Effect of Polyphosphoric Acid on the Chemical Composition and Properties of Different Bitumens

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ABSTRACT: The effects of adding polyphosphoric acid (PPA) to pavement bitumen were studied by determining chemical composition and conventional physical properties like viscosity, softening point, penetration and ductility. The results show that the softening point and viscosity of bitumen are increased linearly with the increasing of PPA content, while the ductility and penetration of bitumen are decreased to some extent. The obvious effect of PPA on chemical composition is the conversion from resins to asphaltenes. The influence of PPA on different bitumens was also investigated. A high correlation was found between the colloidal index of bitumen and the influence of PPA. In one bitumen with lower colloidal index, the chemical composition and physical property are slightly influenced by PPA. In the other two bitumens with relatively higher colloidal index, there are strong interactions between PPA and bitumens which show the higher asphaltenes increment and resins decrement as well as the higher viscosity increment and the lower retained ductility after modification.

KEY WORDS: Bitumen, polyphosphoric acid, physical property, chemical composition.

1 INTRODUCTION

Bitumens are important factors in road construction and roofing systems duo to its very good binding property (Loeber et al. 1998). Specifications on paving grade bitumens have become quite severe in order that the mixes resist climate and traffic (Lesueur, 2009). In an attempt to change its characteristics and improve its performance, bitumen is often modified by elastomers, plastomers, thermosets, sulphur, or mineral acid (Masson, 2008, Polacco et al. 2006, Giavarini et al. 1996, Al-Dobouni et al. 1994, Huang et al. 2003). There is now much

interest in the use of polyphosphoric acid (PPA) to modify bitumen since it permits to significantly harden bitumen in an easily controllable way (Baumgardner et al. 2005, Edwards et al. 2007, Edwards et al. 2006, Orange et al. 2004, Masson and Gagné 2008, Masson et al. 2008, Masson and Collins 2008). Upon the PPA modification, the high temperature rheological properties of bitumen can be improved remarkably without affecting the low temperature grade (Baumgardner et al. 2005). Edwards et al. studied the rheological effects of PPA in bitumen 160/220–high, medium and low temperature performance. Adding PPA especially to a non-waxy bitumen, showed considerable positive effects on the rheological behaviour at higher, medium and low temperatures (Edwards et al. 2007, Edwards et al. 2006).

There are also some studies referred to the reaction mechanism between PPA and bitumen. Orange et al. considered that PPA acted through the neutralization of polar interactions between the stacked asphaltenes molecules, either by protonation of basic sites or by esterification. The overall effect was to increase the solvation of the asphaltenes, increasing in turn the solid fraction and hence, the viscosity (Orange et al. 2004). Baumgardner et al. proposed various bitumen-dependent mechanism of PPA modification which also affected the lower weight components of the bitumen: co-polymerization of the saturates, alkyl aromatization of the saturates, cross-linking of neighboring bitumen segments, the formation of ionic clusters and the cyclization of alkyl-aromatics (Baumgardner et al. 2005). Model compounds, isoquinoline and 1-methyl-2-quinolinone, were reacted with PPA by Masson et al.. It showed that both compounds formed salts with PPA (Masson and Gagné 2008). Other model compounds, such as bisphenol A, butyl phenyl ether, acetophenone, benzoic acid (Masson et al. 2008), and sulfur compounds (Masson and Collins 2008) were also investigated.

However, as mentioned above, more attention of the existed studies has been paid to the PPA modification mechanism. There are relatively few published articles about the effect of PPA on the chemical composition and physical properties of bitumen. Bitumen is a complex system of different constituents, made of hydrocarbons and hetero-atoms. After fractionation of the bitumen by specific solvents, four main chemical families (saturates, aromatics, resins, asphaltenes) are obtained (Corbett, 1969). The property of bitumen is governed by the chemical-physical interactions of these constituents (Masson et al. 2007). So investigating the influence of PPA on chemical composition and physical property of bitumen, especially for different base bitumens, will help to better understand the interaction of PPA with bitumen.

In this paper, the effects of PPA on chemical composition and physical properties of bitumens with different chemical composition were investigated.

2 EXPERIMENTAL

2.1 Materials

Three bitumens, denoted B1 to B3, were supported by SK Corp., Korea, Panjin Northern asphalt Co., Ltd and China offshore (Taizhou) bitumen Co., Ltd, China, respectively. The physical properties and chemical composition of the three bitumens are listed in Table 1. PPA (105 % relative contents of H_3PO_4) was supported by Changzhou Wujin Huayang Chemical Co., Ltd, China.

Table 1: Physical properties and chemical composition of bitumens.

Physical properties and chemical composition		B1	B2	B3
Physical properties	Penetration(25 ℃, 0.1 mm)	92	85	63
	Softening point(℃)	46.3	43.4	51.4
	Ductility (15 ℃, cm)	>150	>150	>150
	Viscosity (60 ℃, Pa·s)	151	124	273
Chemical composition	Saturates(%)	21.82	30.02	18.82
	Aromatics(%)	46.19	30.21	43.20
	Resins(%)	20.45	32.98	25.80
	Asphaltenes(%)	11.54	6.79	12.18
	Colloidal index[a]	2.00	1.72	2.23

[a] Determined according to reference (Loeber et al. 1998).

2.2 Preparation of PPA Modified Bitumen

Bitumen was first heated until it becomes well melting fluid at around 170 ℃ in an iron container. Then a certain amount of PPA was added into bitumen, and the mixture was blended at 2000 r/min rotation speed for 40 min. The pristine bitumen was also processed under the same conditions in order to compare with the PPA modified bitumen.

2.3 Chemical Composition

The chemical composition of bitumen was determined according to JPI-5S-22-83 (Japan Petroleum Institute Standard). First, bitumen was deasphaltened to yield asphaltenes and maltenes which is the n-heptane soluble portion. Then, the maltens were further separated into three fractions, saturate (soluble in n-heptane), aromatic (soluble in toluene) and resin (soluble

in toluene and ethanol mixture), by column chromatography. All fractions were weighed after the complete removal of their respective solvents.

2.4 Physical Properties Test

The physical properties of bitumen, including softening point, penetration (25 ℃) and ductility (15 ℃), were tested according to ASTM D 36, ASTM D 5 and ASTM D 113, respectively. The Brookfield viscometer (Model DV-II+, Brookfield Engineering Inc., USA) was employed to measure the viscosity of the bitumen according to ASTM D 4402.

3 RESULT AND DISCUSSION

3.1 Effect of PPA on Chemical Composition and Physical Properties of Bitumen B1

3.1.1 Chemical Composition

The effects of PPA on the chemical composition (saturates, aromatics, resins and asphaltenes) of bitumen B1 are shown in Figure 1 to Figure 4. It can be seen that the asphaltenes increase linearly from 11.64 wt% to 16.38 wt% with the increasing of PPA content, while the resins decrease quickly from 20.43 wt% to 15.16 wt%. The saturates decrease to a certain proportion and then increase. In contrast to saturates, aromatics increase to a certain amount and then decrease.

Interestingly, the decrease amount of resins is similar to that of the increase of asphaltenes. It indicates that some resins are converted into asphaltenes under the influence of PPA. Orange et al. hypothesized that PPA protonates basic sites, which induces a loss of hydrogen bonding and the disaggregation of asphaltenes, with the result being a greater dispersion of smaller asphaltene domains (Orange et al. 2004). During this process, the cross-linking of reactive segments may exist to form a matrix of covalently linked matter between the resins (perform as asphaltenes stabilizers) and asphaltenes after adding PPA, i.e., resins-PPA-asphaltenes, which will contribute to asphaltenes. Moreover, upon PPA modification of bitumen, the breaking of alkyl aromatics in resins into alkyl and stiff aromatic fragments may occur (Baumgardner et al. 2005), then n-heptane precipitates increase, which also contributes to the decrease of resins and increase of asphaltenes in bitumen.

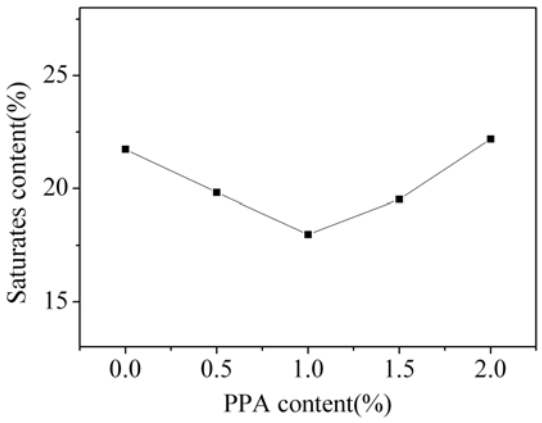

Figure 1: Effect of PPA on the saturates of bitumen B1.

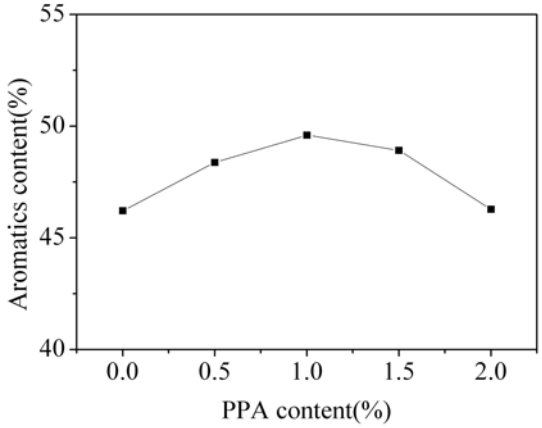

Figure 2: Effect of PPA on the aromatics of bitumen B1.

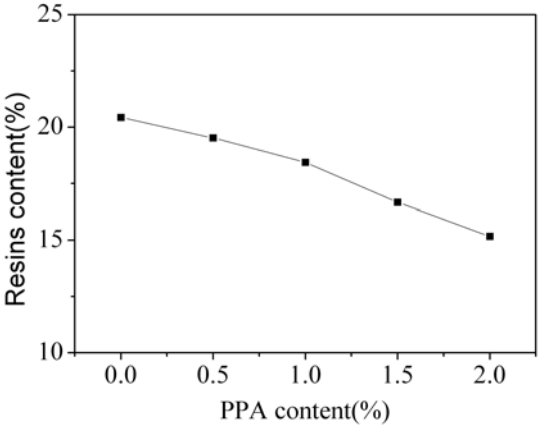

Figure 3: Effect of PPA on the resins of bitumen B1.

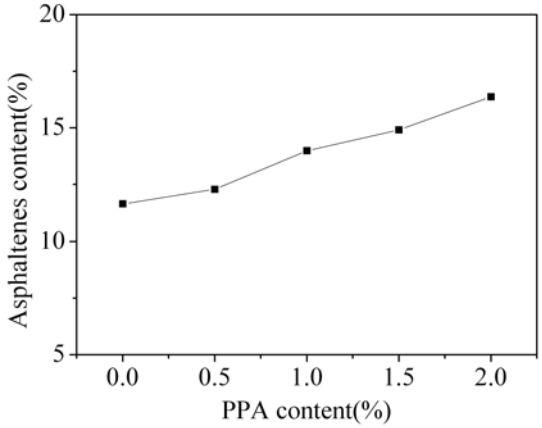

Figure 4: Effect of PPA on the asphaltenes of bitumen B1.

3.1.2 Physical Properties

The physical properties of PPA modified bitumen B1 with different PPA content are shown in Figure 5 to Figure 8. It can be found that the softening point is enhanced quickly with the increasing of PPA content. The viscosity increases gradually when the PPA content is no more than 1 wt%. But when the PPA content exceeds 1 wt%, the viscosity increases linearly. It indicates that the high temperature property of bitumen is improved with the increase of PPA content. According to Figures 7 and 8, the ductility and penetration of bitumen B1 are decreased to some extent, especially when the PPA is increased from 0.5 wt% to 1.5 wt%. However, PPA has a little effect on the ductility with low content (0.5 wt%), and when the

PPA content is more than 1.5 wt%, the decrease rates of penetration and ductility are reduced. It is generally accepted that the ductility of bitumen is largely influenced by the resins content in bitumen. As shown in Figure 3, the resins in bitumen B1 are decreased remarkably with the increasing of PPA, and consequently, its ductility is reduced obviously.

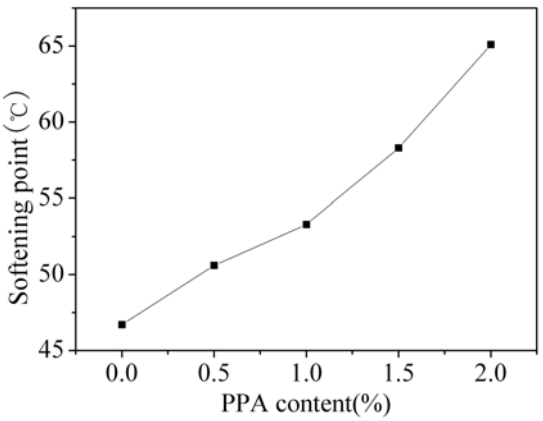

Figure 5: Effect of PPA on the softening point of bitumen B1.

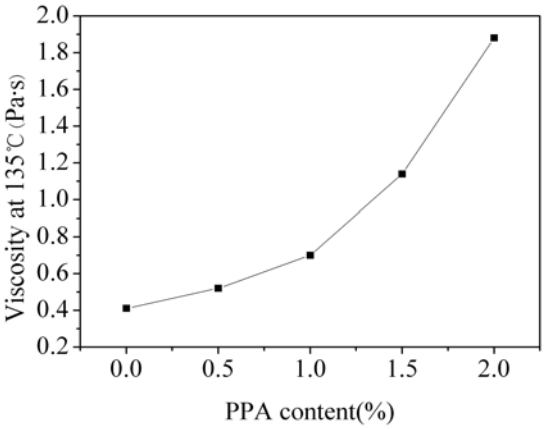

Figure 6: Effect of PPA on the viscosity of bitumen B1.

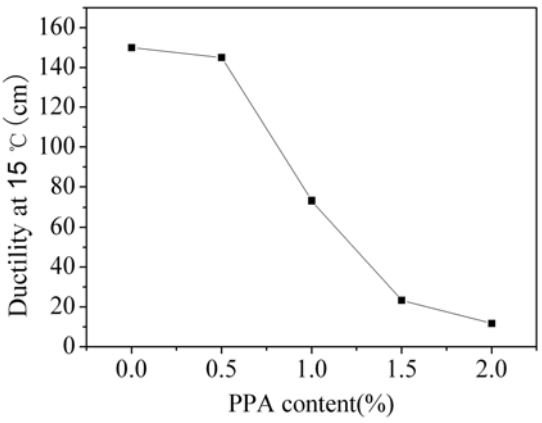

Figure 7: Effect of PPA on the ductility of bitumen B1.

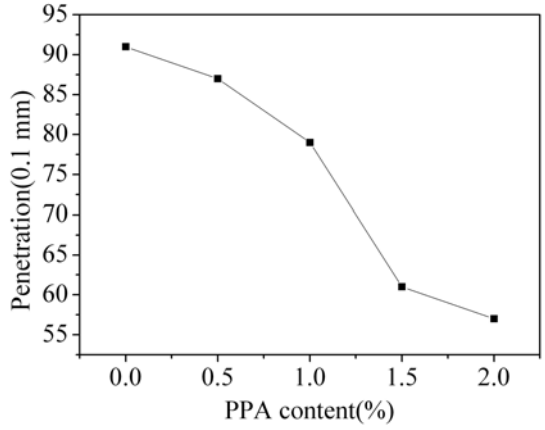

Figure 8: Effect of PPA on the penetration of bitumen B1.

3.2 Effect of PPA on Chemical Composition of Different Bitumens

The effects of PPA on the chemical composition of different bitumens at the same addition content (1 wt%) are shown in Table 2. It can be observed that PPA raises the asphaltenes content and decreases resins content in varying degrees for these three bitumens. With the

introduction of PPA, the most important change is an apparent conversion of resins into asphaltenes, as discussed earlier, which can be attributed to the disaggregation of asphaltenes and breaking of alkyl aromatics in bitumen. However, for other two constituents, namely saturates and aromatics resins, PPA shows different influences on them. It implies that the effects of PPA on the chemical composition of bitumens depend on the base bitumen.

According to Loeber's report (Loeber et al. 1998), the different constituents in the bitumen follow a colloidal law (colloidal index). A higher colloidal index means that the asphahenes are more peptized by the resins in the oil based medium. In this study, the colloidal index of the three bitumens increases in the order: B2 (1.72), B1 (2.00) and B3 (2.23), which is in accordance with the influence order of PPA on the chemical composition and physical properties. We can see from Table 1, the bitumen B2 has the lowest asphalenes and the highest resins. Upon the PPA modification, there are enough resins to act as a stabilizer to asphaltenes. Consequently, PPA has little influence on the colloidal structure of bitumen B2. However, the bitumen B3 has the highest asphaltenes among these three bitumens, more resins are needed as stabilizers, and then the cross-linking reactions between the resins and asphaltenes are more obvious. In addition, on contrary to other bitumens, the saturates content increase after modification, which may be attributed to an acidolysis of the pendant alkyl chains on aromatic nuclei (Baumgardner et al. 2005). Consequently, the changes of chemical component in bitumen B3 are more remarkable than the other bitumens.

Table 2: Changes in chemical composition of different bitumens after PPA modification.

Bitumens	Chemical composition (%)			
	Saturates	Aromatics	Resins	Asphaltenes
B1	21.72	46.21	20.43	11.64
B1/PPA	17.98	49.59	18.44	13.99
Changed values	-3.74	3.38	-1.99	2.35
B2	29.92	30.33	32.85	6.90
B2/PPA	28.48	29.65	32.26	9.61
Changed values	-1.44	-0.68	-0.59	2.71
B3	18.67	43.07	26.00	12.26
B3/PPA	26.93	40.74	16.38	15.95
Changed values	8.26	-2.33	-9.62	3.69

3.3 Effect of PPA on Physical Properties of Different Bitumens

The influences of PPA on the physical properties of different bitumens at the same addition

content (1 wt%) are given in Figure 9 to Figure 12. Changes of softening point, viscosity increment(VI), penetration retention rate (PRR) and retained ductility (RD), which are calculated according to formulas (1) to (3), are used to evaluate the effects of PPA on the physical properties of bitumens.

$$VI = \frac{Modified\ viscosity\ value - Unmodified\ viscosity\ value}{Unmodified\ viscosity\ value} \times 100 \quad (1)$$

$$PRR = \frac{Modified\ penetration\ value}{Unmodified\ penetration\ value} \times 100 \quad (2)$$

$$RD = \frac{Modified\ ductility\ value}{Unmodified\ ductility\ value} \times 100 \quad (3)$$

It can be seen that compared with bitumen B1 and B3, PPA shows a little influence on the physical properties of bitumen B2. Interestingly, the penetration of bitumen B2 is increased to some extent and the ductility is slightly affected by PPA. As mentioned earlier, PPA has little effect on the colloid structure of bitumen B2 duo to its highest resins and the lowest asphaltenes content. Correspondingly, its physical properties are slightly influenced.

Compared with bitumens B1 and B2, there are strong interactions between PPA and bitumen B3 which shows the higher increment of viscosity and softening point and the lower retained ductility and penetration after modification. Bitumen B3 has the highest asphaltenes content and colloidal index, the changes of chemical components in bitumen B3 are more obvious after modification, especially the remarkable decrease of resins which play a crucial role in the stability of bitumen. Accordingly, its physical properties are changed evidently.

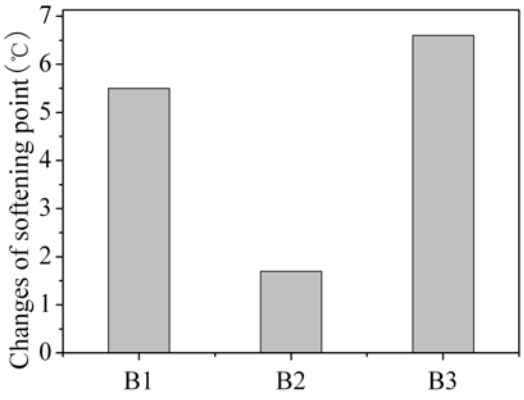

Figure 9: Changes in softening point of different bitumens.

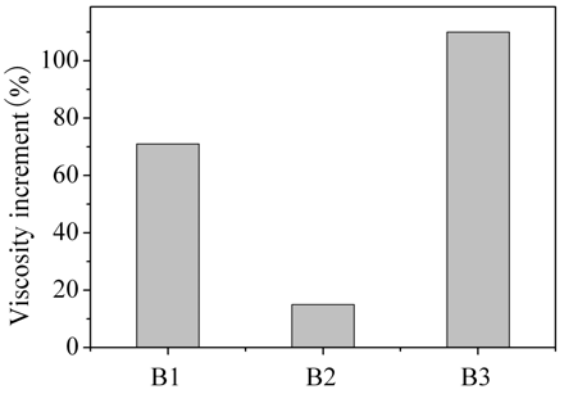

Figure 10: VI of different bitumens.

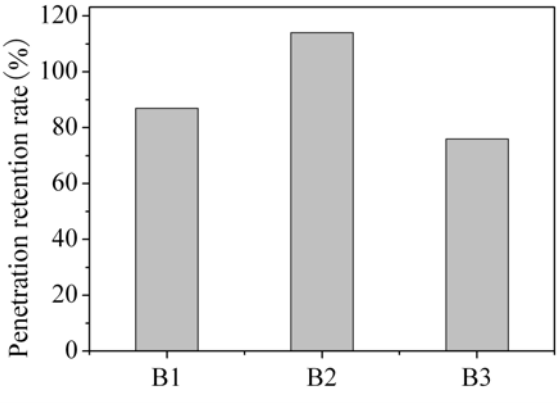

Figure 11: PRR of different bitumens.

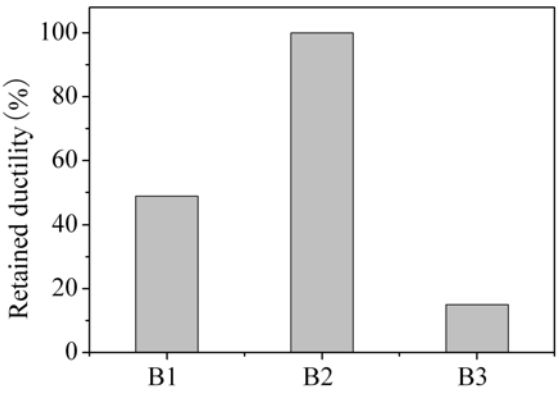

Figure 12: RD of different bitumens.

4. CONCLUSIONS

The effects of PPA on chemical composition and physical properties of bitumen were investigated. The results show that the softening point and viscosity of bitumen are increased remarkably with the increase of PPA, while the ductility and penetration are decreased to some extent. Meanwhile, the obvious change in chemical composition is an apparent conversion of resins into asphaltenes with the increasing of PPA content. The changes of saturates are opposite with the aromatics under the influence of PPA.

The influence of PPA on different bitumens was also studied. The higher the colloidal index of base bitumen, the more obvious effect of PPA on its chemical composition and physical properties. In the bitumen with lower colloidal index, the penetration is increased with the addition of PPA. Furthermore, the ductility is slightly affected by PPA, as well as its slightly influence on the chemical composition. In the other bitumens with relatively higher colloidal index, bitumen shows the higher asphaltenes increment and resins decrement as well as the higher viscosity increment and the lower retained ductility after modification.

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