



Enhancing Thermal Stability of Hybrid-Modified Local Asphalt

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Abstract

Chemical additives and polymeric materials, selected for their compatibility and ability to improve asphalt's performance in demanding environments. Key additives, including Polyphosphoric Acid (PPA), Polyvinyl Acetate (PVAC) beads, Maleic Anhydride (MA), and Ethylene Vinyl Acetate (EVA) resin, were mixed in precise ratios with the asphalt binder. These additives were chosen to evaluate their effects on crucial performance indicators, such as the Penetration Index (PI) and activation energy, which measure the material's thermal stability, flexibility, and resistance to deformation. Results demonstrated that the addition of these materials significantly increased the asphalt's activation energy by up to 45.44%, enhancing its resistance to temperature fluctuations and providing better stability under various environmental stresses. The Penetration Index (PI) also improved notably, indicating that modified asphalt exhibits greater durability and reduced susceptibility to cracking or deformation under thermal changes. These enhancements contribute to lower road maintenance requirements and support greater energy efficiency in asphalt production and application processes. Compared to neat asphalt, the modified asphalt exhibited superior thermal stability, mechanical resilience, and overall performance, making it suitable for use in diverse climatic conditions. This study provides valuable insights into sustainable asphalt modification techniques, emphasizing the role of polymer and chemical additives in extending pavement lifespan and reducing environmental impact through improved material properties.

Keywords: Activation Energy, PI, Asphalt Enhancers, Polymeric Enhancers.

تعزيز الاستقرار الحراري للأسفلت المحلي المعدل الهجين

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الخلاصة:

يهدف هذا البحث إلى تحسين خصائص الأسفلت المحلي من خلال دمج إضافات كيميائية ومواد بوليمرية محددة تم اختيارها لتوافقها وقدرتها على تعزيز أداء الأسفلت في البيئات الصعبة. شملت الإضافات الرئيسية حمض الفوسفوريك ((PPA)، وحببات أسيتات البولي فينيل ((PVAC)، ومادة المالك أميدريد ((MA)، وراتنج إيثيلين فينيل أسيتات ((EVA)، والتي تم مزجها بنسب دقيقة مع رابطة الأسفلت لدراسة تأثيرها على مؤشرات الأداء الرئيسية، مثل مؤشر التغلغل (PI) وطاقة التنشيط، اللذين يقيسان استقرار المادة الحراري ومرونتها وقدرتها على مقاومة التشوه. أظهرت النتائج أن إضافة هذه المواد أدى إلى زيادة كبيرة في طاقة تنشيط الأسفلت بنسبة تصل إلى 45.44%، مما يعزز من مقاومته للتغيرات الحرارية ويحقق استقراراً أفضل تحت الضغوط البيئية المختلفة. كما شهد مؤشر التغلغل تحسناً ملحوظاً، مما يدل على زيادة متانة الأسفلت وقدرته على مقاومة التشققات والتشوهات الناجمة عن التغيرات الحرارية. تساهم هذه التحسينات في تقليل متطلبات صيانة الطرق وتدعم كفاءة أكبر في استهلاك الطاقة خلال عمليات إنتاج وتطبيق الأسفلت. بالمقارنة مع الأسفلت التقليدي، أظهر الأسفلت المعدل ثباتاً حرارياً أعلى، ومرونة ميكانيكية أفضل، وأداءً عاماً متفوقاً، مما يجعله ملائماً للاستخدام في ظروف مناخية متنوعة. يقدم هذا البحث رؤى قيمة حول تقنيات تعديل الأسفلت المستدامة، مسلطاً الضوء على دور المواد البوليمرية والكيميائية في إطالة عمر الرصف وتقليل التأثير البيئي من خلال تحسين خصائص المادة.



1. Introduction

The study of rheology delves into how substances move and change. Specifically focusing on asphalt, it explores the way asphalt responds to pressures and temperatures [1-8]. Understanding rheology is critical to measuring how well asphalt performs in different operational situations, leading to better road design and increased durability [9-12]. Activation energy is the energy needed to initiate a reaction. In asphalt, it refers to the energy required for chemical reactions to occur between asphalt components and additives such as resins when heated [13-18]. This metric is vital for assessing asphalt stability and effectiveness at temperatures that play a role in evaluating and optimizing the quality of modified asphalt [14, 15, 19, 20]. Linhui Cao introduced a method to quantitatively measure activation energy as a measure of the self-healing ability of asphalt materials [16, 21]. Through experiments involving nine asphalt samples and fatigue rest stress tests, the researcher found that activation energy can effectively distinguish between the self-repair capabilities of mastic types while accurately indicating the rates of strength improvement over time [4, 16, 21-23]. Yufan Chen studied the leeway of using viscous flow activation energy (E_a) to evaluate the rheological and aging features of SBS-modified asphalt binders [14, 24-27]. Chen displayed that ingredient with higher activation energy (E_a) values, which were found using Dynamic Shear Rheometer (DSR) and Rotational Viscometer (RV) testing, had better rheological properties and were less likely to break down over time [14, 24, 25, 28-30]. Studies on SBS polymer modification have confirmed augmentation instability at high temperatures and resistance to cracking at low temperatures [31]. The study employed activation energy (E_a) to assess temperature sensitivity and aging resistance. The findings revealed that higher E_a values are associated with superior performance and E_a increases as the material ages [24-26, 32, 33]. Several experts have concentrated on augmenting asphalt using polymers and resins Liu et al. Researchers have formulated improved asphalt mixtures using polymers. Additionally, Pranav et al. investigated the effects of polymers and resins on asphalt maintenance and repair [34]. These studies emphasize the importance of polymers and resins in improving asphalt performance and increasing road durability [16, 24, 26, 35-39]. The research problem lies in the cracks and rutting that occur on roads and asphalt mixtures. This study aims to improve asphalt mixtures by incorporating polymeric and chemical materials to enhance the properties of asphalt and understand its susceptibility to temperature variations. This will be achieved by calculating the activation energy and Penetration Index (PI) to evaluate the performance of asphalt under different conditions.

2. The Meaning of Rheology

Rheology focuses on how materials flow and deform under stress [49-50]. In asphalt, rheology studies how the binder behaves under different temperatures and loads. The properties of asphalt change with temperature: it becomes more plastic at high temperatures, and it can easily deform and at low temperatures, it becomes more brittle and cracks easily. Thus, knowledge about the rheology of asphalt plays a significant role in improving its properties and applying it effectively in road construction.

3. Activation Energy

Activation energy is important in improving asphalt properties through the incorporation of polymeric resins and chemical additives. the strength of these additives is evaluated away measure the activation energy for both optimized and optimized asphalt. activation energy in modified asphalt is typically higher indicating that the additives have stabilized the chemical reactions within the asphalt and this increase in activation energy indicates greater resistance to environmental and mechanical changes and Therefore Improved asphalt resilience.

To calculate activation energy, the Arrhenius equation is used, which relates the reaction rate to temperature and activation energy:

$$K=Ae^{-E_a/RT} \quad \dots\dots (1)$$

where (k) is the reaction rate constant, (A) is the frequency factor, (E_a) is the activation energy, (R) is the gas constant, and (T) is the absolute temperature. To determine activation energy graphically, the reaction rate constant is measured at different temperatures, and the relationship between ($\ln(k)$) and ($1/T$) is plotted. The slope of the resulting line equals ($\{-E_a./R\}$), from which the activation energy can be calculated. Hence, an increase in activation energy indicates enhanced stability and improved properties of the asphalt, demonstrating that the additives effectively enhance the overall performance of the asphalt.

4. Materials and Methodology

4.1 Materials

4.1.1 Asphalt Cement

In this study, a 40-50 penetration grade asphalt binder was utilized, sourced from the Al-Dowrah refinery. Generally, the physical properties of this asphalt binder, along with the specifications used for its analysis, are detailed in Table1.

4.1.2 Asphalt modifier

To prove the hypothesis that resinous materials can improve the properties of asphalt, Polymers, and chemical additives were employed to enhance the properties of asphalt. The specific additives utilized include:

- Ethylene Vinyl Acetate (EVA) resin: Combined at a ratio of 4% with asphalt. EVA is often used to



improve flexibility and durability in asphalt pavements.

- Polyvinyl Acetate (PVAC) Bead: Added at a ratio of 4% by weight of asphalt. PVAC beads can improve the viscosity and adhesion of asphalt mixes.
- Polyphosphoric Polymer was mixed at a ratio of 1% by weight of asphalt, along with Polyvinyl Acetate (PVAC) Bead at a ratio of 4% by weight of asphalt. This blend indicates the use of two different substances to modify asphalt properties. The Polyphosphoric Polymer enhances binding and stability, while PVAC Bead improves the viscosity and adhesion of the asphalt mixture.
- Malic Aldehyde: Added at a ratio of 2% to a mixture containing 4% PVAC Bead. MA is probably utilized for its reactive properties, potentially enhancing chemical bonding within the asphalt mix, similar to its effect on PVAC Bead.

All additives were blended with PG64-16 performance-grade asphalt binder using a mixer for 15 minutes at a rotation speed of 1200[44]. cycles per minute and a temperature of 120°C.

Fig.1 provides an overview of the various types of additional polymers and chemical additives employed in the process.

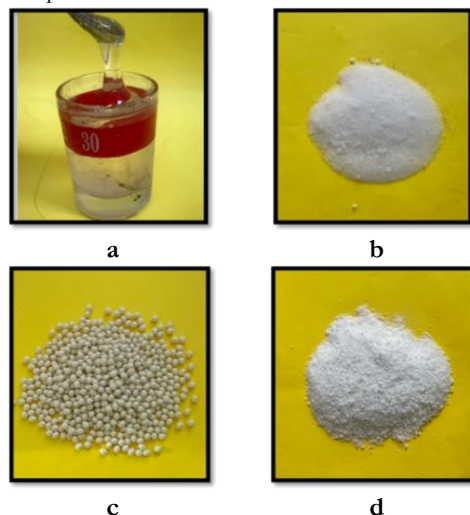


Figure (1): The various types of additional polymers and chemical additives: (a) Polyphosphoric acid (PPA); (b) Polyvinyl acetate (PVAC) bead; (c) Ethylene vinyl acetate (EVA) resin; (d) MA (MA).

4.2 Methodology

In this study, polymers and chemical additives were utilized to enhance the properties of asphalt. Polymeric materials were blended with asphalt at various ratios to achieve optimal results. Two types of polymers, Ethylene Vinyl Acetate (EVA) and Poly vinyl acetate, along with an additional chemical additive, were employed. A mixture containing 1% polyphosphoric acid and 4% EVA, based on the weight of asphalt, was prepared. Additionally, 2% MA was mixed with 4% EVA based on the weight of asphalt. All additives, including EVA, polyphosphoric acid, and MA, were mixed with PG64-16 grade asphalt binder. The combination experienced amalgamation in a mixer for 15 minutes at a rotation speed of 1200 [44].

cycles at a temperature of 120°C. Following the preparation of both pure and modified asphalt, viscosity tests were performed in the laboratory at temperatures of 135°C and 165°C. The viscosity data obtained from these tests were subsequently utilized to calculate the activation energy for both the pure and modified asphalt samples.

Table (1): Physical Features for Asphalt Cement

Test	Specification Term	Units	Results	Specificati on Requirements
Penetration (25°C, 100g, 5sec).	ASTM D 5[41]	1/10 mm	44	40-50
Ductility (25° C, 5 cm/min).	ASTM D 113-07[42]	Cm	122	≥100
Flash Point (Cleveland Open Cup)	ASTM D92[43]	°C	291	≥230
Specific gravity (25°C)	ASTM D 70[44]	---	1.04	-----
Rotational Viscometer @ 135°C	AASHTO TP 48[45]	Pa.s	0.462	Max. 3
Rotational Viscometer @ 165° C	AASHTO TP 48[45]	Pa.s	0.112	
Dynamic Shear Rheometer 10 rad/sec, G/sinδ at 70	AASHTO TP 5[46]	KPa	1.73	Min. ≥ 1
Rolling thin film oven test mass loss (%)	AASHTO TP 240[47]	%	0.456	Max. ≤ 1
Dynamic shear 10 rad/s, G/sinδ @ 64 OC (kPa)	AASHTO TP 5[46]	KPa	2.03	Min. ≥ 2.2
Dynamic shear @ 25 OC, 10 rad/s, G/sinδ (kPa)	AASHTO TP 5[46]	KPa	7421	Max. ≥ 5000

5. Results and Discussion

The connection, between viscosity and temperature is utilized in the Arrhenius equation, which links viscosity and temperature through activation energy [49-51]. This demonstrates that viscosity is greatly influenced by temperature and decreases as the temperature rises requiring energy to surpass the materials resistance. The activation energy was determined for asphalt, without substances, and was measured at 69.3 kJ/mol.

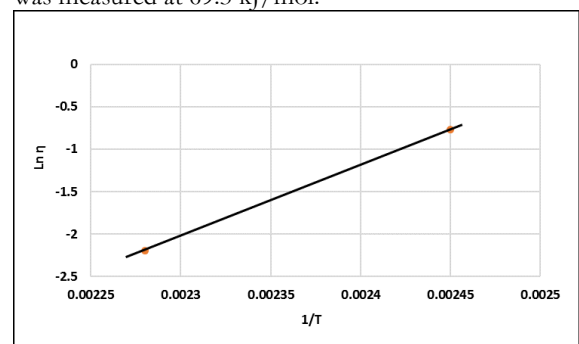


Figure (2): Viscosity vs. Reciprocal Temperature for Calculating Activation Energy of Pure Asphalt.



Convert Data to Logarithmic Form

Calculate the natural logarithm of the viscosity at each temperature

Use the Logarithmic Form of the Arrhenius Equation:

Arrhenius Equation:

$$\ln\eta = \ln A + E_a/R \cdot 1/T \quad \dots\dots(2)$$

Rearrange it to the linear form:

$$\ln\eta = (E_a/R) \cdot 1/T + \ln A$$

This equation is similar to the linear equation:

$$y = mx + b \quad \dots\dots (3)$$

Where:

$$y = \ln\eta, x = 1/T, \text{ and } m = E_a/R$$

5.1 The effect of incorporating EAV resin into asphalt on the activation energy of asphalt.

In this study section, the impact of adding Ethylene-Vinyl Acetate (EVA) resin on asphalt properties was assessed. The activation energy was determined using the Arrhenius equation, correlating reaction rate with temperature. Results compared activation energies of different samples, highlighting changes with EVA-enhanced asphalt. The equation's logarithmic relationship between reaction rate and temperature provided precise activation energy calculations via graph slope. This method is pivotal for analyzing energy changes and enhancing material properties with chemical additives.

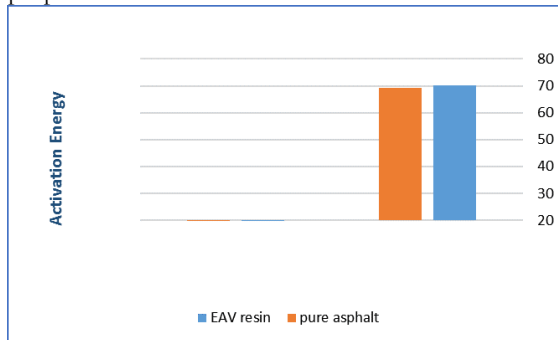


Figure (3): Effect of EAV Resin on The Activation Energy of Asphalt.

Fig.3 shows Insignificant enhancement by adding EVA resin considering asphalt properties. Results indicate a 1.30% increase in activation energy for the improved asphalt, indicating greater resistance to thermal changes and improved chemical stability. This could confirm EVA effectiveness in boosting asphalt performance, making it more suitable for high-performance applications in demanding environmental conditions.

5.2 Effect of the PVAC bead on the activation energy of the asphalt.

The effect of polyvinyl acetate (PVAC) on the activation energy of asphalt has been studied, revealing that the addition of this material alters the asphalt's viscosity and flow properties. This modification enhances the asphalt's concerning under various thermal conditions, the components that may lead to enhancement. durability and flexibility, making it more resistant to cracking and damage.

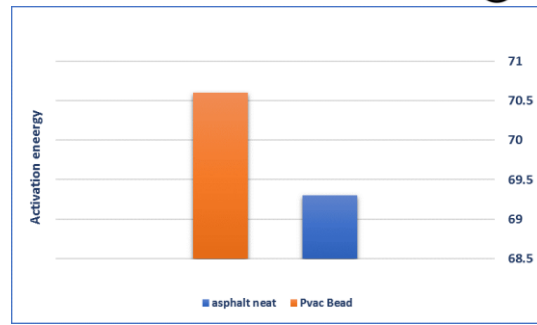


Figure (4): Impact of Polyvinyl Acetate (PVAC) Beads on The Activation Energy of Asphalt.

According to Fig.4, the activation energy of pure asphalt is 69.3 kJ/mol while that of asphalt Improved with PVAC is 70.6 kJ/mol indicating a 1.9% increase in activation energy with the addition of PVAC. This increase can be attributed to the improvement of contact among particles of bitumen, this is due to the addition of PVAC beads which results in the strengthening of various links between the various components of the asphalt. Further, PVAC enhances the thermal stability of asphalt and thus brings more resistance of the material to fluctuations in the temperature as well as increasing the activation energy required to produce similar levels of viscosity and flow of the material. Such characteristics increase the ability of asphalt to perform under different temperatures and therefore enhance the production of paving materials with such characteristics so that they can last longer.

5.3 Effect of MA+PVAC beads on the activation energy of asphalt

Addition of MA mixed with polyvinyl acetate beads (PVAC) significantly improves the activation energy of asphalt through laboratory analysis and the use of the Arrhenius equation. This combination improves the rheological and mechanical properties of asphalt, indicating a noticeable improvement in its performance. The addition significantly increases the activation energy of the mixture which positively affects the rheological properties of the modified asphalt. therefore, hybrid modification can be proposed as an alternative to the traditional methods of optimization which are justified in the use of large amounts of valuable additives, as illustrated in Fig. 5.

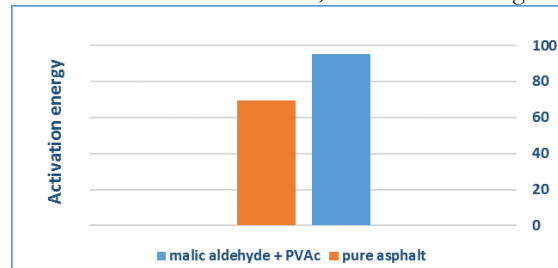


Figure (5): Effect MA + PVAC beads on the activation energy of asphalt

Fig.5 shows that adding MA and PVAC beads to asphalt increases the activation energy by approximately 37.27%, from 69.3 kJ/mol to 95.12 kJ/mol. This could explain how effectively these compounds in enhancing asphalt. Through molecular-level interactions, MA increases the durability of



chemical bonds and makes it more difficult to break them. Polyvinyl acetate (PVA) beads play a critical role in extending the stability and lifetime of asphalt in many applications by strengthening the material's resistance to deformation.

5.4 Effect of polyphosphoric+ PVAC beads on the activation energy of asphalt.

This study investigates the impact of integrating polyphosphoric acid with polyvinyl acetate (PVAC) beads on asphalt activation energy. The primary objective is to enhance the properties of asphalt, thereby increasing its resistance and durability under diverse environmental conditions.

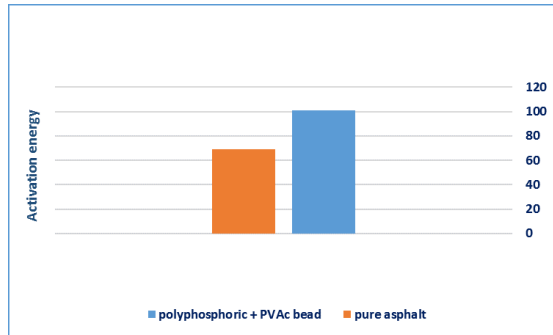


Figure (6): effect of polyphosphoric+ PVAC beads on the activation energy of asphalt.

The research investigates the effect of combining polyphosphoric acid (PVAC) with polyvinyl acetate (PVA) granules on the activation energy of asphalt, the main objective being to improve the properties of asphalt making it more challenging and long-lasting in environmental conditions. Due to the unique properties of polyvinyl particles at normal temperatures, they can effectively interact with host materials. The figure shows that the highest activation energy was obtained when polyphosphoric acid was combined with polyvinyl acetate (PVAC) granules, where the activation energy of the improved asphalt increased by 45.44%, which is the highest increase obtained in the study.

7. Effect of additives on asphalt PI

The PI (PI) was calculated for both neat asphalt and asphalt modified with various additives: PVAC beads, EAV resin, MA combined with PVAC beads, and polyphosphoric acid combined with PVAC beads. The results are as follows: neat asphalt has a PI of -0.57, PVAC beads -0.50, EAV resin -0.53, MA with PVAC beads -0.43, and polyphosphoric acid with PVAC beads -0.51. These results, illustrated in the graph below, highlight the impact of different additives on asphalt properties and their resistance to thermal changes, demonstrating how modifications can enhance the material's performance under varying conditions.

The PI serves as a measure, in the asphalt industry gauging how additives can enhance characteristics when compared to plain asphalt.

For PVAC Bead the PI is 0.50 indicating an enhancement of 12.3%. Meanwhile, EAV Resin has a PI of 0.53 showing a 7.0% increase. A significant enhancement is observed in the combination of aldehyde and PVAC beads with a PI of 0.43

representing an increase of around 24.6%. When polyphosphoric acid is combined with PVAC beads the resulting PI is 0.51 indicating an improvement of 10.5%.

Negative values in the PI signify improvements in the modified asphalt properties compared to neat asphalt, with values indicating enhanced resistance to long term wear and cracking.

These discoveries enrich our understanding of how polymers and additives impact asphalt properties. The integration of polymer networks and PVAC beads leads to heightened viscosity increased softening points and overall enhanced efficiency and performance of asphalt, over durations.

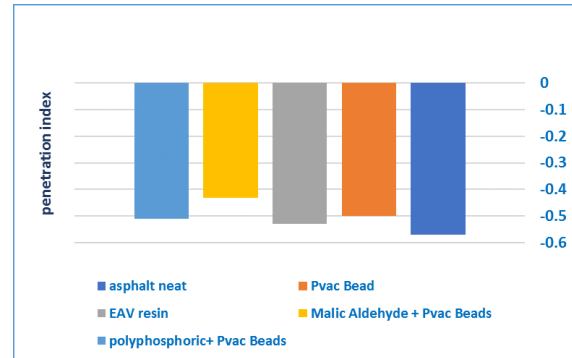


Figure (7): Effect of additives on the asphalt PI

8. Conclusion

Activation energy is a crucial indicator of asphalt's ability to withstand temperature variations during service, directly impacting its durability and stability. Asphalt binders modified with PVAC beads, EAV resin, MA mixed with PVAC beads, and PPA + PVAC beads exhibited higher activation energy values compared to neat asphalt, indicating superior performance in resisting thermal changes.

- It was found an increase in the activation energy of the optimized asphalt over the non-optimized asphalt, where it was found that when EVA resin, MA mixed with PVAC beads, and PPA mixed with PVAC beads were added, the activation energy value increased by 1.9%, 1.30%, 37.27%, and 45.44%, respectively.
- The PI (PI) was assessed for both neat asphalt and asphalt modified with various additives, including PVAC beads, EAV resin, MA combined with PVAC beads, and polyphosphoric acid combined with PVAC beads. The analysis revealed improvements in PI for the modified asphalt relative to neat asphalt, with enhancements of 12.3%, 7.0%, 24.6%, and 10.5%, respectively. These results suggest a superior thermal resistance for the modified asphalt formulations.

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