

Commentary

Research Progress and Prospect of Polyphosphoric Acid Modified Asphalt Technology

Abstract:

In order to clarify the current status of polyphosphoric acid (PPA)-modified asphalt technology, to solve its road problems, and to promote its further popularization and application, the research progress of PPA-modified asphalt technology in scientific research and engineering is summarized. Firstly, the chemical modification mechanism of PPA on asphalt is revealed from the components, chemical reaction and microstructure; the engineering application and service situation of PPA-modified asphalt pavements at home and abroad are evaluated; finally, the future research direction of PPA-modified asphalt is envisioned. The PPA-modified asphalt with dosage of 0.5%,1.0%,1.5%,2.0% was studied, and the presence of PPA was almost indistinguishable from that in the fluorescence micrographs of modified asphalt, and the compatibility between PPA and asphalt was excellent. Atomic force microscopy has a higher resolution relative to fluorescence electron microscopy as well as scanning electron microscopy. The results show that PPA can react chemically with asphalt components to increase the asphaltene content, and the incorporation of PPA helps to improve the high temperature performance, aging resistance, and fatigue characteristics of asphalt. At present, there is no supporting application guide for PPA-modified asphalt technology, and the lack of long-term observation of PPA-modified asphalt test sections restricts the popularization and application of PPA-modified asphalt technology in China.

Keywords: road engineering; polyphosphoric acid; modified asphalt; modification mechanism; compound modification; pavement performance

0 Preface

Polyphosphoric acid (Polyphosphoric Acid, PPA) is a phosphoric acid formed by intermolecular dehydration crosslinking of different degrees of polymerization of inorganic acids, can be used as asphalt modifiers, in petroleum asphalt doping is only 0.5% to 1.0% can significantly improve its high-temperature performance^[1-6], has a high cost-effective. In particular, PPA can improve the storage stability of polymer modifiers in asphalt^[7-9], and easy to add, just a simple mechanical mixing can be, and its modified asphalt has a high popularization value and application prospects. However, combined with the current research and engineering experience found that PPA-modified asphalt there are still some constraints on its further development of the problem, for example, PPA will lead to asphalt low-temperature performance degradation^[10-12], limiting its popularization and application in cold regions. Further improvement of the durability of PPA-modified asphalt and its mixtures is the focus of the current technology of PPA-modified asphalt, and it is also the key to its widespread application.

In recent years, scholars at home and abroad have utilized the existing test equipment in the field of

road engineering and combined with the analytical testing technology in the field of materials, to carry out research on PPA-modified asphalt technology, and have obtained many valuable research results. In terms of the modification mechanism of PPA on asphalt, the focus is on the change of the four components of asphalt before and after the modification of PPA and the chemical reaction between PPA and asphalt components. The doping of PPA makes the asphaltene content of asphalt increase and the gum content decrease, so it is presumed that the PPA will interact with the gums in the asphalt^[13-17]. Baumgardner^[18] also believes that PPA promotes the acidolysis of alkyl aromatic hydrocarbons, which is the most important factor in asphalt modification. The acidolysis of alkylaromatics, which results in the production of small molecular weight asphaltenes. In terms of high temperature performance^[19-20], PPA can improve the softening point, elastic recovery rate and other indicators of asphalt, that is, it enhances the deformation resistance of asphalt at high temperature. However, the low temperature performance and water stability of PPA-modified asphalt and its mixtures are still controversial. In terms of low-temperature performance, it is generally believed that PPA reduces the low-temperature performance of asphalt, but a few studies have shown that PPA can improve the low-temperature performance of asphalt called, which may be related to the test program. In addition the water stability of PPA-modified asphalt is closely related to the type of aggregate and the adhesion properties between asphalt and aggregate. Orange et al^[22] proved that PPA improved the water stability of asphalt mixtures by traditional rutting test and freeze-thaw splitting test; however, Hossain et al^[23] found that the hydrolysis of PPA itself increased the sensitivity of PPA-modified asphalt to water, which would have a negative impact on the asphalt mixtures adversely. In terms of fatigue performance, linear amplitude scanning (LAS) test^[4], beam bending fatigue test^[24] and pavement analyzer testing^[25] have shown that PPA improves the fatigue characteristics of asphalt and its mixtures. Domestic and foreign scholars' research on PPA-modified asphalt technology has matured, providing a new material solution for the high-quality development of asphalt pavements. Summarize the current research found that the research of PPA-modified asphalt has achieved certain results, but most of the research lack of comprehensive consideration, only focus on one or two of the indicators, the scientific research value is higher but not enough attention to the value of engineering applications. In addition, the modification mechanism of PPA-modified asphalt low-temperature performance and water stability performance of the research due to the asphalt source and different test methods, has not yet obtained consistent results^[21-22,26-29], limiting its large-scale popularization and application.

In summary, in order to promote the application and development of PPA modified asphalt technology in the field of road engineering in China, this paper analyzes the modification mechanism of PPA modified asphalt from the perspective of chemical modification. The low temperature performance, high temperature performance, anti-aging performance, water damage resistance and fatigue properties of PPA modified asphalt and its mixture were reviewed. Finally, the existing PPA modified asphalt technology was summarized and prospected, in order to provide reference for the further development and application of PPA modified asphalt.

1 Microscopic mechanism of PPA modified asphalt

PPA is viscous, colorless and transparent at room temperature. It is a mixed acid composed of orthophosphoric acid and various polymerized polyphosphoric acids, as well as a small amount of metaphosphoric acid and polyphosphoric acid, also known as polyphosphoric acid or polyphosphoric acid^[1-3]. According to the percentage of phosphoric acid in PPA, the grade of polyphosphoric acid can be divided^[3]. For example, the phosphoric acid content in orthophosphoric acid (H_3PO_4) is 100%, and its

grade is 100%. The calculation method of other types of polyphosphoric acid grade is as follows : the content of phosphorus pentoxide (P_2O_5) in orthophosphoric acid (H_3PO_4) is 72.4% (calculated by P_2O_5/H_3PO_4 , mass ratio), the content of phosphorus pentoxide (P_2O_5) in tripolyphosphoric acid ($H_5P_3O_{10}$) is 82.6% (calculated by $P_2O_5/H_5P_3O_{10}$ mass ratio), and the grade of tripolyphosphoric acid is $82.6\%/72.4\%=114\%$. At present, 105%, 110% and 115% PPA are often used to modify asphalt.^[2]

Experts at home and abroad have done a lot of research on the modification mechanism of PPA, which is mainly reflected in the four components, chemical reaction and microstructure of PPA modified asphalt.

1.1 Asphalt four components

According to the polarity difference of each molecule in asphalt, Corbett divides it into four components, namely asphaltene, resin, aromatic and saturate.^[30] The macroscopic properties of asphalt will be affected by the properties and proportions of its microscopic components^[31]. Therefore, it is of practical significance to analyze the changes of components in asphalt after adding PPA to PPA modified asphalt. Table 1 is the change of each component in the asphalt after adding PPA, in which the proportion of each component of the asphalt after adding PPA is A_2 , and the proportion of each component of the asphalt before adding A_1 , the calculation formula of the change is $[(A_2-A_1)/A_1] \times 100\%$.

Table 1 The change of four components of asphalt after adding PPA

asphalt type	The dosage of PPA (%)	Asphaltene change amount (%)	Amount of colloid change (%)	Aromatic change amount (%)	Saturate variation (%)
Zhongyou 50# ^[13]	2.00	75.20	-11.31	-2.08	-21.54
Incheon 70 # ^[14]	1.50	118.57	-6.65	-2.41	-39.78
Taizhou 70# ^[15]	1.00	38.13	-30.15	-2.15	30.15
Lu Chang 70# ^[16]	0.50	21.22	13.34	-3.14	-17.55
	1.00	47.19	-18.10	3.39	-19.76
Shell 70# ^[16]	0.50	22.45	11.22	-7.28	-2.86
	1.00	37.88	23.86	-9.73	-11.85
East China Sea 70# ^[16]	0.50	20.07	-0.23	1.54	-8.72
	1.00	27.58	-3.05	5.40	-14.60
SK 90# ^[15]	1.00	59.19	-18.50	1.15	-10.40
	0.25	0.96	-9.33	10.50	-13.20
Canadian asphalt ^[17]	0.50	8.01	-14.25	8.42	-4.20
	0.75	6.03	-1.89	2.67	-16.10
Arabian asphalt ^[17]	0.50	25.46	-18.18	5.63	11.56
	0.75	42.32	-22.67	5.15	8.72
	1.00	46.57	-3.48	-10.68	-2.84

From the calculation results, PPA has different effects on the four components of asphalt from different sources. After the incorporation of PPA, the asphaltenes and resins in the asphalt changed greatly, while the aromatics and saturates changed little. Among them, the asphaltene content increased significantly, and the change of asphaltene content was more obvious with the increase of PPA content. For asphalt with less asphaltene content (such as Incheon 70#, SK90#, East China Sea 70#, etc.), the increase was particularly significant ; the gum content generally showed a decreasing trend. Chen Shouming et al.^[32] believed that PPA played a catalytic role in asphalt and coupled with resins, which increased the molecular weight and polarity of resins and converted them into asphaltenes, so the content of resins decreased. From a chemical point of view, PPA causes the cracking of alkyl aromatic

hydrocarbons in the resin to form aromatic compounds, which are precipitated as asphaltenes^[1].

The problem of poor low temperature performance of single PPA modified asphalt can be improved by compounding PPA with polymer modifiers such as SBS and SBR. Usually, asphaltenes are not compatible with polymers or undergo chemical reactions, while aromatics swell with polymers.^[33] From the results, the PPA modified asphalt mixed with the polymer still maintains the characteristic of increasing asphaltene content. In addition, regardless of whether the PPA is mixed with the polymer modifier, the light components in the asphalt show a decreasing trend as a whole. The changes of each component in asphalt after adding PPA and polymer are shown in Table 2.

Table 2 Changes of each component in asphalt after adding PPA and polymer

asphalt type	Types and dosage of polymer	The dosage of PPA	Asphaltene change amount	Amount of colloid change	Aromatic change amount	Saturate variation
Canadian asphalt ^[17]	2.00%SBS	0.50%	8.00%	6.62%	-8.52%	-5.10%
Arabian asphalt ^[17]	2.00%SBS	0.75%	45.97%	10.44%	-20.28%	-17.55%
Panjin 90# ^[34]	4.20%SBR	1.80%	44.57%	-3.72%	-6.48%	-8.58%

1.2 Chemical modification mechanism of polyphosphoric acid

SBS, rubber powder and other polymer modified asphalt are mostly physical blending modification, and the mixed polymer modifier basically does not react with asphalt, so its storage stability is poor. PPA can react with asphalt components and has great advantages in the storage stability of modified asphalt. At present, the research on the chemical modification mechanism of PPA modified asphalt has achieved certain results at home and abroad, but there is still a lack of systematic research. The main reasons can be summarized as follows^[26]: First of all, the source of asphalt is wide, and the chemical composition of asphalt in different producing areas is quite different, which leads to the lack of uniformity between different research results. It is difficult to explain the interaction between PPA and asphalt through one or several chemical reaction mechanisms, and the research results are less universal. Secondly, PPA reacts with specific functional groups, and asphalt is a complex organic mixture. It is difficult to establish a clear relationship between the chemical reaction of PPA at the molecular angle and the change of the macroscopic properties of asphalt. Even so, the researchers still give a reasonable explanation for the chemical modification mechanism of PPA, which can be used to explain the existing physical and chemical properties of PPA modified asphalt.

Firstly, from the perspective of the interaction between PPA and asphalt components^[35-36]: PPA can interact with functional groups with high dielectric constant. PPA decomposes in asphalt to produce a large amount of $H_2PO_4^-$, and H^+ , which can react with groups such as -OH, -N-, and -S- in asphaltenes, thereby breaking the hydrogen bonds connecting asphaltenes and promoting the decomposition of asphaltene clusters. The formed small molecule asphaltenes are distributed in a continuous phase composed of light components^[37], as shown in Figure 1.

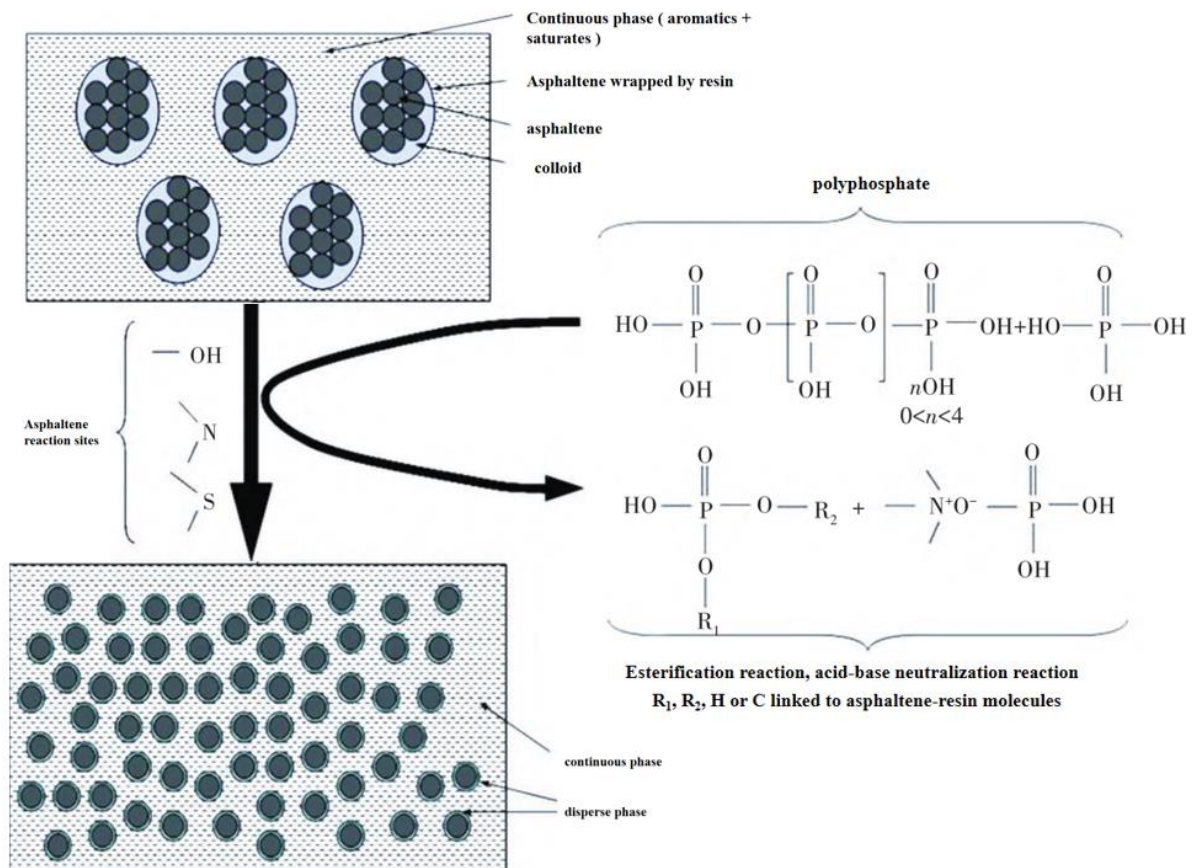


Fig.1 Effect of PPA on asphalt composition^[37]

The source of asphalt is quite different, and the molecular composition of different asphalts is quite different, so the reaction mechanism of PPA and asphalt is different^[35]. Some experts believe that^[36,38-39], PPA replaces weak acids (phenols) and forms ion pairs with weak bases (Pyridine, amphoteric quinolones). The cleavage of hydrogen bonds in the asphaltene cluster structure and the formation of alkylated phenols in the large aromatic structure lead to the decrease of asphaltene molecular weight. The asphaltenes are depolymerized to form small clusters of asphaltenes with polarity. The small cluster asphaltenes cross-linked with PPA to form a covalent compound of 'asphaltene-PPA-asphaltene'.

Baumgardner et al.^[18] explained the decrease of asphaltene molecular weight and the dispersion of low molecular weight asphaltenes from the perspective of chemical reaction. Asphaltene is an aromatic condensation ring structure material, and the addition of PPA makes the alkyl aromatic hydrocarbons in the asphalt acidolysis, as shown in Figure 2.

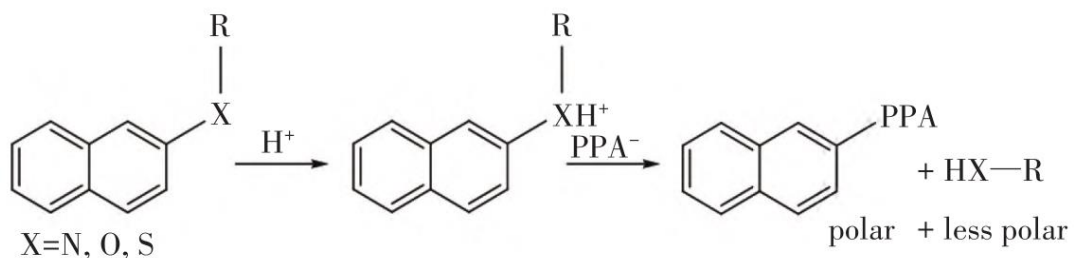


Fig.2 Acidolysis and nucleophilic substitution of alkylarenes

PPA not only reacts with asphaltene, but also reacts with light components, resulting in a decrease in light components, which explains the problem of PPA modified asphalt needle degree decline. Firstly, the cross-linking of the reaction section in the light component forms a covalently cross-linked substance ;

then, PPA catalyzes the cyclization of alkylarenes to form harder naphthalene arenes, as shown in Fig.3.

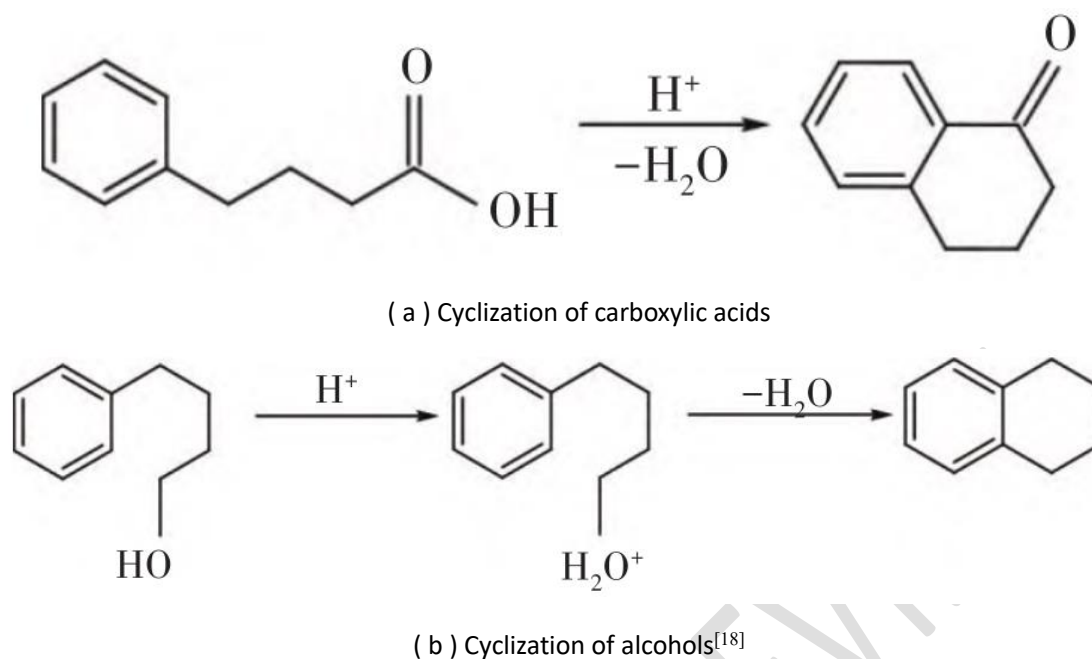


Fig.3 Reaction process of PPA and light components of asphalt

In addition, the esterification of PPA with the chemical components in asphalt and the phosphide formed by acid-base neutralization reaction also lead to the increase of asphalt hardness.^[18,37,40]

1.3 Microstructure of polyphosphoric acid modified asphalt

The microstructure of modified asphalt can be analyzed intuitively by means of fluorescence microscope, scanning electron microscope, atomic force microscope and other characterization methods, so as to analyze the influence of PPA on the macroscopic properties of asphalt. Wang Lan et al.^[41] analyzed the fluorescence of 0.5%, 1.5% PPA modified asphalt and 3% SBS modified asphalt with 0.5%, 1% and 61.5% PPA respectively. The results showed that PPA was evenly distributed in the modified asphalt, and with the increase of PPA content in 3% SBS modified asphalt, the number of SBS particles in the asphalt increased and the average particle size became smaller. PPA can improve the compatibility between SBS polymer and asphalt. Zhang et al.^[42] studied PPA compound SBR modified asphalt by scanning electron microscopy. After adding PPA, the particle size of SBR modifier decreases, and the edge of the particles is blurred, which means that PPA promotes the compatibility of SBR with matrix asphalt. Yu Wenke [3] studied the PPA modified asphalt with the content of 0.5%, 1.0%, 1.5% and 2.0%. The existence of PPA can hardly be distinguished in the fluorescence micrograph of the modified asphalt, and the compatibility between PPA and asphalt is excellent. Atomic force microscope has higher resolution than fluorescence electron microscope and scanning electron microscope. Microscopic analysis of asphalt surface by atomic force microscopy is common in the study of asphalt materials, especially it can intuitively show the 'bee-like' structure in asphalt^[43]. Yu Yanbin^[44] used atomic force microscopy to observe the surface morphology of PPA modified asphalt with 1% and 2% content. After adding PPA, the surface of asphalt becomes rougher. Wang Yongning^[45] observed the surface morphology of SK90 #, Zhenhai 90 # and Xitai 90 # after adding PPA. After adding PPA, the asphalt appeared 'bee-like' structure, and with the increase of PPA content, the size of 'bee-like' structure decreased and became dispersed, which indicated that PPA had a chemical reaction with matrix asphalt.

Through the microscopic analysis of PPA modified asphalt, it can be seen that the compatibility between PPA and matrix asphalt is excellent, and the compatibility between polymer and matrix asphalt

is promoted, which proves that PPA can improve the storage stability of polymer modified asphalt.

2 PPA modified asphalt and its mixture road performance

2.1 Low temperature performance

According to the current research results, the influence of PPA on the low temperature performance of asphalt is still controversial, but it is generally believed that the addition of PPA will damage the low temperature performance of asphalt. For example, Ho et al.^[10] studied 1.0% and 2.0% PPA modified asphalt by direct tensile test (DDT). The results show that the direct tensile failure stress of PPA modified asphalt is the same or slightly lower than that of matrix asphalt, that is, PPA has an adverse effect on the low temperature performance of asphalt. However, some scholars believe that PPA can improve the low temperature performance of asphalt. Baldino et al.^[21] and Ding Haibo et al.^[46] studied the low temperature rheological properties of PPA by dynamic mechanical analyzer (DMA), and obtained similar conclusions, that is, PPA can increase the stiffness of asphalt and improve the low temperature performance of asphalt, and the low temperature performance of PPA modified asphalt is related to the wax and asphaltene content in asphalt. Edwards et al.^[27-28] believed that the influence of PPA on the rheological properties of asphalt is closely related to the composition of asphalt, which means that the influence of PPA on low temperature performance is closely related to the source of asphalt. Sarmowski^[37] used PPA to modify matrix asphalt and SBS modified asphalt respectively. There was no significant difference in low temperature performance between matrix asphalt and SBS modified asphalt before and after modification. Cao Weidong et al.^[47] By changing the content of PPA, the creep results of asphalt low temperature bending beam were analyzed by variance analysis, and it was found that the effect of PPA content on the low temperature performance of modified asphalt was not significant.

At present, the research on the low temperature performance of PPA modified asphalt has two characteristics :

(1) The combination of polymer and PPA is widely used to reduce the adverse effects of PPA on the low temperature performance of asphalt. Among them, SBS and SBR, two polymers with excellent low temperature performance, are commonly used additives^[48-50]. Some people have also tried to use organic warm mix agent Sasobit^[51], dioctyl phthalate (DOP), trioctyl trimellitate (TOTM)^[52], basalt fiber^[53] and other materials to modify, and achieved good compounding effect.

(2) Different researchers evaluated the low temperature performance of PPA modified asphalt by low temperature ductility, low temperature trabecular bending creep, dynamic mechanical analyzer, force ductility and other test methods, but the test results are not uniform. In the follow-up study, it is necessary to systematically study the low temperature evaluation methods and indexes of PPA modified asphalt, so as to better understand the effect of PPA on the low temperature performance of asphalt and guide the actual project.

2.2 High temperature performance

The increase of asphaltene content in asphalt after PPA doping promotes its transformation from sol structure to sol-gel structure, which is helpful to improve the high temperature performance of matrix asphalt. For SK70# asphalt, 1% content of PPA can increase its softening point from 49.5°C to 54.7°C. When the content of PPA is 2%, the softening point can rise to 61.5°C^[19]. Dong Gang^[38] Multi-stress creep recovery test (MSCR) was used to analyze the creep recovery rate and recovery rate difference of PPA modified asphalt with 0.5%, 1.0%, 1.5% and 2.0% content. The higher the recovery rate, the better the elastic deformation ability of asphalt. The smaller the difference of recovery rate is, the smaller the sensitivity of recovery rate to stress is. The results show that the addition of PPA

effectively improves the recovery rate of matrix asphalt, and the recovery rate increases with the increase of PPA content, which means that the resistance of PPA modified asphalt to rutting deformation is improved. The difference of recovery rate decreases significantly with the increase of PPA content, which is beneficial to delay the occurrence of permanent deformation of asphalt pavement. Nuñez et al.^[6] and Domingos et al.^[20] also found that PPA can improve the elastic recovery rate of asphalt. Therefore, the conclusion that PPA can improve the high temperature performance of asphalt is highly recognized and unified at present.

2.3 Anti-aging properties

The anti-aging ability of asphalt affects the performance and service durability of pavement. Domestic and foreign studies have shown that the incorporation of PPA helps to enhance the anti-aging ability of matrix asphalt^[6,12,38]. At present, the research on the aging of PPA modified asphalt mainly includes the performance changes of PPA modified asphalt under ultraviolet light, thermal oxygen and other aging conditions, the aging kinetics of PPA modified asphalt and its anti-aging mechanism.

By analyzing the changes of 5°C ductility softening point, rutting factor and other performance indexes of PPA and PPA compound polymer modified asphalt under different ultraviolet and thermal aging time, Xu Nan et al.^[54] found that PPA can effectively improve the low temperature ductility of matrix asphalt and polymer modified asphalt after aging. PPA can be used as an anti-aging agent to effectively enhance the anti-ultraviolet aging ability of pavement during service. Chen Zhao et al.^[55] analyzed the high and low temperature rheological properties of PPA composite SBS modified asphalt before and after aging by DSR and BBR tests. PPA composite SBS modified asphalt can improve the high temperature anti-aging ability of single PPA or SBS modified asphalt, but its low temperature anti-aging ability is lower than that of single PPA or SBS modified asphalt, which also reflects that the performance of PPA modified asphalt at low temperature needs to be further improved. Through infrared spectroscopy analysis, the sulfoxide index of PPA compound SBS modified asphalt changed little before and after aging, and its anti-aging ability was better^[56].

From the perspective of aging kinetics, Zhang et al.^[9] analyzed the aging kinetics of SK 70# asphalt with 1% PPA. The results show that the aging reaction of PPA modified asphalt follows the first-order reaction. The aging reaction rate of PPA modified asphalt is lower than that of the original matrix asphalt, and the activation energy of PPA modified asphalt is higher than that of the matrix asphalt. Therefore, the anti-aging performance of PPA modified asphalt is also better than that of the original matrix asphalt. Generally, there is a linear relationship between the physical and chemical properties of asphalt and long-term aging oxidation. However, Huang et al.^[40] found that PPA interfered with the linear relationship between the physical and chemical properties of matrix asphalt and long-term oxidation aging by studying the modified asphalt with 1.5% PPA content.

In summary, it is a consensus that PPA can effectively increase the anti-ultraviolet aging and thermo-oxidative aging ability of asphalt. Future research should also focus on in-depth exploration of aging kinetics and aging mechanism.

2.4 Water stability

Generally speaking, the damage to the asphalt pavement caused by the participation of water is called water damage. Water stability is as important as high temperature deformation resistance, low temperature crack resistance, aging resistance and fatigue resistance^[57]. Studies have shown that the reduction of the water stability of the asphalt mixture itself is the internal cause of water damage to the asphalt pavement^[58]. Therefore, it is very important to study the water stability of PPA modified asphalt mixture. The water stability of PPA modified asphalt mixture involves many aspects, such as PPA

modified asphalt itself, aggregate type, adhesion between asphalt and aggregate, etc.

Zhou et al.^[59] compared and analyzed the water damage resistance of different modified asphalt mixtures by using Kentucky Flying Test and Immersion Hamburg Rutting Test. The results show that the modified asphalt mixture with 0.4% PPA content is better than the modified asphalt mixture with 15% rubber powder content, the modified asphalt mixture with 20% TB rubber powder content and the matrix asphalt mixture, but less than the modified asphalt mixture with 20% rock asphalt content and the modified asphalt mixture with 4.5% SBS content. Orange et al.^[22] studied the water stability of PPA modified asphalt by freeze-thaw splitting tensile strength ratio (TSR) and Hamburg wheel tracking test (HWTD). After adding PPA, the TSR value increased from 60% to 70%, and the HWTD rutting test showed that there was no obvious spalling point in the rutting sample after adding PPA. Both tests showed that PPA was helpful to increase the water stability of asphalt mixture.

The adhesion between asphalt and mineral aggregate is also another effective method to evaluate the water stability of asphalt mixture. Due to the addition of PPA, the asphaltene content in the matrix asphalt increases, and the adsorption polarity of the asphalt increases, so the adhesion performance between the asphalt and the aggregate is improved^[59]. Huang et al.^[60] proved that PPA improved the adhesion between asphalt and granite aggregate by bond strength test. The change of adhesion depends not only on asphalt, but also on the type of aggregate. Ali et al.^[61] measured the adhesion work of matrix asphalt with 1.5% PPA content and limestone aggregate, and found that the addition of PPA led to the decrease of adhesion work. Dong^[38] found that the adhesion of PPA modified asphalt was also related to the type of compound polymer. PPA could improve the adhesion of SBS modified asphalt, but had no significant effect on the adhesion of SBR modified asphalt.

Moraes et al.^[62] evaluated the adhesion properties of PPA modified asphalt by means of PATT tensile tester. The addition of PPA improves the tensile strength between asphalt and aggregate, that is, the effect of enhancing the adhesion performance is related to the type of aggregate and the matrix asphalt. Based on density functional theory, Mousavi et al.^[29] explained the change of water stability of PPA modified asphalt. The water in the environment induced the shortening of PPA molecular chain, which weakened the grid effect of PPA in matrix asphalt, thus reducing the elasticity of modified asphalt. At the same time, the hydrolysis of PPA itself also leads to the sensitivity of PPA modified asphalt to water. With the increase of PPA content, the sensitivity of PPA modified asphalt to water is enhanced^[23].

In practical applications, anti-stripping agent can be used to improve the water stability of PPA modified asphalt^[1]. In the test section paved in Altay, Xinjiang, 0.3% PA-1 asphalt anti-stripping agent is added to the asphalt. The residual stability of the section can reach 84.5%, and the freeze-thaw splitting tensile strength ratio can reach 85.0%. The effect is good^[63].

2.5 Fatigue characteristics

Linear amplitude scanning (LAS) test is an effective means to quickly evaluate the fatigue performance of asphalt binders. Jafami et al. ' analyzed the fatigue properties of asphalt binders with different PPA based on LAS test. PPA modified asphalt has better fatigue resistance than base asphalt. With the increase of PPA content, the fatigue performance is significantly improved. At a higher PPA content, the asphalt binder will have a higher fatigue life. Liu et al.^[64] obtained the same test results and believed that PPA would make the asphalt structure more stable. Babago H^[24] found that the combination of PPA and SBR can improve the elasticity of matrix asphalt and increase the fatigue life of binder. At the same time, the four-point trabecular bending fatigue test (FPBF) also proved that PPA combined with SBR improved the fatigue performance of asphalt mixture.^[65] studied the fatigue characteristics of PPA/SBS, PPA/ rubber powder and SBS modified asphalt mixture, and considered that

the fatigue characteristics are related to the initial stiffness modulus. SBS modified asphalt mixture has the largest stiffness modulus and the largest relative hardness, so its fatigue life is the shortest, while PPA/SBS has the lowest stiffness modulus, the longest fatigue life and the best fatigue resistance. Hou^[25] used pavement analyzer (APA) to carry out fatigue test, and found that with the increase of PPA content, the fatigue life of the mixture increased significantly. Most studies have shown that PPA can effectively improve the fatigue properties of asphalt mixtures^[66-68], and Li Chao et al.^[68] pointed out that the PPA/SBS modified asphalt mixture prepared by replacing part of SBS with PPA has excellent fatigue resistance, which can reduce the amount of SBS and reduce the engineering cost.

3 Engineering Applications

In the 1970s, the United States had studied the application of PPA in asphalt modification and gradually applied it to practical engineering. According to statistics, the use of PPA modified asphalt accounted for only 3.5% of the total amount of road asphalt in the United States in 2005, and increased to 14% by 2010. In 2009, the United States held a " PPA modified asphalt seminar, " which discussed the high and low temperature performance, water stability and fatigue performance of PPA modified asphalt. It was pointed out that PPA can be used alone or in combination with polymers for asphalt modification ^[1,69,70]. Arkansas, Alabama, Minnesota and other places in the United States have carried out long-term observation of PPA modified asphalt pavement, which proves that PPA modified asphalt pavement has no quality problem^[71].

China's research on PPA modified asphalt technology started late and SBS, room temperature modified asphalt and other technologies have a large area of application in China is different, PPA modified asphalt only in Hebei Xibaipo^[72], Liaoning Changtu^[67], Inner Mongolia Alashan^[45], Xinjiang Altay^[63] and other places have test section paving records. Considering the shortcomings of the performance of PPA single modified asphalt, these demonstration projects mostly use PPA compound polymer modifier to achieve its high performance. For example, Wang Yongning^[45] first added extract oil and dibutyl phthalate to the matrix asphalt. After heating to 160°C, the PPA and SBS modifier were added to shear at 175~180°C for 30 min. After the shear was completed, it was developed at 175°C for 3 h to complete the preparation of PPA compound SBS modified asphalt.

China has a vast territory, and the climate varies greatly in different regions. Therefore, the application of PPA modified asphalt must first consider the use of partitions. For example, through aging test research, Chen Zhao et al.^[55] suggested that PPA composite SBS modification should be used in high temperature areas, and compound modification should be avoided in cold areas. Xu Nan^[54] recommended that PPA modified asphalt be used in areas with high temperature difference and high ultraviolet radiation, but it is also necessary to limit the use of PPA modified asphalt in cold and rainy areas.

On the whole, although PPA modified asphalt pavement has been paved in China, there is no relevant literature showing that its field observation results should strengthen the observation of its later road performance, especially low temperature cracks and water damage. The feasibility of large-scale popularization and application of PPA modified asphalt technology in China is verified by long-term observation data.

4 Conclusion

At present, PPA modified asphalt technology is recognized by the US transportation department, and a large number of test sections have been paved in the United States. Although China has also carried

out a wealth of related research, it has not been widely applied due to some technical defects. This paper systematically reviews the research progress of PPA modified asphalt and summarizes the problems existing in the current research, hoping to actively promote the further development of PPA modified asphalt technology in China and realize the large-scale promotion and application as soon as possible.

First of all, the current research on the modification mechanism of PPA is not sufficient. The modification effect of PPA has a certain relationship with the source of asphalt. It is not clear what causes the difference in the modification effect of PPA on different asphalts. Scholars in many fields such as roads, chemicals, and materials should work together to further explore the modification mechanism of PPA in asphalt from the molecular level on the basis of the four components of asphalt. In addition, the asphalt mixture is mixed with asphalt, aggregate, mineral powder and so on. The type of aggregate and mineral powder will also affect the final performance of PPA modified asphalt mixture. In the final application, the appropriate aggregate and mineral powder type should be selected according to the mechanism of PPA modified asphalt.

Secondly, there is no clear application specification for PPA modified asphalt technology at present. It still refers to 'Highway Engineering Asphalt and Asphalt Mixture Test Procedures' (JTG E20-2011), 'Highway Asphalt Pavement Construction Technical Specifications' (JTG F40-2004). It is necessary to form a characteristic application guide for PPA modified asphalt technology, and standardize the storage problems, environmental protection problems and production safety problems that may exist in the practical application process. At the same time, there are many polymer categories that can be compounded with PPA. It is necessary to sort out the polymer categories with more stable performance and study their compatibility as the recommended items in the PPA modified asphalt guide. In addition, the design verification process of PPA modified asphalt mixture can be strengthened, and the water stability and low temperature performance indexes can be increased to avoid the problem that the research results of low temperature performance and water stability of PPA modified asphalt are not uniform. Compiling the application guide of PPA modified asphalt will contribute to the large-scale application of PPA modified asphalt.

The high temperature performance and fatigue resistance of PPA modified asphalt are more prominent. It can improve the high temperature rutting resistance of matrix asphalt at a lower cost. It has application advantages in heavy-duty traffic sections and high temperature environments, and has research value and application promotion potential.

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