



Evaluation of Modified Asphalt Binder and Mixtures with Polyphosphoric Acid

Miami M. Hilal¹, Mohammed Y. Fattah^{2*}

Authors affiliations:

1) Civil Engineering
Department, University of
Technology, Baghdad-Iraq.
40092@uotechnology.edu.iq

2*) Civil Engineering
Department, University of
Technology, Baghdad-Iraq.
40011@uotechnology.edu.iq

Paper History:

Received: 21st Dec. 2022

Revised: 29th Dec. 2022

Accepted: 7th Jan. 2023

Abstract

Rutting is the most common distress that most Iraqi asphalt pavements suffer from it. Asphalt binders are modified by using additives and polymers to enhance their physical qualities and fulfill the performance demands. Polyphosphoric acid (PPA) has been used in many countries to enhance the physical and mechanical characteristics of asphalt binders and mixtures that can improve the performance of asphalt pavements. In this paper, evaluation of the Iraqi asphalt binder and mixtures performance by using three percentages of Polyphosphoric acid (PPA) (0.4, 0.8, and 1.2) percent by asphalt binder weight and added to (60-70) penetration grade asphalt binder to show the applicability and suitability of using PPA in asphalt pavement in Iraq. Original asphalt binder and modified are subjected to traditional tests which are penetration, ductility, softening point, and viscosity. Results show better performance and enhancement of the physical properties of the modified binder. Other tests are Marshall Stability and wheel track tests. The results of the addition of PPA to the asphalt mixture show increases in the Marshall Stability and enhance the performance of the asphalt pavement mixtures. The wheel track test is applied to the original and modified mixture at two test temperatures 40°C and 50°C and the results show a decrease in the rut depth when the percentages of PPA increase. It is concluded that %PPA addition will enhance the performance of the Iraqi asphalt pavement and the mixture will be more rutting resistant, especially in high-temperature weather.

Keywords: Modified Asphalt Binder; Polyphosphoric Acid; Marshall Stability; Rut Depth; Performance.

تقييم الرابطة الاسفلتي المعدل والخلاطات الاسفلتية المعدلة مع حمض البولي فوسفوريك

ميامي محمد هلال ، محمد يوسف فتاح

الخلاصة:

يعتبر التخدّد من العيوب الأكثر شيوعاً التي تعاني منها معظم الأرصفة الإسفلتية العراقية. يتم تعديل الروابط الإسفلتية باستخدام المواد المضافة والبوليمرات لتحسين صفاتها الفيزيائية وتلبية متطلبات الأداء. تم استخدام حمض البولي فوسفوريك (PPA) في العديد من البلدان لتعزيز الخصائص الفيزيائية والميكانيكية لروابط ومخاليط الأسفلت التي يمكن أن تحسن أداء رصيف الأسفلت. في هذا البحث تم تقييم أداء رابطة الأسفلت العراقي ومخاليط باستخدام ثلاث نسب من حامض البولي فوسفوريك (0.4، 0.8، 1.2) % من وزن رابطة الإسفلت وإضافته إلى الأسفلت الذي درجة اختراقه (60-70) لإظهار مدى قابلية تطبيق وملاءمة استخدام PPA في رصف الأسفلت في العراق. مادة رابطة الإسفلت الأصلية والمعدلة تخضع لاختبارات تقليدية وهي الاختراق، البوننة، نقطة التلين، واللزوجة. تظهر النتائج أداء أفضل وتحسين الخواص الفيزيائية للرابطة المعدل. الاختبارات الأخرى هي اختبارات استقرارية مارشال ومسار العجلة. تظهر نتائج إضافة PPA إلى خليط الأسفلت زيادة في استقرار مارشال وتحسين أداء مخاليط رصف الأسفلت. يتم تطبيق اختبار مسار العجلة على الخليط الأصلي والمعدل عند درجتي حرارة اختبار 40 درجة مئوية و 50 درجة مئوية وتظهر النتائج انخفاضاً في عمق الشق عند زيادة نسب PPA. نستنتج أن إضافة PPA/ ستعزز أداء رصيف الأسفلت العراقي وسيكون الخليط أكثر مقاومة للتآكل، خاصة في درجات الحرارة العالية.



1. Introduction

Different vehicle types use roads and highways, but large trucks are seen to be the most problematic in terms of loading, which leads to pavement distress such as rutting, and raises the cost of maintenance and restoration [1]. Also, the responses of cyclic loading reveal that as deformation occurs, the damage rate increases. [2]. So, the performance of asphalt binders and mixtures has been improved by many studies over the past few decades, particularly in hot climates like the summer in Iraq. [3]. Various polymers have been used to improve the asphalt mixture's performance [4] such as elastomers, plastomers, thermosets, sulfur, and mineral acids are frequently used to modify bitumen to alter its properties and enhance its performance. Since polyphosphoric acid (PPA) enables bitumen to be extensively hardened in a manageable manner, it has gained a lot of attention recently [5, 6]. Polyphosphoric acid (PPA) is commonly applied to asphalt binders to enhance and increase their elasticity and stiffness [7].

PPA offers advantages including a simple processing technique with low cost, and it has positive benefits in altering asphalt [8], including the improvement of matrix asphalt's temperature sensitivity, high-temperature stability, and antiaging capabilities. Due to the advantages listed above, PPA has received a lot of attention in recent years.

The first mention of PPA's application in asphalt alteration dates back to 1973. Because of how some of the components of asphalt react with PPA, it is categorized as a chemical modifier [9]. In earlier research, phosphorus pentoxide (P_2O_5) was used as a catalyst to oxidize asphalt in the air [10]. Extensive experiments on the usage of PPA with polymers to modify asphalts since the late 1990s are documented in several patents [11, 12]. According to Baumgardner [13], the addition of PPA to polymer plus PPA-modified binders improved their resistance to rutting.

Rutting, a permanent deformation in the wheel path brought on by traffic loads, is more prevalent during hotter months [14]. When choosing pavement materials, high-performance bitumen with high-temperature stability should be taken into consideration to reduce pavement rutting and extend the service life of bitumen pavement [15]. According to Liu et al [16], more rutting resistance than the original binder can be gained by adding the PPA into binders. The benefits of PPA include its low cost and straightforward processing method, as well as the fact that it has a positive modification effect on asphalt, improving the sensitivity to temperature changes, high-temperature stability, and anti-aging properties of matrix asphalt.

This research aims to evaluate and produce a modified Iraqi asphalt binder by adding selected percentages of PPA by the asphalt binder weight and showing the modification effect on the asphalt binder's physical properties by traditional tests. Also, produce modified mixtures to show the stiffness enhancement effect on the modified mixtures by the Marshall stability test and show the effect on rutting resistance by wheel track test to show the PPA effect on asphalt pavements performance.

2. Materials and Methods

2.1 Materials

The asphalt binder used in this study is the (60 – 70) penetration grade from the Al-Dura refinery in Baghdad City in Iraq. Physical properties are presented in Table 1 for the asphalt binder used.

Table (1): Asphalt Binder's Physical Properties

Laboratory Test	Result	Unit	Specification limits	ASTM specification
Penetration	67.5	mm/10	60-70	D5
Ductility @ 25 °C	170	cm	100 min.	D113
Softening point	50	°C	-----	D36
Flash point	290	°C	232 min.	D92
Specific gravity	1.03	----	-----	D70

In this study, three percentages of PPA were added to modify the asphalt binder (0.4, 0.8, and 1.2%) by the asphalt binder weight. The PPA's physical characteristics are presented in Table 2.

Table (2): PPA Physical Characteristics.

Property	Polyphosphoric acid	Property	Polyphosphoric acid
Appearance	Clear	Vapor pressure (hPa), at 20 °C	2.2
Physical state	Liquid	Boiling point, °C	158
Color	Colorless	Specific gravity (kg/m ³)	1685
Solubility	Soluble in ethanol	Relative density	1.7
Odor	Odorless		

For the wearing layer, the aggregate gradation employed in this investigation is 12.5 mm nominal maximum aggregate size according to the Iraqi specifications [17]. Table 3 lists the physical characteristics of the coarse and fine aggregate whereas the selected gradation is presented in Table 4 and Fig.1.

Limestone dust is the filler used in preparing the modified asphalt mixture. Table 5 presents the mineral filler's physical properties.

2.2 Sample preparation

A temperature of roughly 150 °C is applied to the asphalt binder to ensure the melting and flowing state of the binder. Then the PPA is added gradually to the binder and mixed for a period time of about 60 minutes using a shear mixer operating at a speed of 3000 rad/min at a temperature of 160 °C to ensure a full spread of the PPA in the asphalt binder. This process is repeated for all three percentages of PPA (0.4, 0.8, and 1.2%) by asphalt binder weight.

Marshall specimens were prepared to measure the stability of the wearing layer for the modified asphalt mixture. The specified gradation of aggregate was placed in the oven, which was preheated to the mixing



temperature of around 150 °C; the modified asphalt binder was also heated to combine with the aggregate. A Marshall compactor device is used to compact the specimens.

A roller compacter device is used for preparing the slab specimens to be tested with the wheel track test device according to AASHTO T 324.

Table (3): Physical Properties of Coarse and Fine Aggregate.

Property	ASTM specification	Aggregate Result	
		Coarse	Fine
Specific gravity (gm/cm ³)	Bulk	2.62	2.65
	Apparent	2.69	2.72
% Water absorption	C-127	0.45	0.73

Table (4): Aggregate Gradation.

Sieve size		Wearing layer gradation, %.	SCRB specification limit, %.
in.	mm		
¾	19.0	100	100
½	12.5	94	100-90
3/8	9.5	84	76-90
No.4	4.75	59	44-74
No.8	2.36	37	28-58
No.50	0.3µm	12	5-21
No.200	0.075 µm	7	4-10

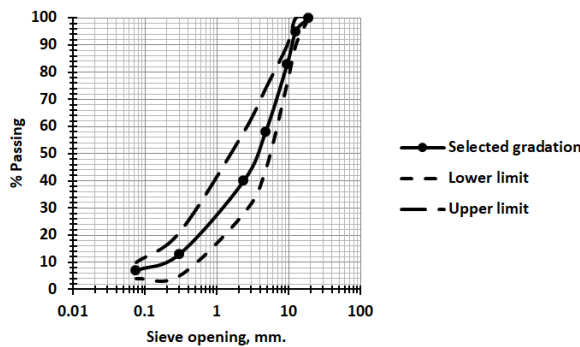


Figure (1): Selected aggregate gradation with limitations.

Table (5): Mineral Filler's Physical Properties.

Property	Result
% passing sieve No. 200	97
Bulk specific gravity, gm/cm ³ .	2.78

2.3 Measurements of physical properties of modified asphalt binder

The laboratory tests used in this research are the traditional tests for asphalt binder which are penetration, ductility, viscosity, and softening point. Other laboratory tests are Marshall stability, and wheel track test for the wearing layer of modified asphalt mixture with each percent of PPA.

3 Results and discussion

3.1 Effect of %PPA on the penetration of modified asphalt binder

Fig.2 depicts how each percent of PPA addition affects the penetration value. The viscosity of the modified binder is assessed using this test. The asphalt is less viscous when the value of penetration for the binder is high.

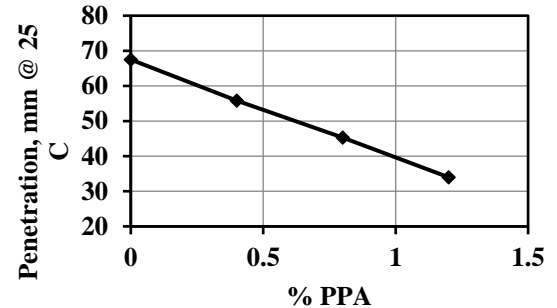


Figure (2): Effect of %PPA on modified asphalt binder penetration at 25 °C.

As presented in Fig.2 the penetration value is decreased linearly with the increase in the percent of PPA, which indicate that the asphalt binder becomes more stiff and viscous because the asphaltene content is increased by adding the PPA to the asphalt binder. This result is complying with Gau et.al. [14] and Liu et.al. [16].

3.2 Effect of %PPA on the ductility of modified asphalt binder

The ductility test carried out by ASTM D113 for asphalt binder involves determining the extent to which it can withstand plastic deformation without rupture or the asphalt binder's capacity to stretch without breaking. Fig.3 shows the %PPA effect on the change in the ductility value for each percent of addition at 25 °C which is the standard test temperature. The figure depicts that the ductility decreases with the increase of %PPA because the PPA leads to a decrease in resin content in the asphalt binder and the bitumen's resin content has a significant impact on how ductile it is. Also, the figure shows that when the percent of PPA is 0.4% of asphalt binder weight the curve is sharply decreased from 170 cm to 110 cm this demonstrates how PPA reduces the asphalt's ability to resist cracking at low temperatures. However, increasing the amount of PPA in the asphalt binder is anticipated to result in worse low-temperature deformation capacity but the figure shows that the ductility didn't decline sharply between the value of PPA from 0.4% to 1.2% by weight of asphalt binder.

It is concluded that the new distinctive peak intensities don't change with the increase of PPA content. The result complies with Jaroszek [18] and Yan et. al. [19].

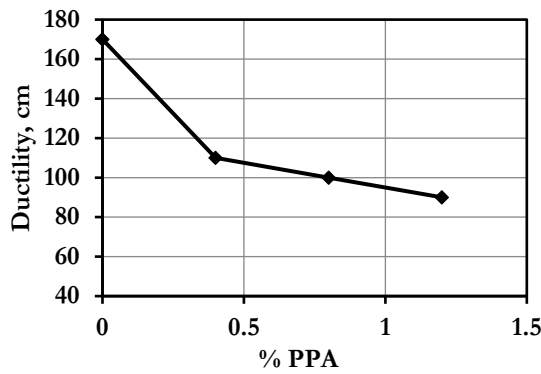


Figure (3): Relationship between the ductility and %PPA.

3.3 Effect of %PPA on the viscosity of modified asphalt binder

The asphalt binder rotational viscosity test assists in making sure that the asphalt binder is adequate fluid for mixing and pumping. ASTM D 4402 is the standard test specification used for measuring the viscosity for each percent of PPA added to the asphalt binder. Using a rotational viscometer instrument, Figure 4 presents the %PPA influence on the change of the viscosity value for each percent of addition at a test temperature of 135 °C, which reflects the fluidity of the binder. The figure illustrates how the binder of asphalt becomes more viscous when the percent of PPA increases and becomes stiffer because of the resin content decrease and increase in the content of asphaltene in the modified asphalt binder. This result complies with Jiang et. al. [20].

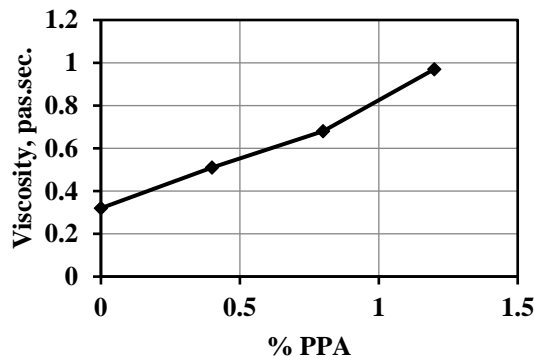


Figure (4): Relationship between the viscosity and %PPA.

3.4 Effect of %PPA on the softening point of modified asphalt binder

Knowing the binder's softening point by ASTM D36 enables the material to be heated to the right temperature for various uses on roads. Fig.5 presents how %PPA affected the change in the softening point value for each percent of addition using the ring and ball device. As presented in Figure 5 the value of the softening point is increased and enhanced with the percent of PPA increase. This result complies with Kodrat et. al. [21].

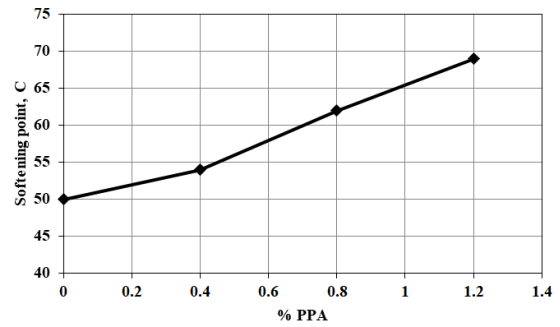


Figure (5): Relationship between the softening point and %PPA.

3.5 Effect of %PPA on the Marshall stability of modified asphalt mixture

Fig.6 presents the Marshall stability for each percent of %PPA by weight of asphalt binder.

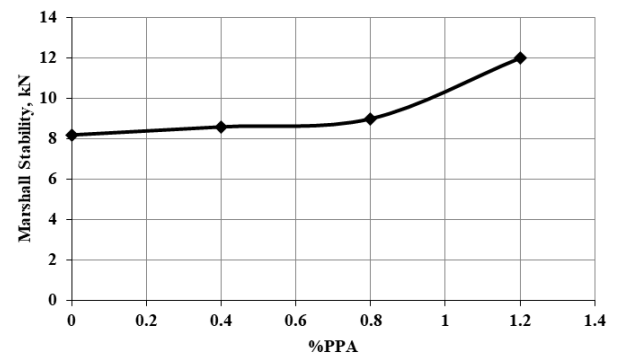


Figure (6): Marshall Stability for each percent of %PPA.

The figure shows that the Marshall Stability increased by 4.88%, 9.76%, and 46.34% for 0.4%, 0.8%, and 1.2% of PPA respectively. As a result, adding PPA to the asphalt mixture improves the Marshall Stability and the functionality of asphalt pavements.

3.6 Effect of %PPA on rut depth for modified asphalt mixture

The wheel track test is carried out by AASHTO T 324 at two test temperatures 40 °C and 50 °C. The test ended when the number of passes reached 20 mm or when the slab failed.

Fig.7 presents the results of rut depth for 40 °C test temperature. As presented in the figure the test continues until the number of passes becomes 10000 passes that have attributed to the test temperature which is 40 °C whereas in Fig.8 the number of passes doesn't exceed 6500 passes because the test temperature is higher which is 50 °C and the slabs failed before reaching 10000 passes.

However, the rut depth decreases with the increase of the percent of PPA because the mixture becomes stiffer with the addition of the %PPA. The rut depth for 0%, 0.4%, 0.8%, and 1.2% PPA is 18.5, 17.5, 16, and 15.2 mm respectively at a test temperature of 40 °C. When the percent of PPA is 0.4 %, 0.8%, and 1.2% of the weight of asphalt binder the rate of decrease is 5.7%, 15.6%, and 21.7% respectively at 40 °C test temperature.

When the temperature test becomes 50 °C, the number of passes is increased when PPA is added to



the asphalt mixture until the slab specimens failed. As illustrated in Figure 8 the number of passes at 0%, 0.4%, 0.8%, and 1.2% of PPA are 4500, 5000, 6000, and 6500 respectively. The rut depth at 4500 passes for 0%, 0.4%, 0.8%, and 1.2% is 23, 19.7, 16.8, and 16.1 mm respectively whereas the rate of decrease is 16.75%, 36.9%, and 42.85% for 0.4%, 0.8%, and 1.2% of PPA respectively.

It can be said that the performance of the asphalt pavement will be improved by the addition of PPA, and the mixture will be more rutting resistant, especially in high-temperature weather. This result complies with Babagoli [22].

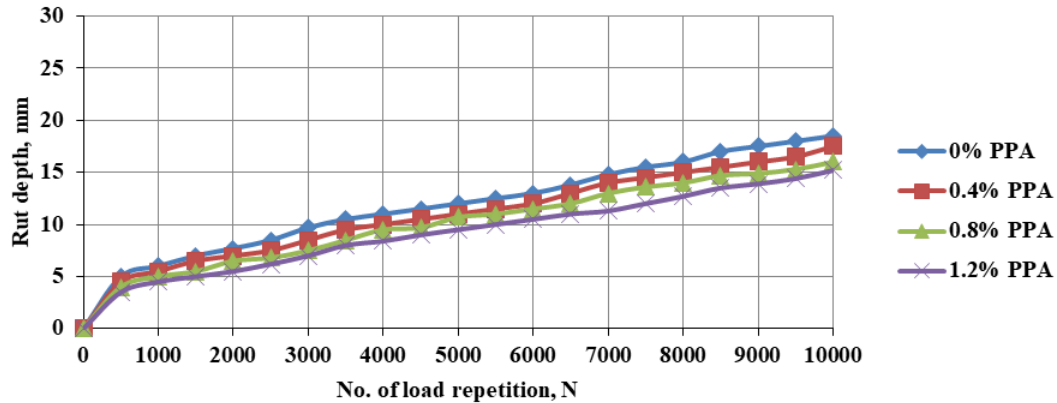


Figure (7): Rut depth at various percent of PPA at 40 °C.

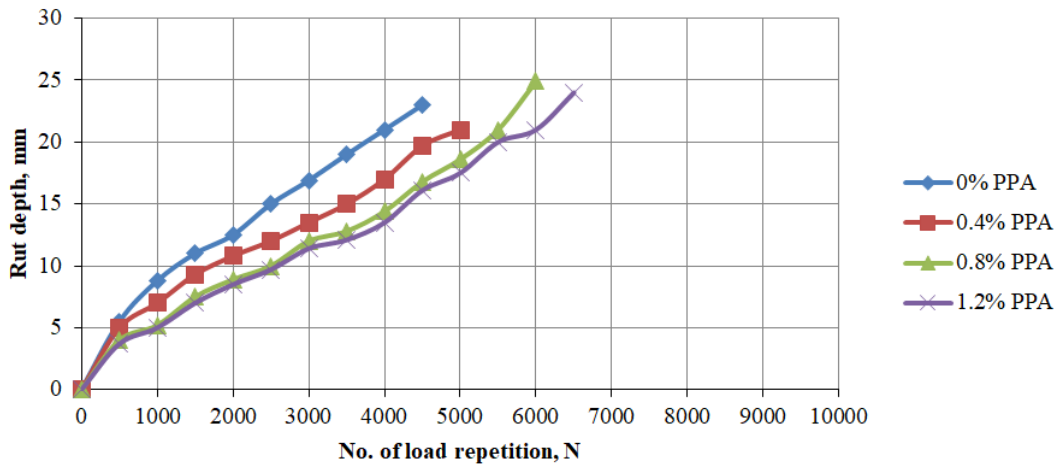


Figure (8): Rut depth at various percent of PPA at 50 °C.

4. Conclusions

To assess the improvement of the asphalt binder and mixes, three percentages of PPA were applied. As a result, the following can be concluded:

1. When adding the PPA to the binder, the content of asphaltene increases while the resin concentration decreases.
2. The asphalt binder penetration value is decreased linearly with the increase in the percent of PPA, which indicate that the asphalt binder becomes more stiff and viscous because the asphaltene content is increased by adding the PPA to the binder.
3. Since the PPA causes the asphalt binder's resin content to decrease, and since bitumen's resin content heavily influences ductility, the asphalt binder's ductility decreases as the PPA percentage increases.
4. As the percentage of PPA rises, the softening point value increases and improves.
5. The addition of PPA to the asphalt mixture increases the Marshall Stability and enhances the

performance of the asphalt pavements by increasing the stiffness of the mixture.

6. The rut depth decreases with the increase of %PPA.
7. At 40 °C test temperature, the number of passes is 10000 and the slab samples are not failed, whereas the number of passes at 50 °C varies with the percent of PPA. The rut depth for 0%, 0.4%, 0.8%, and 1.2% PPA is 18.5, 17.5, 16, and 15.2 mm respectively at a test temperature of 40 °C at 10000 passes. The rut depth at 4500 passes for 0%, 0.4%, 0.8%, and 1.2% is 23, 19.7, 16.8, and 16.1 mm, respectively.
8. The rut depth rate of decrease is 16.75%, 36.9%, and 42.85% for 0.4%, 0.8%, and 1.2% of PPA respectively at 50 °C and 4500 passes whereas the rate of decrease is 5.7%, 15.6%, and 21.7% respectively at a test temperature of 40 °C and 10000 passes.
9. The PPA addition will enhance the Iraqi asphalt pavement performance and the mixture will be more rutting resistant, especially in high-temperature weather.



5. Recommendations

It is recommended to:

1. Investigate the performance of the asphalt binder at other PPA concentrations.
2. Evaluate PPA addition to the asphalt mixtures on fatigue distress of asphalt pavements.
3. Studying the chemical composition of the modified binder with PPA.
4. Studying the effect of using different mineral fillers with polyphosphoric acid on the performance of asphalt pavements.

6. References

- [1] Akram HA, Hilal MM, Fattah MY, “Numerical Simulation of the Effect of Repeated Load and Temperature on the Behavior of Asphalt Layers”, *Engineering and Technology Journal*, 40(5): 1-10, 2022.
<https://doi.org/10.30684/etj.2021.131187.1012>
- [2] Hatem NS, Hilal MM, Fattah MY, “Finite Element Simulation of Repeated Loading Test of Asphalt Concrete”, *Engineering and Technology Journal*, 40 (05), 661-667, 2022.
<https://doi.org/10.30684/etj.v40i5.2128>
- [3] Abdulkhabeer WN, Fattah MY, Hilal MM., “Characteristics of asphalt binder and mixture modified with waste polypropylene”, *Engineering and Technology Journal*, 39(08):1224–30, 2021.
<https://doi.org/10.30684/etj.v39i8.1716>
- [4] H.H. Jony, M.M. Hilal, and D.S. Helan, “Effect of Polymer Additives on Permeability of Asphalt Concrete Mixtures”, *Engineering and Technology Journal*, Vol. 36, Part A, No. 1, pp. 75-83, 2018.
- [5] Baumgardner GL, Masson JF, Hardee JR. “Polyphosphoric acid modified asphalt: proposed mechanisms”, *Proceeding Association Asphalt Pavement Technology*, 74:283–305, 2005.
- [6] Masson JF, Gagne M, Robertson G., “Reactions of polyphosphoric acid and bitumen model compounds with oxygenated functional groups: where is the phosphorylation?”, *Energy Fuels*, 22(6):4151–7, 2008.
- [7] Ziaria, M. A. et al, 2021, “Effect of polyphosphoric acid on fracture properties of asphalt binder and asphalt mixtures”, *Construction and Building Materials*, Volume 310, 6 December 2021.
- [8] Y. Wei, “Research on the Performance and Microstructure of Polyphosphoric Acid Modified Asphalt”, *Kunming University of Science and Technology*, Kunming, China, 2015.
- [9] Orange G., Dupuis D., Martin J.V., Farcas F., Such C., Marcant B., “Chemical Modification of Bitumen Through Polyphosphoric Acid: Properties-Microstructure Relationship”, *3rd Eurasphalt & Eurobitumen Congress*, (2004).
- [10] Alexander S.H., “Method of Treating Asphalt”, U.S. Patent 3,751,278 (1973).
- [11] Hoiberg A.J., “Air-Blown Asphalt and Catalytic Preparation Thereof”, U.S. Patent 2,450,756 (1948).
- [12] Puzic O., Williamson K.E., “Asphalt Compositions and Method for Making”, U.S. Patent 6,414,056 (2002).
- [13] Baumgardner, G, “Why and How of Polyphosphoric Acid Modification”, *Transportation Research Board of the National Academies*, Transportation Research Circular, Polyphosphoric Acid Modification of Asphalt Binders: A Workshop, 2011-2012, Number E-C160, January 2012.
- [14] Gao L., et. al., “Influence of PPA on the Short-Term Antiaging Performance of Asphalt”, *Advances in Civil Engineering*, Volume 2021, Article ID 6628778, 11 pages,
<https://doi.org/10.1155/2021/662877>
- [15] B. Li, X. Li, Marie Judith Kundwa et al, “Evaluation of the adhesion characteristics of material composition for polyphosphoric acid and SBS modified bitumen based on surface free energy theory”, *Construction and Building Materials*, 266 (2021) 121022.
<https://doi.org/10.1016/j.conbuildmat.2020.121022>
- [16] Liu S, Zhou S, Peng A. “Evaluation of polyphosphoric acid on the performance of polymer modified asphalt binders”, *J Appl Polym Sci*, 2020;e48984.
<https://doi.org/10.1002/app.48984>
- [17] SCRIB, General Specification for Roads and Bridges. Section R/9, Hot-Mix Asphalt Concrete Pavement, Revised Edition. State Corporation of Roads and Bridges (2003). Baghdad: Ministry of Housing and Construction, Republic of Iraq.
- [18] Jaroszek, H., “Polyphosphoric acid (PPA) in road asphalts modification”, *CHEMIK*, 66, 12, 1340-1345, 2012.
- [19] Yan K., Zhang H., and Xu H., “Effect of polyphosphoric acid on physical properties, chemical composition and morphology of bitumen”, *Construction and Building Materials*, 47, 92–98, 2013.
<https://doi.org/10.1016/j.conbuildmat.2013.05.004>
- [20] Jiang, X., Li, P., Ding, Z., Yang, L., and Zhao, J., “Investigations on viscosity and flow behavior of polyphosphoric acid (PPA) modified asphalt at high temperatures”, *Construction and Building Materials*, 228 (2019) 116610.
<https://doi.org/10.1016/j.conbuildmat.2019.07.336>
- [21] Kodrat, I., Sohn, D., and Simon, A.M, “Comparison of Polyphosphoric Acid-Modified Asphalt Binders with Straight and Polymer-Modified Materials”, *Transportation Research Record: Journal of the Transportation Research Board*, No. 1998, Transportation Research Board of the National Academies, Washington, D.C., pp. 47–55, 2007.
<https://doi.org/10.3141/1998-06>
- [22] Babagoli R.; “Laboratory investigation of the performance of binders and asphalt mixtures modified by carbon nano tube, poly phosphoric acid, and styrene butadiene rubber”, *Construction and Building Materials*, 275 (2021) 122178.
<https://doi.org/10.1016/j.conbuildmat.2020.122178>