

Improving the Longevity of Locally Modified Asphalt with Polymers Thorough Evaluation of Rheological Properties and Performance.

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Abstract

This research aimed to enhance the longevity of local grade 40/50 cement asphalt pavement by incorporating polymer additives—polyvinyl acetate (PVAc), polymethyl methacrylate (PMMA), and poly cyanoacrylate (PCA)—at varying percentages. The focus was on improving rheological properties to meet Iraqi road and bridge construction standards, specifically the post-thin film oven test (RTFO). The novelty lies in the limited exploration of PCA polymer applications in asphalt. Two scenarios were employed: one with both sulfur and catalyst, anhydrous aluminum chloride (AlCl₃), and the other with only the catalyst, excluding sulfur. Microwave radiation (360watts) for different durations (5, 10, and 15 minutes) was utilized. Various tests evaluated physical, chemical, and aging properties, revealing that while indigenous grade 40/50 asphalt initially met rheological standards, it failed post-RTFO, with PMMA showing no improvement. In contrast, both PVAc and PCA exhibited enhanced rheological properties. The combination of 0.5% of all polymers with microwave treatment resulted in significant improvement, with the best outcomes observed using PCA polymer without sulfur. This study underscores the effectiveness of incorporating PCA without sulfur, addressing the gap in existing research. Rigorous examination of physical, chemical, and aging properties validated the improvements in asphalt performance, highlighting PCA's potential as a valuable polymer additive for pavement enhancement.

Keyword: Polymers, Asphalt, Rheological and Physical properties, RTFO

1. Introduction

Asphaltic materials encompass a diverse range of intricate organic constituents originating from various sources and serving different industrial purposes. These materials can be categorized into two types: natural and industrial asphalts. Natural asphalts are located in proximity to underground crude-oil deposits, while industrial asphalts are obtained through the fractional distillation of crude oil at temperatures between 300°C and 350°C. These industrial asphalts form a distinct class of construction materials, possessing unique properties and applications [1, 2]. Asphalt binder, a crucial element in asphalt pavement, has consistently been a focal point of research within the field of road construction. It is a complex hydrocarbon with a high molecular weight and can be categorized into four primary components: asphaltene, resins, saturates, and aromatics [3]. A key factor that significantly influences the deformation and flow of bitumen binders is their rheological characteristics, commonly represented by their complex viscosity [4].

The characterization of asphalt binders typically involves measuring various physical and rheological properties such as softening point, penetration, and viscosity [5]. Understanding these properties is vital for designing asphalt mixtures that can withstand the stresses of traffic and environmental conditions, ensuring the longevity and safety of roadways. Despite their viscoelastic behavior under specific conditions, conventional asphalt binders often fall short when exposed to increased traffic volume, heavier loads, and challenging weather conditions. Consequently, researchers have turned their attention to modified asphalt binders. Among the various asphalt modifiers available, polymers have gained widespread usage in recent years. They enhance the binders' elasticity, reduce stress and temperature sensitivity, and thus contribute to improved resistance against rutting and fatigue in asphalt binders [6].

Polymers are high-molecular-weight synthetic materials composed of extended chains comprising carbon and various other elements, including hydrogen, oxygen, chlorine, and nitrogen (C, H, O, Cl, and N). These chains are formed by linking together smaller units called monomers. These monomers are chemical substances derived from crude oil and gases [7]. Polymer-modified binders have proven highly effective in areas subject to substantial stress, including busy street intersections, airports, vehicle weigh stations, and race tracks [8–10]. In the high-quality asphalt pavement industry, polymer-modified asphalt (PMA) has become a widely utilized material. PMA has demonstrated its significance as a vital component in the paving process. Among the various polymers used for asphalt modification, SBS (styrene-butadiene-styrene) is the most commonly used, followed by other polymers like GTR (ground tire rubber), SBR (styrene-butadiene rubber), EVA (ethylene vinyl acetate), polyethylene, (poly vinyl acetate) PVAc, (poly methyl methacrylate) PMMA, cyanoacrylate, and several others [8–11].

1.1. Literature review

In the research conducted by Jing Li et al., a preparation of a composite material known as "Polymethyl Methacrylate-Graphene Nanoparticles (PMMA-GNPs)" was performed to enhance the high-temperature rutting resistance of Styrene-Butadiene-Styrene (SBS) modified asphalt. The researchers utilized a microwave heating emulsion polymerization strategy, significantly reducing the reaction time [15]. In another study, Al-Azzawi et al. utilized polymethyl methacrylate (PMMA) and polyphosphoric acid (PPA) to modify Iraqi asphalt with a penetration grade of 40/50. The key finding of their research revealed a substantial enhancement in the softening point of the asphalt, increasing it from 51°C to 66°C. Furthermore, the modification demonstrated notable

improvements in asphalt elasticity, as well as increased resistance to cracking, rutting, and temperature susceptibility [16]. Salih et al. conducted a study aimed at enhancing the rheological properties of bitumen by introducing polyvinyl acetate (PVAc) and spent lubricating oils. Results from their experiments demonstrated the viability of utilizing waste materials to improve bitumen performance, emphasizing the positive influence on physical properties observed after a one-year aging period [7]. Xu et al. utilized the influence of four preventive maintenance materials on porous asphalt over a nine-year period. The results indicated that the CEM (bonding enhanced material) led to enhanced surface roughness and skidding resistance, while GL1 (cyanoacrylate polymer) and RJ (reduced material) notably improved resistance to raveling and low-temperature cracking [14]. Abd El-Rahman et al. formulated an asphalt emulsion using local asphalt 60/70 (Suez Co.) and incorporated various polymers, including epoxy resin, latex styrene butadiene styrene (SBS), and poly vinyl acetate (PVAc). The investigation included exploring polymer combinations for improved emulsion performance. The findings indicated that the modified emulsions surpassed the unmodified version. Particularly, the emulsion modified with a combination of epoxy resin, latex SBR, and PVAc exhibited superior road performance, showing enhanced resistance to fuel and acid [12]. Chavez-Valencia et al. incorporated a polyvinyl acetate emulsion (PVAc) into a cationic quick-set emulsified asphalt as a means of improving the compressive strengths of cold-mix asphalt (CMA) to combat rutting issues. The adjusted CMA, featuring evenly dispersed polyvinyl acetate microparticles, exhibited a notable 31% enhancement in compressive strengths when compared to the unmodified CMA [17].

In the study by Zhen Fu et al. polyphosphoric acid (PPA) significantly enhances the performance of styrene-butadiene rubber (SBR)-modified asphalt. Molecular dynamics (MD) simulation and experimental analysis reveal that PPA increases the complex modulus (G^*), improving elasticity, stiffness, and rutting resistance. Multiple stress creep recovery (MSCR) shows superior high-temperature performance in PPA/SBR asphalt. Molecular dynamics analysis demonstrates PPA's introduction of phosphorus-containing groups, creating a more ordered asphalt structure. Electron density and potential estimation explain the adsorption mechanism, highlighting molecular-level interactions. In summary, PPA positively influences rheological and chemical properties, improving asphalt performance with enhanced stability and molecular order [18].

From the literature, it was observed that most of them took into account either the physical and rheological or chemical properties of modified asphalt to improve various factors like cracking resistance, fatigue, and temperature sensitivity. Notably, the polymer groups found in the existing literature predominantly center on the interaction between C=C bonds and C=O bonds. Consequently, this research introduces novelty by investigating the application of PCA polymer with alternative interactions, such as C≡N bonds. These interactions, relatively underutilized in asphalt modification, present a promising direction for future research. Additionally, addressing the gap involves aligning the asphalt properties with Iraqi standards, particularly following the RTFO process.

Motivated by the gap highlighted earlier, our research endeavors to tackle the aforementioned challenges by improving the physical and rheological traits, chemical attributes, and aging characteristics of indigenous asphalt grade 40/50 sourced from Lanaz Company in Duhok, Kurdistan Region, Iraq. The focus of the study lies in examining the influence of polymers—specifically PVAc, PMMA, and PCAc—on these properties.

2. Materials and Test methods

2.1. Materials

The local asphalt was obtained from Lanaz Company in Duhok, Kurdistan Region, Iraq. The asphalt grade used in this research was 40/50, and its specific characteristics are detailed in Table 1. The enhancement process involves treating the asphalt material with three different polymers: polyvinyl acetate (PVAc) D3 type, polymethyl methacrylate (PMMA), and cyanoacrylate (PCA). The polymers were converted to powder, which included crushing them either through freezing with liquid nitrogen (used for PVAc and PCA) or via thermal methods (applied to PMMA). Different polymer ratios were added to asphalt samples (0.5%, 1%, 2%, 3%, and 4% by weight). The treatment was carried out at a temperature of 180°C for a duration of 30 minutes. Additionally, microwave treatment was applied at 360 watts for different durations (5, 10, and 15 minutes) due to their positive impact and minimal energy consumption [19]. Furthermore, sulfur was incorporated at a weight ratio of 1%. This addition of sulfur served to generate free radicals, guaranteeing the initiation of the chemical reaction and improving the asphalt's plasticity [20]. At a weight ratio of 0.06%, anhydrous aluminum chloride (AlCl₃) functions as a catalyst, serving as a Lewis acid catalyst and facilitating the interaction between polymer molecules and bitumen molecules [21]. The mixture underwent mechanical stirring at 1000 rpm.

Table (1): Rheological and physical properties of asphalt 40/50.

Original Asphalt	Specification value	Standard specification of road and bridge of Iraq government SORP/R9 [22]
Viscosity at 135 C° (CP)	616.7	-----
Flash point C°	282	>240
Sulfur content %	6.14	<8
Ductility cm , 25 C°	+100	100
Softening point C°	51.4	49-60
asphaltene	21	5-25
Penetration 100g,5s,25C°	49.9	40-60

2.1. Test methods

2.1.1. Conventional bitumen tests

The original and modified asphalt underwent comprehensive analyses of their physical rheological characteristics, encompassing penetration, ductility, and softening points. These evaluations were conducted in

accordance with globally recognized standards, namely ASTM D5 for penetration [23], ASTM D113 for ductility [24], and ASTM D36 for softening [25], along with the calculation of penetration index (PI) [26]. All of these represent the degree to which asphalt binders are sensitive to changes in temperature. To assess the effects of aging, selected asphalt samples were subjected to rolling thin film oven testing (RTFO), following ASTM D 2872-12 [27]. Other analyses such as the Marshall test, were applied to test the flow dynamics and durability of asphalt binder, following the globally accepted ASTM D6927 American standard [28]. The rotational viscosity measurement (RV) test was conducted based on ASTM D4402-06 to assess the flow characteristics of a binder and gauge its level of workability [29]. Other tests included asphaltene measurement based on ASTM D4124 [30], sulfur content determination via ASTM D4294 [31], chemical immersion tests based on ASTM D1664 [32], and flash point evaluation according to ASTM D92 [33].

FTIR was employed [34]. TGA represents fundamental analytical tools employed in the examination of the thermal characteristics and functionality of materials [35]. SEM and EDX are utilized to examine the surface structure and makeup of materials, particularly polymer-modified asphalt used in road construction [36]. Dynamic Shear Rheometer (DSR) testing, as per the AASHTO T315 standard, was carried out to assess bitumen's viscoelastic properties under high and intermediate service temperatures [37]. The Bending Beam Rheometer (BBR) test, designed to evaluate bitumen's resistance to thermal cracking and deformation under low air temperatures, was conducted in adherence to AASHTO T313 [38].

3. Results and discussion

3.1. Rheological Properties

This study employed three distinct types of polymers to alter the rheological characteristics of asphalt.

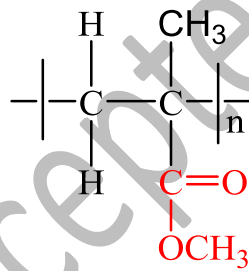
3.1.1. Modification of original asphalt with PMMA

The first polymer was PMMA, which contains three active groups: carbonyl C=O and methoxy groups O-CH₃, which are named ester groups. These groups are responsible for the interactions occurring between the asphalt and the polymer. Figure 1 shows the chemical structure of PMMA [39]. The source of this polymer was waste material obtained from illuminated advertising offices, originating from Sumipex Company in Thailand. Utilizing these additives in the processes contributes to a reduction in environmental pollutants, even at minimal levels. To enhance compatibility between asphalt and the additive, PMMA was subjected to thermal crushing. This process aimed to achieve the lowest possible molecular weight for the polymer. It is noteworthy that the harmony between asphalt and the additive intensifies with a decrease in the molecular weight of the additive [40]. In accordance with the experimental conditions detailed in the experimental section, PMMA was employed. The details of polymer percentages and microwave durations are addressed in Tables 2 and 3, and the result obtained from mixing PMMA is shown in Figures 2 and 3. Diverse polymer percentages were introduced over varying microwave durations, with one set involving solely a catalyst and the other including both a catalyst and sulfur. The outcomes of these mixings illuminate how the polymer impacts the rheological properties of the asphalt binder.

In the experiment set up with 0.5% PMMA and microwave durations of 5 and 10 minutes, both penetration and ductility experienced a decrease, falling beyond the scope defined by the standard specifications for road and bridge construction set by the Iraqi government [22]. In particular, samples labeled As3 and As18, treated with

0.5% PMMA and a 15-minute microwave duration, exhibit excellent penetration and ductility values, aligning with the Iraqi standards. This improvement can be attributed to the favorable interaction between PMMA and the original asphalt under these specific conditions. When considering the addition of the polymer at other percentages (1%, 2%, 3%, and 4%), all instances adhere to the standard specifications for road and bridge construction in Iraq, SORP/R9 [22]. This conformity arises due to the inherent rigidity and lack of flexibility in PMMA. Moreover, the stiffness observed is associated with the interaction between the active side of PMMA and the functional groups present in asphalt. According to FTIR analysis, the C=O group in PMMA may form attachments with the C=O group in asphalt, a connection likely influenced by the disparities in electronegativity between carbon (C) and oxygen (O). This leads to a partial positive charge on C and a partial negative charge on O, facilitating attachment through dipole-dipole interactions [41]. In instances where the PMMA content is at 0.5%, the interaction between asphalt and PMMA is notably weak. Consequently, the rheological properties of the modified asphalt improve. However, as the percentage of PMMA increases, the interaction strengthens, resulting in increased asphalt rigidity. We posit that this heightened interaction is responsible for the asphalt's diminished ability to enhance its rheological properties.

To sum up, among the modified samples, only two, As3 and As18, have successfully met the criteria specified in the treatment of asphalt with PMMA.



PMMA

Figure (1): PMMA Chemical Structure

Table (2): Rheological properties of asphalt treated with PMMA at 180°C in the presence of sulfur 1% by weight and 0.06% by weight of AlCl₃ at (30 min)

Sample NO.	PPMA (wt.%)	Microwave 30min (360W)	Penetration (100gm;5sec;25°C)	Ductility (Cm.25°C)	Softening point (°C)	PI
As0			49.9	+100.0	51.4	-0.860
As1	0.5	5.0	35.3	53.0	55.3	-0.731
As2	0.5	10.0	33.0	58.0	55.4	-0.846
As3	0.5	15.0	43.7	+100.0	55.1	-0.314
As4	1.0	5.0	36.5	43.0	55.4	-0.640
As5	1.0	10.0	35.5	44.0	56.2	-0.530
As6	1.0	15.0	36.3	57.0	55.7	-0.589
As7	2.0	5.0	38.3	36.0	54.0	-0.842
As8	2.0	10.0	35.7	44.0	56.9	-0.374
As9	2.0	15.0	38.1	57.0	55.7	-0.486
As10	3.0	5.0	39.1	36.0	54.0	-0.798
As11	3.0	10.0	34.9	28.0	56.9	-0.422
As12	3.0	15.0	36.7	41.0	56.0	-0.503
As13	4.0	5.0	36.2	28.0	56.0	-0.531
As14	4.0	10.0	30.0	25.0	57.0	-0.707
As15	4.0	15.0	36.0	22.0	59.0	0.065

Table (3): Rheological properties of asphalt treated with PMMA at 180°C in the presence of 0.06% by weight of AlCl₃ at (30 min)

Sample No.	PPMA (wt.%)	Microwave 30min (360W)	Penetration (100gm;5sec;25°C)	Ductility (Cm.25°C)	Softening point (°C)	PI
As0			49.9	+100.0	51.4	-0.860
As16	0.5	5.0	35.6	73.0	54.9	-0.798
As17	0.5	10.0	38.5	69.0	54.5	-0.721
As18	0.5	15.0	45.4	+100.0	53.8	-0.516
As19	1.0	5.0	38.1	49.0	53.1	-1.052
As20	1.0	10.0	40.1	57.0	53.3	-0.900
As21	1.0	15.0	40.4	45.0	54.4	-0.640
As22	2.0	5.0	36.8	43.0	53.8	-0.968
As23	2.0	10.0	40.6	31.0	54.0	-0.718
As24	2.0	15.0	40.3	62.0	54.6	-0.602
As25	3.0	5.0	38.8	21.0	55.5	-0.490
As26	3.0	10.0	38.8	27.0	54.8	-0.640
As27	3.0	15.0	41.0	44.0	54.9	-0.499
As28	4.0	5.0	39.9	25.0	54.5	-0.645
As29	4.0	10.0	38.0	24.0	56.0	-0.429
As30	4.0	15.0	38.2	24.0	57.0	-0.209

3.1.2. Modification of original asphalt with PCA

The PCA polymer was employed as a modification for the asphalt binder. PCA belongs to the cyanoacrylate family, encompassing powerful and fast-bonding adhesives widely applicable in industrial, medical, and household settings. The distinctive property of Polycyanoacrylate, a cyanoacrylate adhesive, is attributed to its cyano group with the chemical formula $C\equiv N$, and the associated esters $R-O-C=OR$ in figure 4 show the chemical structure of PCA. These components play a crucial role in facilitating interactions between the asphalt and the polymers [42]. This specific polymer was sourced from the Ridofix adhesive company in Turkey and underwent crushing through freezing using liquid nitrogen. The impacts of mixing PCA with asphalt are tabulated in Tables 4 & 5, along with visual representations in Figures 5 & 6. As per the Iraqi standards [22], the addition of PCA to the original asphalt reveals that lower percentages have a positive impact on the rheological characteristics, including penetration, ductility, softening point, and penetration index. Four samples were successfully tested, named As33, As46, As50, and As51. However, only As33 and As46 were selected due to the necessity of minimizing polymer percentages for the economic viability of the asphalt binder. In the case of As46, a minimum

percentage of 0.5 was chosen, along with a 5-minute microwave 360W treatment with a catalyst. This choice highlighted a rapid reaction between PCA and asphalt attributed to active groups present in PCA.

Likewise, for As33, the presence of sulfur led to the optimal outcome, with a minimum concentration of 0.5 and a 15-minute microwave 360W treatment resulting in excellent values for penetration, ductility, softening, and penetration index. Other percentages also improved softening to a good extent but did not enhance penetration for some and ductility, primarily due to the stiffness of PCA. Additionally, as indicated by FTIR analysis, the observed peak is associated with the C≡N group, signifying that the interaction primarily stems from the cyano group. This connection is linked to the higher electron density of C≡N compared to C=O. Consequently, the interaction is driven by dipole-dipole forces. In the case of PCA, a lower polymer percentage leads to an enhancement in asphalt properties, aligning them with Iraqi standards. However, as the polymer percentage increases, a robust interaction occurs between the C≡N group and the asphalt's typical functional group, C=O. This interaction impacts the asphalt properties, rendering it more rigid. By comparing a test sample's penetration index with that of a control sample, engineers ensure quality control and identify material variations. Additionally, the penetration index aids in predicting performance, selecting appropriate binders for various projects, assessing durability, and driving research and development in asphalt technology. PI can be calculated according to the following equation [43]:

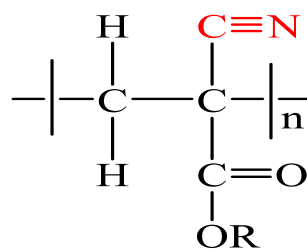
$$\frac{20 - \text{PI}}{10 + \text{PI}} = 50 \left(\frac{\log 800 - \log \text{pent.}}{T_{\text{RB}} - T} \right)$$

PI: Penetration Index.

Pent: Penetration Grade of the asphalt model.

TRB: Softness Grade of the model.

T: The temperature at which penetration is measured, equal to (25) °C. This function is used to determine the sensitivity of the asphalt material to temperature variations[44].



PCA

Figure (4): PMMA Chemical Structure

Table (4): Rheological properties of asphalt treated with PCA at 180°C in the presence of sulfur 1% by weight and 0.06% by weight of AlCl₃ at (30 min)

Sample No.	PCA (wt.%)	Microwave 30min (360W)	Penetration (100gm;5sec;25°C)	Ductility (Cm.25°C)	Softening point (°C)	PI
As0			49.9	+100.0	51.4	-0.860
As31	0.5	5.0	34.7	+100.0	55.0	-0.829
As32	0.5	10.0	34.8	+100.0	56.2	-0.572
As33	0.5	15.0	42.3	+100.0	52.7	-0.922
As34	1.0	5.0	35.4	+100.0	55.0	-0.789
As35	1.0	10.0	35.6	66.0	56.2	-0.525
As36	1.0	15.0	36.7	100.0	54.1	-0.908
As37	2.0	5.0	36.2	80.0	54.6	-0.828
As38	2.0	10.0	37.8	88.0	53.8	-0.913
As39	2.0	15.0	35.3	55.0	56.4	-0.501
As40	3.0	5.0	33.2	67.0	55.8	-0.751
As41	3.0	10.0	33.3	68.0	54.7	-0.976
As42	3.0	15.0	39.3	+100.0	53.2	-0.965
As43	4.0	5.0	34.0	57.0	53.0	-1.303
As44	4.0	10.0	33.6	66.0	55.4	-0.810
As45	4.0	15.0	30.7	50.0	56.4	-0.783

Table (5): Rheological properties of asphalt treated with PCA at 180°C in the presence of 0.06% by weight of AlCl₃ at (30 min)

Sample No.	PCA (wt.%)	Microwave 30min (360W)	Penetration (100gm;5sec;25°C)	Ductility (Cm.25°C)	Softening point (°C)	PI
As0			49.9	+100.0	51.4	-0.860
As46	0.5	5.0	40.9	+100.0	53.0	-0.926
As47	0.5	10.0	35.0	+100.0	55.7	-0.664
As48	0.5	15.0	36.4	77.0	56.2	-0.478
As49	1.0	5.0	36.9	+100.0	54.1	-0.897
As50	1.0	10.0	40.8	+100.0	53.5	-0.818
As51	1.0	15.0	43.4	+100.0	52.5	-0.912

As52	2.0	5.0	39.4	87.0	53.0	-1.004
As53	2.0	10.0	39.8	+100.0	52.0	-1.211
As54	2.0	15.0	42.6	96.0	53.3	-0.770
As55	3.0	5.0	38.2	68.0	53.4	-0.979
As56	3.0	10.0	41.2	91.0	52.6	-1.001
As57	3.0	15.0	36.3	+100.0	53.1	-1.150
As58	4.0	5.0	37.1	77.0	52.0	-1.354
As59	4.0	10.0	38.0	68.0	52.7	-1.147
As60	4.0	15.0	38.3	53.0	53.8	-0.886

3.1.2. Modification of original asphalt with PVAc

The third polymer introduced is polyvinyl acetate (PVAc), which is a clear thermoplastic adhesive formed through the polymerization of vinyl acetate. In PVAc, the active group is the acetate group, However the unique feature of this polymer lies in the ester bonding that occurs between the oxygen (O) and carbon (C) atoms, as illustrated in Figure 7 which depicts the chemical structure of PVAc. This non-toxic adhesive is widely used in various forms such as wood glue, white glue, carpenter's glue, school glue, or PVAc glue. It is notably one of the most commonly used water-dispersed adhesives [45]. The source of this polymer was the VODA BOND company in Turkey, which provided a D3 type wood glue known for its water resistance. The polymer was pulverized through cryogenic freezing using liquid nitrogen. The outcomes of incorporating PVAc for the enhancement of the original asphalt are presented in tables (6 and 7) and figures (8 and 9). In the context of PVAc, a total of nine samples were successfully generated. Among these, two samples involved the incorporation of sulfur, denoted as As63 and As69, while the remaining samples were sulfur-free, and involved only the addition of catalyst and PVAc. These latter samples were identified as As77, As83, As84, As87, As88, As89, and As90. However, due to economic considerations, only two samples were selected for further evaluation, namely As63 and As77, as mentioned earlier.

The outcomes, as depicted in tables 6 and 7 and figures 8 and 9, reveal the positive impact of PVAc addition on the rheological attributes of the original asphalt. With the inclusion of sulfur, there was a reduction in softening, a simultaneous enhancement in penetration, and consistent ductility. Similarly, the introduction of a catalyst without sulfur had minimal impact on ductility yet it led to improvements in both softening and penetration. Moreover, this pertains to the interaction between the C=O groups in PVAc and those in the asphalt structure, as indicated by FTIR analysis. The interaction is observed in the polymer as a chemical interaction, while in the cases of PMMA and PCA, it manifests as a physical interaction. These distinctions will be elaborated upon in the explanation of the FTIR figures. When sulfur is introduced, the chemical bonding is strengthened, creating robust bonds through the free radicals produced during sulfur decomposition. This enhanced bonding may potentially interfere with the interaction of C=O groups present in both PVAc and asphalt, consequently increasing the

asphalt's rigidity. Conversely, in the absence of sulfur when adding PVAc, the interaction is weaker, with only the C=O groups on both PVAc and asphalt engaging in dipole-dipole interactions.

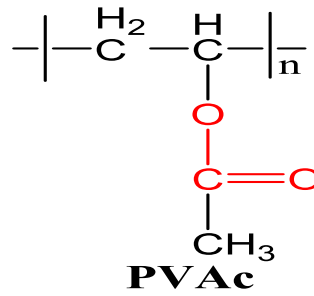


Figure (7): PVAc Chemical Structure

Table (6): Rheological properties of asphalt treated with PVAc at 180°C in the presence of sulfur 1% by weight and 0.06% by weight of AlCl₃ at (30 min)

Sample No.	PVAc (wt.%)	Microwave 30min (360W)	Penetration (100gm;5sec;25°C)	Ductility (Cm.25°C)	Softening point (°C)	PI
As0			49.5	+100.0	51.4	-0.878
As61	0.5	5.0	38.1	+100.0	55.7	-0.486
As62	0.5	10.0	37.2	+100.0	54.6	-0.772
As63	0.5	15.0	45.3	+100.0	50.7	-1.244
As64	1.0	5.0	39.5	+100.0	54.0	-0.777
As65	1.0	10.0	32.6	90.0	54.0	-1.167
As66	1.0	15.0	30.7	+100.0	55.2	-1.029
As67	2.0	5.0	36.2	+100.0	53.3	-1.112
As68	2.0	10.0	38.0	+100.0	53.8	-0.902
As69	2.0	15.0	40.1	+100.0	51.7	-1.265
As70	3.0	5.0	32.5	95.0	54.1	-1.151
As71	3.0	10.0	34.7	77.0	56.0	-0.619
As72	3.0	15.0	34.0	73.0	54.1	-1.063
As73	4.0	5.0	32.1	79.0	55.0	-0.985
As74	4.0	10.0	33.3	59.0	54.7	-0.976
As75	4.0	15.0	37.8	75.0	52.5	-1.203

Table (7): Rheological properties of asphalt treated with PVAc at 180°C in the presence of 0.06% by weight of AlCl₃ at (30 min)

Sample No.	PVAc (wt.%)	Microwave 30min (360W)	Penetration (100gm;5sec;25°C)	Ductility (Cm.25°C)	Softening point (°C)	PI
As0			49.9	+100.0	51.4	-0.860
As76	0.5	5.0	47.4	+100.0	51.2	-1.024
As77	0.5	10.0	44.8	+100.0	52.0	-0.959
As78	0.5	15.0	39.1	+100.0	54.9	-0.602
As79	1.0	5.0	39.7	+100.0	52.4	-1.125
As80	1.0	10.0	38.5	+100.0	52.1	-1.256
As81	1.0	15.0	36.0	+100.0	53.3	-1.123
As82	2.0	5.0	39.2	+100.0	51.2	-1.428
As83	2.0	10.0	41.2	+100.0	52.2	-1.093
As84	2.0	15.0	41.0	+100.0	51.3	-1.312
As85	3.0	5.0	39.6	+100.0	51.4	-1.360
As86	3.0	10.0	37.8	+100.0	52.0	-1.316
As87	3.0	15.0	41.1	+100.0	51.8	-1.190
As88	4.0	5.0	40.5	+100.0	52.8	-0.992
As89	4.0	10.0	41.2	+100.0	53.3	-0.842
As90	4.0	15.0	44.9	+100.0	52.1	-0.931

3.2. Optimization

In this stage, the best six samples were chosen (As3, As18, As33, As46, As63, and As77) for further testing. As0 was selected as a control and compared with the other modified samples. When comparing the softening and penetration values of the modified asphalt with the original asphalt, As0 as shown in table 8, the improvements were evident. Interestingly, ductility remained unaffected. This suggests that adding a small amount of polymers to the regular-grade 40/50 asphalt can be a promising way to enhance it. The modified asphalt could display strong resistance to acid rain, high temperatures, flowing well, staying stable, and aging.

Table (8): Optimal selections from the study

Samples No.	PMMA, PCA, PVAc (wt.%)	Microwave 30min (360W)	Penetration (100gm;5sec;25°C)	Ductility (Cm.25°C)	Softening point (°C)	PI
As0			49.9	+100.0	51.4	-0.860
As3	0.5	15.0	45.4	+100.0	53.8	-0.314
As18	0.5	15.0	43.7	+100.0	55.1	-0.516
As33	0.5	15.0	42.3	+100.0	53.0	-0.929
As46	0.5	5.0	40.9	+100.0	52.7	-0.926
As63	0.5	15.0	45.3	+100.0	52.0	-1.244
As77	0.5	10.0	44.8	+100.0	50.7	-0.959

3.3. Chemical immersion testes

The chemical immersion test was conducted to evaluate the adhesion strength between asphalt and aggregate when exposed to sodium carbonate (Na_2CO_3). This test aims to determine the asphalt's ability to withstand acid rain and high temperatures, as indicated by the Riedel and Weber (R&W) number [32]. This number represents the point at which asphalt begins to detach from the aggregate interface, a phenomenon known as stripping. The procedure of immersion was conducted according to the literature [46].

Based on the findings presented in Table 9, it can be observed that at R&W number 5, with the addition of 0.328 grams of Na_2CO_3 , the original asphalt detached from the aggregates. However, the modified asphalt experienced detachment at R&W numbers 6-8. This implies that the modified asphalt demonstrated higher resilience against both acid rain and elevated temperatures.

Table (9): Chemical Immersion test of modified and original asphalt

Name of samples	R&W No	R&W No for original asphalt	R&W No for modified asphalt	% Na_2CO_3
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	1		0.025
	2		0.041
	3		0.082
	4		0.164
As0	5	5	0.328
As3	6		0.656
As33	7		1.312
As63	7		1.312
As77			
As46	8	8	2.624
As18			
	9		5.248

3.4. Marshal test

The Marshall test represents a comprehensive strategy for mechanical properties that are crucial for designing asphalt pavement mixes. By following a systematic procedure, it determines the optimal asphalt content for a mixture, ensuring the highest level of strength and stability under various loads [47]. Table 10 illustrates a notable enhancement in the stability of modified asphalt compared to that of the original variant. Furthermore, the flow characteristics fall within the range prescribed by the SORP/R0 standard. Consequently, this outcome significantly enhances the asphalt pavement's resistance to deformations induced by the repetitive stresses imposed by vehicular traffic on road surfaces. By effectively mitigating the deleterious effects of these loads, this approach not only improves the overall performance and durability of the pavement but also results in a considerable extension of the lifespan of roadways.

Table (10): Marshal test for modified and original asphalt

Sample NO.	Stability KN	Flow mm	SORP/R9	
			Stability KN	Flow mm
As0	10.5	3.5		
As3	12.1	2.8		
As18	14.1	3.6		
As33	15.5	3.6	Min 8.0	2-4
As46	13.9	3.8		
As63	14.3	3.6		
As77	13.2	3.3		

3.5. Rolling thin film oven test RTFO

This test is utilized to assess the combined impact of heat and air on a thin film of bitumen or bituminous binder. Its objective is to replicate the solidification process that bituminous binders undergo during mixing, transportation, and compaction. This process helps determine the longevity of road surfaces [48]. According to Table 11, the original asphalt As0 has not meet the standard specifications set by the Iraqi government for roads and bridges [22]. Similarly, the asphalt modified with PMMA As3, As18, and PVAc, along with sulfur As63, also falls short of meeting these standards. However, the asphalt modified with PCA As33, As46, and PVAc As77 has demonstrated success, exhibiting excellent values in terms of penetration, ductility, and softening [49]. This suggests that the road's lifespan could be prolonged, as the asphalt mixture displays enhanced resistance to processes that lead to hardening, such as transportation and compaction [50].

Table (11): RTFO test for modified and original asphalt

Sample NO	Penetration (100gm;5sec;25°C)	SORP/R9	Ductility (Cm.25°C)	SORP/R9	Softening (°C)	SORP/R9
As0	50.5		60.0		58.0	
As3	53.5		26.0		60.0	
As18	48.4		22.0		61.5	
As33	62.8	Min 55	37.0	Min 25	58.6	-----
As46	67.4		58.0		57.5	
As63	42.1		20.5		61.0	
As77	55.8		41.0		59.0	

3.6. Rheological and physical properties of original and modified asphalt

As shown in Table 12, numerous alterations were revealed in both the rheological and physical attributes of the original asphalt. The changes in rheological properties were previously outlined. The modifications in physical properties encompass several aspects. With regards to viscosity, Table 12 demonstrates that the addition of PVAc As77 leads to a reduction in viscosity. This reduction may not be conducive to asphalt enhancement. Conversely, the incorporation of PCA As33 and As46 results in an elevation of viscosity, which indicates a favorable enhancement of the asphalt pavement. With respect to flash point, there is a notable increase in the flash point for all samples (As77, As46, and As33) contributing positively to safety. Moreover, when considering the instances of As77 and As33, the introduction of sulfur results in an increase in the sulfur content within the asphalt pavement. Nonetheless, this rise may not necessarily be beneficial for enhancing the asphalt's physical characteristics since elevated sulfur levels can have an adverse effect on the overall performance of the asphalt mixture. In contrast, As46 demonstrates a decrease in sulfur content, leading to an improvement in the performance of the asphalt. Additionally, asphaltene content experiences an increase across all instances. This phenomenon can be attributed to the mixing and aging processes occurring during asphalt modification. Notably, for As77, the asphaltene content surpasses the range specified in the standard regulations of Iraqi road and bridge

authorities [22]. This excess leads to asphalt rigidity, which is undesirable for pavement application. However, both As33 and As46 exhibit asphaltene percentages within acceptable limits, rendering them suitable for pavement use [51]. In conclusion, the optimal choice for asphalt pavement is As46 due to its commendable physical and rheological attributes.

Table (12): Rheological and physical properties of original and modified asphalt

Sample No.	As0	As33	As46	As77	SORP/R9
Viscosity at 135 C° (CP)	616.7	635.0	618.3	611.7	-----
Flash point C°	282.0	298	302	310	>240
Sulfur contents %	6.14	7.25	5.6	6.33	<8
Ductility cm, 25 C°	+100.0	+100.0	+100.0	+100.0	+100
Softening point C°	51.4	53.0	52.7	50.7	49-60
Asphaltene %	21.0	24.2	22.8	30.6	5-25
Penetration 100g,5s,25C°	49.9	42.3	40.9	44.8	40-60

3.7. Performance grade for original and modified asphalt

Recently, the established technique for appraising the low-temperature PG of asphalt binders has been the BBR test. Conversely, the DSR is a widely employed and efficient approach for determining the PG in conditions spanning intermediate to high temperatures, specifically employed for examining the rheological properties of modified asphalt [52]. The procedure entails subjecting samples to an RTOF furnace and PAV in accordance with PG standard M320 [53]. The Dynamic Shear Rheometer (DSR) test has gained recognition for assessing the viscoelastic properties of bitumen under conditions of high and intermediate service temperatures. As stipulated by the AASHTO T315 standard, the DSR test involves the determination of the complex modulus (G^*) and the phase angle ($\sin \delta$) to evaluate the viscoelastic characteristics of binders and their performance within the realm of elevated and moderate temperatures [31]. These measured parameters play a crucial role in foreseeing a binder's ability to withstand fatigue-induced cracking and resist rutting within asphalt pavements. The initial (unaged) binder is required to exhibit a $G^*/\sin \delta$ value of at least 1.00 kPa, while the same binder, after undergoing aging through the RTFOT (Rolling Thin Film Oven Test), should display a minimum of 2.20 kPa. Additionally, the $G^*/\sin \delta$ value is instrumental in addressing fatigue concerns at intermediate temperatures, utilizing both PAV (Pressure Aging Vessel) and RTFOT-aged binders. As per the specifications, the $G^*/\sin \delta$ value must not exceed

5000 kPa. In terms of fatigue resistance, optimal outcomes are linked to low $\sin \delta$ and low G^* values. Conversely, to enhance resistance against rutting, the ideal scenario involves low $\sin \delta$ coupled with high G^* values [54].

Analysis of the outcomes from Tables 13 and 14 indicates that the original asphalt grade As0 and the modified asphalts As33 and As77 all exhibit the same PG of (70-16). This suggests that the introduction of polymers to As0 has a marginal impact. However, As46 achieves a grade of (70-22), indicating a positive enhancement of As0 by incorporating a small percentage of PCA polymer without the addition of sulfur.

As shown in table 13, DSR results are contingent upon the $G^*/\sin \delta$ value. A rise in $G^*/\sin \delta$ signifies an augmentation in the asphalt pavement's resistance to rutting or permanent deformation. For As33 and As46, $G^*/\sin \delta$ values increase, while for As77, they decrease across all conditions, both before and after aging, including after PAV exposure.

The BBR (Bending Beam Rheometer) test was created to assess the ability of bitumen to withstand thermal cracking and ascertain its resistance to deformation under low air temperatures. When bitumen exhibits high creep stiffness, it indicates a propensity for breakage, consequently elevating the risk of cracking [55]. To mitigate this vulnerability, the BBR test standard AASHTO T313 enforces a maximum limit of 300 MPa on the creep stiffness of bitumen. The m-value parameter is utilized to regulate the rate of bitumen stiffness alteration over time in colder conditions. A higher m-value is preferred, as it signifies that the binder's stiffness will transition rapidly with decreasing temperatures and the accumulation of thermal stresses [56]. A notable speed of stiffness alteration implies that the stiffness could escalate to a point where low-temperature cracking becomes plausible. To ensure adequate resistance against cracking at low temperatures, the m-value must surpass 0.300 [57].

As in Table 14, it becomes evident that at -16°C , As33 demonstrates nearly identical stiffness and m-values. In contrast, As46 and As77 showcase the lowest stiffness values, with m-values remaining relatively consistent. As46, with its notably low values among all samples (As0, As33, and As77), exhibits robust resistance to low temperatures, warranting a downgrade to grade -22°C . Consequently, As46 emerges as the optimal choice for enhancing the properties of As0. The tests were conducted according to the standards of AASHTO T315-12 [37], for DSR and AASHTO T313-12 [38], for BBR. Finally, Figure 7 describes the overall proposed methodology that has been used in this study.

Table (13): Results of the DSR Test for Original and Modified Asphalt PG (70-16) (70-22)

Sample No.	Standard specifications	DSR ($G^*/\sin \delta$), kPa.		Requirement	
		Temperature	Result		
As0	AASHTO T315-12	70.0 °C	1.0842	1 kPa, Min	
		76.0 °C	0.5293		
As33		70.0 °C	1.2804		
		76.0 °C	0.6169		
As46		70.0 °C	1.2335		
		76.0 °C	0.5999		
As77		70.0 °C	1.0642		
		76.0 °C	0.5819		
Aging RTFO					
As0		70.0 °C	2.7790		2.2 kPa, Min
		76.0 °C	1.2877		
As33		70.0 °C	3.2175		
	76.0 °C	1.4905			
As46	70.0 °C	2.9220			
	76.0 °C	1.3334			
As77	70.0 °C	2.6859			
	76.0 °C	1.2548			
Aging PAV					
As0	28.0 °C	5175.46	5000 KPa, Max		
	31.0 °C	3723.17			
As33	28.0 °C	5339.95			
	31.0 °C	4695.23			
As46	28.0 °C	4575.72			
	28.0 °C	4115.74			
As77	28.0 °C	4115.74			
	31.0 °C	3526.39			

Table (14): Results of the BBR Test for Original and Modified Asphalt PG (70-16) (70-22)

Sample No.	Standard specifications	BBR			Requirement	
		Temperatures	Stiffness	m-value	Stiffness	m-value
As0		-16.0 °C	120.6040	0.343364		
		-22.0 °C	246.0799	0.294397		
As33	AASHTO T313-12	-16.0 °C	120.9660	0.333945		
		-22.0 °C	247.4730	0.295667	≤ 300	> 0.3
As46		-16.0 °C	114.1896	0.338118	MPa	
		-22.0 °C	251.7316	0.300653		
As77		-16.0 °C	116.7785	0.331528		
		-22.0 °C	230.1580	0.289103		

3.8. Fourier-Transform Infrared Spectroscopy (FTIR)

FTIR is a versatile analytical technique essential for the analysis of polymer-modified asphalt. It is invaluable for multiple purposes, including analyzing chemical composition, ensuring quality control in production, quantifying polymer content, studying molecular-level polymer interactions, evaluating aging and durability, and comparing different polymers for suitability [58]. In this study, we examined three types of polymers, namely PMMA, PCA, and PVAc. The findings revealed that PMMA did not contribute to improving the asphalt properties to meet the Iraqi standard. Consequently, we deemed it unnecessary to delve into the analysis of the interaction between PMMA and asphalt. Our focus shifted to analyzing only those samples that enhanced asphalt properties in line with the Iraqi standard, aligning with the primary objective of our research.

Before scrutinizing the results, it was imperative to identify the stretching regions for the ester group present in both polymer types (PVAc and PCA) through FTIR analysis. Typically, the characteristic absorption for the carbonyl group (C=O) in esters occurs around $\approx 1735 \text{ cm}^{-1}$, while the COO- group exhibits absorption in the range of $1620\text{-}1550 \text{ cm}^{-1}$ [59]. The stretching region for the C≡N group is identified by an absorption band around $\approx 2200 \text{ cm}^{-1}$ in the FTIR spectrum [60]. We selectively considered three main samples, namely As33, As46, and As77, for further analysis. In the case of As33, sulfur underwent a process alongside As0 and PCA. At a temperature of ≈ 110 degrees, sulfur begins to decompose, producing free radicals [20]. A stretching peak appeared in the region of 2250, corresponding to the C≡N in the FTIR of PCA. This peak did not appear in the same region for the original asphalt As0 but manifested in As33 at around 2260, indicating an interaction between As0 and PCA. This interaction may be attributed to the free radical of sulfur decomposition, as the C≡N has more electron density, allowing the free radical to attach to the triple bond of the C≡N.

Furthermore, in the region of 1754 for PCA and 1747 for As0, a peak disappeared, and the peak at 1622 in As0 shifted to 1600 in As33. This suggests the possibility of the double bond π bond of C=O inductive effect, leading to partial negativity on O- and partial positivity on carbon +C, indicating dipole-dipole interaction. The

most accurate representation of this interaction involves T% for both As0 and PCA. The T% in the region of 1745 values decreases for As33 compared to As0 and PCA. As a result, this interaction is supported by two types of active groups. Such interactions contribute to the observed modifications in the PCA and asphalt interactions. Figure 10 visually represents the key findings from the FTIR analysis of As33.

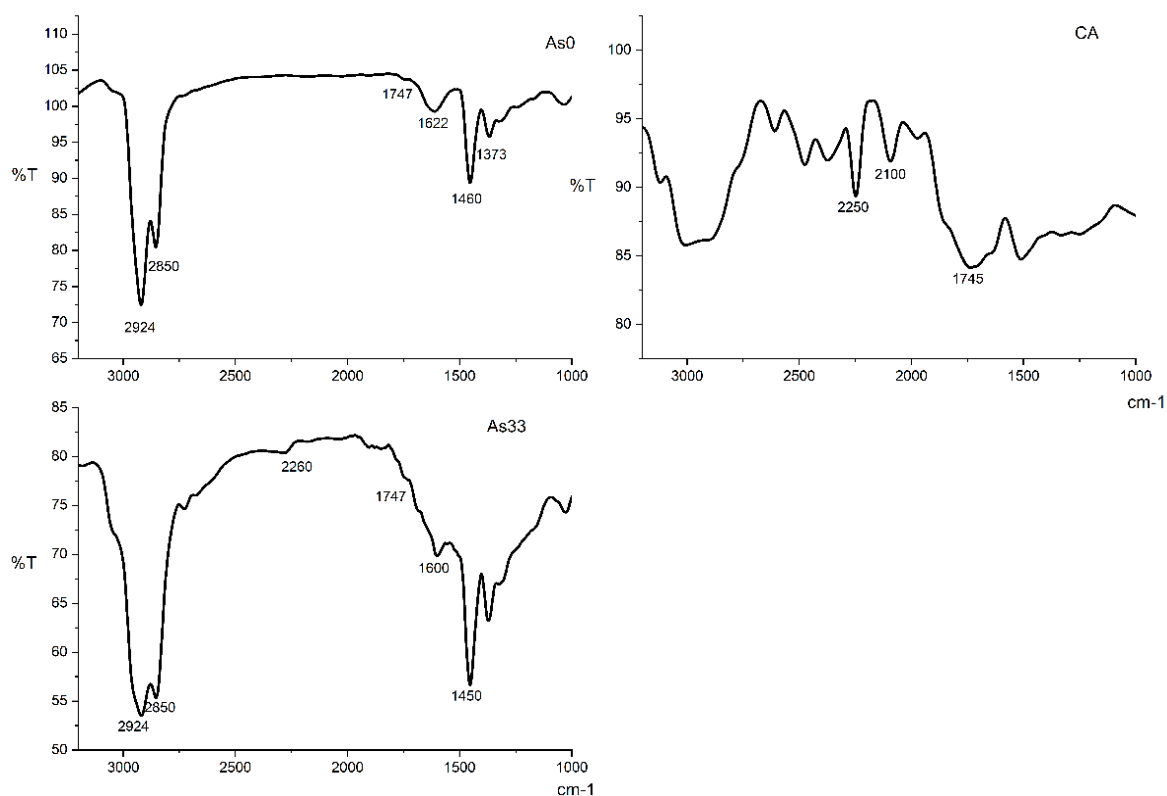


Figure (10): FTIR chart for analysis PCA, As0 and As33

In the case of As46, Figure 11 demonstrates the absence of intensity in the 2250 region, possibly attributed to the lack of sulfur. However, a crucial observation is the placement of the carbon atom within the active groups of C=O, specifically in the configuration $N\equiv C-C-C=O$. In this structure, there is significant electron density, leading to a high Partial +C in the C=O region present in the PCA. This high electron density is conducive to interaction with COO- present in As0, and it is likely that this group is fully engaged. This interaction is believed to contribute to As46 displaying superior enhancement compared to AS33 and As77. A noteworthy observation is the shift from 1622 in As0 to 1600 in As46, as previously mentioned. This shift is attributed to the interaction between the C=O of As0 and the C=O of PCA, resulting in the formation of COO. Consequently, the double bond partially converts to a single bond. Additionally, the shift from 1622 for As0 to 1600 for As46 indicates such interactions occurring in the C=O group or COO- group. The most accurate representation of this interaction involves T% for both As0 and PCA. The T% in the region of 1745 values decreases for As46 compared to As0 and PCA. According to the FTIR analysis, a decrease in T% suggests increased absorption of infrared radiation, indicating a heightened interaction between As0 and PCA. In summary, the interaction in this context primarily involves the ester group in both As0 and PCA. Figure 11 visually summarizes the key findings obtained from the FTIR analysis of As46.

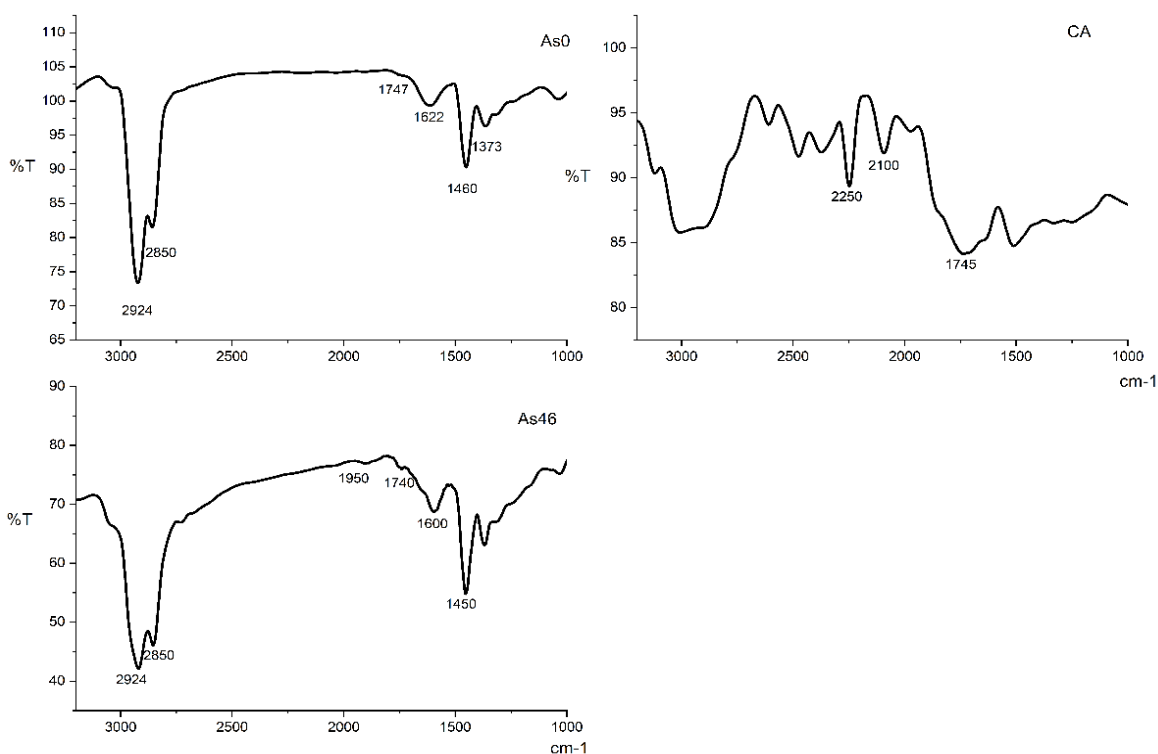


Figure (11): FTIR chart for analysis PCA, As0 and As46

Moreover, it is anticipated that the conduct observed in As77 closely mirrors that of As46. This similarity is ascribed to the fact that As77, with only one active group, promotes interaction between the carbonyl group of PVAc and the carbonyl group of As0 through dipole-dipole interactions. However, the differentiation between As46 and As77 lies in the positioning of the carbon atom center in As77, which is farther away from the electron density of C=O, as depicted in Figure 7. The partially positive charge on the carbon +C in As77 is less than the +C observed in As46. Additionally, the shift from 1622 for As0 to 1600 for As77 indicates such interactions occurring in the C=O group or COO- group. The most accurate representation of this interaction involves T% for both As0 and PVAc. The T% in the region of 1745 values decreases for As77 compared to As0 and PVAc. As a result, the intensity of As77 is lower than both As33 and As46. Hence, we deduce that this distinction could be the cause of the slight enhancement of As77 over As0. For a visual representation of the critical findings obtained from the FTIR analysis of As77, please refer to Figure 12.

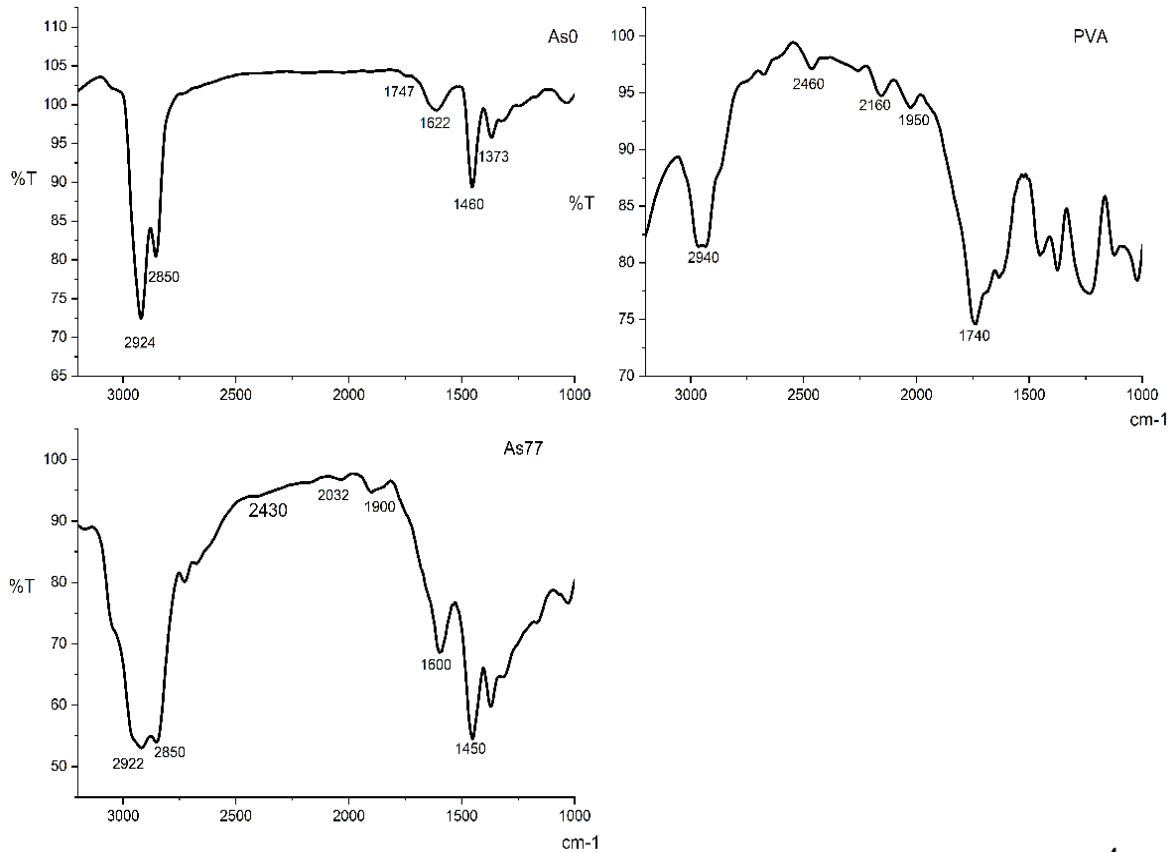


Figure (12): FTIR chart for analysis PCA, As0 and As77

3.9. Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Spectroscopy (EDX)

SEM and EDX play a crucial role in the field of materials science and various research domains. They are utilized to examine the surface structure and makeup of materials, particularly polymer-modified asphalt used in road construction [36]. The SEM test results reveal distinctive interactions in various asphalt samples. In the SEM analysis, (a) As0 exhibits no discernible particles interacting with the asphalt, resembling a black mirror. Conversely, in figure (b) for As33, a conspicuous interaction is observed between As0 and PCA, with particles exhibiting fluctuations alongside the asphalt binder. Moving to figure (c) for As46, the interaction between As0 and PCA appears more homogeneous than in As33. However, in figure (d) for As77, an interaction is present resembling accumulation, and PVAc appears incompletely dispersed. This might be attributed to factors like mixing time or interactions between active groups present in both As0 and PVAc.

The table EDX findings reveal a reduction in the carbon weight percentage when compared to As0. This implies the potential evaporation of low-molecular-weight compounds within the asphalt binder due to heating. Consequently, this phenomenon might be linked to the decline in asphalt's carbon atom percentage [61]. Regarding the weight percentage of oxygen, it increases for As33 and As77, indicating active group interactions between

asphalt and polymers. In As46, the weight percentage surpasses that of As33 and As77, underscoring enhanced interaction with As0. Increased interactions between polymers and asphalt contribute to improved resistance against rutting, fatigue, and deformation.

Additionally, in the case of sulfur, a gradual increase in the weight percentage within a limited range enhances asphalt binder properties [36]. To visualize the key discoveries derived from the SEM analysis of As0, As33, As46, and As77, see Figure 4-11. Additionally, the results of the EDX analysis are presented in Table 4-14.

Table (15): EDX analysis to compare and present the elemental composition of both the original and modified forms of asphalt

Element	Wt. % As0	Wt. % As33	Wt. % As46	Wt. % As77
C	92.89	91.66	90.85	91.54
O	0.76	1.14	2.00	1.28
S	5.97	7.58	7.15	7.17

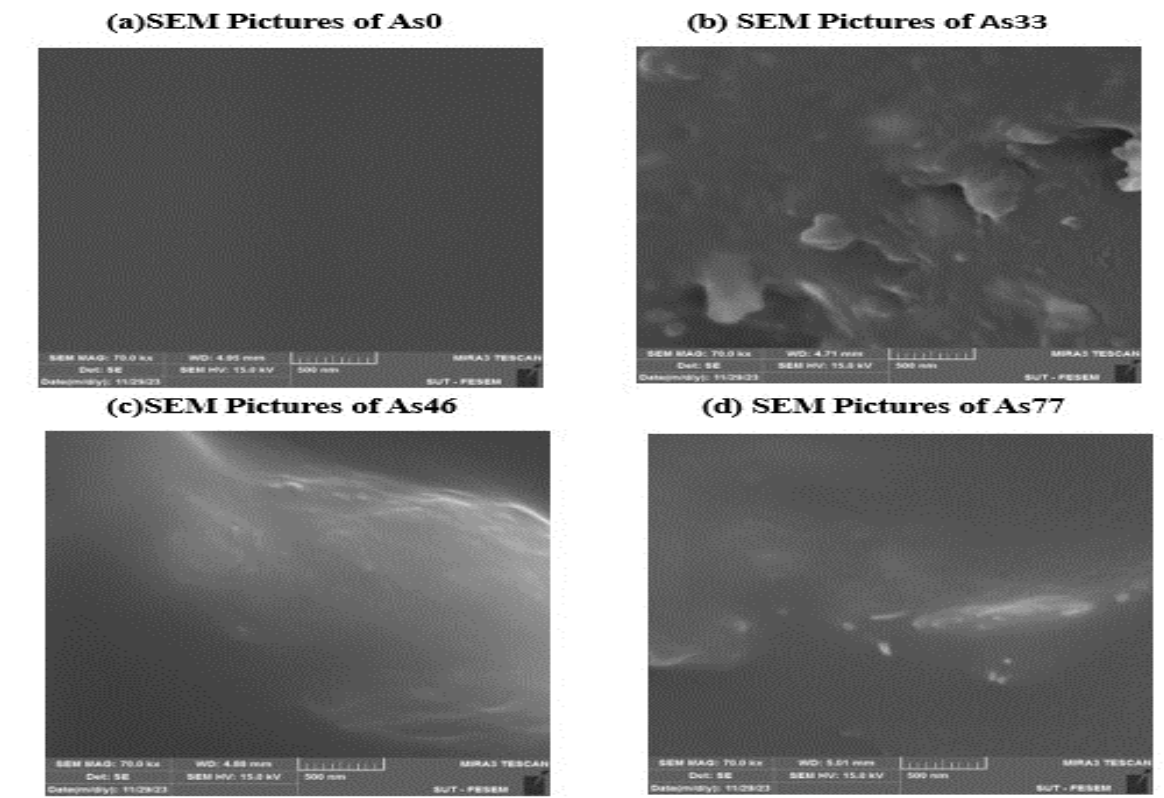


Figure (13): SEM analysis for As0, As33, As46 and As77

3.10. Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC)

Thermogravimetric analysis (TGA) was utilized to evaluate the rate of thermal decomposition in both unaltered and altered asphalt. The investigation focused on understanding the impact of polymer introduction on

the thermal stability of asphalt, exploring whether it has a positive or negative influence. Additionally, the study revealed the degradation occurring over time and temperature due to debonding processes [62]. The binder analysis in Figure 4-13 revealed variations in time and temperature for a 4% weight loss across all samples. For instance, in the case of unmodified asphalt (As0), the time and temperature recorded for a 4% weight loss were 13.10 minutes and 290°C, respectively. Conversely, for As33, the corresponding values were 14.33 minutes and 314°C, indicating enhanced thermal stability and increased duration for weight loss. As46 exhibited even greater resistance to decomposition, with a temperature of 341°C and a time of 16.27 minutes compared to As0. As77 mirrored the behavior of As33, with a temperature of 313°C and a time of 14.72 minutes, indicating improved resistance to high temperatures and prolonged stability. In summary, As46 demonstrated superior enhancements over As0 when compared to As33 and As77, suggesting that the addition of PCA without sulfur yields greater improvements than incorporating PCA with sulfur or adding PVAc to As0. It is observed that the thermal decomposition of PCA at a weight loss of 4% occurs at 180°C, while for PVAc, it takes place at 188°C. Although both exhibit nearly identical decomposition temperature rates, the findings suggest that the interaction between PCA and As0 is stronger than that between PVAc and As0.

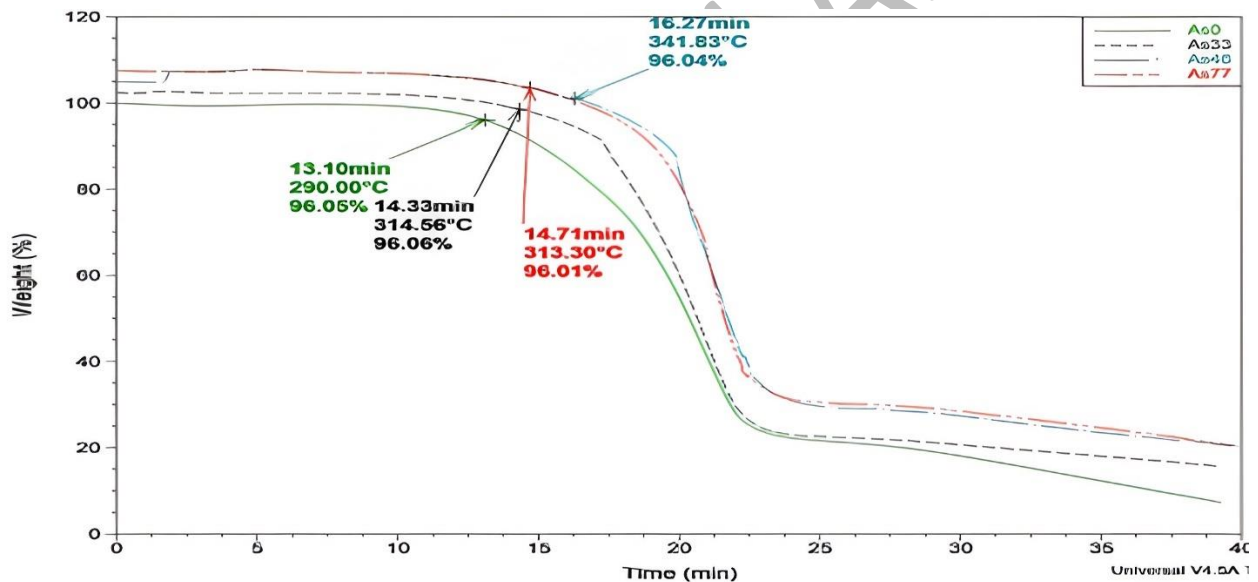


Figure (14): TGA analysis for As0, As33, As46, As77, PVAc, and PCA

4. Conclusion

This study explores the impact of PMMA, PCA, and PVAc additives on bitumen performance. The findings reveal that these additives enhance asphalt stiffness and reduce temperature susceptibility, making modified binders advantageous in hot climates. Chemical immersion tests demonstrate improved resistance against acid rain and elevated temperatures, while Marshal tests indicate enhanced crack resistance and prolonged road lifespan with PMMA, PCA, and PVAc modifications. TFOT tests result in improved aging properties, enabling modified asphalt to meet Iraqi standards, withstand heavy loads, and extend operational life. However, excessive asphaltene content due to PVAc exceeds standards, leading to asphalt hardening and increased road cracking susceptibility. Sulfur addition with PCA and PVAc shows increased overall sulfur content, with favorable chemical

reactions noted without sulfur, reducing phase separation. PG tests suggest improved rutting resistance with PCA and decreased G^* values with PVAc, indicating no enhancement in the original asphalt. BBR tests at -16°C reveal improved low-temperature cracking resistance with PCA without sulfur, while PCA with sulfur and PVAc show minimal improvement. Microwave radiation reduces environmentally harmful gas emissions, contributing to cost savings through extended road lifespan with polymer introduction. Analytical techniques such as FTIR, SEM, EDX, XRD, and TGA provide insights into the interactions between original asphalt and polymers, supporting the overall enhancement of asphalt properties with the addition of PCA and PVAc.

Further research in this area could optimize additive ratios to avoid asphalt hardening issues and extend road lifespans. Long-term field trials are needed to assess durability and environmental impact, while fine-tuning polymer properties can address compatibility challenges. In-depth analysis of chemical reactions and exploration of alternative polymers will enhance understanding and broaden options. Additionally, an economic analysis is crucial for assessing the cost-effectiveness of road construction.

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Appendix

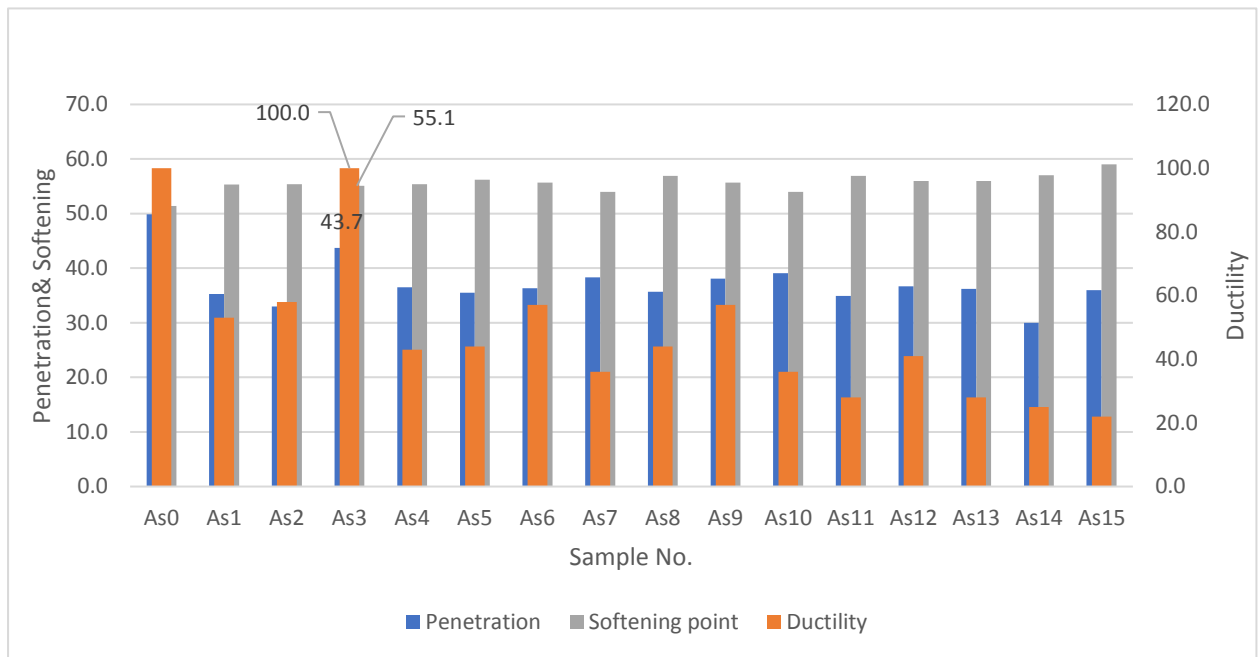


Figure (2): Rheological properties of asphalt treated with PMMA at 180°C in the presence of sulfur 1% by weight and 0.06% by weight of AlCl₃ at (30 min)

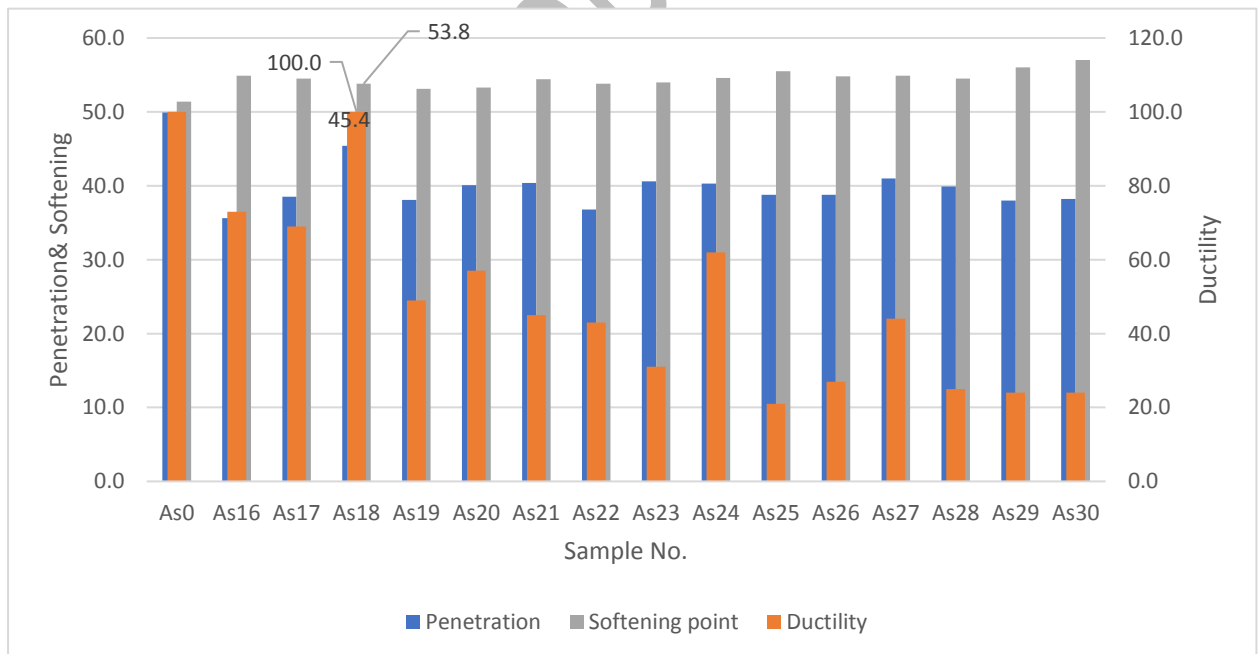


Figure (3): Rheological properties of asphalt treated with PMMA at 180°C in the presence of 0.06% by weight of AlCl₃ at (30 min)

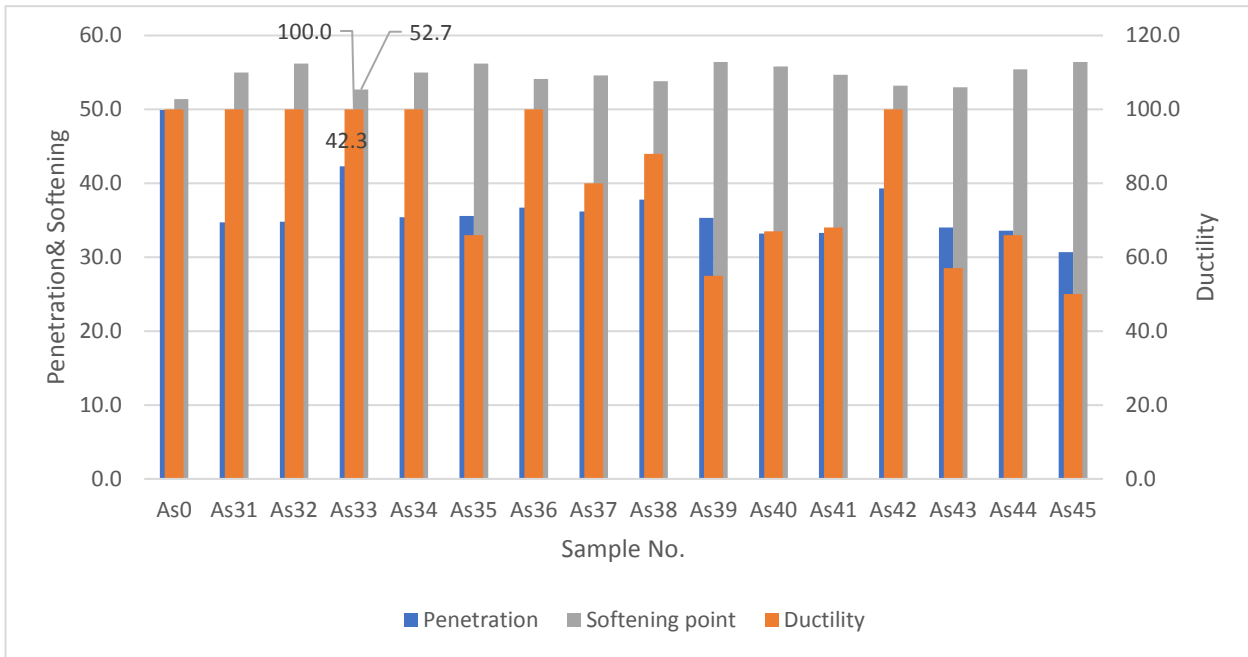


Figure (5): Rheological properties of asphalt treated with PCA at 180°C in the presence of sulfur 1% by weight and 0.06% by weight of AlCl₃ at (30 min)

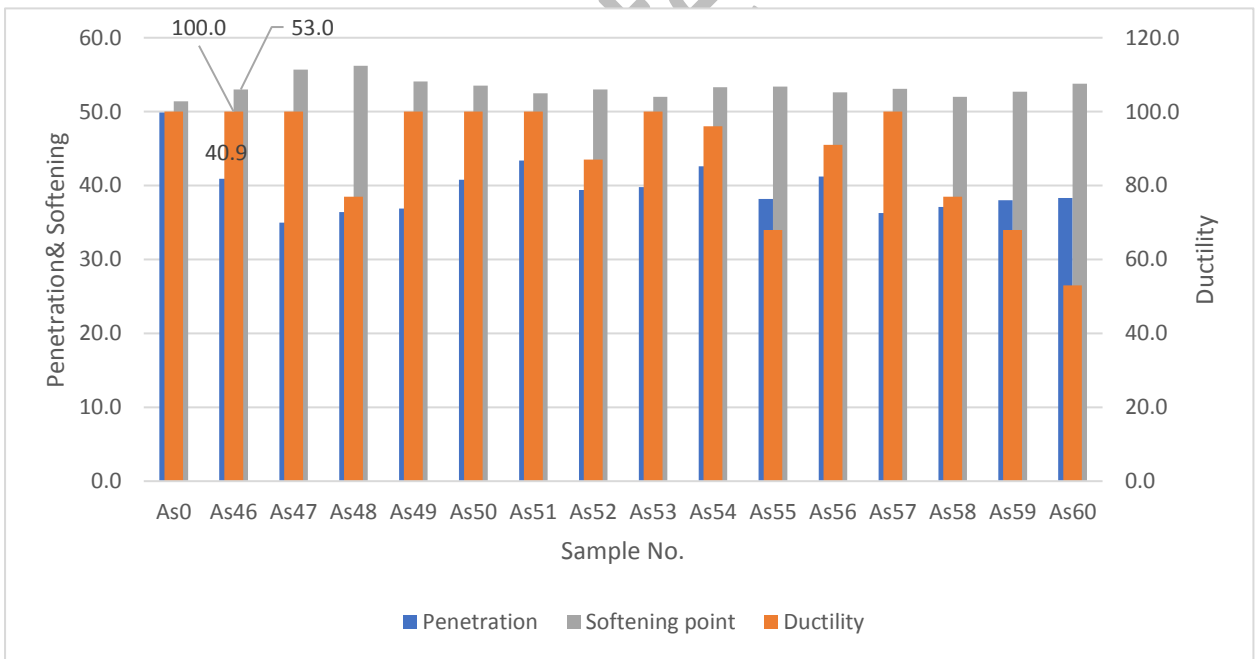


Figure (6): Rheological properties of asphalt treated with PCA at 180°C in the presence of 0.06% by weight of AlCl₃ at (30 min)

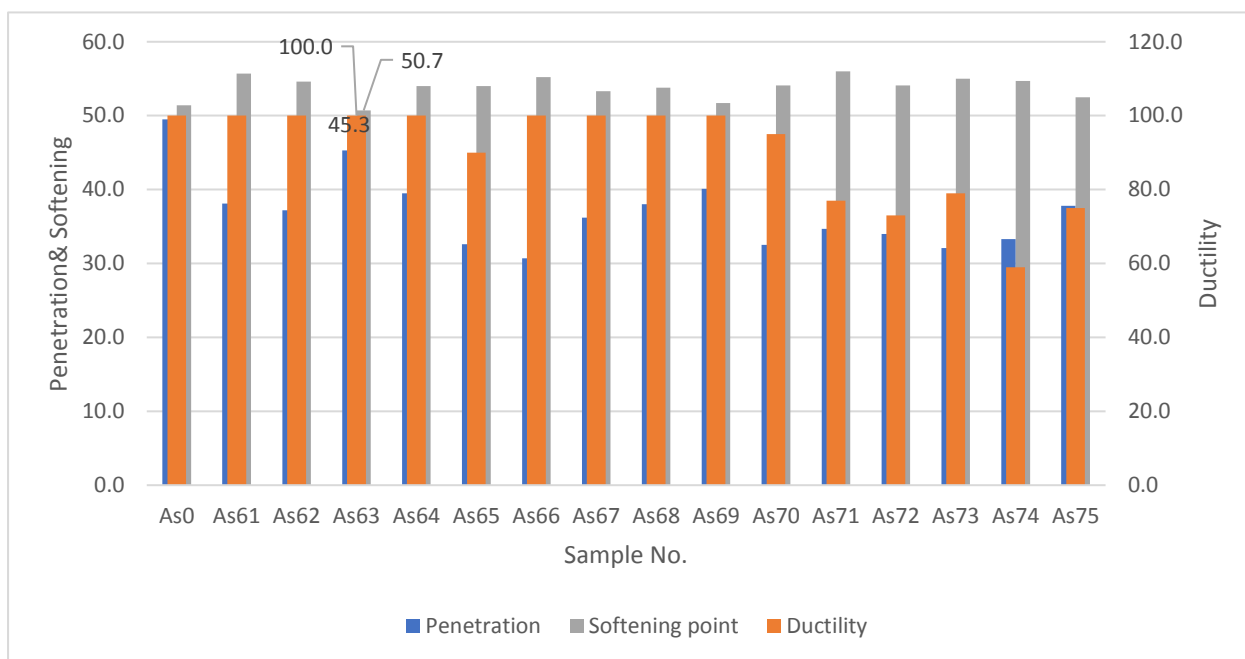


Figure (8): Rheological properties of asphalt treated with PVAc at 180°C in the presence of sulfur 1% by weight and 0.06% by weight of AlCl₃ at (30 min)

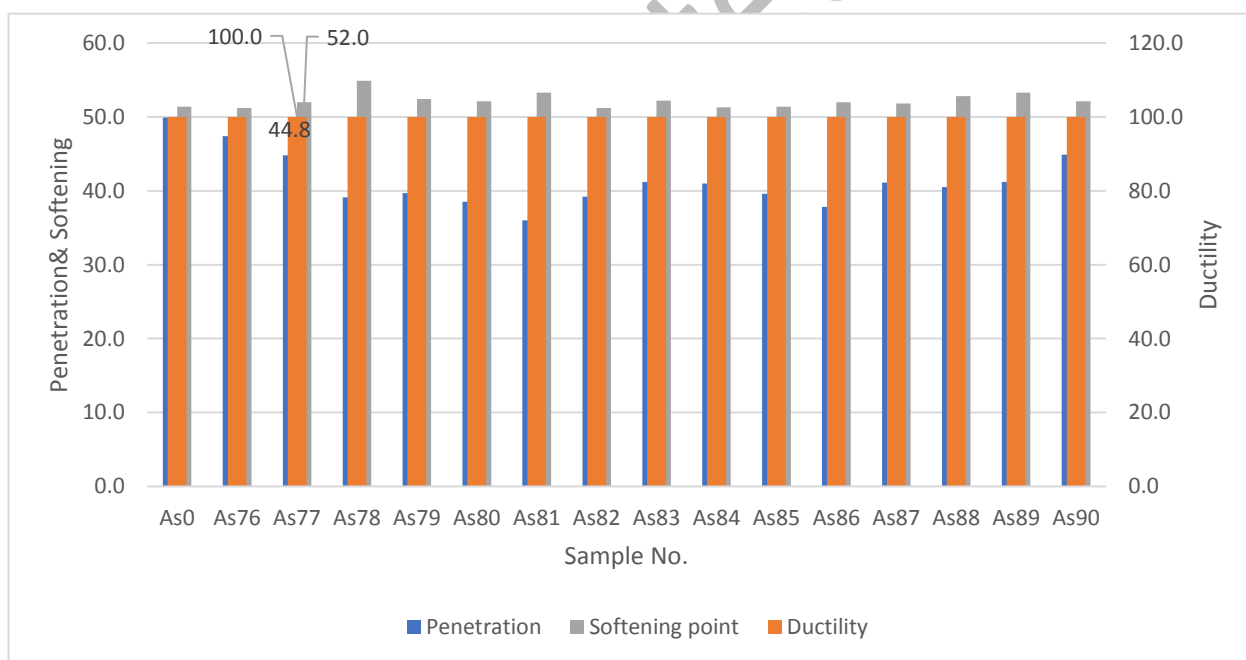


Figure (9): Rheological properties of asphalt treated with CA at 180°C in the presence of 0.06% by weight of AlCl₃ at (30 min)