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Preparation and Evaluation of New Nano-Composites Based on PVA and Thiosemicarbazide for the Enhancement of Iraqi Asphalt Specifications

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ABSTRACT

This work describes the development and broader characterization of a new series of nanostructured polymeric materials derived from thiosemicarbazide and poly(vinyl alcohol) via a multistep synthetic route involving Schiff base formation followed by cyclization reactions. Fourier transform infrared spectroscopy (FTIR) confirmed the successful formation of nano-cross-linked polymer networks. The characterization of proton nuclear magnetic resonance (^{1}H-NMR), thermogravimetric analysis (TGA), X-ray diffraction (XRD), and scanning electron microscopy (SEM). The relationship between temperature and the spontaneous formation of nanostructures on thin films was reported in April 2022. The synthesized polymers can absorb water due to the presence of polar functional groups and a nano-structured architecture, resulting in a higher surface area. Additionally, using these polymeric materials as asphalt modifiers greatly improved the rheological behavior and deformation resistance of the asphalt binder. As shown by the results of this study, the present nano-structured polymers can be successfully used as an alternative (sustainable) asphalt modifier primarily for road pavements subjected to severe thermal and environmental conditions.

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INTRODUCTION

Hot-mix asphalt (HMA) pavements are prone to three major forms of distress—permanent deformation (rutting), fatigue cracking, and low-temperature cracking—throughout their service life, which collectively contribute to premature pavement failure [1]. Fatigue cracking is the most common distress in road pavement, mainly due to repeated vehicular loading (especially heavy axle loads) and environmental conditions [2]. Several distresses hamper the performance of flexible pavements in Iraq and result in premature failure. In flexible pavements, the primary forms of distress are fatigue cracking and rutting [3]. These distresses arise mainly from traffic loading and extreme temperature variations that affect the rheological properties of asphalt binders. Modifying the virgin asphalt binder with polymeric additives has proven to be one of the most effective strategies for enhancing pavement durability and mitigating these forms of distress [4]. The incorporated polymer modifies the viscoelastic and failure characteristics of asphalt, thereby improving its rigidity, elasticity, brittleness

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balance, and storage stability [5].

Polymers are macromolecules formed through the successive linking of small monomeric units into linear, branched, or cross-linked structures [5]. The addition of such polymers can improve the mechanical strength and temperature resistance of asphalt binders [6]. However, the efficiency of this modification depends on the compatibility between the polymer and the asphalt matrix, the type of polymer used, and the interaction mechanism involved (physical blending or chemical reaction) [7].

In Iraq, the continuous increase in vehicle numbers, especially heavy trucks, combined with severe climatic conditions—high ambient temperatures, moisture exposure, and inadequate maintenance—has accelerated pavement degradation [8,10]. These challenges necessitate the development of advanced asphalt modification techniques capable of improving binder performance under such extreme conditions. Given the moisture-related challenges faced by asphalt pavements in Iraq, polymer modification has emerged as a practical approach to improve adhesion and reduce stripping potential, ultimately enhancing the long-term durability of asphalt mixtures under such environmental conditions[11] The structural performance and stiffness of asphalt mixtures are strongly influenced by aggregate gradation, which plays a critical role in controlling load distribution, mixture stability, and resistance to deformation [12]. Asphalt remains the most widely used paving material due to its stability, durability, and waterproofing ability; however, its rheological and mechanical properties can be further enhanced through chemical modification and polymer incorporation [1,6].

Among the various types of asphalt modifiers, polymeric additives have gained significant attention due to their ability to enhance elasticity, reduce temperature susceptibility, and improve resistance to rutting and fatigue cracking [9]. Despite these benefits, conventional polymers such as SBS, EVA, and polyethylene rely primarily on physical blending, often leading to phase separation and limited long-term stability [1,9]. Therefore, there is a growing interest in developing reactive polymers that can chemically interact with asphalt components to form more stable and compatible systems [4,8]. Recent studies in Iraq have focused on synthesizing new Schiff base derivatives and grafted polymeric structures to enhance chemical reactivity and functional performance of polymeric materials [19].

In recent years, significant progress has been made in the field of polymer-modified asphalt, emphasizing the development of reactive systems designed to improve binder–polymer compatibility and performance stability under severe climatic conditions. Recent investigations have highlighted that reactive polymers containing heteroatoms such as nitrogen, oxygen, and sulfur can form strong chemical interactions with bitumen components, leading to enhanced durability and deformation resistance [13].

Polymer modification through copolymerization and functionalization has shown improvements in stability and application-specific performance, indicating the importance of developing reactive polymer systems for industrial applications [20].

Jexembayeva et al. (2024) demonstrated that polymer-modified asphalt mixtures incorporating functionalized polymer chains improved stiffness, thermal stability, and resistance to rutting under high traffic loads [14]. Their findings suggested that the molecular structure and reactivity of the polymer greatly influence its compatibility with asphalt.

According to Emmaima et al. (2024), reactive polymeric systems enhance viscoelastic recovery and storage stability of asphalt binders during prolonged service at elevated temperatures [15]. These properties are particularly beneficial in regions with hot climates, such as Iraq, where high temperature susceptibility is a critical factor in pavement failure.

Riaz (2025) investigated the performance of SBS-based reactive polymer binders and found that their chemical bonding with asphaltenes improved both elasticity and thermal cracking resistance, thereby extending pavement lifespan[16].

Further studies by Zaumanis (2025) proposed a new classification for highly polymer-modified asphalt binders, focusing on their rheological properties and long-term phase stability[17]. This work emphasized the importance of optimizing polymer concentration and blending conditions to ensure stable polymer dispersion.

Lastly, Jaysawal (2025) reported that polymer modification improves asphalt performance even under wet conditions, showing superior adhesion and reduced stripping potential[18]. These results collectively confirm that advanced reactive polymers represent a reliable solution to enhance

the mechanical and rheological performance of Iraqi asphalt binders and ensure longer pavement service life in extreme environmental conditions.

The aim of study is summarized as: 1) To synthesise a novel reactive polymer derived from thiosemicarbazide and 2,4-dihydroxybenzaldehyde through condensation, cyclisation, and subsequent modification with PVA and phthalic anhydride. 2) To confirm the chemical structure of the ynthesized polymer using FTIR, 1H-NMR, and thermal analysis, verifying the formation of Schiff base linkages and heterocyclic functionalities. 3) To incorporate the ynthesized polymer into Iraqi asphalt binder and evaluate its effect on the rheological, chemical, and mechanical performance of the binder. 4) To analyse the interaction mechanism between the reactive polymer and asphalt molecules, focusing on compatibility improvement and the formation of potential chemical bonds. 5) To assess the overall potential of this reactive polymer system as a sustainable and thermally stable modifier for asphalt used in hot-climate regions such as Iraq.

MATERIALS AND METHODS

Materials

Thiosemicarbazide 2,4-dihydroxybenzaldehyde, dimethyl sulfoxide (DMSO), dimethylformamide (DMF), and absolute ethanol were purchased from Fluka Company. Potassium carbonate (K_2CO_3), iodine (I_2), phthalic anhydride, 4-methylbenzaldehyde, glyceraldehyde, poly(vinyl alcohol) (PVA), and sodium hydroxide (NaOH) were of analytical grade and used without further purification.

Experimental Procedure

All chemicals used in this study were of the highest purity and employed as received without further purification. Melting points of the synthesized compounds were determined using a Stuart melting point apparatus. The Fourier Transform Infrared (FT-IR) spectra were recorded using KBr pellets on a Shimadzu FTIR spectrophotometer. The ^{1}H-NMR spectra were obtained in DMSO-d_6 on a Varian 400 MHz NMR spectrometer using tetramethylsilane (TMS) as the internal reference.

Preparation of 2-(2,4-dihydroxybenzylidene) hydrazine-1-carbothioamide (T1) [15]

Thiosemicarbazide (0.5 g) was dissolved in 8 mL of ethanol and reacted with 2,4-dihydroxybenzaldehyde (0.7 g) dissolved in 3 mL of ethanol in the presence of glacial acetic acid (0.5 mL) as a catalyst. The reaction mixture was placed in a round-bottom flask and heated at 78 °C for 11 h under continuous stirring. The product was then dried at room temperature to obtain compound T1.

Preparation of 4-(5-amino-1,3,4-thiadiazol-2-yl) benzene-1,3-diol (T2) [16]

(1 g) of 2-(2,4-dihydroxybenzylidene)hydrazine-1-carbothioamide (T1) was dissolved in 12 mL of ethanol and mixed with (1 g) of K_2CO_3 dissolved in ethanol, then (0.5 g) of I_2 was added. The mixture was placed in a round-bottom flask equipped with a condenser and heated at 78 °C for about 4 hours. The reaction mixture was then cooled, dried, and washed repeatedly with ethanol to obtain compound (T2).

Preparation of (Z)-4-(5-((2,3-dihydroxypropylidene) amino)-1,3,4-thiadiazol-2-yl)benzene-1,3-diol (G) [17]

(0.5 g) of 4-(5-amino-1,3,4-thiadiazol-2-yl) benzene-1,3-diol was dissolved in 10 mL of ethanol and mixed with (1 g) of glyceraldehyde dissolved in 8 mL of ethanol. The mixture was placed in a round-bottom flask equipped with a condenser and heated at 80 °C for about 10 hours. The formed precipitate was washed with ethanol and dried to obtain compound (G).

Preparation of 2-(2,4-dihydroxyphenyl)-5-[(2-pyridyl)methyleneamino]-1,3,4-thiadiazole (Py) [18]

(0.5 g) of 4-(5-amino-1,3,4-thiadiazol-2-yl) benzene-1,3-diol was dissolved in 10 mL of ethanol and mixed with 3 mL of 2-pyridinecarboxaldehyde. The mixture was placed in a round-bottom flask equipped with a condenser and heated at 80 °C for about 10 hours. The formed precipitate was washed with ethanol and dried to obtain compound (Py).

Preparation of 2-(2,4-dihydroxyphenyl)-5-[(2-(3,4-dihydroxy-1,3-dioxoisoindolin-2-yl)propylidene) amino]-1,3,4-thiadiazole-based poly(vinyl alcohol)–phthalate copolymer (T3) [19]

(0.5 g) of poly(vinyl alcohol) (PVA) was dissolved in 12 mL of an ethanol–water mixture (1:1 v/v) under stirring. Separately, (0.5 g) of phthalic anhydride was dissolved in 10 mL of ethanol.

Compound (G) (0.5 g), previously synthesized as (Z)-4-(5-((2,3-dihydroxypropylidene)amino)-1,3,4-thiadiazol-2-yl)benzene-1,3-diol, was dissolved in 15 mL of ethanol and treated with a 5% NaOH solution. The PVA and phthalic anhydride solutions were then added dropwise to the (G) solution under continuous stirring. The reaction mixture was heated at 100 °C for 8 hours under reflux. After completion, the mixture was cooled to room temperature, and the resulting solid product was filtered, washed with ethanol, and dried to afford the modified polymer compound (T3).

Preparation of 2-(2,4-dihydroxyphenyl)-5-[(2-(3,4-dihydroxy-1,3-dioxoisoindolin-2-yl)pyridyl) methyleneamino]-1,3,4-thiadiazole-based poly(vinyl alcohol)–phthalate copolymer (T4) [20]

(0.5 g) of poly(vinyl alcohol) (PVA) was dissolved in 12 mL of an ethanol–water mixture (1:1 v/v) under stirring. Separately, (0.5 g) of phthalic anhydride was dissolved in 10 mL of ethanol. Compound (Py) (0.5 g), previously prepared as €-2-(2,4-dihydroxyphenyl)-5-[(2-pyridyl) methyleneamino]-1,3,4-thiadiazole, was dissolved in 12 mL of ethanol and treated with a 5% NaOH solution. The PVA and phthalic anhydride solutions were then added dropwise to the Py solution under continuous stirring. The reaction mixture was heated at 100 °C for 8 hours under reflux. After completion, the mixture was cooled to room temperature, and the resulting solid product was filtered, washed with ethanol, and dried to afford

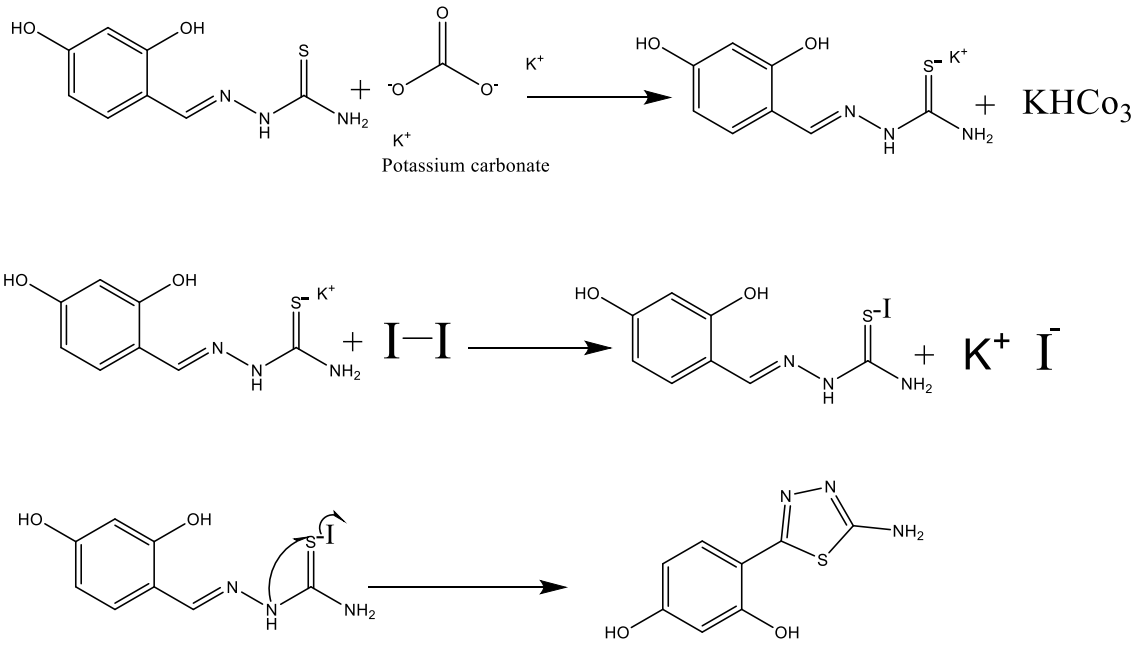

Fig. 1. Ring closure mechanism.

Table 1. FT-IR Spectral Data of Synthesized Compounds (T1–T4, g, and py).

Compound	ν(O–H) cm⁻¹	ν(N–H) cm⁻¹	ν(C–H) aromatic cm⁻¹	ν(C–H) aliphatic cm⁻¹	ν(C=O) cm⁻¹	ν(C=N) cm⁻¹	ν(C–O–C) / ν(C–S) cm⁻¹
T1	3410	3250	–	–	–	1615	1258 / 675
T2	3415	–	–	2950–2870	–	1618	– / 670
G	3380	–	–	2920–2850	–	1616	1248 / 666
Py	3415	–	3010	2960–2850	1715	1620	– / –
T3	3385	–	–	2920–2850	1720	1612	1260 / –
T4	3420	–	3010	2960–2840	1718	1610	– / –

compound (T4).

Fourier Transform Infrared Spectra (FT-IR)

The FT-IR spectra of the synthesized compounds (T1–T4, g, and py) were recorded in the 4000–400 cm^{-1} region and confirmed each step of thesynthesis (Figs. S1-S7).

Compound T1: The spectrum exhibited a broad band at 3410 cm^{-1} for phenolic O–H and a band at 3250 cm^{-1} due to N–H stretching of thiosemicarbazide. The appearance of a new strong band at 1615 cm^{-1} corresponding to C=N (azomethine) confirmed the formation of the Schiff base between thiosemicarbazide and 2,4-dihydroxybenzaldehyde. The peaks at 1258 cm^{-1} (C=S) and 675 cm^{-1} (C–S) supported the presence of the thioamide moiety.

Compound T2: The FT-IR spectrum showed disappearance of the N–H peaks observed in T1, confirming cyclization to form the 1,3,4-thiadiazole ring. A broad absorption near 3415 cm^{-1} indicated O–H stretching, while the sharp peak at 1618 cm^{-1} represented the new C=N bond formed inside the ring. The weak band around 670 cm^{-1} corresponded to C–S stretching, further supporting ring closure.

Compound g: The spectrum revealed a strong band at 1616 cm^{-1} assigned to C=N stretching of a newly formed Schiff base between compound T2 and glyceraldehyde. The broad O–H band at 3380 cm^{-1} and the peaks at 2920–2850 cm^{-1} (C–H) indicated the presence of hydroxyl and aliphatic groups, while additional absorptions at 1248 cm^{-1} (C–O–C) and 666 cm^{-1} (C–S) confirmed condensation with the glyceraldehyde moiety.

Compound py: The FT-IR spectrum showed a distinct C=N stretching band at 1620 cm^{-1}, confirming the second Schiff base formation between compound T2 and 2-pyridinecarboxaldehyde. The peaks at 3415 cm^{-1} (O–H), 2960–2850 cm^{-1} (C–H aliphatic), and 3010 cm^{-1} (C–H aromatic) verified the presence of both hydroxyl and pyridyl groups, while the weak band near 1715 cm^{-1} (C=O) suggested partial conjugation within the system.

Compound T3: The spectrum showed the characteristic bands of the polymeric product. The broad O–H band at 3385 cm^{-1} and C–H stretching at 2920–2850 cm^{-1} were maintained, while new absorptions at 1720 cm^{-1} (C=O) and 1260 cm^{-1} (C–O–C) confirmed the formation of ester linkages during reaction with phthalic anhydride and PVA. The band at 1612 cm^{-1} indicated retained

Table 2. Application of Polymer T3.

Sample ID	Gelatin (g)	Polymer T3 (g)	Mixing Temp (°C)	Time (h)
T3-A	0.5	1.0	100	3
T3-B	1.0	2.0	100	3
T3-C	1.5	3.0	100	3

Table 3. Application of Polymer T4.

Sample ID	Gelatin (g)	Polymer T4 (g)	Mixing Temp (°C)	Time (h)
T4-A	0.5	1.0	100	3
T4-B	1.0	2.0	100	3
T4-C	1.5	3.0	100	3

Table 4. Physical properties of the samples.

Sample	Polymer	Density (g/mL)	Flash Point (°C)	Viscosity (sec)
A0	None	1.043	324	130
T3-C	T3 (High)	1.09	106	130
T3-B	T3 (Medium)	0.9	76	140
T3-A	T3 (Low)	0.87	52	195
T4-C	T4 (High)	0.919	145	166
T4-B	T4 (Medium)	0.88	63	170
T4-A	T4 (Low)	0.89	54	165

azomethine (C=N) groups in the polymer chain.

Compound T4: The FT-IR spectrum displayed a strong band at 1718 cm^{-1} (C=O) and 1610 cm^{-1} (C=N), confirming the successful reaction of polymerization between the pyridyl derivative (py) and phthalic anhydride. The broad O–H band at 3420 cm^{-1} and the aromatic/aliphatic C–H bands (3010 and 2960–2840 cm^{-1}) supported the formation of the final polymer.

Application of Synthesized Polymers (T3 and T4) to Asphalt Binder[27]

Application of Polymer T3 to Asphalt Binder

A quantity of 250 g of base asphalt (penetration grade 40/50) was melted and mixed with 1 L of toluene until complete dissolution. Gelatin was prepared in three concentrations (0.5 g, 1.0 g, and 1.5 g) by dissolving it in distilled water under mild heating and stirring. The synthesized polymer (T3) was dissolved in dimethyl sulfoxide (DMSO) at three different loadings (1 g, 2 g, and 3 g). The polymer and gelatin solutions were gradually added to the asphalt–toluene mixture under continuous stirring at 100 °C for 3 hours. After mixing, the modified asphalt samples were cooled to room temperature and stored in airtight containers for further characterization.

Application of Polymer T4 to Asphalt Binder

The same procedure described for T3 was followed, except that polymer (T4) was used instead of T3. The asphalt (250 g) was dissolved in 1 L of toluene, and gelatin was added at 0.5, 1.0, and 1.5 g concentrations. The T4 polymer was added in 1, 2, and 3 g quantities after being dissolved in DMSO. The mixture was heated and stirred at 100 °C for 3 hours, then cooled and stored for testing.

RESULTS AND DISCUSSION

Table 4 presents the physical properties of the neat asphalt (A0) and the modified asphalt binders incorporating synthesized polymers T3 and T4 at different concentrations. The results clearly indicate that polymer modification influenced the density, flash point, and viscosity of the asphalt binder, reflecting structural and rheological improvements.

The modification of asphalt with thiadiazole-based polymers (T3 and T4) significantly influenced its thermal and rheological behavior. Incorporation of polymer T3 increased the viscosity values, particularly for the lower polymer concentration (T3-A), which reached 195 sec, indicating improved resistance to flow and deformation. This enhancement is attributed to the formation of hydrogen bonding and van der Waals interactions between hydroxyl, carbonyl, and thiadiazole groups in T3 and the polar constituents of the asphalt matrix. Conversely, the density slightly increased with T3 addition (up to

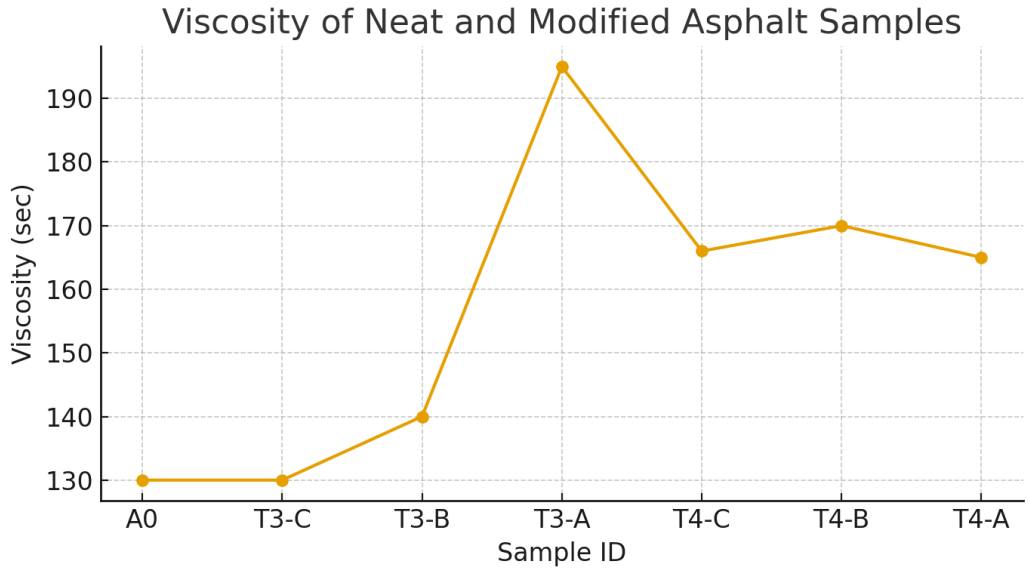

Fig. 2. Variation of viscosity for neat and polymer-modified asphalt samples.

1.09 g/mL), suggesting better molecular packing and dispersion of the polymer chains within the bitumen network. However, the flash point decreased for T3-modified binders due to the possible volatilization of lighter fractions during polymer incorporation.

For polymer T4, the behavior differed: although viscosity values were moderately high (165–170 sec), the flash point significantly increased (up to 145°C), indicating enhanced thermal stability. This improvement is linked to the aromatic pyridyl structure in T4, which contributes to higher resistance against oxidation and volatilization under heating. Thus, T4-modified asphalt binders are more thermally stable and suitable for high-temperature climatic regions.

Comparatively, T3 imparts higher mechanical strength and stiffness due to its thiadiazole and dihydroxy functional groups, while T4 enhances thermal resistance owing to the pyridine-based moiety. These complementary effects make both polymers effective modifiers, with T3 being optimal for heavy-load pavements and T4 for hot-weather applications.

Proton Nuclear Magnetic Resonance (^{1}H-NMR)

^{1}H-NMR spectra of the synthesized compounds were recorded using DMSO-d_6 as solvent, and the obtained spectra confirmed the expected molecular structures. The spectra were illustrated as shown below:

The ^{1}H-NMR spectrum of compound (T1) was shown in Fig. S7, which exhibits the following signals: δ 1.2–1.6 ppm (CH_2 aliphatic, m), δ 2.9 ppm (CH–NH, t), δ 3.6–3.9 ppm (OH–CH, s), δ 6.1–7.9 ppm (aromatic CH, m), and δ 8.2 ppm (C=NH, s). These peaks confirm the formation of the Schiff base between thiosemicarbazide and 2,4-dihydroxybenzaldehyde.

The ^{1}H-NMR spectrum of compound (T2) was shown in Fig. S8, in which the disappearance of N–H signals observed in T1 confirms the cyclization to form the 1,3,4-thiadiazole ring. The spectrum displays peaks at δ 1.6–2.1 ppm (CH_2, m), δ 3.0 ppm (CH, s), δ 6.1 ppm (aromatic CH, s), and δ 7.9–8.2 ppm (OH and aromatic CH, m).

The ^{1}H-NMR spectrum of compound (g) was shown in Fig. S9, showing characteristic signals at δ 1.2–1.5 ppm (CH_2, m), δ 3.0–3.2 ppm (CH–OH, m), δ 4.8 ppm (O–CH_2, s), and δ 7.2–8.1 ppm (aromatic CH, s). These peaks indicate the formation of a Schiff base between compound T2 and glyceraldehyde.

The ^{1}H-NMR spectrum of compound (py) was shown in Fig. S10, which exhibits peaks at δ 1.5 ppm (CH_2, m), δ 3.8–4.0 ppm (CH–NH, s), δ 7.0–8.1 ppm (aromatic CH, m), δ 8.8 ppm (C=NH, s), and δ 10.1 ppm (phenolic OH, s). These signals confirm the successful formation of the pyridyl Schiff base.

The ^{1}H-NMR spectrum of the polymer (T3)

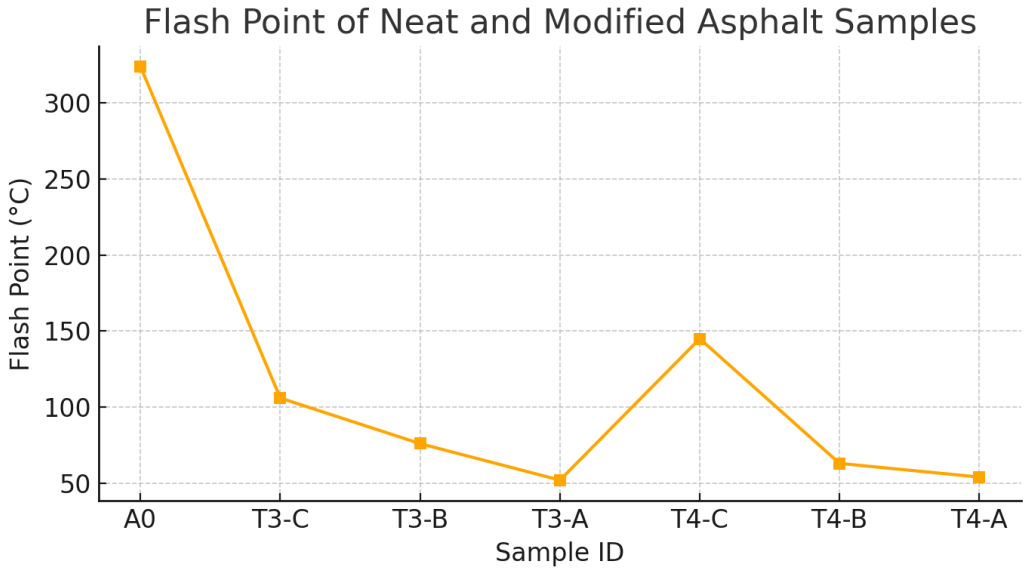

Fig. 3. Flash point comparison for neat and polymer-modified asphalt samples.

was shown in Fig. S11, which displays signals at δ 1.1–1.5 ppm (CH_2–CH, m), δ 2.4 ppm (CH–CO, s), δ 3.8–4.1 ppm (NH–CH, m), δ 7.1–7.9 ppm (aromatic CH, s), and δ 10.5 ppm (Ar–OH, s). These peaks confirm the formation of the polymer obtained from compound g with PVA and phthalic anhydride.

The ^{1}H-NMR spectrum of the polymer (T4) was shown in Fig. S12, which shows characteristic peaks at δ 1.2–1.6 ppm (CH–CH_2, m), δ 2.5 ppm

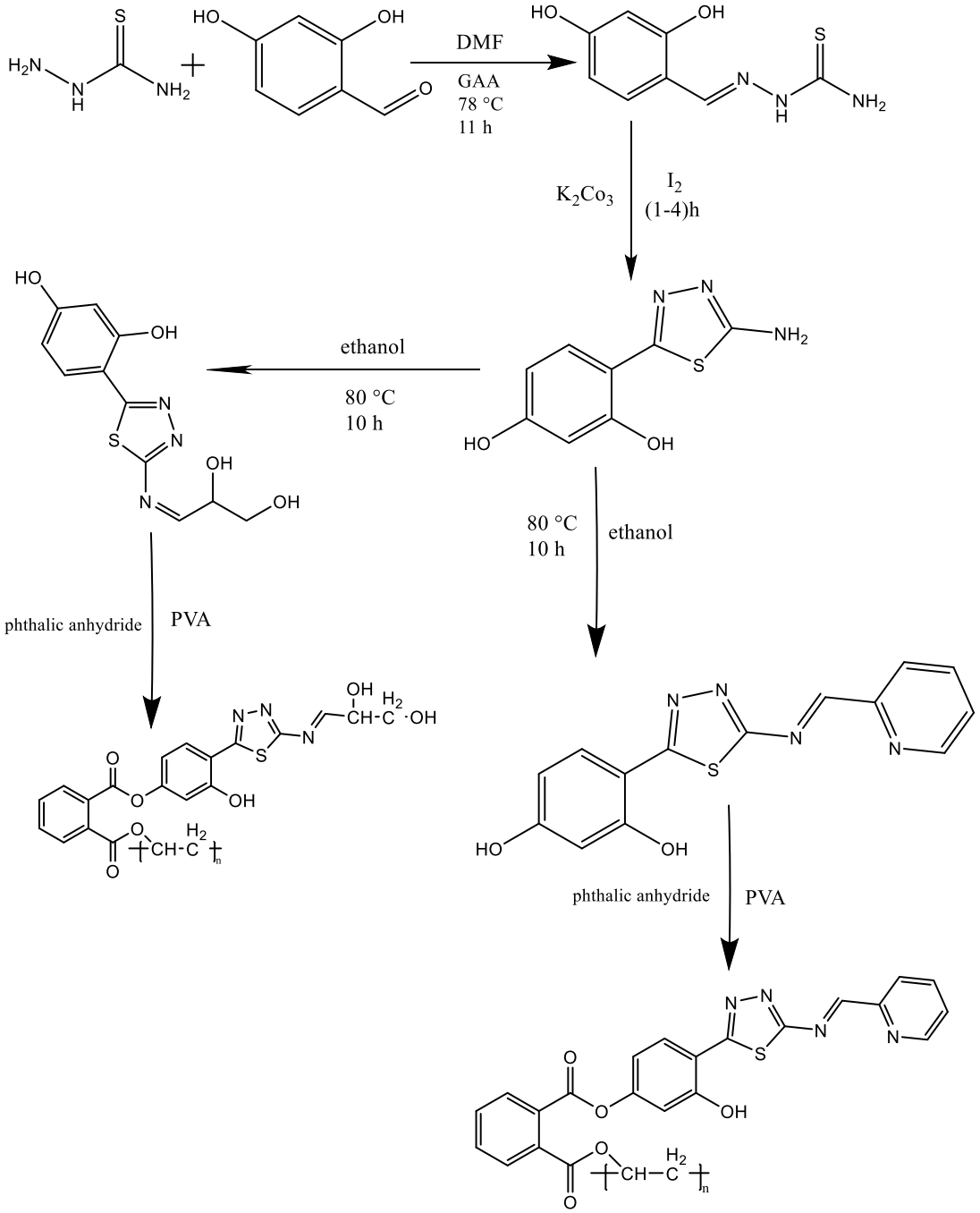

Fig. 4. Synthesis and chemical modification of T3 and T4 polymers. The pathway details the construction of the thiadiazole-functionalized backbone and final cross-linking/modification steps.

(CH_2–CH, t), δ 3.8 ppm (NH–CH, s), δ 4.9 ppm (R–OH, s), and δ 7.9–8.2 ppm (aromatic CH, s). These signals support the formation of the pyridyl-containing polymer derived from compound py and phthalic anhydride with PVA.

Study of Thermal Properties (TGA)

Thermogravimetric (TG) curves of the synthesized polymers (T1–T4) were recorded under an argon atmosphere within the temperature range of 0–1000°C, at a heating rate of 10°C min^{-1}. All the prepared polymers exhibited a multistep decomposition behavior, confirming their good thermal stability.

The TGA curve of compound (T1) in Fig. S13 shows three main stages of weight loss. The first minor loss below 150°C (≈ 5–7%) is attributed to the evaporation of physically adsorbed moisture and volatile substances. The second major weight loss occurs between 200–450°C, corresponding to the decomposition of hydroxyl and carbonyl groups, resulting in a total weight loss of about 41.31%. The final stage above 500°C indicates the breakdown of aromatic and heterocyclic backbones, suggesting good stability of the polymeric framework up to 800°C.

The TGA curve of compound (T2) in Fig. S14 exhibits a similar three-step decomposition pattern. The initial small weight loss below 120°C corresponds to the removal of surface moisture, followed by a second degradation step between 200–400°C, related to side-chain cleavage and decomposition of functional groups. The total weight loss was 71.35%, indicating moderate stability and confirming the formation of a thermally active structure.

The TGA curve of compound (T3) in Fig. S15 shows clear multistage thermal degradation. The first stage under 100–150°C is due to the evaporation of moisture, while the main degradation occurs between 250–500°C, attributed to the decomposition of polymeric linkages and phthalic moieties, with a total weight loss of 78.23%. The final stage beyond 500°C represents the gradual breakdown of aromatic residues, confirming that compound T3 decomposes through multiple successive steps.

The TGA curve of compound (T4) in Fig. S16 demonstrates gradual weight loss with increasing temperature. The initial phase below 150°C indicates moisture evaporation, while the major degradation between 250–600°C results in a total weight loss of 35.29%. This relatively lower mass loss compared to the other polymers suggests enhanced thermal stability, possibly due to the presence of pyridyl and aromatic rings that increase rigidityand resistance to thermal decomposition.

Overall, all compounds (T1–T4) exhibit good thermal stability, particularly compound T4, which shows the highest resistance to thermal degradation, indicating strong crosslinking and aromatic reinforcement in its structure.

SEM Morphological Analysis of the Synthesized Polymers (T3 and T4)

SEM micrographs of the synthesized polymeric additives T3 and T4, before blending with asphalt, are presented in Figs. S17 and S18. The images reveal clear morphological differences between the two prepared structures, reflecting the effect of the chemical composition and the

Table 5. Thermogravimetric (TG) curves.

Codes No.	Temp. °C	Weight Loss %
T1	150	5–7
	200–450	41.31
	500–800	Minor residue
T2	120	5
	200–400	71.35
	>500	Negligible
T3	100–150	5
	250–500	78.23
	>500	Small residue
T4	<150	5
	250–600	35.29
	>600	Stable

nature of functional groups on the final polymer morphology.

The polymer T3 exhibited a semi-crystalline, plate-like morphology, characterized by thin lamellar sheets, fractured surfaces, and stacked layers of irregular geometry. The presence of sharp-edged flakes and multi-layered aggregations indicates partial crystallinity originating from the integrated phthalic anhydride and heterocyclic Schiff-base segments. This morphology resulted in a rough surface with internal voids, suggesting that T3 possesses a high potential for mechanical interlocking and enhanced interaction with asphalt components.

In contrast, the polymer T4 displayed a more aggregated and granular morphology, with the appearance of semi-spherical clusters, compact domains, and heterogeneous surface roughness. The SEM images reveal that T4 forms dense micro-aggregates and porous agglomerations, which may be attributed to the chemical structure of the modified chains and the distribution of heteroatoms (N, O, S) within the polymer network. Compared to T3, T4 showed higher degrees of particle clustering, reflecting differences in polymer chain packing and intermolecular interactions.

Overall, the SEM analysis confirms that both T3 and T4 exhibit heterogeneous, rough, and non-uniform surface textures, which can significantly improve their compatibility with asphalt binders. The plate-like morphology of T3 and the granular porous nature of T4 provide abundant surface irregularities and active interaction sites, facilitating enhanced dispersion within the asphalt matrix. These structural features suggest that the prepared polymers are capable of contributing to improved rutting resistance, higher stiffness, and better thermal stability when incorporated into asphalt formulations.

XRD Analysis of the Synthesized Polymers T3 and T4

XRD patterns of the synthesized polymers T3 and T4 are presented in Figs. S19 and S20. Both diffractograms exhibit several sharp and intense peaks superimposed on a relatively low background, indicating that the prepared materials possess a semi-crystalline nature rather than being completely amorphous.

For polymer T3, multiple reflections are observed mainly within the range of $2\theta \approx 20–40°$, with particularly intense peaks appearing around 30° and in the vicinity of 33–36°. The presence of these sharp peaks suggests the formation of ordered crystalline domains, which can be attributed to the regular packing of the aromatic rings, thiadiazole units, and phthalate segments within the polymer backbone. In addition, the existence of several weaker peaks at higher angles (above 40°) indicates a certain degree of structural ordering at shorter interplanar distances. The combination of sharp peaks and a slightly broadened baseline confirms that T3 contains both crystalline and amorphous regions, consistent with its semi-crystalline morphology observed by SEM.

The XRD pattern of polymer T4 shows a similar distribution of peaks, but with higher peak intensities and slightly sharper profiles, especially for the main reflection near $2\theta \approx 30°$. This behavior indicates that T4 exhibits a higher degree of crystallinity compared to T3. The enhanced crystallinity in T4 can be related to the presence of the pyridyl Schiff-base moieties, which promote more efficient chain packing and stronger intermolecular interactions within the polymer network. The additional reflections appearing between $2\theta \approx 30–40°$ further support the formation of well-organized domains in T4.

Overall, the XRD analysis confirms that both T3 and T4 are semi-crystalline polymers with pronounced crystalline domains embedded in an amorphous matrix. The slightly higher crystallinity of T4, as evidenced by the sharper and more intense diffraction peaks, is expected to contribute to its higher thermal stability and stiffness, in agreement with the TGA and rheological results obtained for the asphalt blends modified with this polymer.

CONCLUSION

In this study, a series of new polymers derived from thiosemicarbazide were successfully synthesized through multi-step reactions and characterized by FTIR, ^{1}H-NMR, and TGA analyses. The spectroscopic data confirmed the successful formation of Schiff base and 1,3,4-thiadiazole derivatives, while the thermal analyses revealed good thermal stability for all synthesized compounds. The polymers (T3 and T4) were further blended with asphalt binder in different proportions to evaluate their effect on the physical and rheological properties of Iraqi asphalt. The

modification process significantly improved the asphalt's consistency, softening point, and resistance to deformation, especially at high temperatures. Among the prepared polymers, T4 exhibited the best performance, showing higher thermal stability, lower weight loss in TGA, and superior enhancement in asphalt characteristics. This behavior can be attributed to the presence of pyridyl and aromatic rings in its structure, which provide additional rigidity and crosslinking within the polymeric network. Overall, the developed polymer (T4) can be considered a promising synthetic modifier for improving the performance of Iraqi asphalt under different climatic and loading conditions.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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