Modification of the rheological properties of chlorinated asphalt by treatment with Degraded Polystyrene

Mahmood K. Saleem [1]
mahmoodsaleem@ntu.edu.iq

Huda A. Younis [2]
hudaa.younis@ntu.edu.iq

[1] Northern Technical University, Mosul, Iraq
[2] Northern Technical University, Mosul, Iraq

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Abstract

This study explores the possibility of modifying the rheological properties of chlorinated asphalt by introducing pyrolyzed polystyrene. Pyrolyzed polystyrene was introduced into the asphalt mixture, resulting in three distinct samples, each containing varying proportions of pyrolyzed polystyrene blended with chlorinated asphalt. Subsequent laboratory tests, conducted included evaluations of ductility, penetration, and softening point. The results indicated significant changes in asphalt properties due to the introduction of pyrolyzed polystyrene. Additionally, the chlorination process also was affected on the thermal properties of the original asphalt.

This study has obtained asphaltic samples with rheological properties suitable for various asphalt application, including paving, platinating and mastic accordance to the standard specifications.

Keywords: Asphalt, Rheological properties, Modify, Chlorination of asphalt, Processing with polystyrene.

Introduction

Asphalt is a highly viscous liquid material whose viscosity increases with temperature. It is a complex mixture of various hydrocarbon materials with different molecular weights, typically ranging from 400 to 500 [1,2]. Asphalt's constituents are bound together through physical and chemical forces, providing a homogeneous appearance and making it seem like a single substance.

Asphalt possesses stable rheological properties crucial for engineering and construction applications, widely used in road construction, airport runways, bridge building, and more [3,4]. However, to develop asphalt with distinctive properties suitable for applications beyond traditional asphalt, numerous researchers have undertaken experiments [5].

Mosckopedis and Speight [6] conducted research involving the addition of chlorine to asphalt, using iron chloride as a chlorination aid. The goal was to obtain halogenated derivatives of asphalt with dark color and resistance to solubility in various solvents such as benzene, nitrobenzene, and carbon tetrachloride.

Makarckiuk and Antonistn [7] studied the impact of heat on chlorinated asphalt derivatives. The results indicated that high temperatures facilitate HCL particle removal, resulting in a easily breakable solid material. These transformations occurred due to the formation of high-carbon olefinic structures, deviating from typical asphalt properties and developing quasi-coal systems.

Shaymaa AL-Mutalq and others [8] evaluates the fuel resistance and morphology of asphalt that has been physicochemically modified using waste polymers, specifically high-density polyethylene and chlorine gas. The high-density polyethylene waste polymer and chlorine gas are utilized to modify the asphalt. The asphalt is modified through a physicochemical process involving the blending of the waste polymer and chlorine gas with the original asphalt. The objective of the research is to investigate the impact of these modifications on the fuel resistance of the asphalt and analyze the resulting changes in its composition and morphology.

While numerous studies have explored the modification of asphalt with various polymers such as rubber, research involving the incorporation of broken polystyrene into asphalt remains relatively limited. Hailong et al. attempted to enhance the stability of stored asphalt by adding styrene-butadiene-styrene (SBS) with sulfur to the mix [9]

In 2005, AL-Dubony and Ahmad [10] successfully prepared asphalt modified with polystyrene and sulfur, resulting in a homogenous blend of asphalt, polystyrene, and sulfur.

Mousa Bani Baker et al. [11] added polystyrene waste by volume to bitumen in ratios of 0%, 5%, 10%, and 15%. Tests measuring penetration, softening point, ductility, flash point, and ignition point were conducted. The results showed that increasing the polystyrene ratio in asphalt directly affected bitumen properties by reducing penetration and ductility while increasing softening point, flash point, and ignition point. Modified asphalt could be used in hot climate areas for various construction purposes such as waterproofing materials for basements, retaining walls, surfaces, or as a material for paving garage floors, car parks, sidewalks, playgrounds, and gardens.

As mentioned by Korshat Yeldiz et al. [12], waste polymers are widely used in asphalt modification, especially to mitigate their environmental impact. This research discusses the possibility of using expanded polystyrene (EPS) waste foam in asphalt modification. EPS foam waste produced during production and use was mixed with bitumen in weight ratios of 2%, 4%, 6%, and 8%, using the dry modification method. The physical and mechanical properties of the original bitumen were compared with asphalt modified by EPS foam waste. A strong relationship between the physical properties of the modified asphalt and the EPS foam ratio was observed. Decreases in penetration and ductility values were noted. Additionally, statistical analyses indicated that a 2% increase in the additive ratio was not sufficient to make a significant difference in the physical properties of bitumen.

Nader Nciri et al. [13] introduced wastes EPS foam into asphalt mixtures used in road construction. Different ratios of waste from EPS foam, such as 2%, 4%, 6%, and 8% by weight were mixed with asphalt binder. The physical and mechanical properties of the modified asphalt mixtures were then evaluated.

Khaled Ramadan et al. [14] collected polystyrene in its wastes form, shredded it, washed it, and then dried it before mixing it with original asphalt. A 70-80 penetration grade asphalt binder was used and mixed with processed wastes polystyrene. The mixing ratios between polystyrene and asphalt (S/A) were: 0.0% (reference sample), 0.2%, 0.4%, 0.6%, 0.8%, 1.0%, 1.2%, and 2% by weight of the asphalt binder.

Building on previous research, this study aims to investigate the dual impact of chlorine and polystyrene on the rheological properties of asphalt binder.

Materials and Methods:

Thermal degradation of polystyrene :

The thermal degradation of polystyrene was achieved by direct heat exposure, breaking down the polymer into approximately 60% of its original weight in the form of styrene.

This resulting product has potential applications as a car fuel improver or could be used in reprocessing the same polymer.

Additionally, the remaining styrene, once ground into fine particles, was blended into chlorinated asphalt at three different ratios (1%, 2%, and 3%) while maintaining a temperature at 150 degrees Celsius for two hours.

Here are the experimental methods [15,16,17,18,19]:

- Ductility: ASTM (D6-70)

- Penetration: ASTM (D5-83)

- Softening point: ASTM (D36-83)

- Thin Film Oven Test (TFOT): ASTM (D6-80)

Chemical materials used :

The chlorination process of asphalt was facilitated by iron chloride as a catalyst. Different temperature levels were used during the chlorination process, as outlined in Table 1.

Degraded Polystyrene.

Devices Used:

- Softening point (ring and ball)

- Penetration

- Ductility

- Simple distillation apparatus for crushing

- Oven for Thin Film Oven Test (TFOT)

Sample Preparation :

Polystyrene was subjected to thermal degradation through direct heating, breaking down the polymer into approximately 60% of its original weight in the form of styrene, the main component of the polymer. The remaining material was then ground into fine particles and added to chlorinated asphalt at three different ratios (1%, 2%, and 3%), with the process conducted at a temperature of 150 degrees Celsius for 2 hours.

Testing Methods:

Asphalt binder samples were tested using penetration tests at 25 degrees Celsius (ASTM D6), softening point tests (ASTM D36), ductility tests at 25 degrees Celsius (ASTM D113), and Thin Film Oven Test (TFOT) ASTM (D6-80) to determine the optimal polymer content.

Results and Discussion:

The thermal cracking process was implemented due to the polystyrene's difficulty in dissolving within asphalt systems and its lack of compatibility with them. Consequently, partial cracking was employed using heat and direct heating. In this process, the polystyrene is subjected to high temperatures to break down its chemical bonds and convert it into smaller, less-ordered molecules. This is achieved by heating the polystyrene to a temperature above its melting point, causing it to crack into smaller, more reactive components. This procedure enhances the polystyrene's ability to blend with asphalt and improves its mechanical properties and adhesion to other materials within the asphalt system.

Chlorinated asphalt is a modified type of asphalt that is enhanced by adding chlorinated compounds to it. Through this modification, asphalt acquires improved properties and additional benefits. Here are some key characteristics of chlorinated asphalt:

Chemical resistance: Chlorinated asphalt enhances resistance to chemical corrosion resulting from asphalt's reactions with harmful chemicals, such as acids and bases. This makes it suitable for use in applications exposed to strong chemical substances, such as chemical industries and water treatment plants.

Thermal resistance: Chlorinated asphalt is known for its resistance to thermal corrosion caused by high temperatures and sudden temperature changes. Therefore, it can be used in applications exposed to extreme thermal conditions, such as thermal industries and tropical regions.

Durability and flexibility: Chlorinated asphalt improves the durability of asphalt and its resistance to cracking and deterioration. It also increases its flexibility, allowing it to withstand movements and vibrations without rapid deterioration. As a result, chlorinated asphalt is used in road, pavement, and sidewalk applications to provide a durable and corrosion-resistant surface.

Water resistance: Chlorinated asphalt has good resistance to water and moisture. It forms a water-resistant layer on the surface, maintaining its stability and preventing water from penetrating into the underlying asphalt. This makes it ideal for use in road, pavement, and plaza applications that require water protection[19].

Table 1 presents the physical properties of chlorinated asphalt using 1.5% from ferric chloride at different temperatures. Meanwhile, Table 2 compares the physical properties of chlorinated asphalt before and after adding 1% powdered polystyrene.

Table (2):Physical properties of chlorinated asphalt after adding (1%) of crushed polystyrene

Sample Number	The Chlorinated asphalt in different Temperatures			The Chlorinated asphalt after adding (1%) of polystyrene		
	Softening point oC	Penetration (0.1mm/ 5 sec, 25°C)	Ductility (Cm, 25 °C)	Softening point °C	Penetration (0.1mm/5 sec , 25 °C)	Ductility (Cm, 25 °C)
1 (25 ◦C)	45	52	+100	45	52	+100
2 (90 oC)	58	38	+ 100	61	32	70
3 (130 oC)	63	30	65	65	20	30
4 (160 oC)	76	16	0	77	3	0

The data reveals the impact of adding polystyrene on the properties of chlorinated asphalt. With an increase in polystyrene ratio as a solid substance, the asphalt's softening point rises while penetration decreases. This result can be attributed to the increased hardness of the asphalt due to higher polystyrene content, affecting penetration values and softening point. Furthermore, high temperatures adversely affect asphalt models, stimulating reactions that remove HCl particles and begin forming olefinic systems and double bonds, resulting in the development of more solid structure.

The comparison of results confirms the significant effect of polystyrene on the properties of chlorinated asphalt, especially in terms of flexibility. Adding 1% polystyrene reduces flexibility to 70 cm, indicating that polystyrene reduces the adhesive properties of asphalt. Additionally, the impact of high temperatures encourages the removal of HCl particles, making samples (1 and 2) suitable for use as gap-filling and roof covering materials.

When asphalt systems are exposed to heat and over time, oxidation reactions occur. These reactions result in the removal of hydrogen from asphalt molecules and the formation of olefinic bonds between the remaining molecules. As a result, the hydrogen-to-carbon ratio in asphalt systems decreases, and their hardness increases.

Over time, the oxidation and hydrogen removal process continues in asphalt systems, leading to a decrease in the hydrogen content relative to carbon. The molecules become more intertwined and bonded as more olefinic bonds are formed, thereby increasing the hardness of asphalt systems.

In general, heat and time affect asphalt systems through oxidation reactions and chemical changes that occur. These processes result in a reduction in the hydrogen-to-carbon ratio and an increase in the hardness of asphalt systems.

Conversely, Table 3 shows that adding 2% and 3% degraded polystyrene to chlorinated asphalt leads to an increase in softening point and a decrease in penetration and flexibility. This change occurs due to prolonged exposure to high temperatures, leading to the removal of HCl particles and leaving a higher proportion of olefinic structures in the presence of polystyrene.

This, in turn, results in the formation of more complex and rigid structures compared to chlorinated asphalt alone.
Due to the extreme hardness and susceptibility to fracture at low temperatures, these asphalt systems cannot be effectively used for other purposes such as paving.

When temperatures decrease, the rigid asphalt transforms into a brittle form that is prone to breaking. This means that it may crack and fracture under pressure or load. Consequently, it is not suitable for use in paving applications that require withstanding traffic movement and mechanical stresses.

It is important to note that there are different types of asphalt systems used in paving, each with varying compositions and properties. Flexible asphalt systems, specifically designed to withstand low temperatures and accommodate expansion and contraction, are commonly employed in regions with cold climates where temperatures are low.

Choosing the appropriate type of asphalt system is crucial for specific operating conditions.

In the case of chlorinated asphalt treated with 2% and 3% degraded polystyrene (samples 1 and 2), the significant changes in penetration, ductility and softening point make them suitable for use as waterproofing and thermal insulation materials.

Table (3) :Physical properties of chlorinated asphalt after adding (2% and 3%) of crushed polystyrene

Sample Number	The chlorinated Asphalt before adding the Polystyrene			The Chlorinated Asphalt and 2% Polystyrene			The Chlorinated Asphalt and 3% Polystyrene		
	Softening	Penetration	Ductility	Softening	Penetration	Ductility	Softening	Penetration	Ductility

	point oC	(0.1mm/, 5 sec , 25 oC)	(Cm, 25 oC)	point oC	(0.1mm/, 5 sec , 25 oC)	(Cm, 25 oC)	point oC	(0.1mm/, 5 sec , 25 oC)	(Cm, 25 oC)
1	45	52	+ 100	45	52	+ 100	45	52	+ 100
2	58	38	+ 100	64	28	35	67	17	10
3	63	30	165	68	15	20	73	6	0
4	76	16	0	80	0	0	82	0	0

able 3 illustrates with greater precision that, with an increase in the poly-styrene ratio, the properties of asphalt change significantly, especially when exposed to higher temperatures. This alteration is attributed to the formation of olefinic systems, leading to a reduction in oil and resin content in the model. As a result, the values for permeability and flexibility reach zero (5.6).

Polystyrene is a type of solid polymer material with a high melting point compared to asphalt. It has a molecular structure characterized by strong bonds between the particles, resulting in increased hardness and rigidity of the models made from it.

The solid nature and high melting point of polystyrene enhance the hardness and stiffness of the models. Polystyrene exhibits high resistance to corrosion and mechanical impacts, making it an ideal material for applications that require strength and rigidity.

However, it's important to note that polystyrene and asphalt are completely different materials in terms of composition and properties. The hardness and stiffness of the models are not solely determined by one component but can also be influenced by other factors, such as the chemical composition of the materials, operating conditions, and manufacturing processes.

In summary, polystyrene with its high melting point and hardness contributes to increased hardness and rigidity of the models. However, it is necessary to consider other factors that may affect the hardness and rigidity in asphalt applications.

Figure 1 visually demonstrates an increase in the softening point for various asphalt samples, including regular asphalt, chlorinated asphalt, and chlorinated asphalt treated with 1%, 2%, and 3% of shattered poly-styrene. Conversely, Figure 2 shows a decrease in penetration for chlorinated asphalt after treatment with different proportions of poly-styrene, comparing it to natural asphalt.

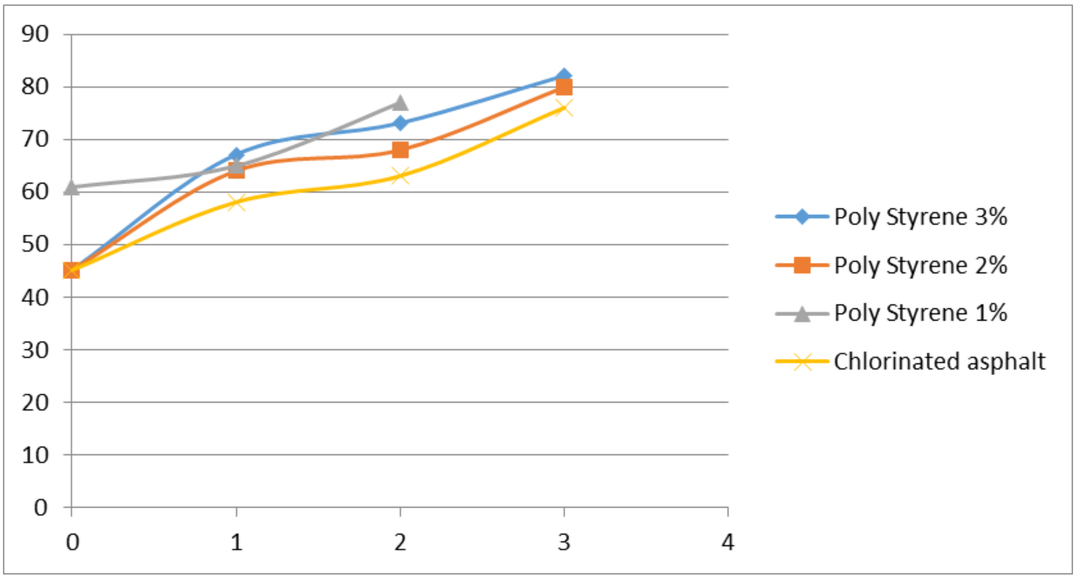

Figure 1: The softening point for the different types of asphalt.

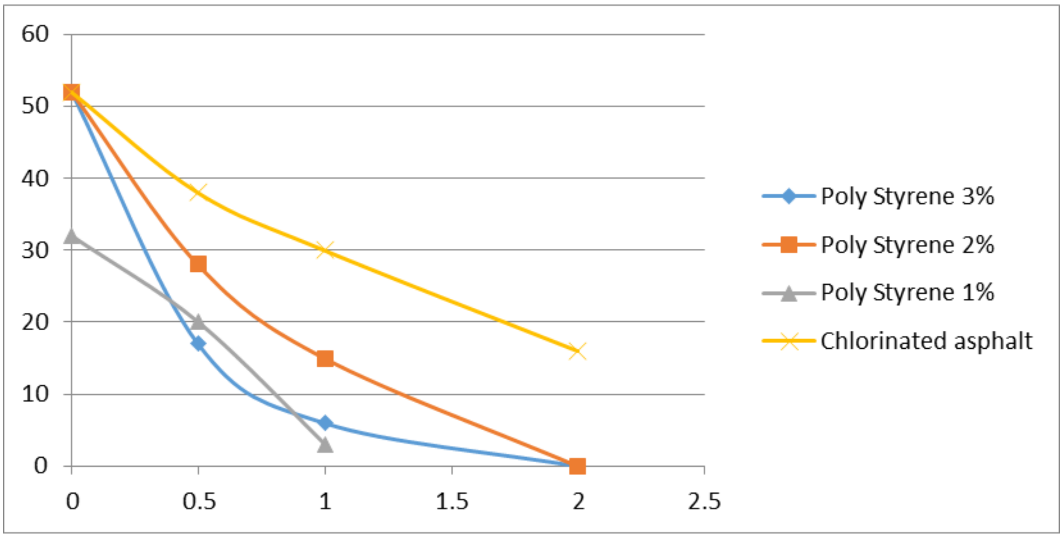

Figure 2: penetration values for the different types of asphalt

Conclusion

Adding chlorine to asphalt increases its melting point, and the degree of this impact is directly related to the temperature used in the chlorination process. Simultaneously, the penetration and flexibility of asphalt decrease, and the extent of this change depends on the temperature increase. Suitable asphalt for road paving in high-temperature areas can be obtained by chlorination at lower temperatures. Substituting hydrogen atoms with chlorine atoms allows asphalt to maintain its properties across a range of temperatures. Chlorinating asphalt at high temperatures leads to an increase in the double bond ratio, primarily due to the removal of HCl particles from the interconnected asphalt formation. This, in turn, enhances cross-linking, resulting in a more rigid form of asphalt applicable in various fields, such as filling gaps in different construction contexts. Adding shattered poly-styrene to chlorinated asphalt raises its melting point while reducing penetration and flexibility. The decrease in flexibility values becomes more pronounced when the poly-styrene content exceeds 1%, eventually reaching zero.

Treating chlorinated asphalt with poly-styrene yields more complex and rigid results compared to chlorinated and regular asphalt. These outcomes present promising samples suitable for use as construction materials in tasks such as gap filling, water insulation, and thermal insulation.

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