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Evaluation of Rheological and Thermal Behavior of Polymer Modified Asphalt.

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Abstract

This research work has evaluated the modification effects of adding the reactive polymer (poly methyl methacrylate - (PMMA)) at different contents with Iraqi asphalt in the presence of poly phosphoric acid (PPA) at constant ratio as cross-linking agent on the thermal and rheological behavior of asphalt material with penetration grade 40/50. Moreover, the chemical structure of Iraqi asphalt and its fractions (asphaltene and maltene) was analysed using FTIR analysis. Combination of PMMA/PPA with asphalt has been presented as a new alternative approach to modify the rheological and thermal behavior of modified asphalt binders via forming chemical bonds and the changing in rheological and thermal characteristics of blended materials. Ten different PMMA percentages ranging from 0.5% to 5% by weight with 0.2% PPA for each sample were blended with 40/50 asphalt binder, the rheological properties of modified asphalt samples at different contents were examined by standard testing including ductility, penetration, softening point and penetration index. It was noted that due the addition of high loadings of PMMA into asphalt, the softening point value increased from 51 ˚C to 66 ˚C, whereas the ductility and penetration values decreased from 150 cm and 41 mm to 33 cm and 12 mm respectively. The result obtained revealed that the incorporation of PMMA/PPA with asphalt at specific level significantly improved elasticity and strengthens of asphalt mixture, which finally enhances the cracking and rutting resistance performance as well as temperature susceptibility of asphalt pavement. The thermo gravimetric analysis (TGA) indicated that the modified asphalt samples had less evaporation and higher thermal stability compared to virgin asphalt, this means that the thermal attitude of modified asphalt was improved. X-ray diffraction (XRD) patterns were performed to study the morphological properties of asphalt and modified one, these results showed that modified asphalt sample possessed homogeneous surface as a result of uniform dispersion of polymers into asphalt morphology due to chemical interaction between polymers and asphalt.

Keywords: Polymer modified asphalt (PMA); Poly Phosphoric Acid (PPA); Poly Methyl methacrylate (PMMA).

1. Introduction

Asphalt binder is an essential material used in the flexible pavement construction, it displays both viscous and elastic features, the viscoelastic properties of asphalt dominate at the higher temperature,[1] whereas asphalt layer in the road behaves as an elastic solid material at the lower temperature, this would be responsible for resistance to deformations of the asphalt pavement. In hot climate areas, the most common shapes of failure is asphalt rutting which is considered as a serious mode of distress in asphalt pavement as a result of applying heavy traffic loading from slow-moving loaded trucks, this leads to increase the viscous behavior of asphalt binder hence making it sensitive to rutting during the summer. [2-4]

The performance of flexible pavements has been improved by modification of asphalt via polymers, these additives aim to enhance the durability and sustainability of asphalt pavement by enhancing the performance at high- and low-temperature.[3] Over the past decades, polymer modified asphalt (PMA) has received a great attention in both research and industrial communities as a result of its potential advantages such as reducing the susceptibility of asphalt to high and low temperatures.[5] Incorporation of thermoplastic or elastomeric polymers into asphalt binder has been conducted to produce the polymer modified asphalt. PMA in flexible pavement has exhibited better resistance to rutting, thermal cracking and temperature susceptibility. [6, 7] Many studies have investigated the effect of polymer modification on pavement performance, this strategy has motivated research communities to develop and evaluate the asphalt binder performance by incorporation a wide range of polymers including: poly ethylene, poly ethylene vinyl acetate, styrene-butadiene-styrene rubber,

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styrene-butadiene rubber and others.[8] Modified asphalts with polymers have shown better mechanical behaviors and higher durability than the unmodified ones.

Reactive thermoplastics polymers are also employed to modify asphalt in order to enhance the rigidity of binder and minimize all the deformation shapes of asphalt when it be under load. It is speculated that the reactivity of polymers is probably due to the presence of functional groups which are likely able to interact with asphaltene segment into the binder.[9-12] The presence of polar functional groups into polymer structures as modifier would increase the polarity of polymers that improves its compatibility and solubility with asphalt as a result of interaction with the polar constituents into asphaltene.[13] Therefore phase separation between asphalt binder and polymer additive is prevented, which turns to improve the materials consistency, and reduces oxidative ageing.[12] One of the most common polar polymer as asphalt modifier is poly methyl methacrylate (PMMA), it displays important aspects to be considered in its properties such as having high mechanical strength and thermal stability. Moreover, it exhibits low elongation at break and moisture absorbing capacity. PMMA is considered as chemical stable compound with low degradation rate especially when exposes to sun and UV light, thus these characteristics make the polymer as suitable product for weathering and erosions.[14, 15] Previous studies revealed that incorporation of waste PMMA powder in an asphalt mixture has improved performance characteristics and mechanical properties of asphalt mixture which can enhance the durability of road pavement.[16] Other study was achieved by Haggam and his group where they synthesized two different molecular weight (Mw) of PMMA, molecular weights of PMMA were estimated to be 21000 and 30000, respectively. The results indicated that the mechanical performance of modified binder has been improved with low Mw of PMMA. Furthermore, the compatibility between asphalt binder and PMMA was enhanced upon further aging especially with low molecular weight of PMMA.[17] Recently, asphalt binder has turned into a highly technical material with additives like polymers and acids, with gaining relevance in the control of the performance properties of modified asphalt.[18] Poly phosphoric acid (PPA) is ortho-phosphoric acid (H_3PO_4) which can be used by itself as suitable polymer for modification.[19] Generally, the PPA modifiers ranging from 0.2% to 1.2% by weight are added to unmodified asphalt. [20] Moreover, PPA plays a crucial role as cross-linking agent to control the rheological attitude of the polymer modified asphalt binder. The PPA modification mechanism of binder has been subjected to many research studies during recent years, these studies have suggested that PPA interacts with asphaltene fraction which leads to disperse the asphaltene fraction into the asphalt binder.[21, 22]. Consequently, the asphaltene fraction is disrupted into the asphalt components thus the asphalt will turn into a more elastic gel-type structure, resulting in producing a homogeneous mixture of the binder and the polymer. [21] Previous study indicated that the addition of the PPA not only provides the role of a cross-linker but also leads to essential changes in rheological properties of the polymer modified asphalt. [23] It is worth mention that the combination of PPA with other polymer modifiers into asphalt stiffens the modified asphalt at higher temperature, improving the permanent deformation resistance without any negative impacts at low temperatures, this approach has enhanced the rheological performance of modified asphalt.[24]

The aim of this research work is to utilize PPA and PMMA as modifiers in asphalt binder for improving its performance properties. Asphalt binder/PMMA/PPA blends were prepared and evaluated in the laboratory. The effect of PMMA loading (0.5%, 1%, 1.5%, 2%, 2.5%, 3%, 3.5%, 4%, 4.5% and 5% beside of 0.2% by weight for each modified asphalt sample) is vastly studied in terms of the properties of PMMA/PPA modified asphalt including rheological, morphological and thermal characteristics.

2. Materials and Methods.

2.1 Materials.

2.1.1 Asphalt binder.

In this work, asphalt binder from Refinery of Dourah, Baghdad, Iraq with a penetration grade of 40/50 were used as the base binder. The physical properties of Iraqi asphalt binder used are listed in Table 1.

Table 1:Physical properties of Iraqi asphalt.

Properties	**Value**	**ASTM Standard specification**
Ductility @ 25 °C (cm)	100+	ASTM D113-86
Softening point	49-58	ASTM D-36
Penetration (25 °C , 100 g , 5 min)	40-50	ASTM D5-83
Flash point °C (min)	240	ASTM D-92
Solubility in trichloroethylene (C_2HCl_3) wt. (min)	99.0	
Density (g/cm^3) @ 15.6 °C	1.04	ASTM D-70

2.1.2. The reactive polymer (PMMA).
The reactive polymer (PMMA) was provided by the dental product supplier (Manufactured by New Stetic S.A-Colombia), and used as the modifier. Its characteristics are listed in Table 2.

2.1.3 Poly phosphoric acid (PPA).
PPA was used as a catalyst in order to accelerate the chemical reaction between asphalt and the reactive polymer. PPA was supplied from the internal chemical store (Sigma-Aldrich). The characteristics of PPA are presented in Table 3. According to previous studies,[21, 22] PPA plays a main role to break the asphaltene agglomerates into asphalt for a better distribution of asphaltene in the molten phase. As a result, it contributes to the elastic attitude of the binder by converting asphaltene clusters into individual particles.

All common organic solvents are available in the internal chemical store of chemistry department.

Table 2: Properties of PMMA.

Properties	**value**
Physical form	powder
Melting point (°C)	190

Table 3: Physical properties of PPA

Properties	**Values**
Physical form	viscous liquid
Boiling point	300 °C
Melting point	16 °C
Density	1.9 g/ml at 25 °C

2.2 Methods.
2.2.1 Asphaltene Separation Technique.
100 ml conical flask was charged with a mixture containing (1 gm) asphalt and (40 ml) n-heptane (1:40 mass :volume), the resulting mixture was carefully dissolved and stirred vigorously under dark condition at ambient temperature for 2 hours. The n-heptane insoluble fraction (asphaltene) was filtered off through filter paper and washed with n-heptane until the filtrate turn into colourless in order to remove co-precipitated maltenes. The precipitate on filter paper was dried in air then vacuum to afford the product as a black material with a reasonable yield (0.19 gm, 19%). Furthermore, the n-heptane soluble portion, which contains maltene fraction, was evaporated in rotary evaporator to produce a sticky black product (0.81 gm, 81%). Asphalt binder and its fractions were characterised by Fourier transform infrared (FTIR) spectroscopy. It is important to separate and identify the asphaltene fraction and its percentage into base asphalt before any modification process, the less asphaltene content into asphalt is considered to be more stable modified product with polymer and more compatible system and high content of asphaltene into asphalt binder decreases polymer/asphalt compatibility.

2.2.1 Sample Preparations.
To study the effect of the polymer and cross linking agent on the performance of binder, the base Iraqi asphalt binder 40/50 pen grade was heated up and stirred vigorously using a mechanical stirrer at 180 °C then PPA was slowly added as a cross linking agent in a proportion of 0.2 % by weight into the melt asphalt sample and mixed for 2 hour in order to gain homogenous asphalt binder. The modified binder samples were prepared by adding 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, and 5.0 % of PMMA polymer modifiers to the PPA-base asphalt binder at 180 °C. The mixture for each sample was allowed to react for 90 minutes at 180 °C with constant stirring. This reaction time is enough to complete the chemical reaction between binder and PMMA to form homogenous products and permanently modified binders. After completion, the PMMA/PPA modified binder samples were removed from reaction vessel into small aluminium cans which covered with aluminium foil and stored for conventional tests.

2.2.2 Fourier Transform Infrared Spectroscopy (FTIR) test.
FTIR spectroscopy is widely employed in quantitative and qualitative analysis of organic materials, in this study, this technique was effectively used to characterise and identify the functional groups into chemical structure of the base asphalt binder and its fractions (extracted maltene and asphaltene) using a Spectrum Two- N (Perkin-Elmar) FT-IR spectrometer with spectral range from 450 to 4000 cm^{-1}, the infrared spectroscopies of the base asphalt and its fractions were tested.

2.2.3 Conventional tests of unmodified and modified asphalt.
The PMMA/PPA modified binders were subjected to standard conventional tests in order to determine the rheological characteristics of modified asphalt, the binder without modifier was also investigated via conventional tests for a comparison. The conventional rheological tests were performed to evaluate the elastic behavior of polymer modified asphalt. these tests include the softening point test (the ring and ball), the penetration and ductility, the tests were carried out in accordance with ASTM D36,[25] ASTM D5 [26] and ASTM D113-86,[27] respectively. The obtained result values of these tests are presented in Table 4. Moreover, the penetration index (PI) value was calculated from the softening point and penetration data in order to predict temperature susceptibility of the modified binder. PI value is obtained according to following equation:

$$\left\{PI = \frac{1952 - 500\log\ pen\ - 20\, softening\ point}{50\log pen - softening\ point - 120}\right\}$$

Where Pen is considered to be the value of penetration at the temperature of 25 °C, SP represents the softening point temperature of the binder. A lower PI value indicates a higher temperature sensitivity of the binder and vice versa.[28]

Table 4: Rheological data of PMMA/PPA modified asphalt.

Content of PMMA (%)	Content of PPA **(%)**	Ductility (cm) at 25 °C	Softening Point (°C)	Penetration (mm) at 25 °C	penetration index (PI) value
0	0	150	51	41	-1.40
0.5	0.2	150	58	21	-1.17
1	0.2	150	58	21	-1.17
1.5	0.2	150	59	21	-0.99
2	0.2	135	59	22	-0.91
2.5	0.2	130	59	22	-0.91
3	0.2	114	59	24	-0.74
3.5	0.2	67	60	15	-1.38
4	0.2	42	62	13	-1.24
4.5	0.2	40	65	12	- 0.88
5	0.2	33	66	12	-0.74

2.2.4 Thermogravimetric analysis (TGA) test.

Thermo gravimetric analysis (TGA) was conducted to investigate the thermal behavior of the base asphalt and modified asphalt via decomposition process of these samples at a higher temperature. TGA analysis was performed using a TGA/DTA thermal analyser (BHAR STA 503-Germany) to study the thermal stability of samples in the temperature rate of 30-600 °C at 10 °C/min verifying heating rate under a constant flow of nitrogen gas.

2.2.5 X-ray Diffraction (XRD) Test

XRD is a method to analyse and identify the crystallographic structure of a solid material, it is a rapid analytical technique that widely utilised to determine the crystallite parameters of base asphalt and modified asphalt binder via peak intensity and position of the structural parameters in the asphalt binder samples. The X-ray diffraction (XRD) patterns of base asphalt and selected polymer modified asphalt sample were recorded by a Philips Panalatical X'Pert (Holland) using diffractometer with Cu Kα radiation.

3. Results and discussion.

3.1. FTIR analysis.

FTIR spectra of the asphaltene (ASP) and maltene (Ma), which were extracted from 40/50 pen virgin asphalt, are shown in Figure 1, and interpreted based on previous studies [29, 30] . It can be observed that FTIR spectra patterns for asphalt and its fractions look similar except few changes in peaks. The functional groups, which are presented in the molecules of the virgin asphalt and its fractions, were studied by FTIR spectrum in the wavenumber range from 450 to 4000 cm^{-1} as depicted in Table 5 and Figure 1. For further interpretation of these results, the FTIR spectra of the virgin asphalt (Figure 1 a) showed strong absorption peaks at 2922, 2851, 1457 and 1376 cm^{-1}. These strong peaks were also observed in the spectrum of extracted maltene and asphaltene fractions (Figure 1 b and c) with minor shift. (Figure 1 a) exhibited a broad peak in the range between 3500 and 3100 cm^{-1} for the virgin asphalt, indicating to absorption of functional groups (O-H) and (N-H) stretch in aromatic and cyclic compounds. Other peak was observed at 3050 cm $^{-1}$ as shoulder which may be attributed to (=C-H) stretch in an aromatic compounds. The high intensity peaks at 2922 and 2851 cm^{-1} were also observed which may be due to (C-H) stretch in CH_3, CH_2 and CH in aliphatic chains, while the absorption bands at 1457 and 1376 cm^{-1} correspond to (C-H) stretch in aliphatic groups and (C-H) bend in methyl groups, respectively. Furthermore, a shoulder peak, which appeared at around 1600 cm^{-1}, corresponds to C-C stretch (in-ring) aromatic compounds, the peaks observed, at around 860, 811and 752 cm^{-1}, which appeared as shoulders, are related to the presence of (C-H) bend in aromatics.

It is interesting to compare the FTIR spectra of the base asphalt and its fractions separated, the FTIR of maltene spectrum (Figure 1 b) showed that there was disappearance of peaks between (3500- 3100 cm^{-1}), (860-752 cm^{-1}) and at near 3050 cm $^{-1}$ in comparison to the base asphalt and asphaltene (Figure 1 a and c) respectively, this can be attributed to absence of polycyclic aromatic compound into maltene unlike asphaltene fraction. The asphaltene spectrum (Figure 1 c) showed peaks at 3434, 3050 and 807 cm^{-1} which could be due to the aromatic stretching absorption as a result of the high content of polycyclic aromatic compounds. It can be concluded from the spectral results obtained that the asphaltene fraction is more aromatic than maltene. Furthermore, the spectral features of precipitated fraction confirm and identify the structure of asphaltene.

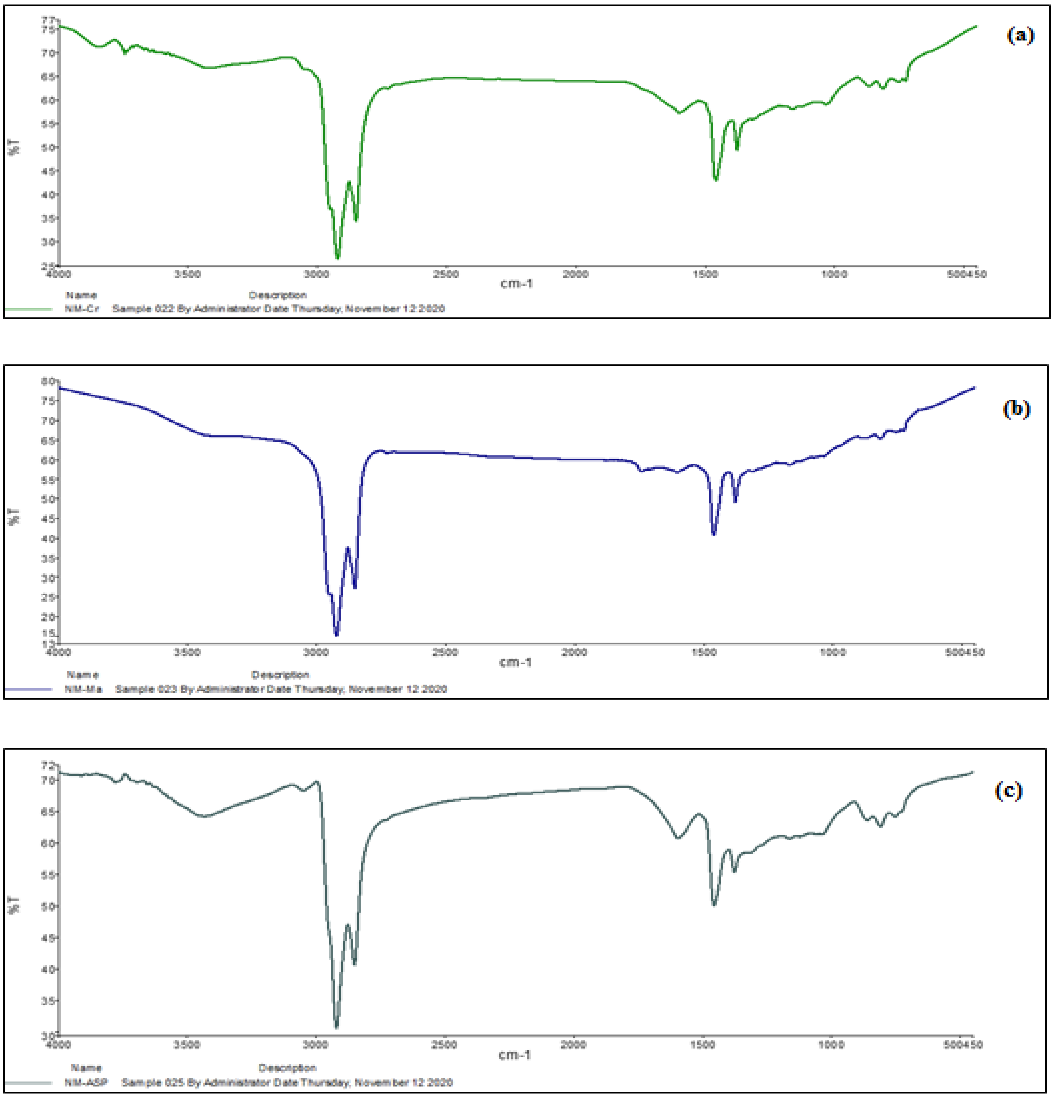

Figure 1: FTIR spectrum of virgin asphalt (a), extracted maltene (b) and extracted asphaltene (c).

Table 5: FTIR assignments of absorption peaks of the virgin asphalt and its fractions (asphaltene and maltene).

Wavenumber (cm^{-1})	**Functional group**	**Virgin asphalt**	**Asphaltene fraction**	**Maltene fraction**
3500-3100	O-H and N-H (str)	3423 (br)	3434 (br)	---
3050-3040	=C-H (str) in aromatics	3040 (w)	3050 (m)	---
2924-2851	C-H (str) in aliphatic	2922-2851 (s)	2922-2852 (s)	2924-2853 (s)
1603-1594	C=C (str) in aromatics	1598 (m)	1594 (s)	1603 (w)
1461-1375	-CH_3 (ben) in aliphatic	1457-1376 (s)	1455-1375 (s)	1461-1377 (s)
860-752	C-H (ben) in aromatics	811 (w)	807 (m)	---

Stretching absorption = (str), bending absorption = (ben), Broad peak = (br), strong peak =(s), medium peak (m) and weak peak= (w).

3.2 Rheological analysis.

It is important to investigate the influence of blending of the asphalt binder with reactive polymer (PMMA) at different ratios and linking agent PPA at constant concentration on the rheological properties of PMMA/PPA modified binder. Rheological characterizations for the base asphalt and modified samples were carried out in accordance with ASTM D36,[25] ASTM D5 [26] and ASTM D113-86,[27] respectively. In this study, the effect of mixture PMMA/PPA was very obvious on elastic attitude of the binder when it was added to the virgin asphalt at the mixing temperature of 180 C. The results obtained indicated that the modified asphalt with higher PMMA content had lower penetration values compared to unmodified asphalt as depicted in Table 4, this can be attributed to loss of fluidity within asphalt binder, resulting in adopt high-temperature consistency of modified asphalt.[31] It can be noted from Figure 2 that the penetration (Pen) value of the unmodified asphalt was 41 (mm) which dramatically declined at half by increasing the PMMA ratio between 0.5% to 3% with constant ratio of PPA 0.2 % for each sample, then the penetration value of modified asphalt decreased to 15, 13, 12 and 12 (mm) at 3.5%, 4%, 4.4% and 5% loadings of PMMA, respectively. The decrease in penetration values of modified asphalt samples with increased PMMA concentration indicates that addition PMMA/PPA into binder leads to a considerable change on the physical properties of the modified asphalt as a result of substantial hardening. The lower penetration grade of samples can probably improve the resistance of the modified asphalt against high temperature-susceptible defects which enhance the rheological performance of asphalt especially in hot climate areas.[32] However, the flexibility of the modified asphalt might be affected by making the asphalt less softer, and thus the resistance to fatigue cracking can be affected.[17]

As expected, the modified asphalt binder samples with higher PMMA content had higher penetration values. As shown in Figure 3, the softening point of the virgin asphalt was 51 °C, which jumped up to 58 °C, 59 °C and 66 °C at PMMA loading of 1%, 3% and 5%, respectively. This increase ranges from 7˚C to 15˚C with the addition of 1% to 5% of PMMA, respectively, compared to unmodified asphalt. Generally, the softening point of asphalt binder represents its thermal behavior which is related to the temperature susceptibility of asphalt materials and the resistance of the binder to the effect of heat. This means that the high polymer content into asphalt increases the softening point value, resulting in less temperature susceptibility. Therefore, the asphalt with a higher softening point is preferred in warmer places.

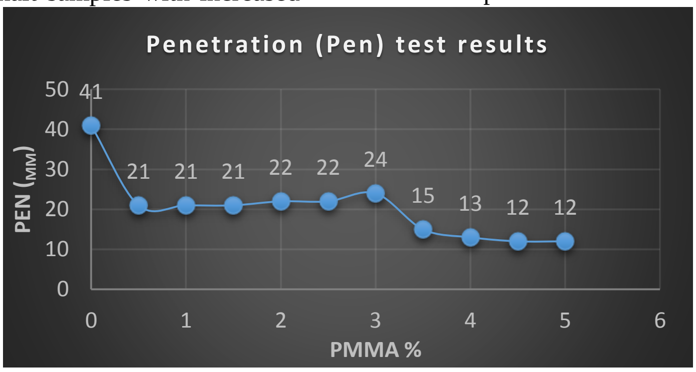

Figure 2: Penetration results of base asphalt and PMMA modified binder at different ratios + 0.2% PPA.

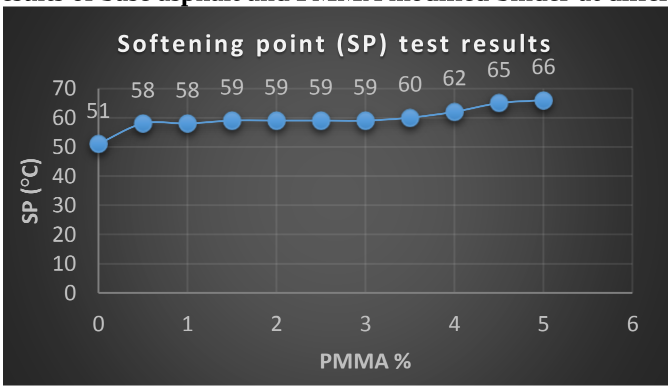

Figure 3: Softening point (SP) values of unmodified asphalt and PMMA modified binder at different ratios + 0.2% PPA.

As seen in Table 4 and Figure 4, the ductility values of modified asphalt samples were kept constant without any change at 150 (cm) at 25 °C when PMMA was added to virgin asphalt of 0.5%, 1% and 1.5% respectively. Afterward, the ductility values notably dropped when PMMA ratio increased steadily. The ductility value of virgin asphalt was

150 (cm), which decreased to 135, 114, 42 and 33 (cm) at 2%, 3%, 4% and 5% loadings of PMMA, respectively, unlike other PMMA contents which exhibited poor performance of ductility of modified asphalt. The ductility value of the virgin binder was 150 cm, which dramatically declined the tensile properties of binder to 42 and 33 cm at 4% and 5% loadings of PMMA, respectively. Presumably this can be attributed to adding PMMA at different contents and PPA at constant content which probably reduces the homogeneity and increases the stiffness of the modified asphalt samples thereby decreasing of the ductility.[33]

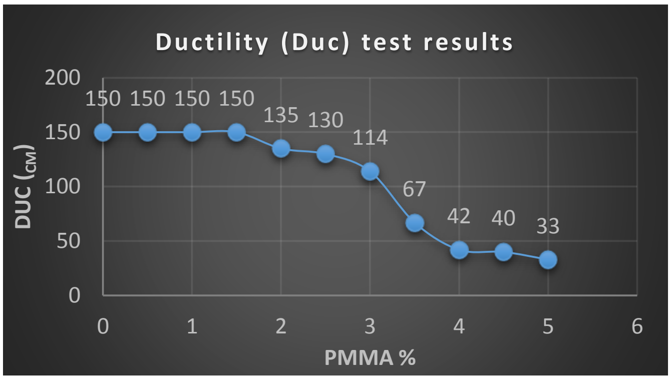

Figure 4: Ductility (Duc) values of unmodified asphalt and PMMA modified binder at different ratios + 0.2% PPA.

The results of PI are obtained from the relation between penetration and softening point results. As shown in Figure 5, the values of PI fluctuated up and down when PMMA was added to the base asphalt. It can be observed that modified asphalt samples have much higher values compared to the virgin asphalt, this rate of increase was 100% at 3% and 5% loading of PMMA, respectively. This indicates that the higher PI values of modified asphalt samples are more resistance to permanent deformation at high temperature and cracking at low temperature which can be categorized as less susceptibility asphalt to temperature, this helps to overcome the general issues of asphalt pavement in hot climate region such as rutting and fatigue.

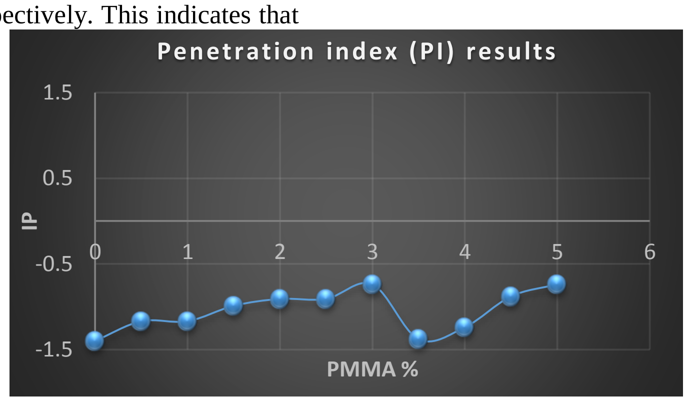

Figure 5: Penetration index (PI) values of unmodified asphalt and PMMA modified binder at different ratios + 0.2% PPA.

In summary, incorporation of PMMA/PPA into virgin asphalt would potentially improve the rheological properties of asphalt and be more favorable for hot climate. Reducing of penetration value and increasing of softening point of the modified asphalt with good elastic properties would eventually enhance the cracking and rutting resistance, anti-deformation ability and temperature susceptibility of asphalt pavement. According to the rheological results above, the modified asphalt samples collected between 0.5% and 3% loading of PMMA and 0.2 % PPA by weight can be recommended and applied successfully on road pavement to produce a suitable asphalt construction in the tropics, higher ratio is not recommended.

3.3 Thermo gravimetric analysis (TGA) analysis.

To better investigate the effect of reactive polymer (PMMA) on the thermal attitude of asphalt binder, thermal degradation properties of polymer modified asphalt samples through TGA in nitrogen atmosphere has been carried out and the results obtained are shown in Figure 6. It is well-known that TGA technique is an effective approach for thermal analysis providing valuable information when materials become to decompose during heating, and this leads to loss in weight of material against temperature. The TGA curves (Figure 6) of the virgin asphalt and PMMA/PPA polymer modified asphalt samples, at different loading (1%, 3% and 5%) of PMMA with constant loading of PPA (0.2 %), revealed that polymer modified asphalt samples have thermal stability with decomposition temperatures. the virgin asphalt showed several degradation steps compared to modified asphalt, the first weight loss in the degradation temperature above 300 ˚C indicated that the unmodified asphalt has lost more weight during the TGA test than the modified binders with PMMA/PPA. At this stage, it can be observed that modified asphalt at lower PMMA concentration (1%) exhibited higher weight loss relative to those samples with higher content of PMMA (3% and 5%). This suggested that PMMA/PPA modified binder samples possess less evaporation and greater thermal stability against decomposition temperature due to the increase of asphaltene content for modified asphalt as compared to unmodified asphalt.[34] Generally, the weight loss in the first degradation stage can be ascribed to the volatilization of the light components of asphalt, such as the saturated and aromatic compounds as well as to decomposition of large molecules of asphalt and polymers at this stage. The TGA plots of PMMA/PPA modified asphalt except unmodified asphalt exhibited similar thermal decomposition patterns as presented in Figure 6, it can be noted that the major weight loss for both virgin asphalt and modified asphalt samples takes place in the temperature range of 300 ˚C and 480 ˚C. These results are consistent with previous studies that exhibit the relationship between polymer modified asphalt and degradation kinetics.[29, 35]

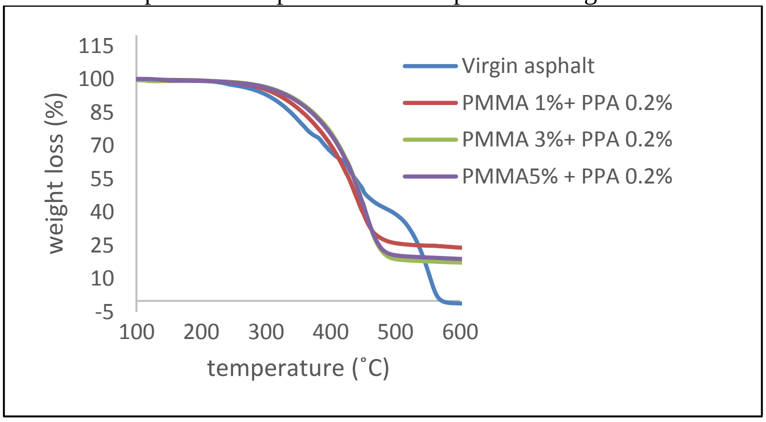

Figure 6: TGA analysis of virgin asphalt and PMMA/PPA modified asphalt binder at different concentrations of PMMA

3.4 X-ray diffraction (XRD) analysis.

X-ray diffraction (XRD) patterns of unmodified asphalt and modified asphalt by PMMA/PPA were obtained (Figure 7 a and b) using Panalatical Xpert XRD diffraction in the range of 2-theta 10° to 80°, this characterization technique was utilized to determine and investigate the modification in morphological features of modified asphalt by PMMA/ PPA. The selected 3% PMMA/0.2% PPA ratio is further investigated, which demonstrated promising performance in rheological properties, as ideal sample tested for morphological characteristics. It can be seen that the base asphalt and modified one exhibit a wide absorption band in XRD patterns at 2-theta ranging from 10 to 30, which indicates to a dominant macromolecular amorphous structure as first amorphous phase. While the second amorphous phase appears at 2-theta between 40 and 50 which is small amorphous phase relative to first amorphous phase in same patterns.

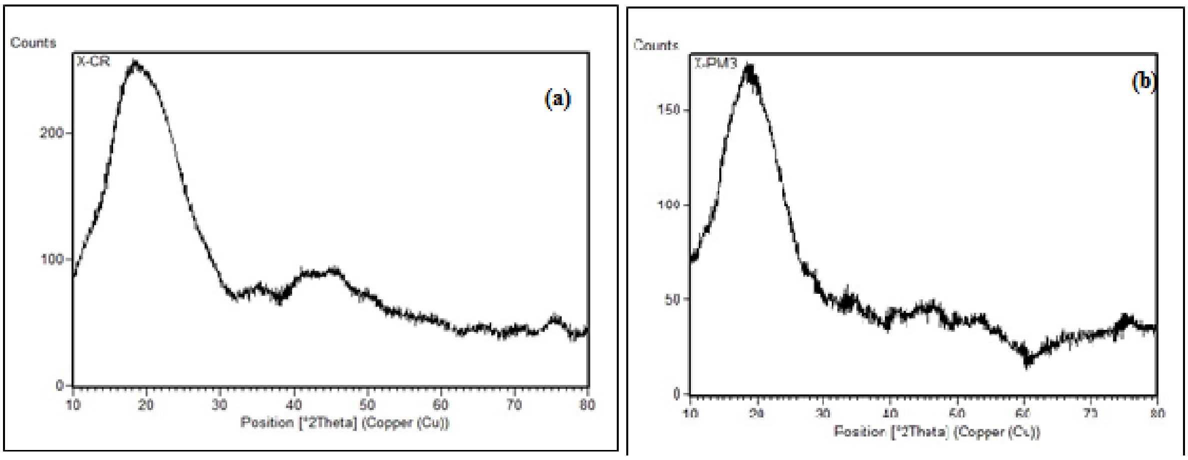

Figure 7: XRD patterns of unmodified asphalt (a) and modified asphalt by PMMA/PPA (b).

In summary, both pure asphalt and modified asphalt have a macromolecular structure in two separate amorphous phases. Generally, XRD results show same patterns of asphalt and modified sample, but the intensity of peaks at first and second amorphous phase for polymer modified binder declined compared to pure asphalt. This can be ascribed to chemical interaction between the main macromolecular groups in the binder and PMMA/PPA polymers, resulting in a uniform distribution within the modified asphalt sample.

4. Conclusion

In this paper, a deeper insight into the properties of Iraqi asphalt 40/50 used in pavement application has been made. It can be seen clearly that FTIR spectroscopy is an integral approach to identify and confirm the functional groups in asphalt especially after separation of binder to asphaltene and maltene fractions. This current study also attempts to improve the performance of asphalt via modification approach. The PMMA/PPA modifiers were added to unmodified asphalt in the range of 0.5-5.0% by weight. A comparative study revealed that the manner of adding PMMA at different ratio with 0.2% PPA into virgin asphalt was helpful to enhance the overall rheological performance of asphalt. Based on results obtained in this current study, it may be concluded that the addition of PMMA/PPA increased the softening point and penetration index values, it also decreased the penetration values of modified samples. However, the ductility values of modified asphalt samples kept constant above 100 (cm) when PMMA was added to virgin asphalt ranging from 0.5% to 3%. Therefore the blending of PMMA with asphalt can significantly increase the cracking and rutting resistance beside good elastic behavior. It is worth mentioning that the optimum modifier content of PMMA was found to be 3% which has more pronounced effect on the rheological properties than other contents of modified asphalt binders specimens. Moreover, The XRD patterns indicated that PMMA and PPA interacted with the functional groups in the virgin asphalt, this leads to behave as homogeneous single phase structure as a result of the chemical reaction in the asphalt blend. In term of thermal study, the modified asphalt samples by PMMA/PPA have generally higher thermal stability compared to the non-modified asphalt sample

Conflicts of interest.

The authors declare that there is no conflict of interest.

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