

Article

Mechanical Properties and Modification Mechanism of Thermosetting Polyurethane-Modified Asphalt

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Abstract

To study the mechanical properties and modification mechanism of thermosetting polyurethane (PU)-modified asphalt, the effects of polyurethane dosage on the workability of polyurethane-modified asphalt were analyzed by means of rotational viscosity tests. The mechanical properties of polyurethane-modified asphalt with different polyurethane dosages were explored using tensile tests and dynamic mechanical analysis (DMA). In addition, the thermodynamic behavior and micromorphology of polyurethane-modified asphalt were also thoroughly investigated using the test results of differential scanning calorimetry (DSC) and scanning electron microscopy (SEM). The results showed that PU obtained the optimum workability when the polyurethane dose was 50%: at 120 min, its rotational viscosity was 1005 cp, which was lower than 2800 cp (40% PU) and 760 cp (60% PU). Additionally, the results of fracture elongation and fracture strength indicated that the PU-modified asphalt had good flexibility and strength. Compared with base asphalt, the tensile strength of 50% PU-modified asphalt increased by 509%, which was significantly higher than 157% (40% PU) and more balanced than 897% (60% PU) in terms of strength and flexibility. Added PU can significantly improve the elasticity of asphalt at high temperatures, while increasing the proportion of asphalt adhesive components, enhancing the deformation ability and temperature stability of asphalt. As the dose of PU increases, the interface between asphalt and PU blended more fully, and the surface became smoother. When the dose of PU was 50% or more, the interface between asphalt and PU was well integrated with a smooth and flat surface, forming a more uniform and stable cross-linked network structure.

Keywords: polyurethane; modified asphalt; tensile property; dynamic mechanical performance; modification mechanism; microscopic characteristics



Academic Editor: Valeria Vignali

Received: 28 June 2025

Revised: 14 July 2025

Accepted: 31 July 2025

Published: 4 August 2025

Citation: Zhuang, W.; Ding, T.; Pang, C.; Jiao, X.; Geng, L.; Sun, M. Mechanical Properties and Modification Mechanism of Thermosetting Polyurethane-Modified Asphalt.

Coatings **2025**, *15*, 912. <https://doi.org/10.3390/coatings15080912>

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1. Introduction

Asphalt pavement is prone to early damages including rutting, cracks, and potholes due to the combined effects of complex factors such as traffic loads, temperature, light, and moisture during long-term service [1–3]. Furthermore, the increasing traffic volume and vehicular loading are imposing more stringent demands on the pavement performance of asphalt-surfaced roads [4,5]. The asphalt pavement is made by mixing asphalt binder, coarse aggregate, fine aggregate, and filler, followed by the processes of paving

and compaction. Although asphalt accounts for a small proportion of the asphalt mixture, it is a key component that affects the road performance of the asphalt pavement [6–8]. With the worsening of the natural environment, frequent extreme weather, serious overloading and heavy loading all over the world, higher demands are placed on asphalt pavement. Conventional petroleum asphalt fails to fulfill the current performance requirements of asphalt pavements. It has been demonstrated through research that the addition of modifiers, through specific processes, constitutes an effective approach to enhancing the road performance of asphalt materials [3,9]. Among these, polymer modifiers are most extensively utilized owing to their outstanding modification effects, particularly styrene-butadiene-styrene (SBS)-modified asphalt, crumb rubber (CR)-modified asphalt, and styrene-butadiene rubber (SBR)-modified asphalt [1,5,9]. SBS-modified asphalt demonstrates superior high-temperature and low-temperature characteristics, thereby considerably enhancing pavement durability. However, SBS is prone to thermal-oxidative aging and is more expensive [10]. CR can enhance resistance to cracking and rutting of asphalt, and is also cost-effective and environmentally friendly due to recycling [3,5]. Nonetheless, added CR can significantly increase the viscosity of the asphalt, making it more difficult to construct [3,5,10]. SBR-modified asphalt provides good low-temperature flexibility and resistance to fatigue cracking, but it may not perform as well at high temperatures [11]. Therefore, there is an urgent need for an ideal modifier to achieve a comprehensive improvement in road performance of asphalt.

Polyurethane (PU) represents a class of polymers in which the main chain features urethane bonds (-NHCOO-) as recurring structural units. The principal raw materials for PU synthesis are isocyanates bearing isocyanate groups (-NCO) and polyols possessing active hydroxyl groups. As an organic polymer, PU possesses advantages such as good elasticity, excellent resistance to aging, outstanding wear resistance, sufficient low-temperature ductility and high tear strength. These exceptional properties of PU provide an effective way to solve early damages associated with asphalt pavement [11–13]. In terms of physical properties, PU can be classified into two major categories: thermoplastic polyurethane and thermosetting polyurethane. Thermosetting polyurethane has a complex chemical cross-linked network structure, containing both hard segments and soft chain segments in its molecular structure, which confer corresponding rigidity and flexibility. Compared to thermoplastic polyurethane-modified asphalt, thermosetting polyurethane-modified asphalt has garnered widespread attention due to its superior modification effects, good compatibility with asphalt, and lower construction temperatures [12–15].

Some studies on thermosetting polyurethane-modified asphalt (PU-modified asphalt) have already been reported, and they found that thermosetting polyurethane forms a cross-linked network configuration within the asphalt system, thereby modifying the internal composition of asphalt and conferring outstanding mechanical capabilities onto the asphalt mixture [9,12–16]. C. Edward Terry et al. [17] carried out a succession of performance evaluations on their self-developed PU-modified asphalt. The findings indicated that the PU-modified asphalt exhibited commendable adhesion properties and resilience against moisture-induced damage. Awazhar et al. [18] investigated the influence of PU on the engineering attributes and leaching performance of warm-mix asphalt mixture. The results indicated that PU increased the viscosity and hardness of the asphalt and enhanced the interfacial adhesion between the binder and aggregate. Additionally, based on the heavy metal content of leachate from the asphalt samples, PU-modified asphalt had no adverse environmental impact, and the leachate did not exceed drinking water standards. Zhang et al. [19,20] explored the preparation procedures and pavement performance of PU-modified asphalt tailored for bridge deck surfacing. The research findings disclosed that PU substantially enhanced the high-temperature performance and mechanical characteristics

of asphalt. Moreover, in comparison with epoxy asphalt, the PU-modified asphalt manifested pre-eminent low-temperature performance and cost-effectiveness. Q He et al. [21] synthesized composite-modified asphalt, employing PU and epoxy resin as modifiers. The work revealed that these two modifiers established a continuous interpenetrating network architecture within the asphalt matrix. This structure remarkably improved the asphalt's high- and low-temperature stability, along with its resistance to moisture.

It can be seen from existing studies that the incorporation of PU can substantially enhance the high-temperature stability, low-temperature crack resistance, and moisture damage resistance of asphalt. However, the aforementioned studies have primarily focused on investigating the macroscopic properties while lacking systematic analysis of mechanical properties such as tensile strength and dynamic viscoelasticity, as well as their intrinsic correlation with microstructures. Thermosetting polyurethane-modified asphalt forms a permanent covalent network structure through irreversible chemical reactions between polyurethane prepolymers, asphalt, and curing agents. This unique structure endows it with superior temperature stability and durability, while exhibiting distinct mechanical characteristics and modification mechanisms compared to thermoplastic polyurethane-modified asphalt that have not been thoroughly elucidated. Moreover, existing research on other polymer modifiers has revealed their limitations such as susceptibility to thermal-oxidative aging, excessive viscosity increase, or inadequate high-temperature performance, yet the mechanism by which thermosetting PU achieves comprehensive performance improvement compared to these modifiers remains insufficiently explored. Therefore, further research is still needed to systematically explore the mechanical properties and modification mechanisms of thermosetting polyurethane-modified asphalt.

To study the workability, road performance, and modification mechanism of thermosetting polyurethane-modified asphalt, rotational viscosity tests were conducted, and the mechanical properties of PU-modified asphalt were systematically appraised through utilization of the tensile test and dynamic mechanical analysis (DMA). The thermal behavior and microscopic characteristics were assessed to deeply investigate the modification mechanism of thermosetting polyurethane-modified asphalt.

2. Materials and Methods

2.1. Raw Material

In this paper, base asphalt with penetration grade 70 #, produced by Sinopec Qilu Petrochemical Company (Zibo, China) was used. The modifier used for this study was a PU prepolymer and curing agent provided by Wanhua Chemical Group Co., Ltd. (Yantai, China). The raw materials are presented in Figure 1. The property indexes of the base asphalt and PU prepolymer are shown in Tables 1–3.

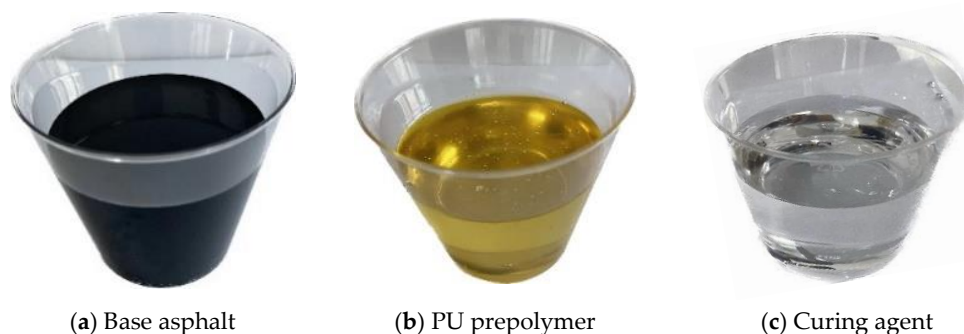


Figure 1. Raw materials.

Table 1. The property indexes of base asphalt.

Indicators	Penetration (25 °C)/0.1 mm	Ductility (10 °C)/cm	Brookfield Rotational Viscosity (135 °C)/mPa·s	Softening Point/°C	Flash Point/°C	Dynamic Viscosity (60 °C)/Pa·s	Density (15 °C)/(g·cm ⁻³)
Test value	65.3	56	2200	48	330	203	1.036
Standard value	60~80	≥10	—	≥43	≥260	≥180	—

Table 2. Property indexes of the PU prepolymer.

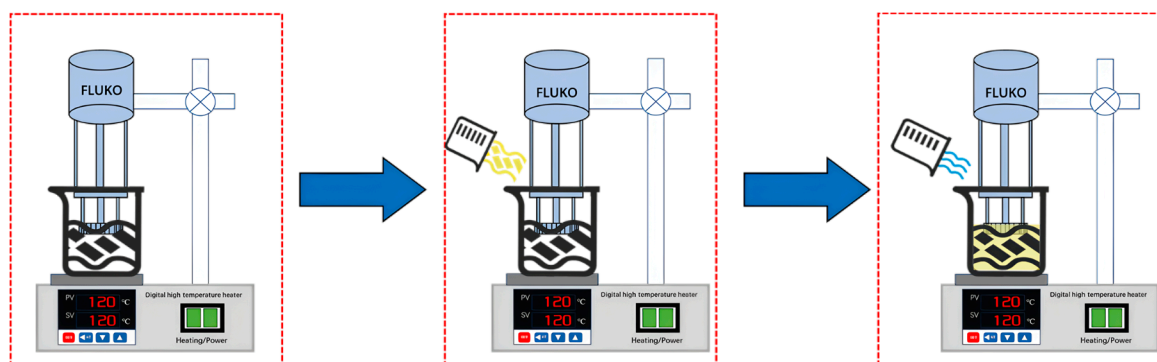
Indicators	Unit	Standard Value	Test Value
Ambient state	/	/	Yellow liquid
Viscosity (25 °C)	mPa·s	800–2200	1660
Density (25 °C)	g·cm ⁻³	1.05~1.11	1.10
Tensile strength (25 °C)	MPa	≥5	11.9
Elongation at break (25 °C)	%	≥80	330

Table 3. Performance indicators of curing agent.

Name	Molecular Formula	Appearance (25 °C)	Density (25 °C)	Purity
Diethylene Glycol	C ₄ H ₁₀ O ₃	Colorless, transparent, viscous liquid	1.118 g/cm ³	≥99%

2.2. Sample Preparation

The research team's preliminary studies have demonstrated that using the polyurethane prepolymer and modifier described in this study, when the polyurethane prepolymer content exceeds 40%, thermosetting polyurethane-modified asphalt can be successfully prepared [9]. Thus, three types of thermosetting polyurethane-modified asphalt with polyurethane content ratios of 40%, 50%, and 60% were prepared and tested. The samples were designated as A (base asphalt), PU (pure polyurethane), and PUA-40, PUA-50, and PUA-60 for asphalt modified with 40%, 50%, and 60% PU, respectively. The specific preparation procedure is as follows, and the procedure is depicted in Figure 2.

**Figure 2.** Preparation process of the PU-modified asphalt.

(a) The base asphalt was heated until it reached a molten state and then decanted into the metal container. The base asphalt was stirred by electric agitator for 20 min at 120 °C.

(b) A specified mass of PU prepolymer was introduced into the base asphalt. The PU contents of 40%, 50%, and 60% refer to the mass fractions, and the corresponding

mass fractions of the base asphalt are 60%, 50%, and 40%, respectively. Subsequently, the resultant mixture was agitated for a duration of 10 min.

(c) The curing agent amount, which is 3% of the polyurethane amount, was added to the asphalt containing the polyurethane prepolymer, and the mixture was stirred for 5 min.

All mechanical and thermal tests were conducted on fully cured polyurethane-modified asphalt. The preparation and curing conditions of the specimens are as follows: after the preparation process, all samples were cured at 25 °C with 50% humidity for 10 days to complete the curing reaction. During the curing period, it is necessary to avoid excessive air humidity, which could cause excessive isocyanates in the polyurethane-modified asphalt to react rapidly with water and release carbon dioxide, resulting in specimen expansion.

2.3. Experimental Methods

2.3.1. Rotational Viscosity Test

Based on ASTM D4402 [22], rotational viscosity tests were carried out to evaluate the workability of the asphalts by using an AMETEK Brookfield DV2T viscometer (Middleboro, MA, USA). A spindle (S27) and shearing rate (20 r/min) were used in this paper. Viscosity value was recorded every 10 min until the required testing time was reached. The viscosity values of PU prepolymer, base asphalt, and asphalts with different PU prepolymer doses (40%, 50% and 60%) were documented.

2.3.2. Tensile Test

According to the GB/T 528-2009 standard, the tensile test was used to characterize the resistance to cracking and deformation of the asphalts. The sample was poured into mold and left for 24 h at room temperature for testing [23]. This test was conducted using the WDL-2000 electronic tensile testing machine (Jinan Chenchi Instrument Co., Ltd., Jinan City, China), with a tensile rate of 500 mm/min and a testing temperature of 23 ± 2 °C. The tensile strength (TS) and elongation at break (E) of the samples were calculated using Equations (1) and (2):

$$TS = \frac{F_{max}}{w \times t} \quad (1)$$

$$E = \frac{L_1 - L}{L} \times 100 \quad (2)$$

where F_{max} is the maximum force at fracture, kN; w is the width of the narrow section, mm; t is the thickness of the narrow section, mm; L is the length of the narrow section; and L_1 is the length at fracture, mm.

2.3.3. Dynamic Mechanical Analysis Test

In this study, a TA Instruments DMA Q800 dynamic mechanical analyzer (TA Instruments, New Castle, DE, USA) was used to perform a temperature scan on base asphalt, pure PU, and PU-modified asphalt samples. The asphalt samples were prepared into disc-shaped specimens with a diameter of approximately 10 mm and a thickness of 2–3 mm. The shear mode was used with a scanning temperature range from -100 °C to 160 °C, a frequency of 10 Hz, and a temperature change rate of 4 °C/min. As the temperature approaches and reaches the glass transition temperature (T_g), the molecular chains of the material begin to move, which is reflected in parameters such as the storage modulus (G') and loss modulus (G'') [24]. The loss factor ($\tan\delta$) can be calculated by Equation (3), which reflects the viscoelastic state of asphalt.

$$\tan \delta = \frac{G''}{G'} \quad (3)$$

2.3.4. Microscopic Analysis Test

The differential scanning calorimetry (DSC) test was conducted. A Ta DSC Q-2000 differential scanning calorimeter (TA Instruments, New Castle, DE, USA) was used to carry out the test in a nitrogen environment with a nitrogen purge rate of 60 mL/min; liquid nitrogen was used as an efficient coolant with a heating rate of 10 °C/min, and the test temperature range was set between −100 °C and 100 °C.

The scanning electron microscopy (SEM) test was used to observe the effect of PU on the microstructure of asphalt. Since asphalt is a non-conductive material, the samples were sprayed with metal. The asphalt samples were placed in a 5 mA vacuum diffraction coating machine for metal spraying for 8 min before SEM testing to improve conductivity of asphalt. The voltage for SEM test was set as 5 kV, and SEM micrographs at different magnifications were obtained.

3. Results and Discussion

3.1. The Viscosity of Polyurethane-Modified Asphalt

In order to examine the workability of PU-modified asphalt, the rotational viscosity tests were carried out at 120 °C, and the results are presented in Figure 3.

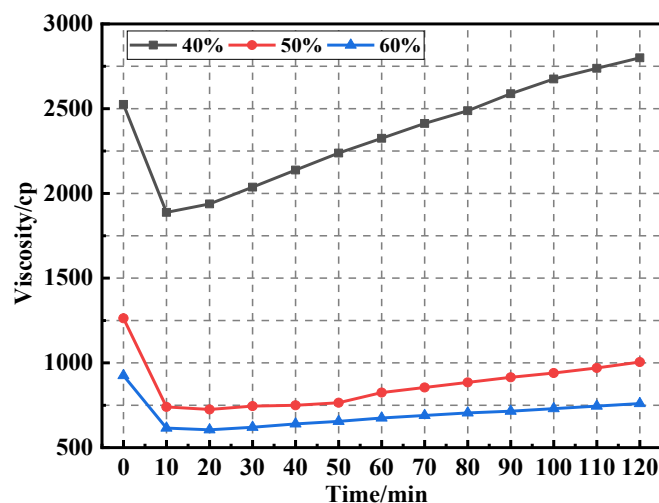


Figure 3. The viscosity of the modified asphalts containing different doses.

The viscosity of the three PU-modified asphalt samples first decreased and then increased over time, with an inflection point at 10 min. After that, the viscosity of the modified asphalts gradually increased with time. This result may be attributed to the initial phase where PU and asphalt were not yet fully integrated, forming a two-phase system that resulted in higher viscosity of PU-modified asphalt samples. As the PU and asphalt blended into a more homogeneous system, the internal shear resistance of the asphalt decreased, leading to a reduction in the viscosity of the modified asphalts. Over time, the PU underwent a curing reaction within the asphalt matrix, forming a cross-linked network structure, which gradually increased its viscosity. Additionally, the viscosity of the modified asphalts decreased with the increase in dose of PU. At 120 min, the rotational viscosity of the modified asphalt containing 40% PU was 2800 cp. When the PU dose increased to 50% and 60%, the initial viscosity dropped to 1005 cp and 760 cp, respectively. Therefore, PU-modified asphalt exhibited a lower viscosity when PU dose was 50% or higher, providing a longer workable time, which was beneficial for its application in construction.

3.2. Tensile Property Analysis

The base asphalt, PU, and modified asphalt samples containing 40%, 50%, and 60% PU were named A, PU, PUA-40, PUA-50, and PUA-60, respectively. The samples after tensile fracture are shown in Figure 4, and the E and TS values of the asphalt samples are shown in Figure 5.

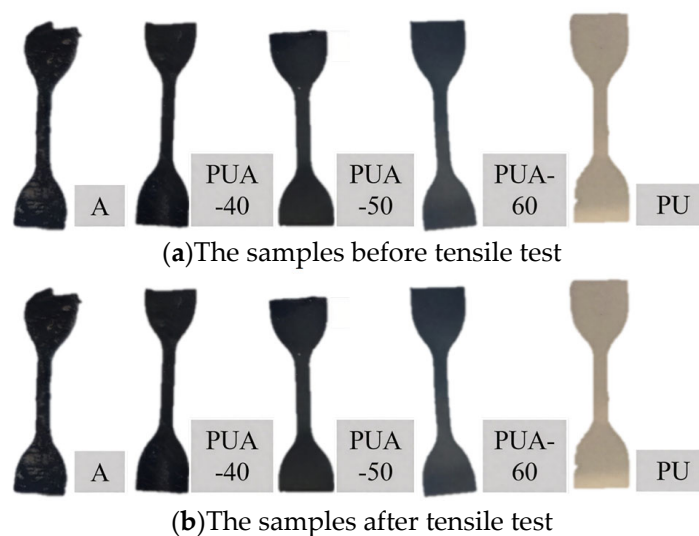


Figure 4. Tensile test samples.

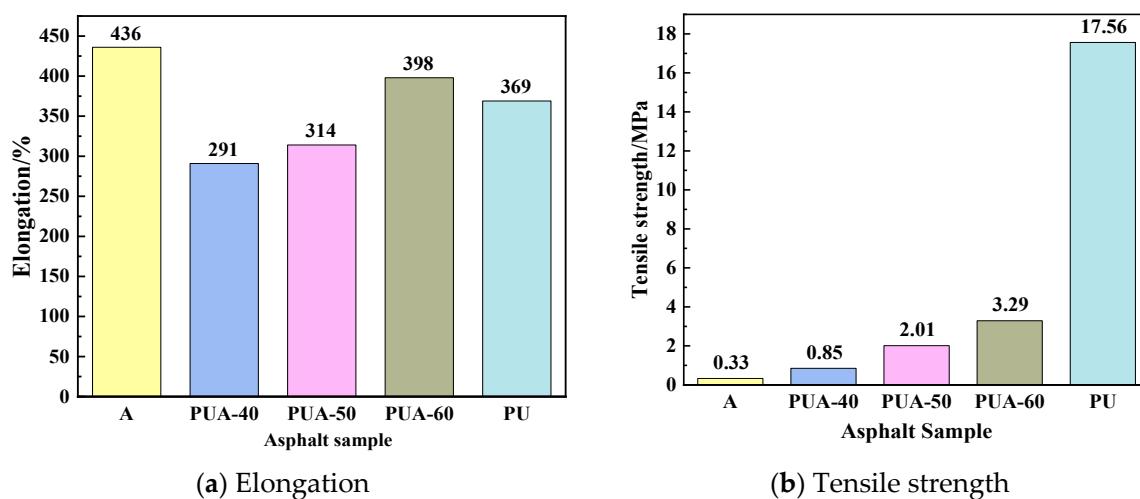


Figure 5. Elongation and tensile strength of the test samples.

The base asphalt sample exhibited flexible tensile failure, whereas the modified asphalts showed brittle fracture when the dose of PU exceeded 50%. The added PU modifier reduced the E of the asphalt when the PU dose was 40%, while the E of the modified asphalt samples showed an increasing trend as the PU dose increased from 40% to 60%. This result may be due to the strong ductility of base asphalt, while when the polyurethane dose is 40%, the initially formed cross-linked network has a relatively high proportion of hard segments, and its rigid characteristics limit the free movement of asphalt molecular chains, resulting in a decrease in elongation compared with the base asphalt. However, with the increase in PU content, the cross-linked network structure within the PU–asphalt system continuously develops, and the tensile fracture strength shows a progressive enhancement trend. When the PU content increases to 50% and 60%, the cross-linked network structure tends to be perfect, and the proportion of soft segments in the network increases accord-

ingly. The flexibility of the soft segments improves the mobility of the molecular chains, so the elongation increases with the increase in PU dosage.

Moreover, the addition of PU significantly increased the TS of the asphalt. As the dose of PU increased, the TS of the modified asphalts showed an upward trend. In comparison with the base asphalt, the TS values of asphalts modified with 40%, 50%, and 60% PU exhibited increases of 157%, 509%, and 897%, respectively. These results showed that the increased PU dose resulted in a stronger cross-linked structure within the asphalt, significantly improving the tensile performance of the modified asphalt.

3.3. Dynamic Mechanical Property Analysis

3.3.1. G' and G''

The value of G' can reflect the elasticity of asphalt binder. If the G' value is higher, the deformation resistance of asphalt is stronger. G'' represents the viscous component of asphalt binder. A higher G'' value indicates stronger viscous characteristic of asphalt [25,26]. The G' and G'' values of asphalt samples at different temperatures are shown in Figure 6.

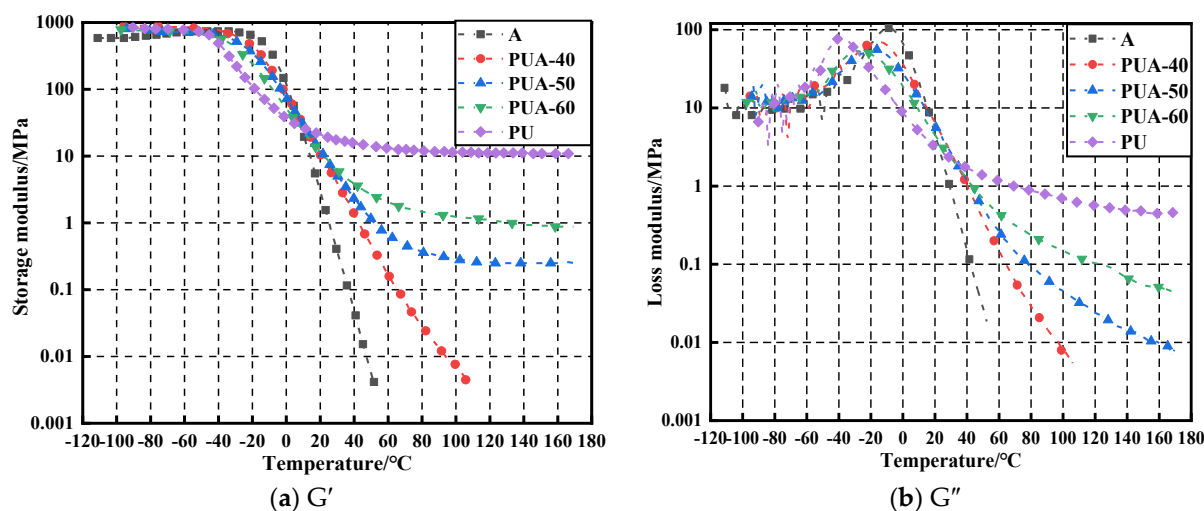


Figure 6. The curves of G' and G'' with temperature variation.

The G' of PUA-50, PUA-60 and PU samples decreased initially with increasing temperature and then stabilized. In contrast, the G' of PUA-40 and base asphalt exhibited a slight increase followed by a rapid decrease as the temperature rose. This may be attributed to the insufficient formation of a stable network structure between PU and asphalt when the dose of PU was low. As the temperature increased, the enhanced molecular vibrations did not significantly disrupt the internal structure of the material. At low temperatures, the differences in G' of all asphalt samples were minimal. However, as the temperature rose, G' decreased and the differences became more pronounced. The G' of the modified asphalts increased with a higher dose of PU, indicating that PU enhanced the elasticity of the asphalt.

The G'' curves of all samples showed an initial increase followed by a decrease as the temperature rose. The differences in G'' among the samples were negligible at low temperatures but became increasingly significant with increasing temperature. This may be due to the distinct glass transition temperature (T_g) presenting in these amorphous polymer materials. When the temperature exceeded T_g , the internal components of the material began to move, leading to a phase transition. Among the samples, the G'' of base asphalt decreased most rapidly with increasing temperature. As the dose of PU increased, G'' value of asphalt increased, indicating that the added PU enhanced the viscosity of the asphalt and improved its low-temperature flexibility.

Figure 7 illustrates the G' value at low temperatures and high temperatures. In the temperature range of $-20\sim 0\text{ }^{\circ}\text{C}$, the G' values were ranked from highest to lowest as base asphalt, PUA-40, PUA-50, PUA-60, and PU. In the temperature range from 30 to $50\text{ }^{\circ}\text{C}$, the G' values were ranked from highest to lowest as PU, PUA-60, PUA-50, PUA-40, and base asphalt. The addition of PU reduced the G' at low temperatures, with a greater reduction observed as the PU dose increased. This resulted in the asphalt becoming more prone to deformation. It is likely that the PU may alter the microstructure of base asphalt, making its internal structure more uniform and improving its low-temperature flexibility. However, at high temperatures, added PU significantly improved the G' value of asphalt. This indicated that PU effectively improved the permanent deformation resistance of asphalt at high temperatures.

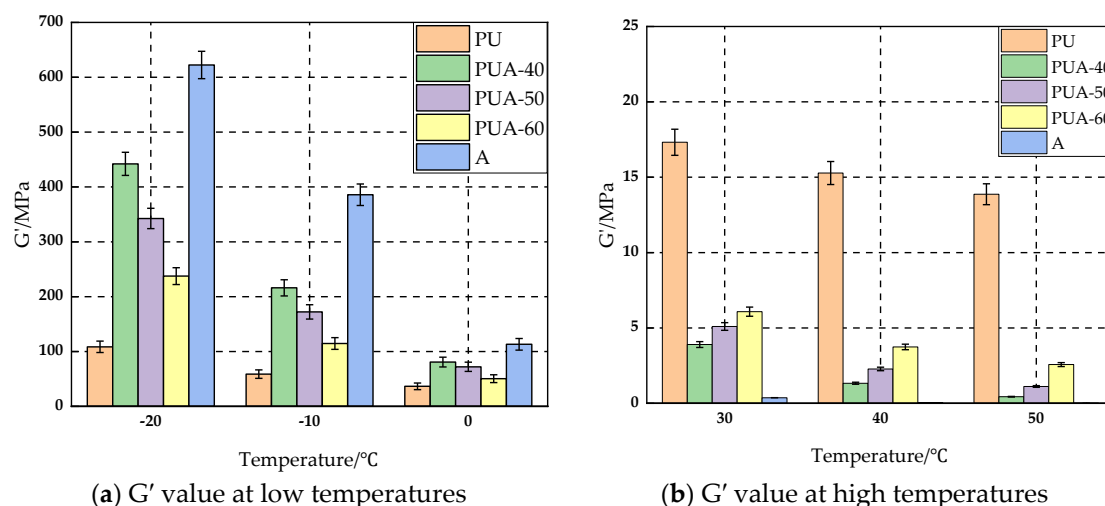


Figure 7. The G' value at different temperatures.

3.3.2. $\tan\delta$

As shown in Figure 8, the curve of the modified asphalt containing 40% PU increased with rising temperature, while the curves of the other modified asphalts initially increased and then decreased. This result may be attributed to the incomplete curing reaction between the small amount of PU and base asphalt. The urethane groups in the molecular chains of PU had a high polarity, leading to a stronger intermolecular interaction and increased viscosity of asphalt. Consequently, the loss angle (δ) increased with temperature, without showing a distinct peak. As the temperature continued to rise, the rate of irreversible deformation surpassed that of reversible deformation, meaning that the G'' decreased faster than the G' , causing the $\tan\delta$ of all the modified asphalt samples except PUA-40 group to decrease.

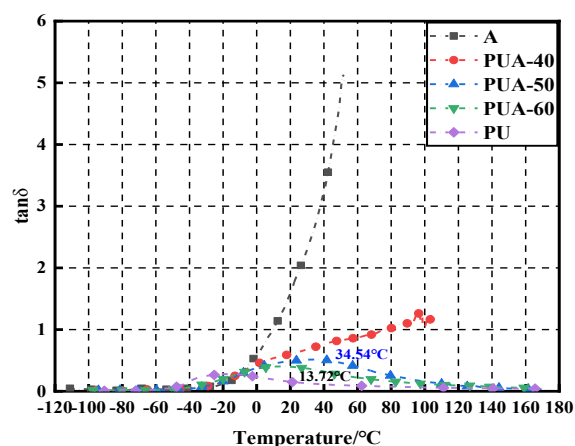


Figure 8. The $\tan\delta$ of the samples at different temperature.

The $\tan\delta$ primarily reflected the viscoelastic state of polyurethane-modified asphalt at high temperatures. With the addition of PU, the maximum value of the glass transition temperature range of polyurethane-modified asphalt changed. The softening onset temperature (T_s) value of PUA-50 was 34.54 °C, while the T_s value of PUA-60 was 13.72 °C. This implied that PUA-50 exhibited excellent compatibility and uniformity, along with improved strength and toughness, contributing to better high-temperature stability. Moreover, the result of $\tan\delta$ demonstrated that the addition of PU improved both the viscosity and elasticity of base asphalt. Especially, when the dose of PU was 50%, the $\tan\delta$ of asphalt reached the maximum value, indicating that PUA-50 had the highest viscosity. This may benefit the adhesion between the asphalt and aggregates and reduce the occurrence of cracks at low temperatures.

3.3.3. Tg

The Tg of polymer composites is detected using DMA analysis by observing the variation in G' and G'' with temperature [27–29]. The temperatures corresponding to the G'' peak values differ significantly among the samples. Therefore, the temperature corresponding to the G'' peak was used as the Tg of the samples in this study, as shown in Table 4. The Tg values of the samples were ranked as follows: base asphalt > PUA-40 > PUA-50 > PUA-60 > PU. From Table 4, the Tg of polyurethane-modified asphalt was significantly lower compared to base asphalt, with reductions of 33.0%, 48.7%, and 67.2% for the three different PU doses, respectively. This indicated that the addition of PU significantly improved the thermal stability of asphalt. The higher the PU dose, the greater the reduction in modified asphalts in Tg, enabling the asphalt to maintain the stability of its internal components at low temperatures, thus reducing the likelihood of deformation in cold environments and improving its low-temperature crack resistance.

Table 4. Tg values of the samples.

Samples	Asphalt	PUA-40	PUA-50	PUA-60	PU
Tg/°C	−9.95	−14.86	−19.39	−30.38	−39.46

3.4. Thermal Behavior and Microscopic Morphology of Polyurethane Asphalt

3.4.1. DSC Analysis

The DSC curves of the five materials during the heating stage are shown in Figure 9.

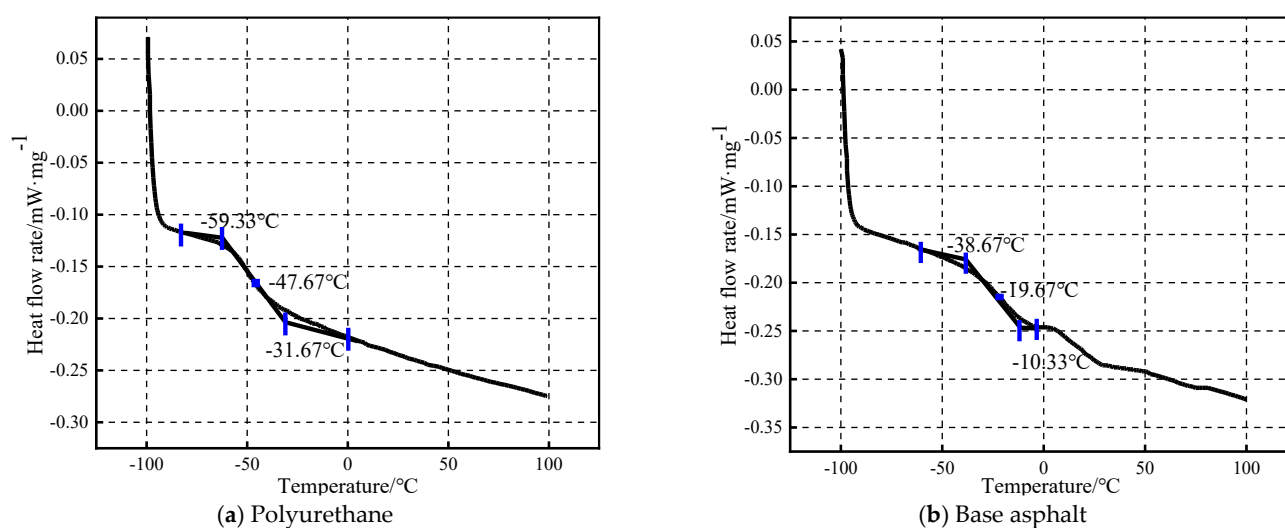


Figure 9. Cont.

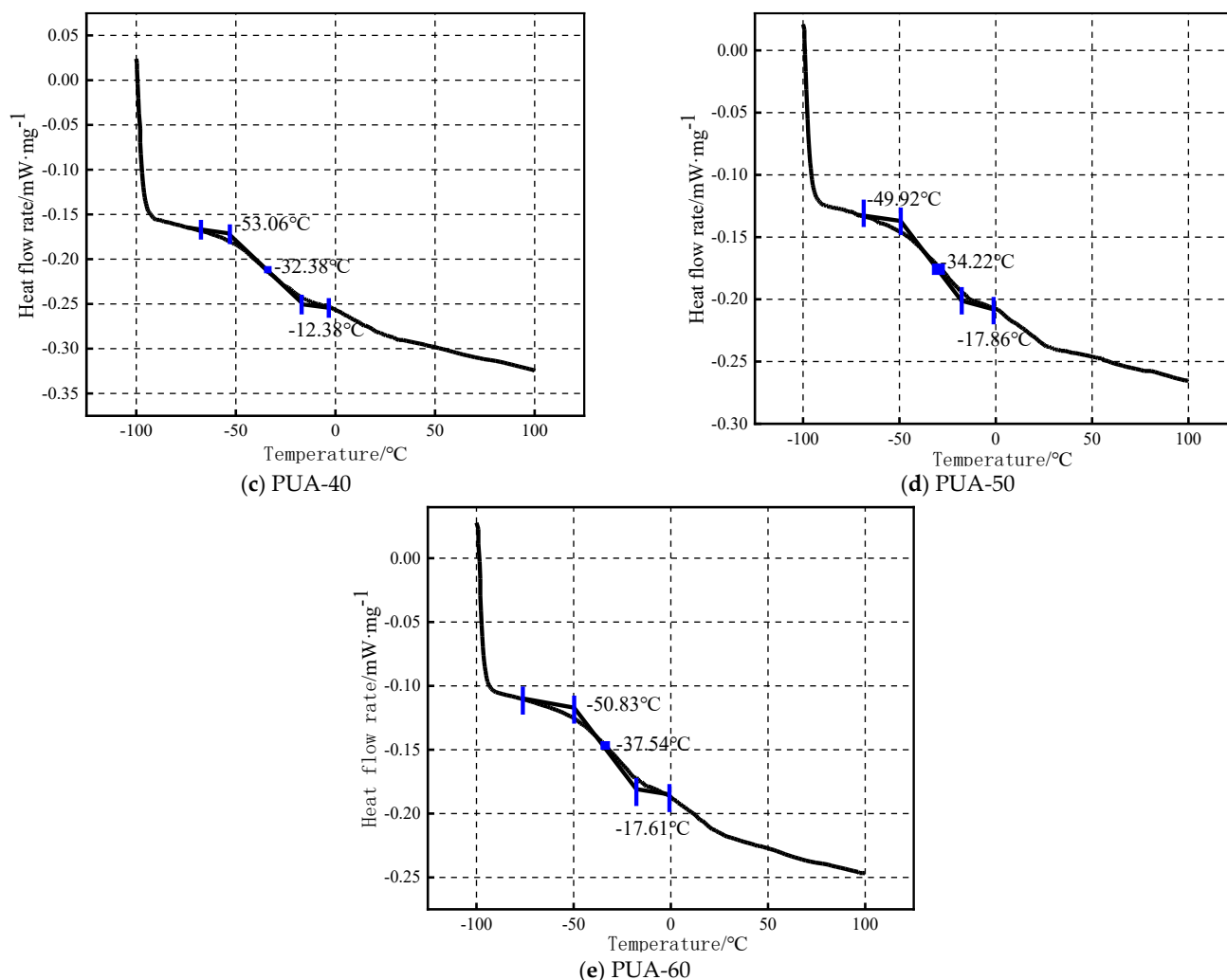


Figure 9. The DSC curves of different materials.

When conducting a differential scanning calorimetry (DSC) test on the base asphalt, the DSC curve is characterized by two broad endothermic peaks. This phenomenon reveals that the base asphalt undergoes multi-stage phase transitions within a relatively wide temperature range. As a mixture composed of various chemical components, each component of asphalt has its specific phase-transition point. As the temperature gradually rises, each component undergoes structural changes one by one according to its own glass transition temperature. In the DSC spectrum, these individual phase transitions are superimposed to form a broad endothermic peak shape. As can be seen from Figure 8, the endothermic peak of the polyurethane material in the DSC curve only appears as a relatively small peak. The possible reason for this, upon analysis, is that the polyurethane material consists of relatively homogeneous substances, resulting in a relatively concentrated phase-transition temperature range. With the incorporation of polyurethane, the influence of the phase transitions of various components in the original base asphalt gradually weakens. The overall phase-transition behavior of the modified asphalt becomes more concentrated and resembles the single-phase-transition characteristics of the polyurethane material. The glass transition temperatures and the initial transition temperatures from the highly elastic state to the viscous-flow state measured by the DSC curves are shown in Table 5.

Table 5. Polyurethane-modified asphalt DSC test results.

Material	Glass Transition Temperature from Glassy State to Highly Elastic State/°C	Initial Transition Temperature from Highly Elastic State to Viscous-Flow State/°C
Base asphalt	−19.67	−4.67
PUA-40	−32.38	−3.37
PUA-50	−34.22	−0.83
PUA-60	−37.54	−0.66
Polyurethane	−47.67	2.33

As shown in Table 5, the glass transition temperature of polyurethane-modified bitumen decreases with increasing polyurethane dosage. In this case, the Tg of matrix bitumen was −19.67 °C, whereas the Tg of polyurethane material was −47.67 °C. The Tg of the three thermoset polyurethane asphalt materials is between them. The temperature in the low-temperature transition zone of the thermoset polyurethane asphalt is lower than that of the matrix asphalt. It shows that the incorporation of polyurethane effectively adjusts the arrangement and interaction mode of asphalt molecular chain, so that the asphalt has better elasticity and viscosity at low temperature, and increases the low-temperature flexibility of asphalt.

When the asphalt transforms from the highly elastic to the viscous-flow state, the onset temperature increases with the increase in polyurethane dosing, indicating that the polyurethane-modified asphalt needs a higher temperature than the matrix asphalt to transform from the highly elastic state to the viscous-flow state, and it is thus seen that the polyurethane dosing helps to improve the high-temperature performance of the bitumen. From the data, it can be seen that there is not much difference between PUA-50 and PUA-60 in the onset temperature of the transition from the high-elasticity to viscous-flow state, which indicates that the effect of polyurethane on the high-temperature performance of asphalt tends to be stable when the polyurethane dosage reaches 50%, which is in line with the conclusion of the DMA test.

3.4.2. SEM Analysis

The SEM images of PU-modified asphalts with different PU doses are presented in Figure 10. The base asphalt exhibits a relatively rough and uneven surface morphology with no obvious network structure, reflecting that its microstructure lacks a continuous binding phase. The surface morphology of PUA-40 showed the numerous protrusions of varying sizes, with a clear two-phase interface between PU and asphalt, indicating that PU had not fully integrated with the asphalt to form a stable structure. For the PUA-50, the micromorphology revealed a reduction in the number of protrusions compared with that of PUA-40, but a distinct separation between PU and asphalt phases was still observable. Compared to that of PUA-40, the two-phase interface in PUA-50 was more fully integrated. When the dose of PU reached 60%, the SEM image of the asphalt showed a significant reduction in protrusions, with the interface almost entirely fused, resulting in a smooth and even surface, forming a uniform network structure. This suggested that a higher dose of PU signified a smoother interface and more homogeneous and stable microstructure of the modified asphalt. This result further verified the test results of tensile properties and dynamic mechanical properties.

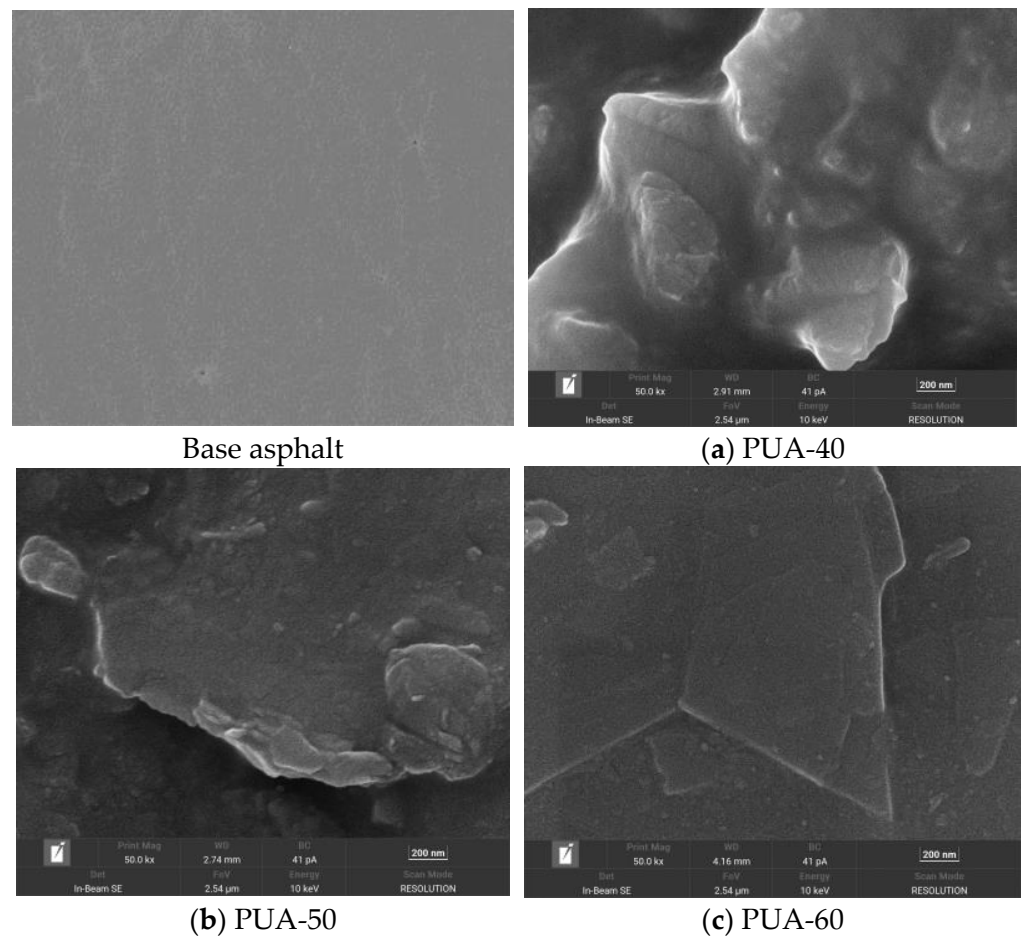


Figure 10. The SEM images of PU-modified asphalt.

4. Conclusions

- (1) The addition of PU significantly enhanced the elasticity of asphalt at high temperatures, thereby improving its permanent deformation resistance in high-temperature environments. Added PU increased the viscous components of asphalt at low temperatures, ameliorating its low-temperature flexibility.
- (2) The tensile properties of asphalt were significantly improved by PU addition. Compared with the base asphalt, the tensile strength of PUA-50 increased by 509%, which was significantly higher than the 157% increase in PUA-40 and achieved a more balanced performance between strength and flexibility than PUA-60. This highlights that 50% PU content optimizes the trade-off between tensile strength and elongation at break.
- (3) The incorporation of PU significantly enhanced the elastic properties of asphalt at high temperatures, thereby improving its resistance to permanent deformation in high-temperature environments. In the high-temperature range, the storage modulus of PU-modified asphalt increased with higher PU content, with PUA-50 and PUA-60 exhibiting substantially higher G' values compared to the base asphalt and PUA-40, indicating a marked improvement in high-temperature deformation resistance. At the same time, PU increased the viscous components of asphalt at low temperatures, effectively improving its low-temperature flexibility.
- (4) When the dose of PU was 50% or more, the interface between asphalt and PU was well integrated with a smooth and flat surface, forming a more uniform and stable cross-linked network structure.

Author Contributions: Conceptualization, W.Z.; methodology, W.Z.; data curation, T.D., C.P. and X.J.; writing—original draft preparation, M.S.; writing—review and editing, W.Z.; visualization, M.S.; supervision, M.S. and L.G.; project administration, T.D.; funding acquisition, W.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Shandong Provincial Natural Science Foundation Youth Project (ZR2022QE054), Shandong Provincial Natural Science Foundation General Program (ZR2024ME093), Shandong Provincial Natural Science Foundation Joint Fund Program (ZR2024LZN020) and Science and Technology Plan Project of Shandong Province Transportation Department (2023B60).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: No new data were created or analyzed in this study.

Conflicts of Interest: Authors Wei Zhuang, Tingting Ding, and Xuwang Jiao were employed by the company Shandong Provincial Communications Planning and Design Institute Co., Ltd. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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