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Improvement Marshall Properties of Hot Mix Asphalt Concrete Using Polyphosphoric Acid

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ABSTRACT

Modified asphalt is considered one of the alternatives to address the problems of deficiencies in traditional asphalt concrete, as modified asphalt addresses many of the issues that appear on the pavement layers in asphalt concrete, resulting from heavy traffic and vehicles loaded with loads that exceed the design loads and the large fluctuations in the daily and seasonal temperatures of asphalt concrete. The current study examined the role of polyphosphoric acid (PPA) as a modified material for virgin asphalt when it was added in different proportions (1%, 2%, 3%, 4%) of the asphalt weight. The experimental program includes the volumetric characteristics associated with the Marshall test, the physical properties, and the FTIR spectroscopy examination of virgin asphalt and polyphosphoric acid (PPA) modified asphalt. This study showed that mixtures with modified asphalt using polyphosphoric acid (PPA) by 3% achieved the typical Marshall properties at the optimal asphalt content of 4.8%, recording a 10% decrease in the optimum asphalt content for the mixtures made with virgin (unmodified) asphalt, whose proportion was 4.9% is the optimum asphalt content. PPA is available in the local markets and is considered cheaper than polymers. It is also regarded as economical as it reduces the optimum content of asphalt.

Keywords: Polyphosphoric acid (PPA), FTIR, Fraction group

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تحسين خصائص مارشال للخلطة الاسفلتية الساخنة باستخدام حامض البولي فوسفورك اسيد

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الخلاصة

يعتبر الاسفلت المعدل احد البدائل لمعالجة اوجه القصور في الخرسانة الاسفلتية التقليدية, حيث يعالج الاسفلت المعدل العديد من المشكلات التي تظهر على طبقات الاكساء في الخرسانة الاسفلتية والناتجة عن الازدحامات المرورية والمركبات المحملة باحمال تفوق الاحمال التصميمية والتقلبات الكبيرة في درجات الحرارة اليومية والموسمية للخرسانة الاسفلتية. كشفت الدراسة الحالية دور حامض البولي فوسفورك كمادة معدلة للاسفلت البكر عند اضافته بنسب مختلفة (1%,2%,3%,4%) من وزن الاسفلت. يتضمن البرنامج التجريبي الخصائص الحجمية المرتبطة باختبار مارشال ,الخواص الفيزياوية , الفحص الطيفي للاسفلت البكر والاسفلت المعدل بحامض البولي فوسفورك اظهرت الدراسة ان الخلائط التي اعدت باستخدام الاسفلت المعدل باستخدام حامض البولي فوسفورك بنسبة 3% حققت خصائص مارشال النموذجية عند محتوى الاسفلت الامثل 4.8% مسجلة انخفاض بنسبة 10% في محتوى الاسفلت الامثل مقارنة بالخلائط التي اعدت باستخدام الاسفلت البكر (الغير معدل)والذي محتوى الاسفلت الامثل له 4.9%. PPAمتوفرفي الاسواق المحلية ويعتبر منتج رخيص مقارنة بالبوليمر كما يعتبر اقتصادي لانه يقلل المحتوى الامثل للاسفلت.

الكلمات المفتاحية: حامض البولي فوسفورك(PPA),اختبار فوريية للطيف بالاشعة تحت الحمراء

1. INTRODUCTION

The durability of asphalt-concrete pavements is measured by how long they can be used while still performing under traffic loads, weather, and climate. Asphalt significantly affects the durability of asphalt concrete, and it is the main ingredient in the bonding process in asphalt concrete. As a result of the fluctuating specifications for asphalt produced in crude oil refineries led to issues affecting the durability of asphalt concrete used in Iraqi road pavement. Modifying asphalt is one of the most effective methods to increase the durability of asphalt pavements **(Hamdou et al., 2014; Al-Hadidy et al., 2020; Ismael, 2022)**. Among the problems that affect the durability of the roads that are covered with asphalt concrete is moisture damage, so the researchers directed to address this problem by using improved additives for the bonding material; for example, **(Al-Saadi and Ismael, 2023)** used ceramic fibers and the researcher and **(Taher and Ismael, 2023)** used nano-silica. One of the methods used in this field is to improve the properties of asphalt by adding Polyphosphoric acid (PPA), which is available in the local markets. It is economically feasible compared to other improvers or additives **(Baumgardner et al., 2023)**.

Polyphosphoric acid (PPA) is a liquid mineral polymer used as one of several additives to modify and enhance the quality of asphalt. This substance is an inorganic polymer. It is produced through the condensation of Mono-phosphoric acid or the hydration of P_2O_5 **(Baumgardner et al., 2023)**. The results obtained from the use of PPA as an improver for asphalt properties found that there is a strong interaction between asphalt and PPA that leads to a change in the chemical composition (an increase in the percentage of asphaltene and a decrease in resins materials), as well as a change in the physical properties and a change in the morphology, and this depends on the type of asphalt **(Yan et al., 2013)**.

As asphalt has a complex structure, it is generally regarded as a colloidal system of high molecular weight asphaltene micelles dispersed in a lower molecular weight maltene medium. The degree of bonding is determined by the polarity of each component of the asphalt, mainly through hydrogen bonding **(Lesueur, 2008)**. Note when adding PPA with different ratios of asphalt, increase the asphaltene content and reduce the resin concentration simultaneously **(De Filippis et al., 1995; Ramasamy, 2010)**, unlike the typical asphalt oxidation process, but to an increase of the polarity of asphaltene-PPA-resin complex **(Huang et al., 2008)**. The asphalt modified with Polyphosphoric acid significantly affects the rheology of the asphalt binder, which gives the modified asphalt the ability to resist high temperatures and stress level conditions more than the unmodified asphalt **(Jafari et al., 2016; Zhang et al., 2018; Abdulkhabeer et al., 2021; Hilal and Fattah, 2023).**

According to the results obtained from the study of **(Raof and Ismael, 2019)**, the use of Polyphosphoric acid (PPA) as an improver for asphalt reduced the optimum asphalt content AC (40-50) by 0.4%, 1.45%, and 1.87% compared to the traditional OAC asphalt, when used (PPA) in proportions of 1%,2% and 3% by weight asphalt, respectively. **(Khader et al., 2015; Raof and Ismael, 2019)** concluded that adding 3% of Polyphosphoric acid as an improvement material to the traditional asphalt was the highest Marshall stability value.

According to **(Yan et al., 2013)**, the effect of Polyphosphoric acid on the physical properties, chemical composition, and asphalt morphology depends on the different types of asphalt produced in crude oil refineries. The type of asphalt with a low colloidal index interacts with polyphosphoric acid slightly. At the same time, it was noted that the types of asphalt with a high colloidal index showed a strong interaction between polyphosphoric acid and asphalt, which led to an increase in the percentage of asphaltene and a decrease in resins, in addition to the rise in viscosity and a reduction in ductility. Changes in morphology correspond to physical properties and chemical composition. The addition of Polyphosphoric acid (PPA) to the asphalt **(Yu et al., 2009; Gao et al., 2021),** as indicated, turns the asphalt from a colloidal solution into a gel, and this helps to significantly delay the aging of the asphalt, which was observed by infrared spectra (FTIR).

This work sought to investigate experimentally the feasibility of using polyphosphoric acid as an improver by adding it to asphalt in four proportions to improve the performance of hot asphalt mixtures. Marshall's method was used to determine the optimum polyphosphoric acid content and to study the effect of polyphosphoric acid on the physical properties of asphalt. The FTIR assay was carried out to study the changes in the asphalt fraction group after adding polyphosphoric acid as an asphalt improver.

2. MATERIALS AND METHODS

2.1 Asphalt Cement

Asphalt produced locally from the Dora refinery, class 40-50, was used in road paving operations in Iraq. All test results meet the Iraqi specification **(SCRB/R9, 2003)**. **Table 1** shows its physical properties.

Table 1. Physical properties of virgin asphalt binder

Test	Unit	ASTM	Result
			Virgin asphalt
Penetration @ 25 °C	0.1 mm	D5	46
Softening Point	°C	D36	54
Ductility @ 25°C	cm	D113	151

2.2 Aggregates

The coarse aggregate and fine aggregate used in this study are local aggregates from the quarries of the Al-Nabai area in Salah Al-Din Governorate and conform to the requirements of **(SCRB/R9, 2003)** as shown in **Table 2.** Limestone dust was used as a filler. **Table 3** shows its physical properties.

2.3 Polyphosphoric Acid (PPA)

PPA is an oligomer of H_3PO_4. High-purity material is produced either from the dehydration of H_3PO_4 at high temperatures or by heating P_2O_5 dispersed in H_3PO. PPA is available in various grades. The grade of polyphosphoric acid used in this research is 115%, available in the local markets. **Table 4** shows its physical and chemical properties.

Table 2. Physical Properties of Fine and Coarse aggregate

Property	ASTM Designation Method	Coarse Aggregate	Fine Aggregate
Bulk Specific Gravity	C-127 & C-128	2.633	2.559
Water Absorption, %	C-127 & C-128	0.28	0.81
Los Angeles Abrasion, %	C-131	17	-----
Soundness Loss by Magnesium Sulfate Solution, %	C88-13	0.1	-----
Flat & Elongated (5:1), %	D-4791	4	-----
Fractured Pieces, %	D-5821	97	-----

Table 3. Physical Properties of Mineral Filler

Property	Test Result	SCRB Specification
Sieve No.30 (0.6mm)	100	100
Sieve No.50(0.3mm)	95	95-100
Sieve No.200(0.075mm)	75	70-100
Specific gravity	2.72	-

Table 4. Physical and chemical properties of PPA

Appearance	Color	Odor	Solubility	Assay P_2O_5 basis	Assay H_3PO_4 basis	Density (g/ml) @20^0c	Boiling
Viscous liquid	Colorless, clear	Odorless	Soluble in ethanol and water	85%	115%	2.05	~550 ^{0}c

2.4 Mixing Polyphosphoric Acid (PPA) with Asphalt

The asphalt was modified with polyphosphoric acid at four ratios of 1%, 2%, 3%, and 4% by asphalt weight. The asphalt was heated at 150 °C to ensure a flowing state. Then, Polyphosphoric acid was slowly added and mixed for 40 minutes at a temperature of 160°C using a high-shear mixer at a speed of 1000 rpm **(Gao et al., 2021).**

2.5 Physical Test

According to ASTM D36, ASTM D5, ASTM D113, and ASTM D92, the physical parameters of asphalt, including softening point, penetration (at 25 °C), ductility, and flash point, respectively, were evaluated.

2.6 FTIR Test

Fourier transform infrared spectroscopy (FTIR) samples were measured by an attenuated total reflectance (ATR) method scanning at 400–4000 cm^{-1}. FTIR examination is necessary to know the effect of adding PPA to the asphalt in terms of the frictional group of the asphalt components and the extent of interaction between the asphalt and PPA due to it being a chemical enhancer

2.7 Marshall Test

The optimum asphalt content was obtained using the Marshall method according to the standard ASTM D6927, where samples were prepared from cylindrical Marshall blocks with a diameter of 101.6 mm (4 inches) and a height of 63.5 mm (2.5 inches) with a weight of not less than 1200 grams, where each face was compacted 75 times by the Marshall hammer 4.5 kilograms (10 pounds), Asphalt concrete mixtures were prepared with different asphalt contents (4.5%, 5%, 5.5%, 6%), where three Marshall template were prepared for each ratio, and the optimal asphalt content was found, which gives an air void ratio of 4%, according to the design of the asphalt mixtures using the Marshall, and a stability test was conducted. **(Ismael and Al-Harjan, 2018). Fig. 4** shows the process of work.

(a)Preparing mixture (b) Group of Marshall specimens (c) Marshall test

Figure 4 Marshall procedure

3. RESULTS AND DISCUSSION

3.1 The Penetration Test

The penetration test for modified and unmodified asphalt is used to evaluate the viscosity of the asphalt. The higher the percentage of Polyphosphoric acid in the asphalt, the less penetrable it becomes. This indicates that the modified asphalt has become more viscous, as the addition of the acid led to an increase in the asphaltene content, which is responsible for the change. **Fig. 5** shows the effect of acid on penetration testing; the penetration decreased from 46mm at 0% PPA to 37mm at 3% PPA; this is consistent with other studies, for example **(Gao et al., 2021)**.

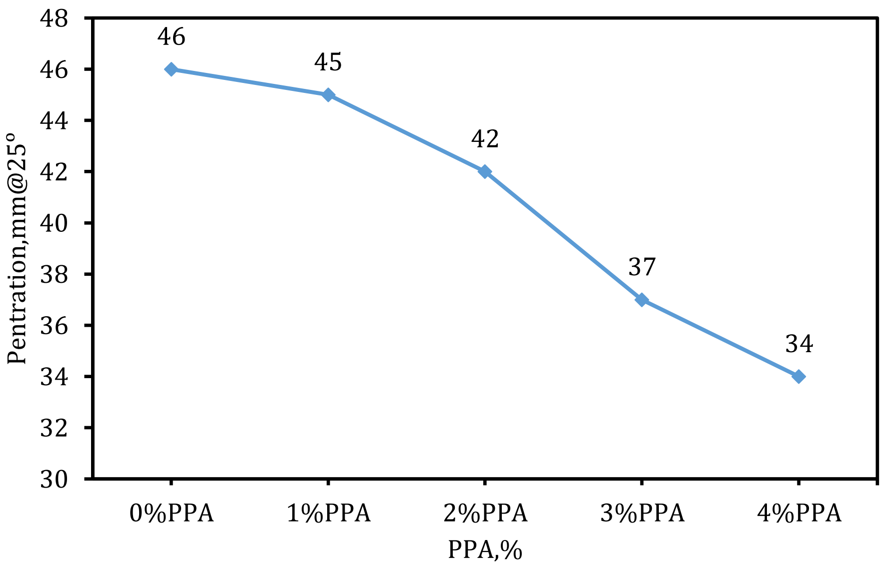

Figure 5. Effect of PPA content on penetration at 25°C

3.2 The Softening Point

The softening point of asphalt indicates its tendency to flow at high temperatures. **Fig. 6** shows the softening points of asphalt with different Polyphosphoric acid contents. The higher the PPA percentage, the asphalt softening point increased from 54 to 59 when adding 3% of the PPA. This indicates that the PPA has a hardening effect on the asphalt, which is associated with a significant change in the structure of the asphalt from liquid to gel, as shown in **Fig. 7.** The decrease in the penetration test is another factor that supports this conclusion. Adding the PPA increases the stability of the asphalt at high temperatures, and this dramatically suits the paving of roads in our country, Iraq, due to its hot weather **(Hilal and Fattah, 2023; Kodrat, 2007),** which is in agreement with the present study.

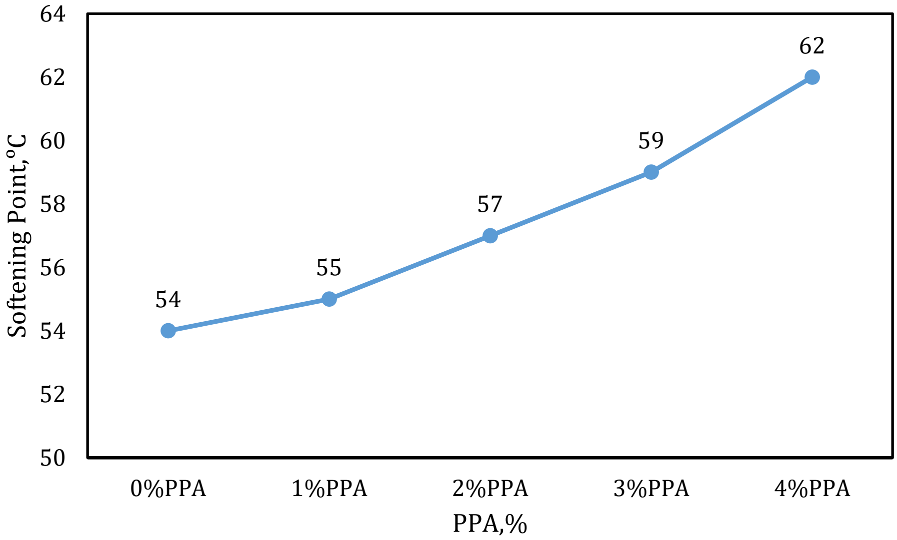

Figure 6. Effect of PPA content on softening point

Figure 7. Virgin asphalt and modified asphalt

3.3 The Ductility

The ductility test demonstrates the asphalt binder's capacity to stretch without breaking. **Fig.8**. displays the ductility of asphalt binders with various PPA contents. The ductility substantially fills from 151 to 123 cm when 3% wt. PPA was added, demonstrating that PPA improves asphalt performance in high-temperature conditions, but it is anticipated that adding more PPA will result in a lower low-temperature deformation capacity,

(Jaroszek, 2012; Gao et al., 2021; Hilal and Fattah, 2023) agree with the present study.

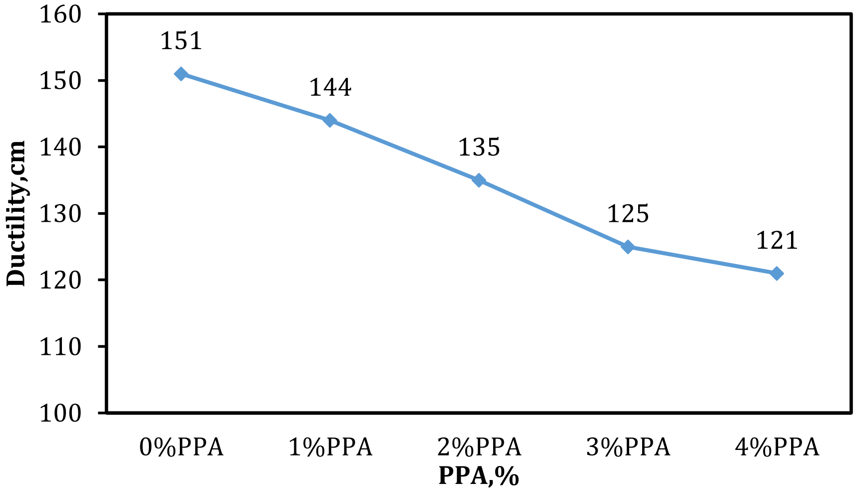

Figure 8. Effect of PPA content on ductility

3.4 FTIR Test

The basic properties of asphalt depend on its microstructure, so the difference in the overall properties between virgin and modified asphalts is due to the addition of polyphosphoric acid, as the FTIR examination showed the difference in the microstructure of virgin and modified asphalt, as in **Figs. 9 and 10**.

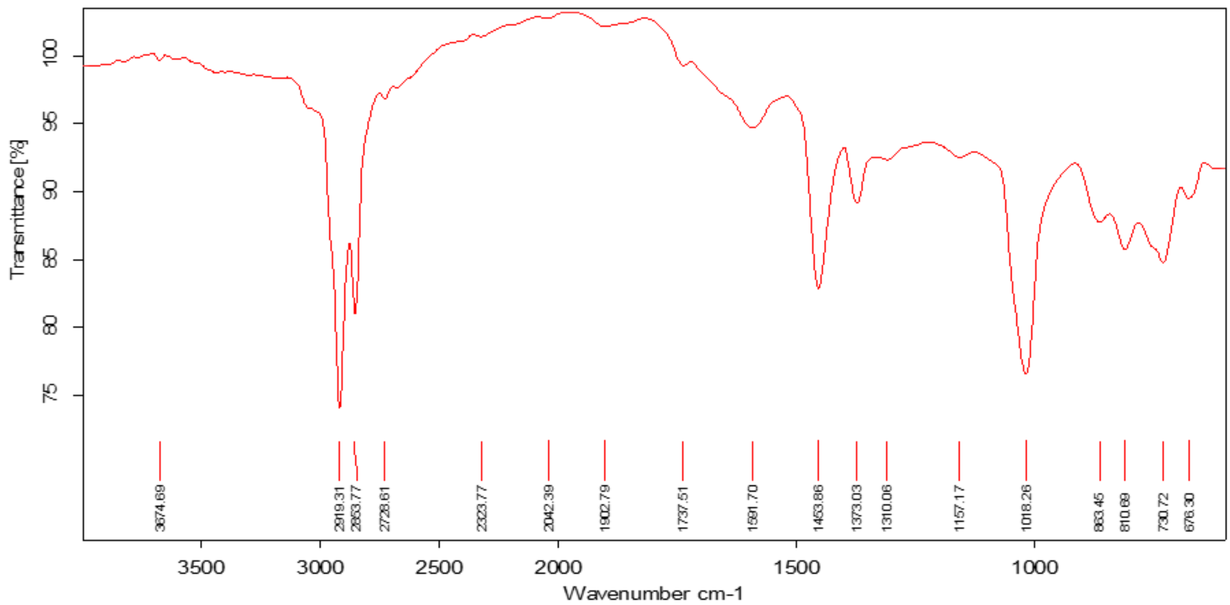

Figure 9. FTIR for virgin asphalt (0%PPA)

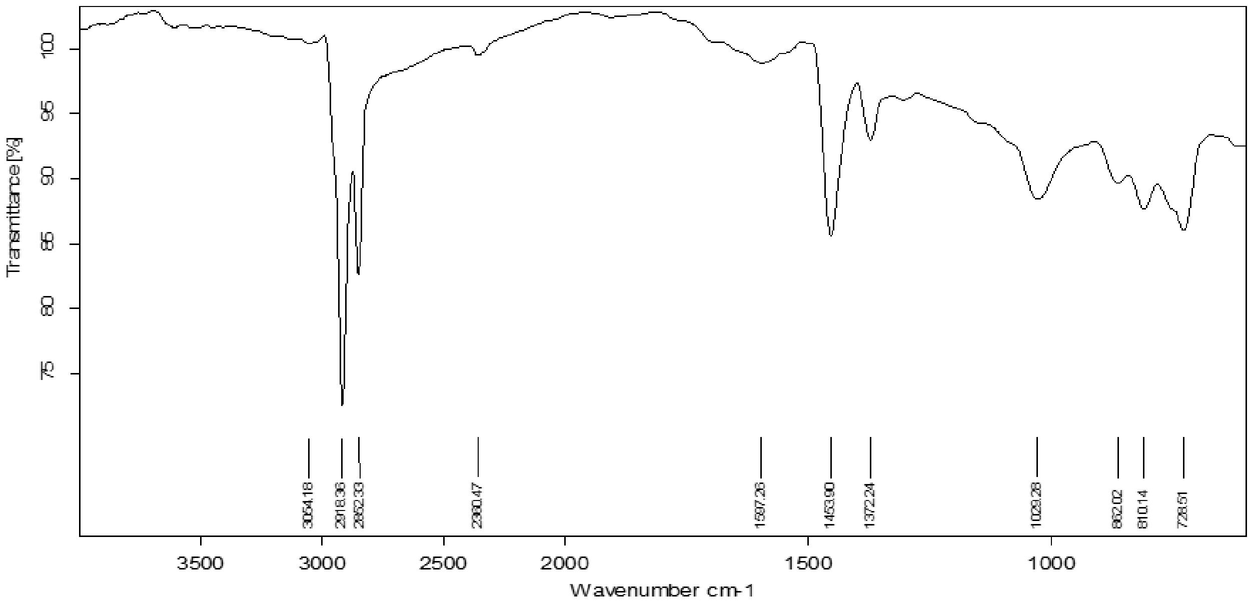

Figure 10 FTIR for modified asphalt (3%PPA)

The absorption peaks at 2919 cm^{-1} and 2853 cm^{-1} in **Fig. 7** FTIR spectrum of virgin asphalt are identified as symmetric and asymmetric C-H stretching vibrations, respectively **(Zhang et al., 2018).** The peak at 1591 cm^{-1} is attributed to C-C aromatic expansion vibrations, while the peak at 1453 cm^{-1} is the signal of C-H bonds and is attributed to asymmetric deformation in CH_3, CH_2, and the peak at 1373 cm^{-1} which is the peak of C-H bonds is classified as symmetric deformation vibrations in CH_3 and minor peaks at 810 cm^{-1} and 730 cm^{-1} "where from the C-H" as a result of the vibrations of the benzene ring. The FTIR spectrum of the treated asphalt with 3% PPA is shown in **Fig. 8**, and there are obvious changes between it and virgin asphalt. First, the P-OH peaks at 1737 cm^{-1} and 2728 cm^{-1} did not appear in the asphalt, proving that the -OH group has interacted with some groups there. With the addition of PPA, the intensity of the P-O-C signals increased, and a new peak in the range of 497 cm^{-1} to 511 cm^{-1} was found in the asphalt that had been modified with PPA. This peak is attributed to the bending vibrations of P-O-P **(Olabemiwo et al., 2016).**

Additionally, the multiple peaks at 800 cm^{-1} are slightly shifted, indicating that P-OH's more substantial absorption peak undergoes asymmetric expansion. In phosphates, P-O-C, 3P = O (RO), It is evident that PPA and asphalt interact chemically **(Zhang et al., 2018)**. The above results proved that the acid reacts with some asphalt components, consistent with the changes in the essential properties. FTIR analysis confirms that it is possible to determine whether or not a binder has been modified **(Lim et al., 2022; Masson and Collins, 2014)**.

3.5 Marshall test

To obtain the optimum percentage of improvement of the virgin asphalt by adding PPA, several rates (1%, 2%, 3%, 4%) were tested, where the highest value of the stability strength 12 kN was obtained by 3% at 4.8% asphalt content according to the design of the Marshall method, as shown in **Fig. 11**, It was also observed that the higher the percentage of PPA addition, the lower the optimum content of asphalt, which fulfills Marshall's best requirements because The process of adding improvers and polymers, including PPA, adds a percentage of the asphalt weight, meaning that it will reduce the percentage of asphalt added. Meaning that it will reduce the percentage of asphalt added as in **Fig.12**, where for mixtures modified with PPA, the optimum content of asphalt was 4.8% at 3% PPA, and for unmodified mixtures, the optimum content of asphalt was 4.9%, where the optimum asphalt content decreased by 10% for the same coarse and fine aggregate and filler used.

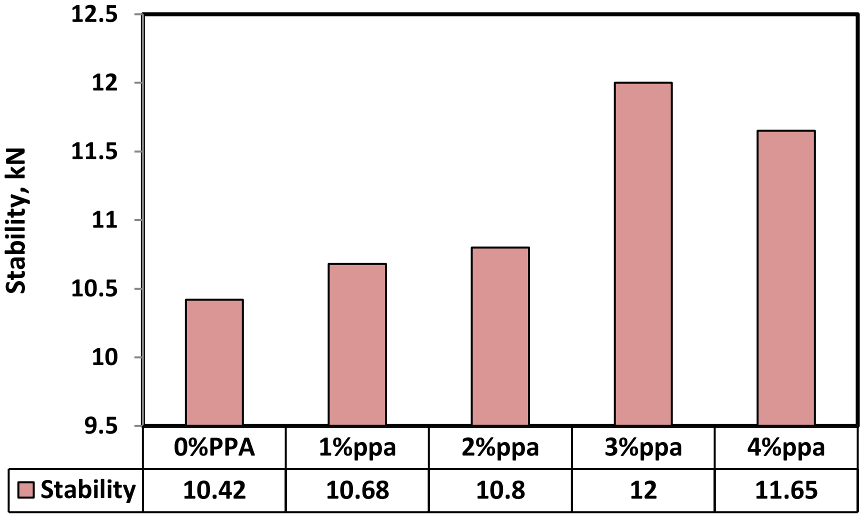

Figure11. Effect of PPA on Stability

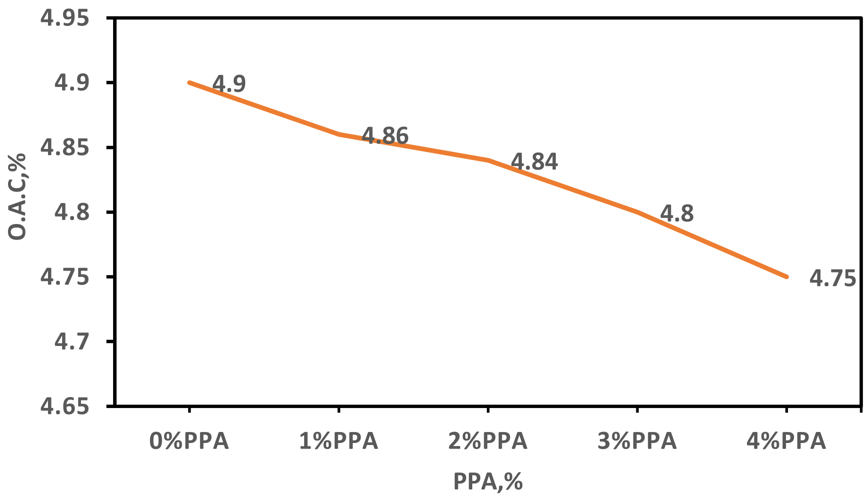

Figure 12. OAC vs. PPA contents

In **Figs. 13 to 17**, the results of the volumetric analysis and the requirements of Marshall's method are presented for mixtures that include virgin asphalt and modified asphalt with 3% acid. The results revealed that the modified asphalt produced mixtures that showed high levels of volumetric properties, as the stability value increased from 10.42 kN in mixtures containing virgin asphalt to 12 kN in modified asphalt mixtures at the optimum content of asphalt. **Fig. 13** shows this; the flow decreased from 3mm in virgin asphalt mixtures to 2.3mm in modified asphalt mixtures, as shown in **Fig. 14**. Perhaps this is because PPA reduced the optimum content of asphalt. The density increased with the addition of PPA, as demonstrated in **Fig.15**, and the air voids decreased. This is considered acceptable because the addition of PPA increases the solid mass as well as the nature of the asphalt gel by changing the dissolution constant of asphaltene in the malate matrix, and this behavior causes most voids to be filled with asphalt, and this is consistent with what **(Poorna, 2014)** concluded. **Fig. 16** shows the effect of PPA on air voids, and the voids increased in the mineral aggregate, as shown in **Fig.17**. These results agree with many previous studies **(Khader et al., 2015; Raof and Ismael, 2019)**.

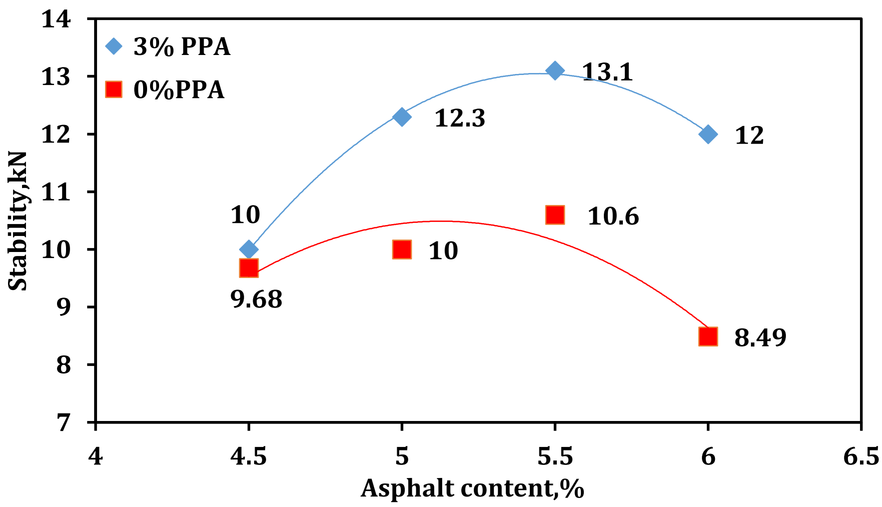

Figure13. Effect of Asphalt Content on Stability

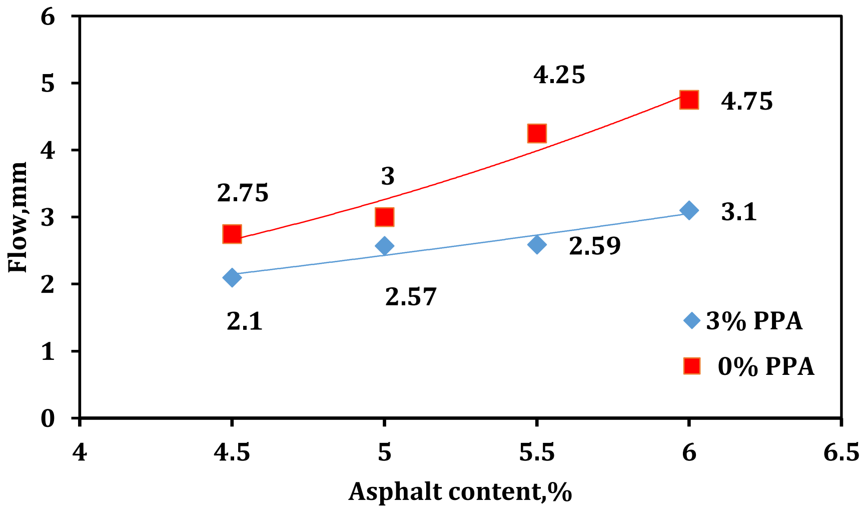

Figure14. Effect of asphalt content on Flow

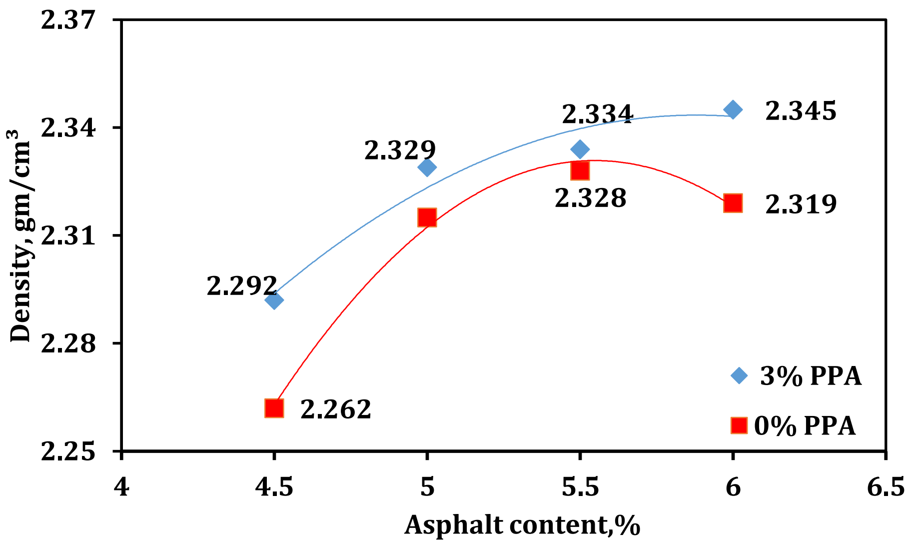

Figure15. Effect of asphalt content on Density

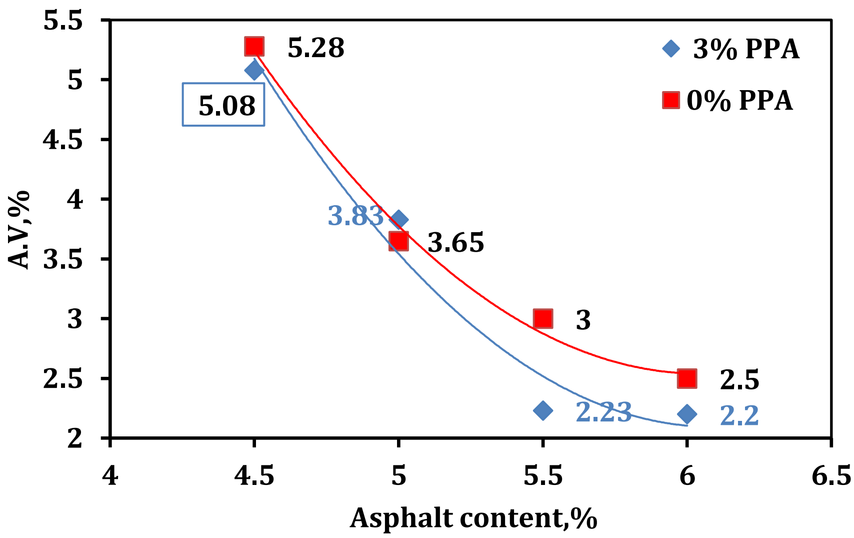

Figure16. Effect of asphalt content on air voids

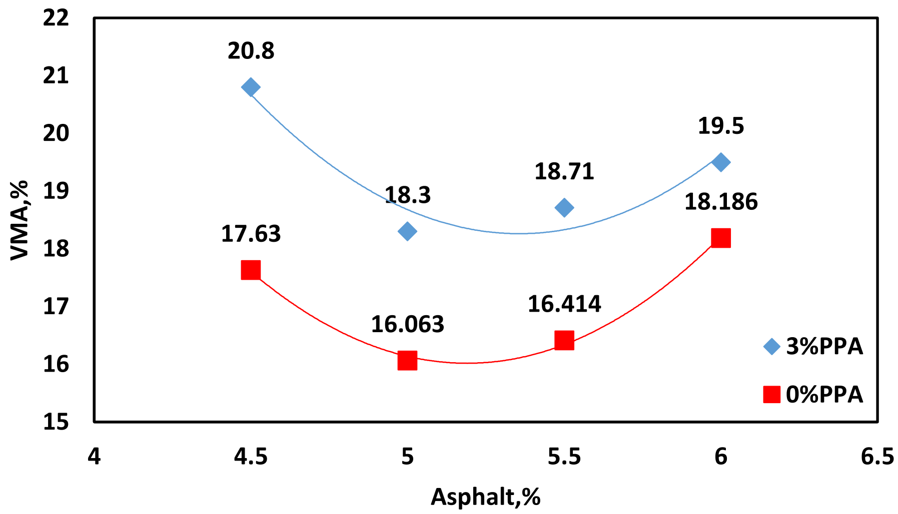

Figure 17. Effect of asphalt content on VMA

5. CONCLUSIONS

In this study, various amounts of Polyphosphoric acid were added to asphalt mixes to modify the asphalt to observe the role of Polyphosphoric acid in improving the physical properties and Marshall properties through changes in the fractional group due to the interaction of polyphosphoric acid with the asphalt components; the following conclusions were obtained:

1. The addition of Polyphosphoric acid makes the asphalt more viscous. The higher percentage of the acid leads to less penetration, and the softening point increases the addition of the PPA, increasing the stability of the asphalt at high temperatures. And this dramatically suits the paving of roads in Iraq due to its hot weather.
2. The application of acid lowers the optimum asphalt content, which is economically advantageous.
3. Compared to mixtures including conventional asphalt, which obtained stability of 10.4 kN with 4.9% optimum content of asphalt and density2.305gm/cm^3, adding 3% PPA produced the maximum value of stability of 12kN and density2.312gm/cm^3 with 4.8% optimum content of asphalt. Stability increased by 15.38%. The density also increased by 0.3%.
4. According to the results of the FTIR, it was found that there is a strong interaction between the acid and the asphalt components. This is compatible with the lines' enhanced physical characteristics and Marshall qualities due to the acid modification of the asphalt.
5. PPA is available in the local markets and is considered cheaper than polymers. It is also regarded as economical as it reduces the optimum content of asphalt. The PPA mixing temperature is 160˚c, within the temperature of heating the asphalt required according to Marshall's specification for class 40-50 PPA is considered better from an operational point of view than the rest of the polymers that are used as improvers for asphalt concrete, as it requires high temperatures during the mixing process.
6. Modern asphalt concrete production plants are suited for adding improvers without incurring additional costs because modified asphalt is commonly used in laboratories across the globe.

NOMENCLATURE

Symbol	Description	Symbol	Description
A. V	Air voids	O.A.C	Optimum asphalt content
AASHTO	American Association of	P_2O_5	phosphorus pentoxide
C-C	Aromatic (Carbon-Carbon)	P-O-C	Conjugated (phosphor-oxygen carbon)
C-H	Aliphatic (Carbon-Hydrogen)	P-O-P	Conjugated (phosphor-oxygen-phosphor)
CH_2	Aliphatic index	PPA	Polyphosphoric Acid.
CH_3	Aliphatic branched	SCRB	State Corporation for Roads and Bridges
H_3PO_4	phosphoric acid	VMA	Void in mineral aggregate

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