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Rheological properties of warm mix asphalt binders and warm mix asphalt binders containing polyphosphoric acid

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Abstract

This paper presents the laboratory investigation of properties of warm mix asphalt (WMA) binders and WMA binders containing polyphosphoric acid (PPA).Two types of warm mix additives were used to produce the WMA binders. Superpave tests were carried out on original and short-term aged binders through the rotational viscometer, the dynamic shear rheometer (DSR), and the bending beam rheometer (BBR). The results indicated that the WMA binders with different warm mix additives showed different viscosity values, however, the addition of PPA remarkably increased the viscosity values of these two kinds of WMA binders used, in the present study, to a similar level. The WMA additive type and the PPA had significant effects on the complex modulus (G^*), phase angle (δ) and $G^*/\sin\delta$ regardless of the binders' aging state (without aging or short-term aging). In addition, two WMA binders with different additive types showed significant differences on the creep stiffness and *m*-value, and the addition of PPA degraded the low temperature rheological properties of the WMA binders.

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Keywords: Warm mix asphalt; Polyphosphoric acid; Rheology

1. Introduction

New technologies have been developed due to the importance of environmental concerns in the manufacture of hot mix asphalt (HMA). Warm mix asphalt (WMA) is one of the new technologies with the objective of minimizing CO_2 emissions in the production and placement process of HMA by reducing the temperatures at which these are mixed and compacted [1–3].

WMA Technologies that allow lower HMA production temperatures may demonstrate positive impacts on pavement performance. Because the lowered mixing temperature reduces oxidative hardening of asphalt binder, it should reduce susceptibility to cracking by improving pavement flexibility and longevity [3].

Reducing production (mixing) and paving (compaction) temperatures by using WMA in place of HMA yields beneficial environmental effects [3]:

- Reduced emissions and odors from plants;
- Reduced smoke; and
- Improved working conditions at the paving site.

WMA can be produced with organic additives and chemical additives or through the foaming technologies (water-bearing additives or water-based processes) [4]. By now, considerable research on WMA has been conducted in many countries [5–11]. The application of organic

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additives produces a decrease in asphalt viscosity when the mixing and placement temperatures are above the melting point of the wax, while the chemical additives reduce the surface tension of the asphalt binder without modifying the rheological properties [12,13]. The foaming technologies are based on the injection of small amounts of water along with the liquid asphalt binder during the mixing process which in-turn causes the asphalt binder to expand in volume and foam at a given temperature. The foaming process helps the liquid coat the aggregate at reduced temperatures [12]. In this study, WMA binders were produced with one type of chemical additive and one type of organic additive.

The considerably lower cost of polyphosphoric acid (PPA) compared with polymer modifiers has made PPA modification a popular choice for pavement applications. The PPA allows to significantly harden bitumen in an easily controllable way. PPA-modified asphalt binders could increase early resistance of the pavement to rutting by increasing initial stiffness and may extend the in-service life of the pavement by improving the low-temperature flow properties. These improved properties may result in both reduced fatigue and low temperature cracking [14–16]. Edwards et al. observed that adding PPA especially to a non-waxy bitumen showed considerable positive effects on the rheological behavior at higher and medium temperatures and little effect at low temperatures [17,18]. Some researchers even reported that addition of 1% PPA by weight of asphalt binder improves the high-temperature performance by approximately 10 °C and the low-temperature performance by approximately 2 °C [19,20]. Although the properties of WAM binders and PPA modified binders were separately investigated in many previous studies, not many studies looked into the properties of WMA containing PPA.

Hence, the main objective of this study was to experimentally investigate the effect of PPA on WMA binders with different WMA additives. In this study, the WMA binders were produced with two different warm asphalt additives. The viscosity properties for the binders in the original state, the high temperature rheological properties in the original state and after rolling thin film oven (RTFO) short-term aging state, and the low temperature properties for the binders after RTFO procedures were evaluated. Fig. 1 shows a flow chart of the experimental design used in this study.

2. Materials and test program

2.1. Materials

In this study, AH-70 asphalt (70 means the penetration of the asphalt binder at 25 °C ranging from 60 to 80 × 10^{-1} mm) was used as the base asphalt with properties shown in Table 1. PPA was used as asphalt modifier, which is a kind of colorless transparent sticky liquid, and $H_6P_4O_{13}$ is its molecular formula. Table 2 lists its basic properties.

This study included an evaluation of two WMA additives (hereinafter called additive-1 and additive-2, respectively). Additive-1 is a product of Sasol Wax, which is a long chain aliphatic hydrocarbon obtained from coal gasification using the Fischer–Tropsch process. After crystallization, it forms a lattice structure in the binder which is the basis of the structural stability of the binder containing additive-1 [21]. Additive-2 is an asphalt emulsion, which is a chemistry package that contains materials to improve workability, adhesion promoters and emulsification agents [22]. Table 3 presents the properties of WMA additives.

2.2. Binders preparation

In this study, 3%, 3% and 1% (by weight of base asphalts) were selected as the contents of additive-1, additive-2, and PPA, respectively in making WMA binders and WMA binders containing PPA (WMA-PPA), based on recommendations from suppliers and previous studies [14,20].

The preparation process of WMA and WMA-PPA binders was developed in the laboratory. The first phase of the process is the preparation of WMA binders. 3% additive-1 pellets (by weight of base asphalt) was added to the heated neat asphalt to prepare the WMA binder with additive-1 (hereafter called WMA-1). A shear mixer was used to stir with a shearing speed of 3000 rpm at about 150 °C for about 30 min. The preparation of WMA binders with additive-2 (hereafter called WMA-2) requires a slow addition of WMA additive. During the addition process, the shearing speed of the shear mixer should be about 800 rpm (if the speed is too high, it will be foaming). After finishing, the shearing speed was turned up to 1500 rpm for another 30 min stirring at 150 °C.

The second phase is the preparation of WMA-PPA binders. The WMA-PPA binders were produced by adding the PPA to the WMA binders in quota with a shearing speed of 1600 r/min at a temperature of 160 °C for 30 min.

Asphalt binders were artificially short-term aged through an accelerated aging process (rolling thin film oven test (RTFOT)). RTFOT was executed at 163 °C for 85 min according to ASTM D 2872.

2.3. Binder tests

The asphalt binder tests were conducted to quantify the binders' performance at two states of its life: in its original state and after mixing and construction. Rheological properties of WMA binders and WMA-PPA binders were evaluated using selected test procedures including rotational viscosity test, dynamic shear rheometer (DSR) test, and bending beam rheometer (BBR) test.

To identify the rotational viscosities of binders, an 8.5 g of binder sample was tested with a number 21 spindle in the

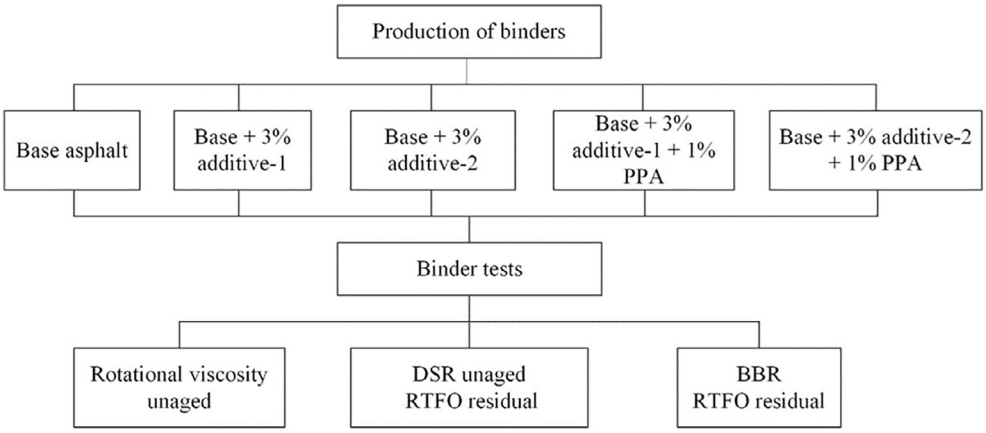


Fig. 1. Flow chart of experimental design procedures.

Table 1
Basic properties of base asphalt.

Parameter measured	Results
Penetration at 25 °C (100 g, 5 s) (0.1 mm)	66.8
Penetration index (PI)	−1.19
Ductility at 15 °C (5 cm/min)(cm)	149.8
Softening point (R&B) (°C)	48.6
Viscosity, (135 °C) (Pa·s)	0.502

Table 2
Basic properties of PPA.

Parameter	Units	Values
Concentration of P_2O_5	%	>84
Specific heat capacity	J/(g °C)	1.434
Density at 25 °C	g/cm^3	2.052
Boiling point	°C	550

Table 3
Properties of WMA additives.

	Parameter measured	Results
Additive-1	Melting point (°C)	99
	Flash point (°C)	285
	Density at 25 °C (g/cm^3)	0.94
	Penetration at 65 °C (0.1 mm)	7
Additive-2	Solid content (%)	12
	Amine value (mg/g)	210
	PH	8.5

rotational viscometer at 135 °C. The rotational viscosity test was performed according to ASTM D4402.

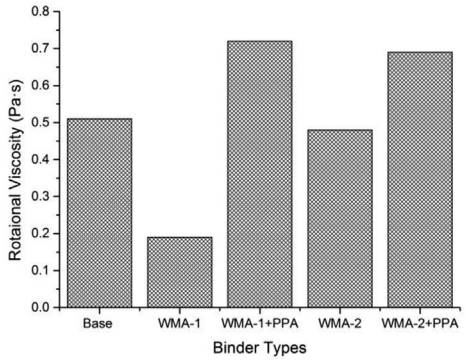
High temperature rheological properties were measured using a dynamic shear rheometer (DSR) according to AASHTO T315. The samples were set between two parallel plates with a diameter of 25 mm and a gap of 1 mm. The temperature sweeps were applied with a fixed frequency of 10 rad/s, the stress level was fixed at 12% for unaged samples, 10% for RTFO aged sample, and the temperature range from 30 °C to 80 °C with an increment of 2 °C/min. The equilibration time was 30 min.

Low temperature creep tests were conducted using bending beam rheometer (BBR) to determine the low-temperature rheological properties of binders according to AASHTO T313. Usually, asphalt binders experience low temperature conditions only after the pavement has been constructed. Thus, in this study, asphalt binders firstly went through rolling thin-film oven test (RTFO) before the low temperature creep test to simulate the aging effect during pavement constructions. In this study, the BBR test was conducted on a binder beam ($102 \times 12.5 \times 6.25$ mm) at −6 °C, −12 °C and −18 °C respectively, and creep stiffness and *m*-value of the binders were measured at a loading time of 60 s.

3. Results and discussion

3.1. Rotational viscosity

The viscosity of an asphalt binder is used to determine the flow characteristics of the binder to provide some assurance that it can be pumped and handled at the hot mixing facility. Fig. 2 shows the experimental values of the viscosities measured by Brookfield viscometer at 135 °C. The results clearly demonstrated that the addition of additive-1 into asphalts decreased the asphalt's viscosity, compared to the base asphalt. And this finding was consistent for the addition of additive-2, but the decreased extent is far less than the addition of additive-1. When the PPA was added to the WMA binders, it was observed that the WMA-PPA binders showed quite higher viscosity values than the WMA binders without PPA, and the viscosity of two types of WMA- PPA binders were almost the same. In Superpave, there is a maximum limit for the rotational viscosity value at 135 °C, that is 3 Pa·s to avoid cracking in asphalt pavements [23]. Consequently, the rotational viscosity values of all binders in this study meet requirements.



*WMA-1: Base asphalt with 3% additive-1; WMA-1+PPA: Base asphalt with 3% additive-1+1%PPA
WMA-2: Base asphalt with 3% additive-2;
WMA-2+PPA: Base asphalt with 3% additive-2+1% PPA

Fig. 2. Rotational viscosity of all WMA binders and WMA-PPA binders.

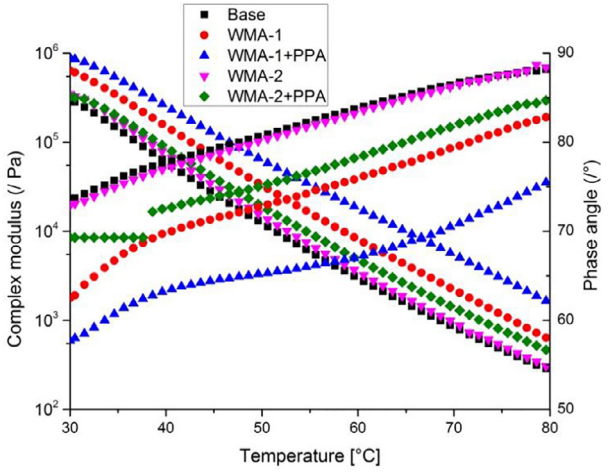


Fig. 3. G^* and δ of asphalts versus changing temperature: no aging.

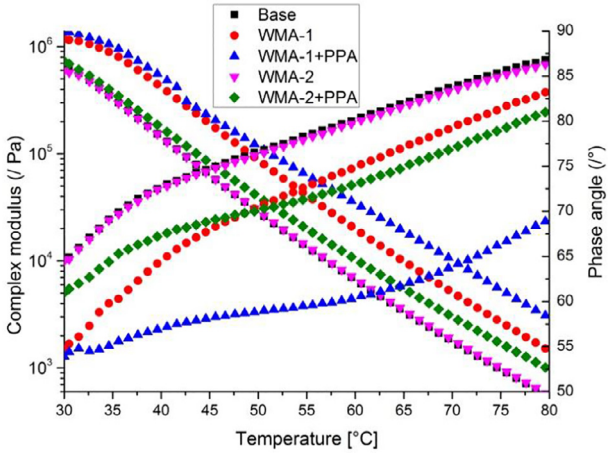


Fig. 4. G^* and δ of asphalts versus changing temperature: RTFO residual.

3.2. High temperature rheological properties

There are four rheological parameters including complex modulus (G^*), phase angle (δ), storage modulus (G'), and loss modulus (G'') can be obtained in the dynamic shear tests. Of these parameters, G^*, is the ratio of total shear stress to total shear strain as defined in Superpave system. The G^* value of asphalt binder and mixture is a fundamental property of the material. In general, asphalt binder and mixture with higher complex modulus value at a given service temperature will exhibit lower permanent deformation value than similar binder and mixture tested at the same temperature that have lower complex modulus values. Phase angle, δ, is an indicator of viscosity and elasticity characteristics of an asphalt binder in Superpave system.

3.2.1. Temperature sweep

The temperature sweep was conducted to simulate variations of rheological properties under changing temperature conditions. The G^* and δ of WMA binders and WMA-PPA binders in original state (i.e., without aging) and after RTFO aging were measured and Figs. 3 and 4 provide the results. The results indicated that the increased temperature results in a reduced complex modulus and an increase phase angle regardless of aging state (no aging and RTFO aging). As shown in Fig. 3, similar complex modulus values trends with the variation of temperature can be observed for the different binders tested in this work, while WMA binders had a greater complex modulus than the base asphalt especially the WMA binder with additive-1. Besides, the WMA-1 + PPA had a greater complex modulus than the WMA-1 and the WMA-2 + PPA had a greater complex modulus than the WMA-2. Interestingly, the WMA-1 even had a greater complex modulus than the WMA-2 + PPA. In addition, the various binders had different phase angles under an increased temperature. It seems that the WMA-2 and the base asphalt had similar phase angle results, and the WMA-1 had a lower phase angle than base asphalt. The addition of PPA deceased the phase angle of WMA binders and the WMA-1 + PPA showed the lowest phase angle values. It should be noted that the phase angle of WMA-2 + PPA at 30–38 °C almost keep stable and suddenly increased at higher temperatures. This phenomenon may attribute to the addition of PPA decreased the visco-elastic temperature sensitivity of WMA binder with additive-2 at relatively low temperatures. Or just because of the using of 25-mm plates and 1-mm gap of DSR when testing at temperature below 40 °C, which were supposed to use the 8-mm plates and 2-mm gap. Therefore, the data presented in Fig. 3 at test temperatures from 30 to 40 °C were for reference only. As indicated by the heading, the purpose of this section is to investigate the high temperature properties of WMA binders and WMA binders containing PPA.

Similar trends in complex modulus and phase angle for RTFO aged binders can be found in Fig. 4, it can be observed that the WMA-2 (RTFO aged) and the base asphalt (RTFO aged) had similar temperature sweep

results. It can be concluded that, for the binder tested, the complex modulus and phase angle characteristics of binders are mainly dependent on the WMA additive type, and the WMA-1 + PPA shows better high temperature properties (higher G^* values and lower δ value than other tested binders at same temperature, which means higher stiffness and more elastic property).

3.2.2. $G^*/\sin\delta$ (Rutting parameter)

The specification defines and places requirements on a rutting parameter, $G^*/\sin\delta$ (where G^*, is the complex modulus and δ, the phase angle) which presents the high temperature viscous component of overall binder stiffness that $G^*/\sin\delta$ should be no less than 1.00 Kpa for the tank asphalt binder and a minimum of 2.20 Kpa for the RTFO aged binder. The $G^*/\sin\delta$ of WMA and WMA-PPA binders in original state (i.e., without aging) and after RTFO aging was measured with a fixed frequency of 10 rad/s (1.59 Hz) at different temperatures and Figs. 5 and 6 provide the results. As shown in Fig. 5, regardless of a test temperatures, the WMA-1 + PPA binder had the highest $G^*/\sin\delta$ value, whereas the base asphalt showed the lowest one. At a higher test temperature, $G^*/\sin\delta$ values of various binders were close. This is because the binder generally exhibits the liquid properties. Moreover, the base asphalt and WMA-2 had $G^*/\sin\delta$ value less than 1 kPa at 70 °C. $G^*/\sin\delta$ values of WMA-1 and WMA-1 + PPA are greater than 1 kPa at 76 °C. It can be concluded that the addition of additive-1 had a significant effect on improving the rutting resistance of base asphalt at a high performance temperature and the affection is far more than the addition of additive-2. The rutting resistance of WMA binders has increased greatly with the addition of PPA. The $G^*/\sin\delta$ values of various RTFO binders at different test temperatures are shown in Fig. 6. Similar to the unaged binders, the WMA-1 + PPA exhibited the highest $G^*/\sin\delta$ values at each test temperatures. The base asphalt and WMA-2 had $G^*/\sin\delta$ value less than 2.2 Kpa at 70 °C, and the

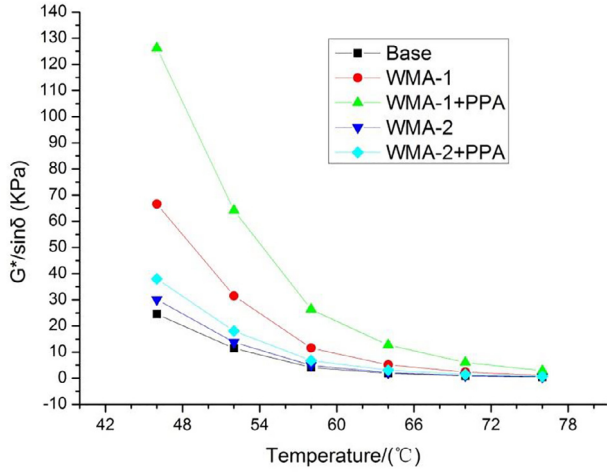


Fig. 5. $G^*/\sin\delta$ values of binders at various test temperatures: no aging.

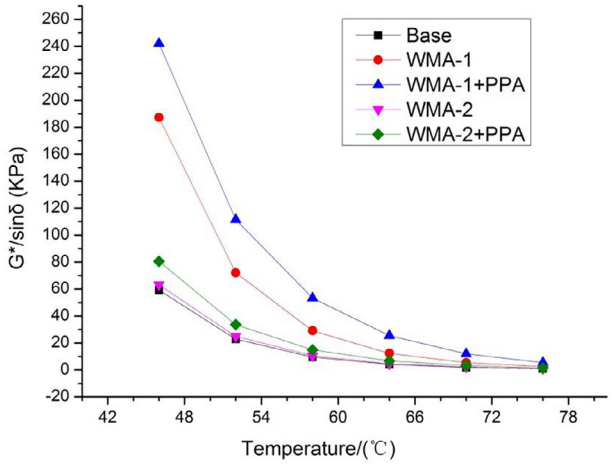


Fig. 6. $G^*/\sin\delta$ values of binders at various test temperatures: RTFO residual.

$G^*/\sin\delta$ values of WMA-1 and WMA-1 + PPA were greater than 2.2 kPa at 76 °C. In addition, the $G^*/\sin\delta$ value of RTFO binder is obviously higher than the value of the unaged binder because of the binder aging process.

3.3. Low temperature rheological properties

Creep stiffness and *m*-value can well characterize the cracking resistance of asphalt binder at low temperatures, generally a low value of creep stiffness and a high value of *m*-value are desired to improve the low-temperature performance of asphalt binder, since a lower stiffness and higher *m*-value can make the asphalt more flexible and perform better to disperse the accumulated stress. It is required in Superpave specification (AASHTO M 320) that the creep stiffness should be no more than 300 MPa and *m*-value should be no less than 0.30.

Fig. 7 shows the creep stiffness of WMA binders and WMA binders containing PPA (RTFO residual) at different low temperatures. As presented in this figure, all the binders' creep stiffness except for the WMA-PPA binders, meet the requirement of Superpave specification at −18 °C. The addition of WMA additive increased the low temperature stiffness of asphalt binder, which may decrease the asphalts' flexibility and increase the possibility of cracking at low temperatures. Similarly, the addition of PPA into WMA binders increases the low temperature stiffness of WMA binders.

The change of *m*-value versus temperature is shown in Fig. 8. Decreases of *m*-value with decreasing temperature were observed for all the asphalts, and the highest *m*-value belonged to the base asphalt at each test temperature, which indicate that the addition of WMA additive into the base asphalt may weaken the asphalts' ability to disperse the accumulated stress. The results also indicated that the addition of PPA into WMA binders decreases the *m*-value of WMA binders. In addition, it can be found that

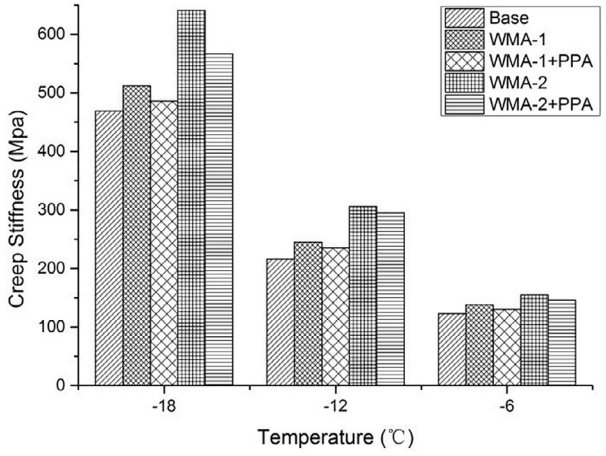


Fig. 7. Creep stiffness of the binders at different temperatures: RTFO residual.

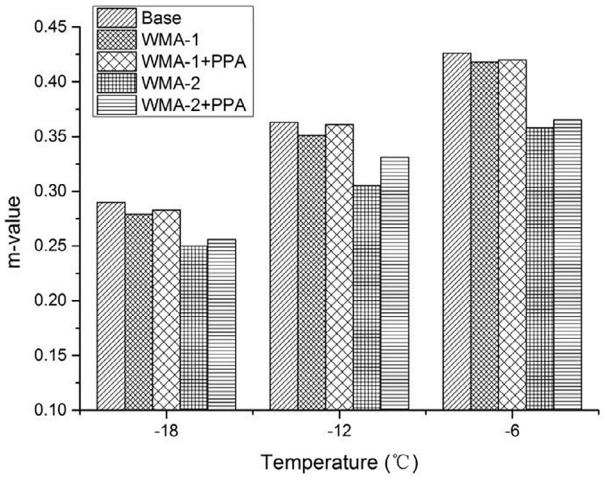


Fig. 8. *m*-value of the binders at different temperatures: RTFO residual.

all the binders' *m*-value failed the requirement of Superpave specification at −18 °C.

4. Conclusion

To characterize the properties of WMA binders and WMA-PPA binders, a series of tests including rotational viscometer test, DSR test, and BBR test were carried out.

The addition of additive-1 significantly decreased the viscosity at 135 °C, which can reduce both mixing and compaction temperatures of mixes. And the additive-1 was observed to be effective on increasing deformation resistance and making the asphalt have more viscous properties, while the effect of additive-2 on these properties was less significant.

Laboratory investigation of WMA-PPA binders in this study identified some benefits of WMA-PPA binder over WMA binders in terms of high temperatures. WMA containing PPA showed the highest viscosity values at 135 °C and best rutting resistance.

However, the WMA binders were observed to have significantly lower resistance on low temperature cracking compared to base asphalt (measured by the BBR test). Also, the addition of PPA decreased the low temperature cracking resistance of the WMA binders. The decreases in values of creep stiffness and *m*-value introduced by PPA weaken the WMA binders' ability to disperse the accumulated stress and decrease the asphalts' flexibility, thus making the low temperature rheological properties worse.

It is suggested to conduct a study to investigate the effect of binder type and binder source on properties of WMA binders and WMA-PPA binder.

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