

## **Laboratory performance comparison of the polypropylene (PP) modified bitumen with different additives**

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### **ABSTRACT**

Polymer modified bitumen (PMB) is widely studied to discover the possibility of road application in order to satisfy the sustainable construction requirement in worldwide. However, the common polymer applied in the bitumen required coupling agent to achieve better mixing to avoid segregation between polymer and bitumen due to the polar interaction in between. This study presents a research to investigate the properties of PMB with different additives by using wet mixing method and obtain the optimum binder-polymer-additive ratio for practical construction usage. Polypropylene (PP), commonly used in daily, is taken as the polymer modifier into bitumen, while phosphoric acid (H<sub>3</sub>PO<sub>4</sub>), carbon black (CB) or waste engine oil (WEO) were treated as the additive to resolve the polar and non-polar heterogenous reaction. The polymer modifier contents vary from 2 - 15% with 1 – 5% additives in different portions incremental according to the polymer and additive combination. The experiment samples have undergone several standard tests (Softening point, ductility and penetration test). The test results showed improvement of rheological properties on PMB after adding additive. Several numerical relationships were concluded to find out the optimum mixing ratio in different application senecio.

Keywords: polypropylene modified bitumen, PMB, phosphoric acid, carbon black, old engine oil, performance test, laboratory performance

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## **1. INTRODUCTION**

Bitumen is the main construction material used in road pavement related work, which treated as a flexible pavement in order to provide a more comfort driving experience comparing to the rigid pavement. With excellent adhesiveness, water resistance, thermoplastic and viscoelastic property, bitumen is suitable for the binding material in pavement on traffic. Bitumen is semisolid under room temperature, which gradually softens when the heat is applied. Molten bitumen is converted into asphalt concrete by mixing with aggregates. Apart from the semi-solid form of bitumen, there is also a liquid form of bitumen primarily for maintenance and repairing Portland cement and asphalt pavement. Common liquid Asphalt includes asphalt cutback and emulsion (Mamlouk and Zaniewski 2011).

Bitumen contains large portion of hydrocarbon (almost 90%) with some sulphur, nitrogen, and oxygen molecules that forms four main functional groups, which are saturates (paraffins), aromatics, resins, and asphaltenes (SARA fractions) (Peralta 2009). With different polarity and chemical composition, the ratio of asphaltenes and maltenes in bitumen gives rise to bitumen's most rheological properties due to the spherical molecular structure of asphaltene. (Hunter, Self et al. 2015) Hydrocarbons with a higher polarity tend to associate into a more robust matrix, which gives the bitumen a more elastic behaviour. In contrast, the non-polar molecules act to disperse the polar molecules, which gives the bitumen a viscous characteristic. (Robertson 1991) Maltenes are composed of resin and heavy oils which are soluble in most solvents. The aromatic portion (non-polar) in oil generally consists of three to four naphthenic carbon rings per molecule, dispersing the polar agglomerations of asphaltenes and resin to maintain stable viscosity and fluidity of the bitumen. On the other hand, asphaltene fraction is highly polar and insoluble in most solvents, acting as a viscosity-enhancing component in bitumen. It is observed that the stiffness, viscosity, and softening point increase significantly with the concentration of asphaltene. (Peralta 2009)

To mitigate the typical failure mechanisms of asphalt pavement such as rutting and cracking, polymer modifiers are commonly supplemented to bitumen using the wet mix method to alter the rheological properties of base binder. Polymer modified bitumen can be further classified into plastomers and elastomers, in which plastomers demonstrate stiff but brittle characteristics when subject to a sudden load. Numerous research suggested that polypropylene (PP) powder, a plastomer commonly found in plastic bags, can substantially improve the high-temperature performance and deformation resistance of bitumen by forming a bi-phasic structure in bitumen matrix. (Zhu, Birgisson et al. 2014) Considering the fact that PP modified bitumen can reduce the amount of plastic waste meanwhile improving the asphalt pavement's durability, the effect of PP's concentration on the base binder are investigated in this research. Even though PP can enhance the stiffness of the bitumen, the non-polar nature of PP and the difference in density may result in instability problems, including partial segregation and coarse dispersion. With the increase in PP's concentration, more and more light non-polar component (i.e. aromatic oil) in the bitumen is absorbed by the PP, which results in the phase inversion. The regular long chain of polyolefin material tends to pack closely

and crystalize, weakening the adhesion between bitumen and PP.

The study aims to evaluate the influence of different types of additives with different content to the polymer modified bitumen on the base of the base material properties of binders in order to achieve the sustainable pavement application in Hong Kong.

## 2. MATERIAL

### 2.1 Bitumen

Bitumen, a by-product from the crude oil extraction or distillation process, is defined as the compound with long carbon chain hydrocarbon. The properties of the bitumen are different in terms of the region and manufacturing process, but also respect to the extraction morphology and crude oil composition. The bitumen from the local supplier is stated as in 50/60 grade, and the material properties examined with the experiments in laboratory were shown in Table 1.

Test	Value	Unit	Method
Penetration@25°C	48.9	dmm	ASTM D5
Softening point	49.3	°C	ASTM D36
Ductility	>1500	mm	ASTM D113
Penetration index	-1.4	N/A	N/A
Viscosity at 135°C	0.48	Pa.s	ASTM D4402
Viscosity at 175°C	0.1	Pa.s	ASTM D4402
Rutting factor, $G^*/\sin\Delta$	1.40	kPa	ASTM D7175
Performance graded	PG56	N/A	ASTM D6373

Table 1. Material properties of the pure bitumen

### 2.2 Polymers and Additives

Polypropylene (PP), one of the common thermoplastics, caused the environmental problem in worldwide due to the long degradation time. The treated PP waste is taken as polymer modifier into the bitumen to enhance the performance of the bitumen. PP is expressed as  $(C_3H_6)_n$  and it is a product from polymerization of polyolefin or saturated polymer. The stability and compatibility are one of the major concerns after adding PP into bitumen. The PP for modification contains particle size gradation after sieving which were shown in Fig. 1. The variation of the particles may vary the ductility performance of PMB. The density and the melting point of the PP is 0.9-0.91 g/cm<sup>3</sup> and 170-176 °C, respectively, which may affect the value of softening point and the hardness of the PMB. Table 2 and Fig. 2 show the linear relationships on softening temperature, penetration values and inverse relationship on ductility variation of the bitumen under different portions of PP content.

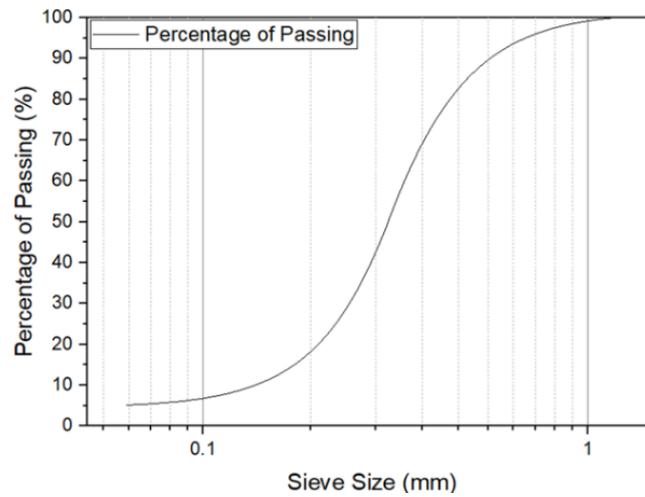


Fig. 1. Gradation curve of PP powder in the experiment

PP CONTENT	5%	10%	15%	Unit	Method
Penetration@25°C	55.8	49.3	53.3	dmm	ASTM D5
Softening point	50.3	53.2	54.4	°C	ASTM D36
Ductility	531	401	220	mm	ASTM D113
Penetration index	-0.9	-0.5	0.0	N/A	N/A
Viscosity at 135°C	0.566	0.714	0.744	Pa.s	ASTM D4402
Viscosity at 175°C	0.343	0.486	0.681	Pa.s	ASTM D4402

Table 2. Properties of PMB with different PP content

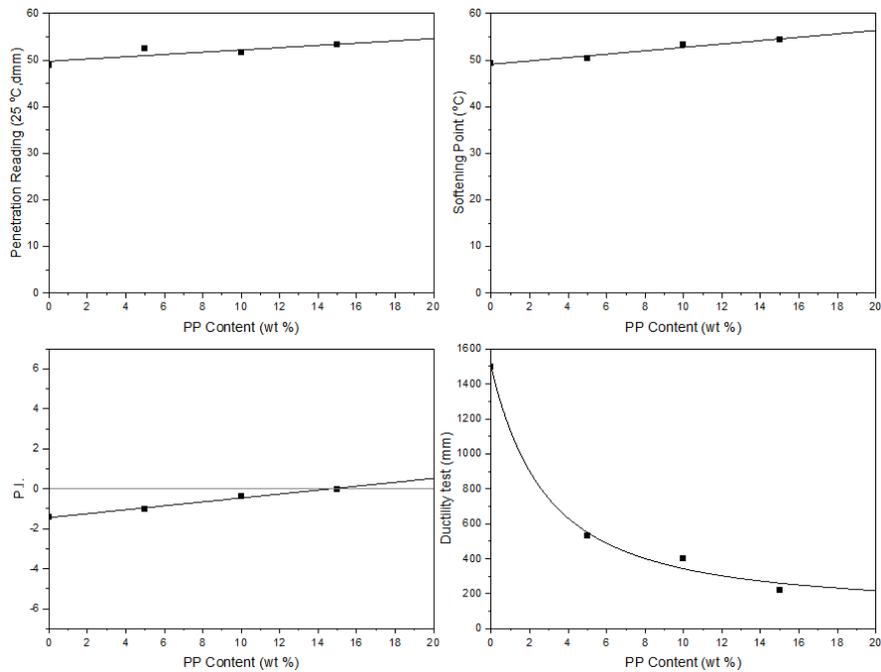


Fig. 2. Overall results for PMB with different PP content

Adding polyphosphoric acid( $H_3PO_4$ ) can solve the heterozygous instability problems between PP and bitumen (Giavarini, De Filippis et al. 1996). The density of polyphosphoric acid is  $2.06 \text{ g/cm}^3$  in  $20 \text{ }^\circ\text{C}$  and soluble in water or bitumen. For the reaction of polyphosphoric acid and bitumen, it showed that addition of polyphosphoric acid can modify the stiffness of bitumen in the experiment (Baldino, Gabriele et al. 2013). Second potential additives is carbon black (CB), which is a high surface-area-to-volume ratio material that produced by the incomplete combustion of crude oil. The melting point, size and density of the carbon black are over  $3000^\circ\text{C}$ ,  $\sim 100\text{nm}$  and  $0.38\text{g/cm}^3$ . For the addition of carbon black in the PP modified bitumen, the main considerations should be the change on penetration values point and ductility due to the high melting point of CB. The final additive in this paper is waste engine oil (WEO). It is collected from the car engine. For the mechanical properties of engine oil, the specific gravity of oxide engine oil is 0.9261 and virgin oil is 0.8818 (Hamawand, Yusaf et al. 2013). In the PP modified bitumen, WEO will be added into the PP modified bitumen in 0 to 3% concentration.

### 3. METHODOLOGY

To study the feasibility for PMB to be used in Hong Kong for non-frictional course purpose, ductility, penetration, and softening point is conducted according to standard ASTM D113, ASTM D5, ASTM D36, and ASTM D4402, respectively. A standardized mixing and testing procedure are to ensure the accuracy and consistency of the result. The samples were prepared using melt blending technique (High shear Mixing). The bitumen (about 400g) was heated in oven till liquidised texture. Afterwards, polypropylene is added and mixed, while the speed of the mixer is maintained at 4000 rpm and temperature needs to be kept between  $160^\circ\text{C}$  and  $180^\circ\text{C}$ . Additive (WEO, CB or  $H_3PO_4$ ) were added and mixed for another 15 minutes after the 15 minutes mixing process of PMB. 0%, 5%, 10% and 15% by weight of the bitumen binder PP were combined with either 1%, 3% and 5% CB or 1%, 2% and 3% WEO respectively, and 1%, 3% and 5% of  $H_3PO_4$  were mixed with 2 -7 % of PP content. Details of the sample preparation procedure are illustrated in Fig. 3.

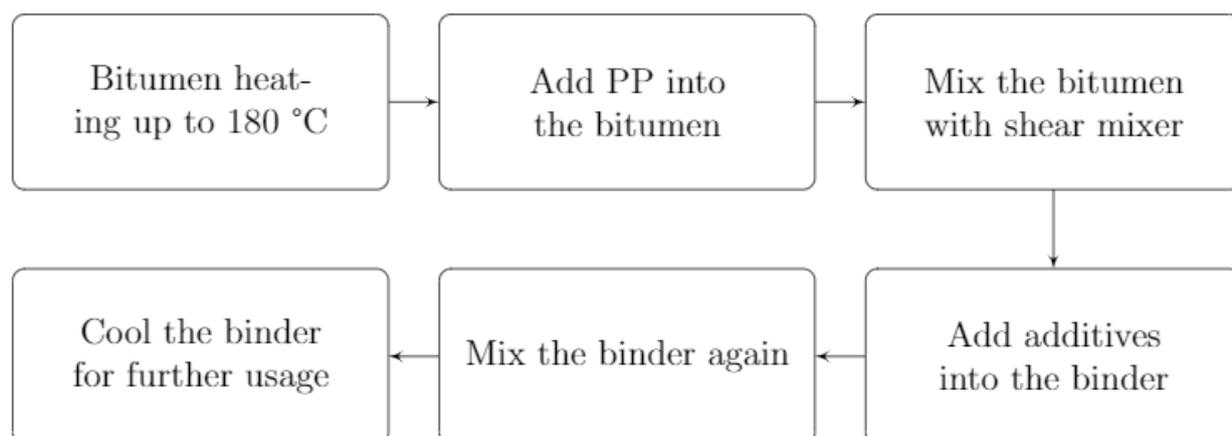


Fig. 3. Schematic Diagram of Binder Sample Preparation

#### 4. EXPERIMENTAL RESULTS AND DISCUSSION

##### 4.1 0 - 15% PMB with 1- 3% waste engine oil (WEO)

Waste engine oil lower the softening point of the pure bitumen significantly from 49.3°C to 45.9°C ,44.2°C and 42.3°C with 1,2 and 3% content, but the rising trend of the penetration value matched the lubrication properties of the engine oil. Although there are large variations on softening point and penetration value, the penetration index and the ductility elongation give the same trend as pure PMB with similar values. It shows WEO changes the thermal related properties of the PMB without affecting bond strength between the molecules.

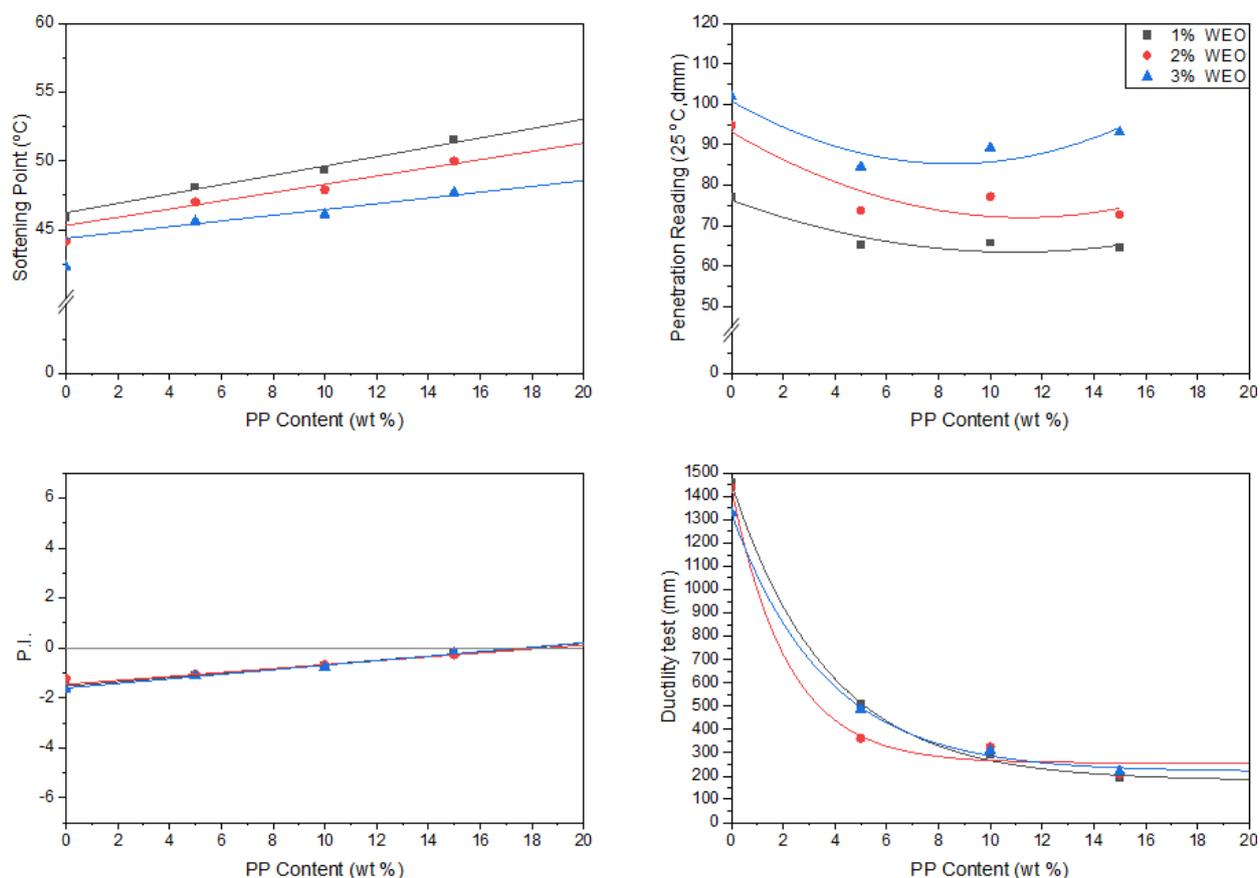


Fig. 4. Overall results for PMB with WEO

##### 4.2 2 - 7% PMB with 1, 3 & 5% phosphoric acid ( $H_3PO_4$ )

The softening temperature of the PMB had an increasing trend according to the polymer content as predicted. Other than that, the softening temperature of PMB with 5% PP content is 50.3°C and increases to 59.5°C, 62.5°C and 77.1°C with 1,3 and 5%  $H_3PO_4$  additive content respectively. The decreasing trend of the penetration value shows the hardness of the PMB is inversely proportional to the PP content and  $H_3PO_4$  content, but the PMB with higher  $H_3PO_4$  content had less rate of change in penetration values. It shows that the  $H_3PO_4$  improves the stability and heterozygous problem between the polymer and bitumen, which enhanced the strength of the bonding structure of the PMB. The ductility of the PMB with  $H_3PO_4$  gives the greatest decreases compare to pure PMB,

which represents the brittleness of samples increases according to the PP content and  $H_3PO_4$  content.

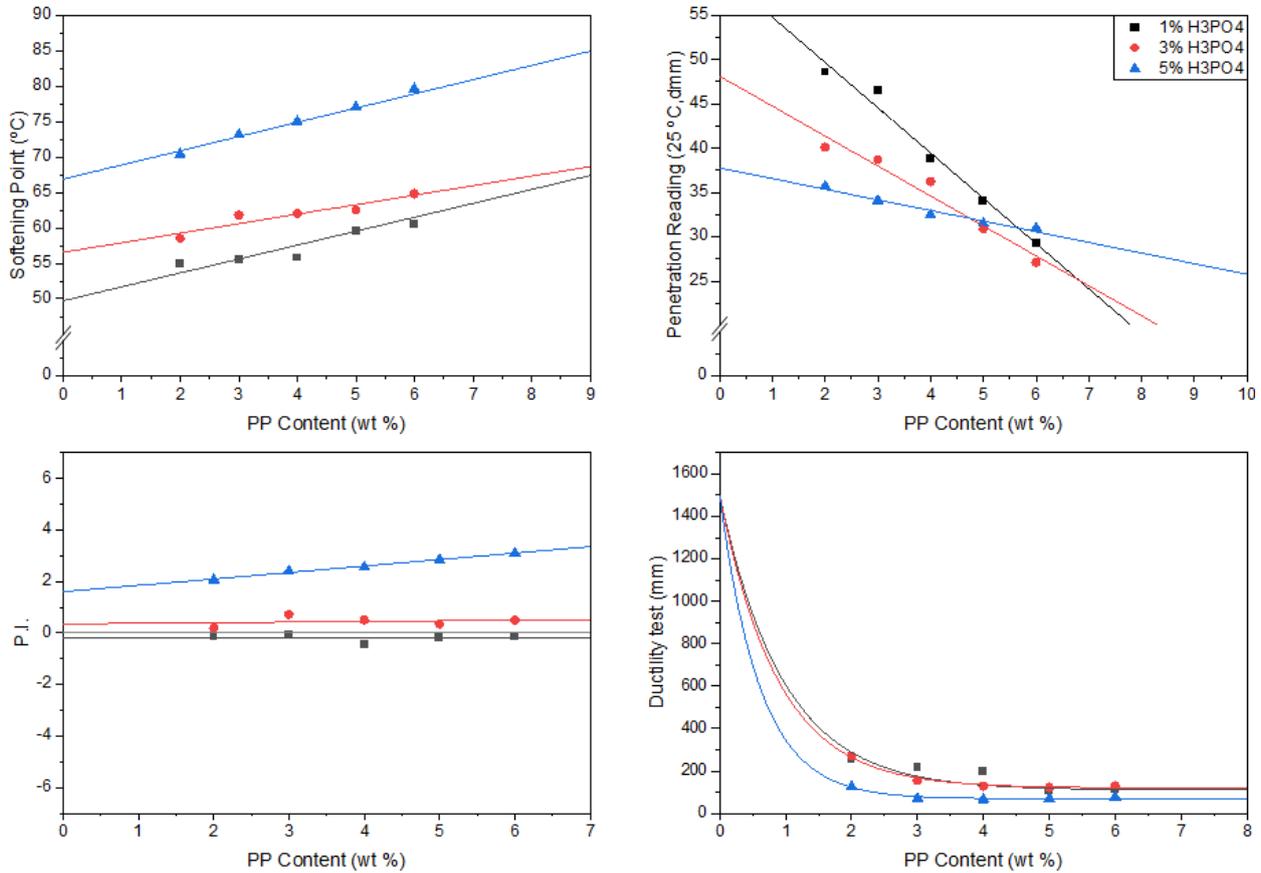


Fig. 5. Overall results for PMB with  $H_3PO_4$

#### 4.3.0 - 15% PMB with 1, 3 & 5% carbon black (CB)

As CB is another type of by-products from the incomplete combustion of heavy petroleum, it is predicted to give the similar increasing trend as polymer additives. However, the different content of carbon black influences very little to the softening point, where it linearly increases 1°C from average 49.3°C to 52.5°C with every 5% PP content increment. The experimental results on the penetration test, ductility test gave a similar result as the softening point test shown, while the content of CB added to PMB does not affect the experimental result. The penetration values of pure bitumen with CB (without polymer content) are in large variation and affected the trendline determination, which indicated that CB may increase the instability of bitumen. PMB with CB shows the parabolic curved result trend with the highest penetration value of 66.5dmm. The penetration index of the PMB with CB slightly elevated from -0.9 to 0.1 with respect to the increment on the percentage content of PP added. The ductility drops significantly before PP content reaches 5% and gets smoothed afterwards. The ductility of the PMB decreases when the PP content increases, and a more serious decreasing trend when CB is added. It probably due to the influence on the difference of the particle size distribution between PMB and PMB with CB.

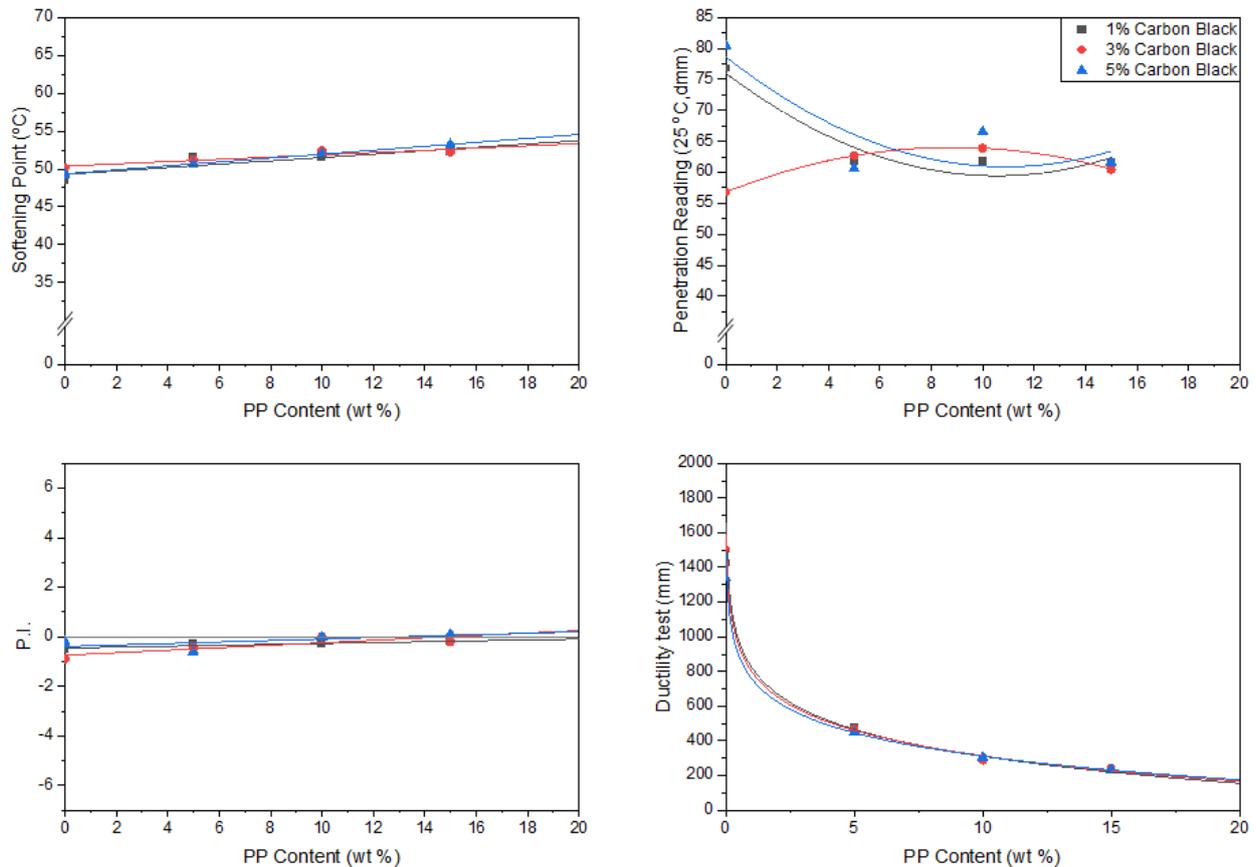


Fig. 6. Overall results for PMB with CB

#### 4.4 The overall performance of PMB with different additives

Fig. 7 is the summary of all the test results. Fig. 8 shows the test results of the 5 % PP bitumen mixing with different percentage of additives in order to investigate the effectiveness of the additives. The softening point test is to determine the temperature of the bitumen sample that fail to resist the 35g steel ball freely. The high softening point of the bitumen ensures that asphalt binder will not bleed or flow in hot weather and in tropical areas, which enhances the rutting resistance of the road pavement. Although Fig. 7 shows the positive correlation to three types of additives, Fig. 8 shows the  $H_3PO_4$  gives positive effect, CB is in neutral and WEO is in negative. It is possible that  $H_3PO_4$  and WEO varies PMB chemically by changing the bond strength of the PMB molecule. However, CB does not vary the thermomechanical properties of the PMB probably due to the high melting point of CB, which shows the mixing between PMB and CB is without chemical change. Similarly, hardness of PMB is mainly dependent on the chemical bond strength and the particle distribution of the PMB binder. The steep increasing trend of penetration value shows the lubrication properties of WEO and the fine particle size of the CB weaken adhesiveness between the penetration needle and samples. Inversely,  $H_3PO_4$  relieves the polar repulsion between the molecules so that the hardness of PMB increases. As the hardness of PMB increases, the brittleness increases and elongation ratio (ductility) decreases.

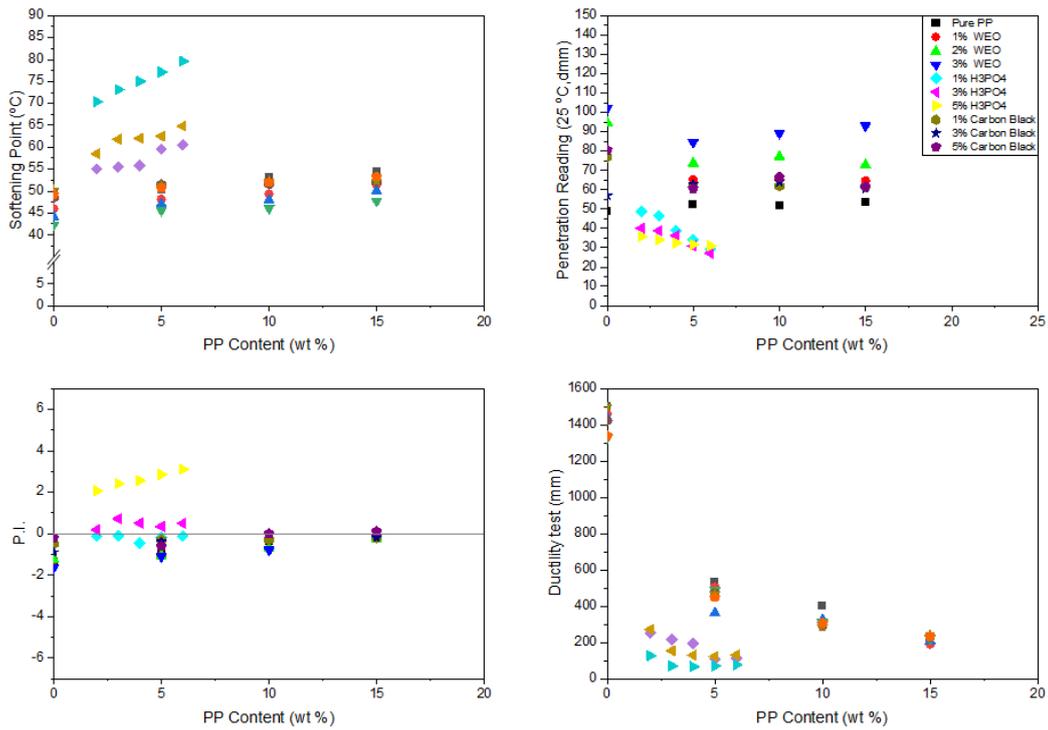


Fig. 7. Overall results for PMB with three additives

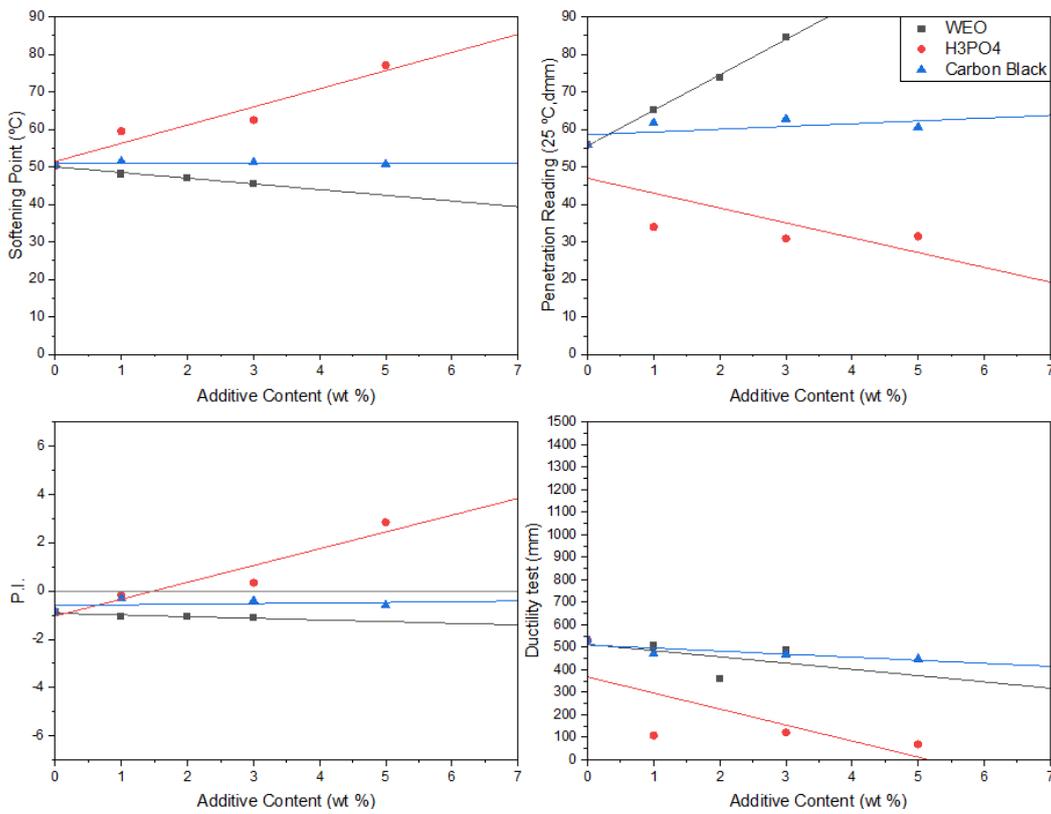


Fig. 8. Overall results for 5%PP content mixed bitumen with three additives

ADDITIVES	WEO	H <sub>3</sub> PO <sub>4</sub>	CB
Softening point	Negative	Positive	Neutral
Penetration@25°C	Positive	Negative	Slightly Positive
Penetration index	Neutral	Positive	Neutral
Ductility	Slightly Negative	Negative	Neutral

Table 3. Influence on PMB by three types of additives

## 5. CONCLUSIONS

The relationships between PP, additives and bitumen binder were investigated by softening point, penetration values and ductility elongation test. The following conclusions can be drawn in terms of the application of PMB with three kinds of additives.

- 1) The increase of PP content in PMB results in enhancement of penetration and softening point but deterioration in ductility. It shows PP improved the hardness, susceptibility and rutting resistance, but it leads the heterogeneous problem.
- 2) CB is observed as a neutral additive to PMB as it caused mechanical properties enhancement without any significant chemical variation. H<sub>3</sub>PO<sub>4</sub> may reinforce the chemical bond between the molecule to enhance stiffness and temperature resistance. WEO acts reversely to H<sub>3</sub>PO<sub>4</sub> as oil particles isolated the interface between the PP and bitumen molecule.
- 3) Based on the current experimental study, the optimum binder-PP-additive ratio by considering the weather condition in Hong Kong (sub-tropical area) can be concluded. 5% PP with any percentage of H<sub>3</sub>PO<sub>4</sub> works well, but the adding process of H<sub>3</sub>PO<sub>4</sub> cannot be done in-situ or factory easily (Special facility is required). CB can be treated as filler but not additive in road pavement as it acts neutral in the experiments. The optimum ratio of PP and WEO added to bitumen should be 5:1 (in percentage of binder weight), which acts like the pure bitumen.

## ACKNOWLEDGMENTS

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