversible aging in asphalt binders. *Energy Fuel* **21(2)**: 1112-1121.
- Šušteršič, E., Tušar, M. & Zupančič Valant, A. 2013.** Rheological and mechanical characterization of waste PMMA/ATH modibitumen. *Construction and Building Materials* **38(2013)**: 119-125.
- Roberts, F.L., Kandhal, P.S., Brown, E.R. & Lee, D.Y. 1991.** Hot mix asphalt materials, mixture design, and construction. NAPA Educational Foundation, Lanham, Maryland, USA.
- Yadollahi, G. & Mollahosseini, H.S. 2011.** Improving the performance of Crumb Rubber bitumen by means of Poly Phosphoric Acid (PPA) and Vestenamer additives. *Construction and Building Materials* **25(7)**: 3108-3116.
- Yu, J.Y., Feng, P.C., Zhang, H.L. & Wu, S.P. 2009.** Effect of organo-montmorillonite on aging properties of asphalt. *Construction and Building Materials* **23(7)**: 2636-2640.
- Zhang, H., Yu, J. & Kuang, D. 2012.** Effect of expanded vermiculite on aging properties of bitumen. *Construction and Building Materials* **26(1)**: 244-248.

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تأثير الوقود المستخرج من زيت النخيل كمعدل لمادة البيتومين لأجل تحسين مقاومة التهالك

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خلاصة

إن الزيادة المطردة للمخلفات الناتجة من مصانع زيوت النخيل سبب مشكلة تلوث في البيئة ويمكن التعامل مع هذه المشكلة بالتدوير وإعادة الاستخدام . في هذه الورقة تم استخدام رماد وقود زيت النخيل- وهو ناتج جانبي في مصانع زيوت النخيل - كمادة معدلة للبيتومين . تم دراسة خواص البيتومين المعدل من حيث إمكانية الاحتراق ونقطة الliquene ، وجدول الاحتراق ، ورقم لزوجة الاحتراق وفحوصات الزوجة . تم تفريذ طريقتين لتمثيل التهالك (aging) في هذه الدراسة. الأولى الطريقة التقليدية فحص الفلم الرقوق بالفرن . والثانية فحص وعاء الصغط . أظهرت النتائج المخبرية زيادة في نقطة الliquene وانخفاض في الاحتراق لعينة البيتومين بعد خلطها برماد وقود النخيل . إن إضافة هذا الرماد- وخاصة بكميات كبيرة - زاد من تحمل البيتومين للحرارة .

إن استخدام هذا الرماد أدى بصورة عامة إلى نقصان أثر معدل التقادم على الخواص الفيزيائية والأنسيوية للبيتومين كما ظهر من نقصان مؤشر العمر لدرجة الزوجة .