

PERFORMANCE CHARACTERISTICS OF THERMOSETTING POLYURETHANE MODIFIED ASPHALT BINDER AND ITS MIXTURES

UPORABNE LASTNOSTI TERMIČNO STABILNEGA POLIURETANA ZA MODIFIKACIJO ASFALTNEGA VEZIVA IN MEŠANIC

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A new thermosetting polyurethane modified asphalt (TPUA) pavement material was developed to solve the unbalanced performance of traditional bridge deck pavement materials. Compared with the conventional bridge deck pavement materials, this work comprehensively evaluates the pavement performance of the TPUA binder and its mixture. The results indicate that the TPUA binder gradually shows elastic material properties at high temperatures and has excellent deformation resistance. The low-temperature flexibility of the TPUA binder is much better than that of SBS asphalt and epoxy asphalt (EA) binders. The TPUA binder is a viscoelastic material at low temperatures, and its creep meets the Burgers constitutive model. Moreover, the TPUA binder also has excellent mechanical properties and flexibility. In addition, the TPUA mixture has excellent mechanical properties, high-temperature deformation resistance and moisture stability. Its crack resistance at room temperature and low temperature is much better than those of SBS asphalt and EA mixture. This work will help us continue the development and performance research of TPUA pavement materials.

Keywords: thermosetting polyurethane, modified asphalt, mixture, bridge deck pavement, pavement performance

Avtorji opisujejo novo vrsto s termično stabilnim poliuretanom modificiranega asfalta (TPUA; angl.: thermosetting polyurethane modified asphalt), uporabnega kot rešitev oziroma zamenjava za neuravnotežen (slabe kakovosti) konvencionalni material za prevleke pločnikov na mostovih. Avtorji so med seboj primerjali konvencionalni material s termično stabilnim poliuretanskim vezivom modificirani material. Rezultati raziskave so pokazali, da ima termično stabilno poliuretansko vezivo elastične lastnosti tudi pri visokih temperaturah in posledično odlično odpornost proti deformacijam. Nizko temperaturna fleksibilnost (elastičnost) termično stabilnega poliuretana je mnogo boljše vezivo kot so SBS asfaltna in/ali epoksidna asfaltna (EA) veziva. TPUA je viskoelastični material pri nizkih temperaturah in proces njegovega lezenja opisuje Burgerjev konstitutivni model. Poleg tega ima TPUA odlične mehanske lastnosti in prilagodljivost, visoko temperaturno odpornost proti deformacijam in stabilnost v vlagi. Njegova odpornost proti pokanju pri vseh temperaturah uporabe je mnogo boljše kot jo imata SBS asfalt in EA mešanice. Izvedena raziskava bo lahko služila tudi drugim raziskovalcem pri razvoju novih kvalitetnih s termično stabilnim poliuretanskim vezivom modificiranih materialov za prevleke pločnikov.

Ključne besede: termično stabilni poliuretan, modifikacija asfalta, mešanice, asfaltna prevleke pločnikov za mostove, lastnosti in kvaliteta pločnikov

1 INTRODUCTION

A bridge deck pavement layer plays a role in protecting a bridge deck, providing driving comfort and dispersing vehicle loads, but it is one of the critical factors affecting the durability of a bridge deck.¹⁻⁴ The existing bridge deck pavement systems include poured asphalt concrete, asphalt mastic concrete, and epoxy asphalt (EA) concrete, which can be divided into two main categories based on the type of asphalt binders: thermoplastic polymer modified asphalt^{5,6} and thermosetting resin modified asphalt.^{7,8} The former is a thermoplastic material. Although polymers (SBS, SBR, rubber powder, etc.) can improve the viscoelasticity of asphalt, the perfor-

mance of modified asphalt is still greatly affected by temperature. The latter is a thermosetting material, and the representative material is EA. In China, epoxy asphalt concrete has been further applied to other large-span bridges since its successful application at Nanjing Yangtze River Second Bridge in 2000. Although epoxy resin can significantly improve the mechanical properties, high-temperature deformation resistance and fatigue performance of asphalt, the EA pavement material has poor flexibility and a high risk of cracking.⁹ The imbalance in the pavement performance of the existing pavement materials has also led to distresses such as cracking, pushing and rutting in the pavement layer, which affects the durability of a bridge deck.

Thermosetting polyurethane is a polymer material with a continuous carbamate (-NHCOO-) structure formed by the reaction of the isocyanate group (-NCO)

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and polyol (-OH). It has excellent mechanical properties, flexibility, high elasticity, chemical stability resistance and other advantages. It is considered to be the next generation of asphalt modifiers and is widely researched because its molecular structure and performance are easy to control.^{10–13} Thermosetting polyurethane modified asphalt (TPUA) refers to a high-performance material with a certain strength PU skeleton structure formed by adding a high amount of the PU modifier into the asphalt through a polymerization reaction. Scholars conducted an in-depth research of the modification mechanism of TPUA and its binder properties. Yang et al.¹⁴ analyzed the polymerization process and modification mechanism of thermosetting polyurethane in asphalt and found that small-molecule modifier monomers can undergo a polymerization reaction in asphalt to form a polyurethane skeleton structure. Moreover, the isocyanate group in polyurethane can react with the active hydrogen group in asphalt, proving a chemical modification. Zhang et al.¹⁵ studied the effects of the curing temperature and diluents on the viscosity change of the TPUA system. The results indicate that the curing temperature can significantly increase the viscosity growth rate and shorten the construction reservation time of the TPUA system, while the effect of the diluent is opposite to that of the curing temperature. In addition, it is also found that thermosetting polyurethane can significantly improve the

high-temperature and mechanical properties of asphalt, while its high-temperature rutting resistance and tensile strength are significantly better than those of SBS modified asphalt. He et al.¹⁶ prepared composite modified asphalt using thermosetting polyurethane and epoxy resin and found that the composite modified asphalt has excellent high- and low-temperature stability and waterproof performance. Cong et al.¹⁷ studied the polymerization process, microstructure and macroscopic properties of the TPUA binder. The microstructure showed that the modifier is dispersed in the form of particles in the asphalt during the initial solidification stage. As the reaction progresses, the modifier gradually undergoes cross-linking and forms a network structure, while the mechanical properties of TPUA are positively correlated with the conversion rate of isocyanates.

Previous studies indicated that thermosetting polyurethane can significantly improve the mechanical properties, high-temperature deformation resistance and low-temperature stability of asphalt. However, current research mainly focuses on analyzing the pavement performance of the TPUA binder, while exploration of the comprehensive performance of its mixture is limited. This work compared traditional bridge deck paving materials, analyzed the rheological properties, low-temperature flexibility, mechanical properties and crack resistance of the TPUA binder and its mixture, and

Table 1: Basic properties of asphalts

Properties	Virgin asphalt		SBS asphalt		Test methods
	Test value	Specification	Test value	Specification	
Penetration (25 °C, 0.1 mm)	65.1	60–80	50.2	40–60	T 0604
Softening point (°C)	48.0	≥46	76.3	≥60	T 0606
Ductility (15 °C, cm)	>100	≥40	>100	—	T 0605
Viscosity (cp, 135 °C)	226	—	926	≤3000	T 0625
Density (15 °C, g/cm ³)	1.012	—	1.008	—	T 0603

Table 2: Basic properties of PTMG

Molecular weight	Viscosity (cp, 40 °C)	Melting point (°C)	Hydroxyl value (mgKOH/g)	Molecular structure
2000	1225	32	54.7–57.5	H-(OCH ₂ CH ₂ CH ₂ CH ₂) _n -OH

Table 3: Basic properties of BDO

Molecular weight	Density (g/cm ³)	Melting point (°C)	Boiling point (°C)	Molecular structure
90.12	1017	16	230	HO-CH ₂ CH ₂ CH ₂ CH ₂ -OH

Table 4: Basic properties of isocyanate

NCO (%)	Equivalent weight	Viscosity (cp, 23 °C)	Diluent	Appearance
23.0	183	1200	Solvent-free	Water clear

Table 5: Aggregate gradation

EA-10	Passing rate/%								
	13.2	9.5	4.75	2.36	1.18	0.6	0.3	0.15	0.075
Upper limit	100	100	85	70	55	40	32	23	14
Lower limit	100	95	65	50	39	28	21	14	7
Target gradation	100	99	72.1	60.9	47.7	32.7	22.8	16.4	10.7

comprehensively evaluated the pavement performance of TPUA bridge deck paving materials.

2 EXPERIMENTAL DESIGN

2.1 Raw materials

This work used traditional SBS asphalt and epoxy asphalt (EA) as control groups to comprehensively evaluate the pavement performance of the TPUA binder and its mixture. The PG64-22 virgin asphalt binder was used as the raw material for preparing TPUA in this research, and SBS asphalt (5 % SBS) was used as the control group, both from Shanghai Urban Construction Rili Special Asphalt Co., Ltd. The thermosetting polyurethane modifier system consists of polytetrahydrofuran glycol (PTMG-2000), 1, 4-butanediol (BDO, AR) and polyisocyanates, respectively, provided by BASF (China) Co., Ltd. and Covestro Polymer (China) Co., Ltd. Two component epoxy asphalt (EA) from ChemCo Systems in the United States was also used as the control group. The aggregates in this work are all limestone and meet the requirements of JTG F40-2004 specifications. The mixture gradation was selected from the commonly used EA-10 for bridge deck pavement. The basic properties and gradation of raw materials are shown in **Tables 1–5**.

2.2 Preparation

The TPUA binder used in this paper consists of components A and B. Component A is a mixture of PTMG-2000, BDO and virgin asphalt, while Component B is polyisocyanate. The proportion of raw materials is consistent with the previous research.¹⁴ The dosage of thermosetting polyurethane is 50 % (polyurethane:asphalt = 1:1). The preparation process of the TPUA mixture is as follows: 1) Place the dry aggregate in a 100–110 °C oven for at least 4 h of insulation; 2) Heat component A to 100 °C and component B to 60 °C; 3) Mix components A and B evenly in proportion, then

mix them with the aggregate and form a test piece; 4) Place the test piece in a 100 °C oven for 7 h before conducting relevant performance tests. The preparation process is shown in **Figure 1**. The polymerization reaction of thermosetting polyurethane involves the reaction of isocyanate (-NCO) with hydroxyl groups (-OH) in PTMG and BDO, as shown in Equation (1):



Component I of the EA binder is epoxy-based, and component II is composed of the curing agent, asphalt and additives. The preparation of the EA mixture is as follows: 1) Heat the aggregate to 120–130 °C; 2) Heat components I and II to 85 °C and 120 °C, respectively, and mix them in a ratio of I:II = 1:4; 3) Mix the EA binder with the aggregates and compact the specimens. Place the test piece in a 120 °C oven for 4 h before conducting relevant performance tests. The preparation process is shown in **Figure 1**.

The preparation process of the SBS asphalt mixture was based on the JTG E20-2011 specification. To make the performance of the three mixtures comparable, all selected mixtures had an asphalt content of 7.3 %.

2.3 Methods

2.3.1 Asphalt binder

A dynamic shear rheometer (DSR) was used to study the high-temperature deformation resistance of SBS asphalt, EA and TPUA binder. Referring to ASTM D638, tensile testing was applied to test the mechanical properties of the EA and TPUA binder. According to ASTM D6648, the low-temperature crack resistance performance of the three modified asphalt binders was analyzed using a bending beam rheometer (BBR), and their low-temperature creep constitutive model was studied based on the Burgers model. The Burgers model comprises the Maxwell and Kelvin models^{18–20} in a series, as shown in **Figure 2**.

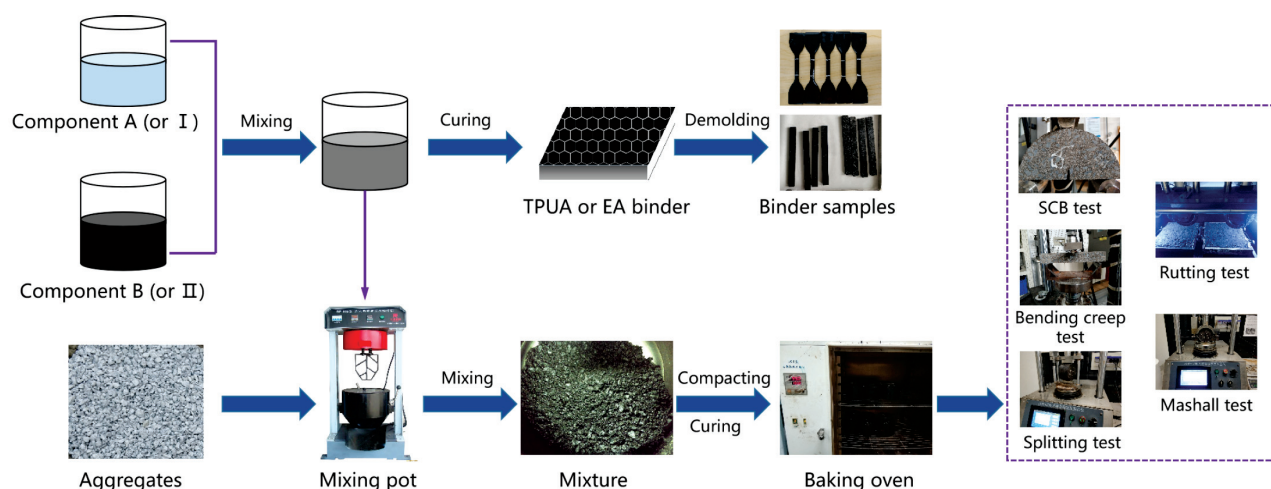


Figure 1: TPUA or EA mixture preparation process

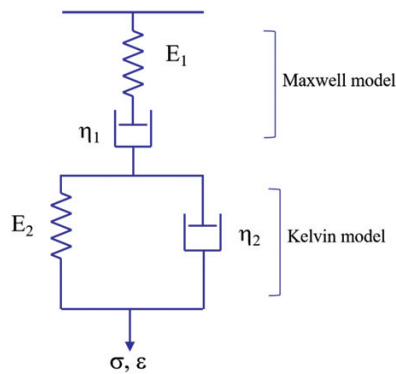


Figure 2: Burgers model

The Burgers creep constitutive model is shown with Equation (2):

$$\varepsilon = \sigma_0 \left[\frac{1}{E_1} + \frac{t}{\eta_1} + \frac{1}{E_2} \left(1 - e^{-\frac{E_2 t}{\eta_2}} \right) \right] \quad (2)$$

where ε represents the strain, σ_0 represents the constant stress, E_1 and η_1 represent the elastic and viscous parameters of the Maxwell model, and E_2 and η_2 represent the elastic and viscous parameters of the Kelvin model, respectively.

Due to the relationship between stiffness modulus $S(t, T)$ and creep compliance $J(t, T)$ satisfying Equation (3), the constitutive model of creep compliance under constant temperature conditions is shown in Equation (4).²¹

$$S(t, T) = \frac{1}{J(t, T)} = \left(\frac{\sigma}{\varepsilon} \right)_{t, T} \quad (3)$$

$$J(t) = \frac{1}{E_1} + \frac{1}{E_2} \left(1 - e^{-\frac{E_2 t}{\eta_2}} \right) + \frac{t}{\eta_1} \quad (4)$$

2.3.2 Asphalt mixture

The mechanical properties, moisture stability, low-temperature crack resistance and other pavement performance of the above three asphalt mixtures were tested with reference to the JTG E20-2011 specification. According to ASTM D8844, a semi-circular bending test (SCB) was conducted to analyze the crack resistance performance of the three mixtures. Firstly, a $\phi 150 \text{ mm} \times 170 \text{ mm}$ cylindrical specimen was prepared with the rotary compaction method and cut into a semi-circular specimen with a thickness of 50 mm. Secondly, a crack with a depth of 15 mm and a width of 1.5 mm was cut at the center of the semi-circular specimen. Finally, after leaving the specimen at room temperature for 4 h, its crack resistance was tested using a MTS machine at a loading rate of 50 mm/min. The maximum tensile stress and fracture energy were calculated as follows in Equations (5) and (6):^{22,23}

$$\sigma_t = \frac{4.976 F}{BD} \quad (5)$$

$$G_f = \frac{W_f}{B(D/2 - a)} \quad (6)$$

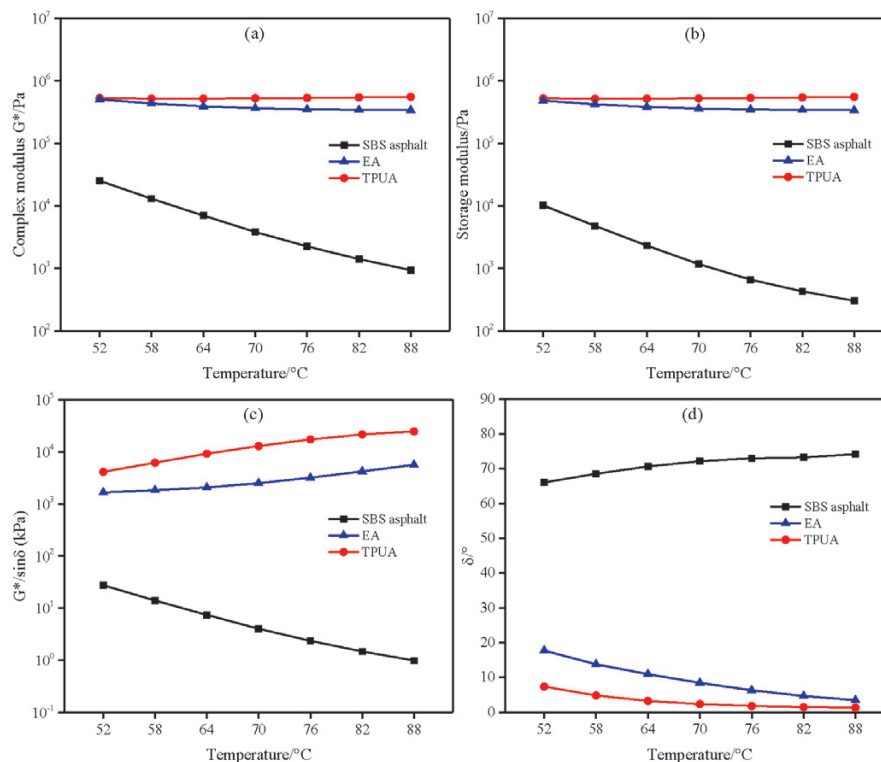


Figure 3: Variation patterns of high-temperature deformation resistance performance of different binders: a) complex modulus, b) rutting factor, c) storage modulus, d) phase angle

where σ_t is the tensile strength, F is the maximum loading force, B is the thickness of the specimen, D is the diameter of the specimen, a is the depth of the incision, G_f is the fracture energy, W_f is the fracture work ($W_f = \int F du$) and u is the displacement at fracture.

3 RESULTS AND DISCUSSION

3.1 Performance analysis of the binders

3.1.1 High-temperature deformation resistance

The surface temperature of bridge deck pavement is higher than that of traditional asphalt pavement under high-temperature weather in summer, which puts forward higher requirements for the high-temperature stability of bridge deck pavement materials. The rheological properties of SBS asphalt, EA and TPUA binder were studied using the time scanning mode within 52–88 °C. Due to the high modulus of EA and TPUA, rheological properties were studied using 8 mm parallel plates. The test results are shown in **Figure 3**.

Figure 3a shows that the complex modulus of thermosetting resin modified asphalt binders such as epoxy asphalt and TPUA varies little with the temperature at high temperatures. The research results of Kang et al.^{24,25} also indicated that after the temperature exceeds 50 °C, the complex modulus change curve of thermosetting resin modified asphalt tends to be horizontal (the platform zone). The main reason for the above results is that a high dosage of thermosetting resin modifiers can form a skeleton structure with a certain mechanical strength in asphalt, causing the physical properties of asphalt to change from viscoelasticity to elasticity at high temperatures. On the contrary, the complex modulus of SBS asphalt significantly decreases with an increasing temperature. The test results of the storage modulus (**Figure 3b**) also indicate that EA and TPUA binders exhibit elastic characteristics at high temperatures, while SBS asphalt still exhibits significant viscous characteristics.²⁶

The rutting factor index is often used to evaluate the high-temperature deformation resistance of modified asphalt. The larger the rutting factor, the better is the high-temperature stability. The rutting factor curves of three asphalt binders with temperature are shown in **Figure 3c**. As the temperature increases, the rutting factor of these two binders gradually increases as well. This result is very different from that for general asphalt viscoelastic materials. It seems to be contrary to the fact that the rutting factor of traditional asphalt materials decreases with an increase in the temperature. This is because a high thermosetting resin content forms a continuous network structure in asphalt, and the performance of asphalt at high temperatures exhibits the elastic properties of modifiers. From **Figure 3d**, it can also be concluded that the phase angle of the EA and TPUA binder gradually decreases and approaches 0° with an increasing temperature. This conclusion is consistent with the research re-

sults by Zhou et al.,²⁷ that is, thermosetting resin modified asphalt gradually exhibits the characteristics of an elastic material at high temperatures, and the phase angle gradually decreases. Due to a slight change in the complex modulus of thermosetting resin modified asphalt at high temperatures and the gradual decrease in the phase angle, the rutting factor of the EA and TPUA binder gradually increases with temperature. In summary, the high-temperature deformation resistance of the EA and thermosetting resin modified asphalt binders such as TPUA is much better than that of traditional thermoplastic polymer modified asphalt, and the traditional rutting factor indicators cannot be used to evaluate their high-temperature deformation resistance performance.

3.1.2 Low-temperature creep performance

Studying the constitutive model of asphalt is significant for understanding its viscoelasticity. The BBR test was used to test the low-temperature (−24 °C) crack resistance of SBS asphalt, EA and TPUA asphalt binders, and each group included 4 samples. Based on the Burgers model, the low-temperature creep constitutive models of the three modified asphalt binders were analyzed. The experimental results are shown in **Figure 4**, and the model fitting parameters are shown in **Table 6**.

As shown in **Figure 4a**, all three types of binders exhibit creep under a constant stress. The stiffness modulus of the EA binder is much higher than that of the other modified asphalt. This is caused by the poor low-temperature flexibility of epoxy resin modifiers. **Table 6** shows that the stiffness modulus of the TPUA binder is much lower than the other two types of asphalt, indicating that the TPUA binder has excellent low-temperature flexibility.

The Burgers viscoelastic constitutive model was used to study the low-temperature creep characteristics of the three asphalt binders mentioned above, as shown in **Figures 4b–d**. The Burgers creep model has an excellent fitting effect on the creep curves of the three asphalt binders (R^2 is greater than 0.98). It is also indicated that the three types of modified asphalt still exhibit viscoelastic material properties at low temperatures.^{24,25} **Table 6** shows that the viscoelastic parameters of the EA binder are much greater than those of the SBS asphalt and TPUA binder, indicating that the EA binder has a larger modulus. This conclusion was also verified with Xue's research,²⁸ showing that the viscoelastic parameters of epoxy asphalt are significantly greater than those of the traditional asphalt materials because epoxy resin significantly increases the modulus of asphalt, which theoretically explains the reason for the high brittleness of epoxy asphalt. In addition, the viscoelastic parameters of the TPUA binder are also lower than the other two types of asphalt binder, with the best low-temperature flexibility. The reason is that the soft segment of the PU modifier uses polyether polyols and theoretically its glass transition temperature is lower than −80 °C. Therefore, the PU

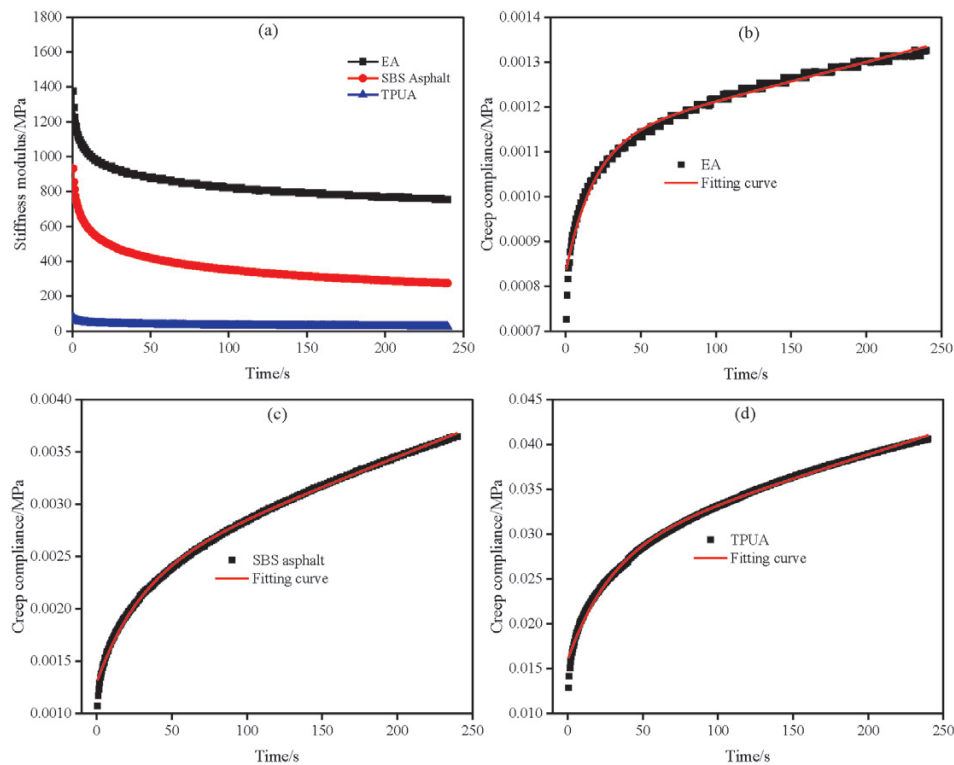


Figure 4: Change curves of the stiffness modulus and creep compliance of different binders: (a) stiffness modulus, (b) EA, (c) SBS asphalt, (d) TPUA

Table 6: Low-temperature crack resistance and Burgers model parameters

Asphalt	Low-temperature crack resistance(60 s)		Model parameters				
	Stiffness modulus/MPa	Creep rate	E_1 /MPa	E_2 /MPa	η_1 /MPa·s	η_2 /MPa·s	R^2
EA	865	0.095	1203.9	3377.9	1152920.2	64097.2	0.989
SBS asphalt	404	0.243	771.3	985.4	175212.8	28916.3	0.998
TPUA	34	0.216	62.6	81.4	18814.8	2366.5	0.997

modifier maintains high elasticity and flexibility at the testing temperature.

3.1.3 Tensile mechanical properties

The thickness of a general bridge deck pavement layer is less than 80 mm, causing greater stress on the bridge deck pavement under load, thus also putting higher requirements on the mechanical performance of the bridge deck pavement.²⁹ SBS asphalt undergoes significant deformation before demolding and testing due to its soft material, resulting in inaccurate final test results. This work only used direct tensile testing to analyze the mechanical properties of the EA and TPUA binder, and each group includes 5 samples. The results are shown in **Figure 5** and **Table 7**.

The macroscopic stretchability of polymer chains strongly relies on the structural evolution during the elongational flow. Different polymer chains (i.e., short chain, long chain, very long chain, among others) play different roles in the stretching process.³⁰ **Figure 5** shows that the stress-strain curves of the TPUA and epoxy asphalt binder are similar to those of an ideal crosslinked

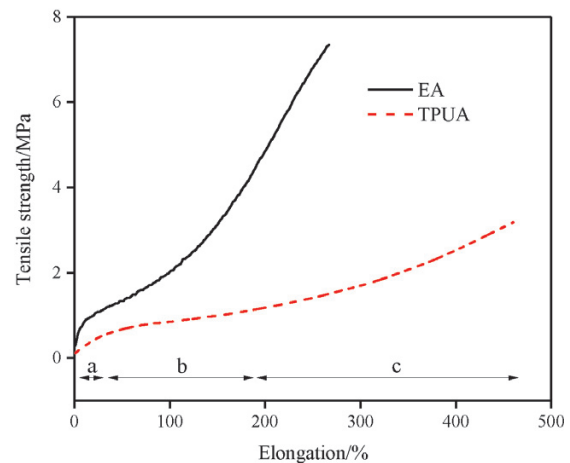


Figure 5: Stress-strain curves of the tensile test

Table 7: Tensile test results

EA		TPUA			
Strength /MPa	Elongation /%	Fracture energy /J·m ⁻²	Strength /MPa	Elongation /%	Fracture energy /J·m ⁻²
7.3	270	2.18×10^5	3.2	460	1.71×10^5

rubber.³¹ Although the tensile strength of the TPUA binder is lower than that of the EA binder, its elongation at break is much higher than that of the EA binder. The stress-strain curve of TPUA can be divided into three stages: elastic, yield, and strengthening ones. In the elastic stage, the stress-strain curve of TPUA tends to a straight line at minor strains in accordance with Hooke's law. The research by Vaidya et al. shows that polymers only meet Hooke's law when subjected to small deformations (strain less than 5 % or even lower).³² During the yield stage, the strain significantly increases while the stress slowly increases. The main reason is that the crimped PTMG soft segments in the PU molecular structure are straightened and gradually arranged in order. At this stage, the stress change rate with the strain is relatively low. In the strengthening stage, the stress of TPUA increases rapidly with the increase in the strain. This is because breaking the TPUA binder requires a greater force. When the ultimate stress is reached, the material is destroyed. Although the tensile strength of TPUA is lower than that of the EA binder, the difference in the fracture energy between the two materials is not significant. Therefore, TPUA has excellent flexibility and fracture resistance.

3.2 Evaluation of asphalt mixture pavement performance

3.2.1 Mechanical properties

The thickness of bridge deck pavement is thinner than that of traditional pavement, causing the pavement material to undergo greater tensile and compressive stresses under repeated loads and temperatures. The study investigated the mechanical properties of traditional bridge deck pavement materials and TPUA mixtures based on a Marshall test and splitting test, and each group includes 4 samples. The results are shown in **Figure 6**.

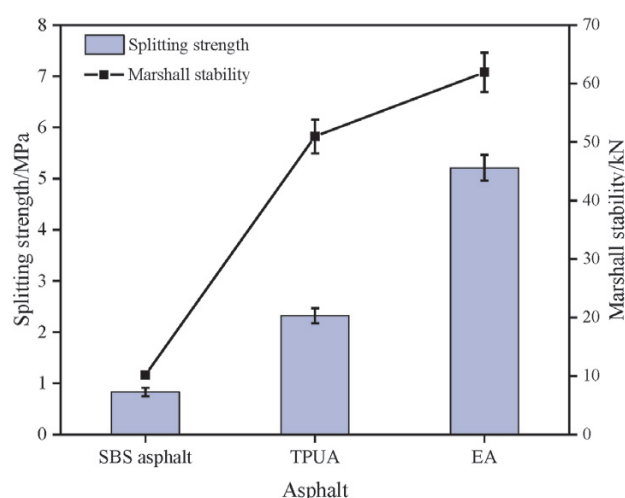


Figure 6: Mechanical properties of three asphalt mixtures

Thermosetting resin modified asphalt (e.g., TPUA and EA) is a composite material with a continuous skeleton structure formed by the polymerization reaction of small molecule modifier monomers in the asphalt.^{8,14} Traditional thermoplastic polymer modified asphalt is a mixture with a certain network structure formed due to a simple dispersion of polymers in asphalt. The former is a chemical crosslinking of the modifier in asphalt, while the latter is a physical crosslinking of the polymer. Therefore, the strength of a thermosetting resin modified asphalt mixture is several times higher than that of thermoplastic polymer modified asphalt. The research by Liu and Wei et al.^{33,34} found that the Marshall stability of an epoxy asphalt mixture is over 50 kN. **Figure 6** shows that the mechanical properties of the TPUA mixture are between those of SBS asphalt and EA mixture. Its Marshall stability exceeds 50 kN, and its splitting strength is greater than 2 MPa, demonstrating excellent mechanical properties. Although the mechanical properties of the TPUA mixture are slightly lower than those of the EA mixture, its Marshall stability is five times that of a traditional SBS asphalt mixture, and its splitting strength is also close to three times that of the SBS asphalt mixture, far exceeding the mechanical performance requirements of an asphalt mixture. Therefore, the TPUA mixture is a high-strength paving material.

3.2.2 High-temperature stability

Due to the small thickness of bridge deck pavement and great impact of the temperature field, it is significant for rutting damage in high-temperature environments. It also puts forward higher requirements for the high-temperature deformation resistance of bridge deck pavement materials. GB/T 30598-2014 requires the dynamic stability of epoxy asphalt mixture at 60 °C to be greater than 8000 cycles/mm. JTG F40-2004 requires the dynamic stability of the SBS asphalt mixture to be greater than 3000 cycles/mm. This paper analyzes the high-temperature stability of the TPUA mixture and its control groups using the rutting test, and each group includes 3 samples. The results are shown in **Figure 7**.

The traditional bridge deck pavement layer must meet the requirements of a dense structure, so the content of the binder used in the pavement material is relatively large. It adversely affects the high-temperature stability of traditional thermoplastic polymer modified asphalt mixtures. As shown in **Figure 7**, the dynamic stability of the SBS asphalt mixture is only 3089 cycles/mm. Although it meets the pavement performance requirements, more is needed for a bridge deck pavement in complex environments. The dynamic stability of the TPUA and EA mixture exceeds that of the SBS asphalt mixture by one order of magnitude, and their rut depth is also close to 0 mm. This also indicates that the TPUA and EA mixture can maintain the deformation resistance of bridge deck pavement under continuous high-temperature conditions. The reason for the above results is the high-performance thermosetting resin modified asphalt.

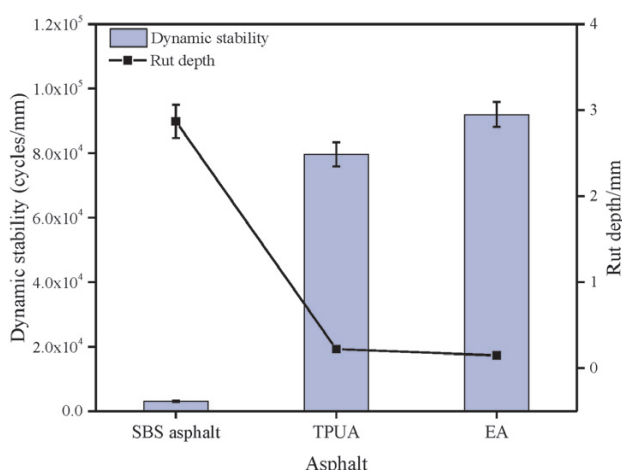


Figure 7: Rutting test results

The research by Xue and Qian et al.^{35,36} also indicated that after the formation of a network structure by thermosetting resin modifiers, the dynamic stability of the modified asphalt mixture is higher than 10,000 cycles/mm. The above results also reveal that the high-temperature stability of thermosetting resin modified asphalt pavement materials is much better than that of thermoplastic polymer modified asphalt.

3.2.3 Moisture stability

At present, the distresses of a bridge deck pavement are mostly directly or indirectly related to the moisture stability of the pavement material. This work used the immersion Marshall test to analyze the TPUA mixture and its control groups, and each group includes 4 samples. The results are shown in **Figure 8**.

Thermosetting resins are mostly polymerized from polar small molecule monomers, which also endows them with strong polarity. Therefore, thermosetting resins have strong adhesion to substrates, especially polar substrates. In addition, thermosetting resins can also improve the polarity of modified asphalt and its adhesion to aggregates, thereby improving the moisture stability of

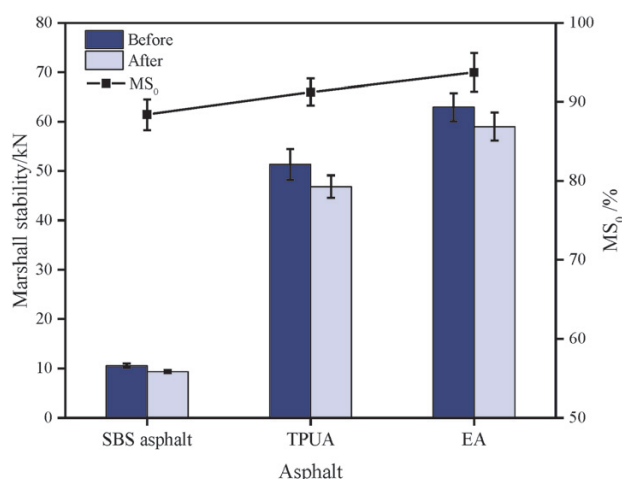


Figure 8: Immersion Marshall test results

the mixture.^{14,27} Qian et al.^{35,36} found that the moisture stability of a thermosetting resin modified asphalt mixture is much higher than that of a traditional SBS asphalt mixture, and its Marshall residual stability and indirect tensile strength ratio are not less than 90 %. **Figure 8** shows that the Marshall residual stability of SBS asphalt, TPUA and EA mixtures is 88.4, 91.3 and 93.8 %, respectively, much higher than the specification requirements (not less than 80 %). After immersion, the TPUA and EA mixtures still have a much better mechanical strength than the SBS asphalt mixture, meeting the bridge deck pavement's high bearing capacity requirements. This indicates that thermosetting resin modified asphalt pavement materials have excellent moisture stability. The reason is that thermosetting resin modifiers can form a denser skeleton structure in asphalt and prevent water from entering the interior of the mixture. In addition, thermosetting resin modifiers are mostly polar materials, able to improve the adhesion between asphalt and aggregate and reduce water erosion on the cement aggregate interface.

3.2.4 Crack resistance

Cracking distresses caused by repeated effects of temperature fields, loads and other factors account for over half of bridge deck pavement distresses. After being subjected to loads and environmental factors, asphalt pavement with existing cracks will experience stress concentration at the top of the cracks. If the strength and toughness of the asphalt mixture are insufficient, cracks will extend along the weak areas of the mixture until they penetrate the entire road surface. Traditional fatigue tests make evaluating the crack resistance performance of asphalt mixtures after existing cracks difficult. ASTM D8044 indicates using semi-circular bending (SCB) testing to evaluate the cracking resistance of asphalt mixtures at intermediate temperatures. Gong and Jiang found that using fracture energy indicators in SCB tests, they can effectively evaluate the crack resistance performance of asphalt mixtures.^{22,23} Therefore, a SCB test was used to study the crack resistance performance of TPUA and its control group mixtures in the presence of cracks, and each group included 4 samples. The results are shown in **Figure 9**.

As shown in **Figure 9a**, the force of the EA mixture significantly increases with displacement during the loading process. The ultimate strength is reached at a displacement of about 1 mm, and the loading force rapidly decreases. At this point, the specimen undergoes brittle fracture. This result is consistent with Fan's research findings, which indicate that the EA mixture exhibits strong resistance to crack initiation and weak resistance to crack propagation (similar to brittle fracture).³⁷ On the contrary, the stress of the SBS asphalt and TPUA mixture slowly decreases after reaching their ultimate strength. The fracture mode is a ductile fracture. The above results also indicate that the EA mixture has a

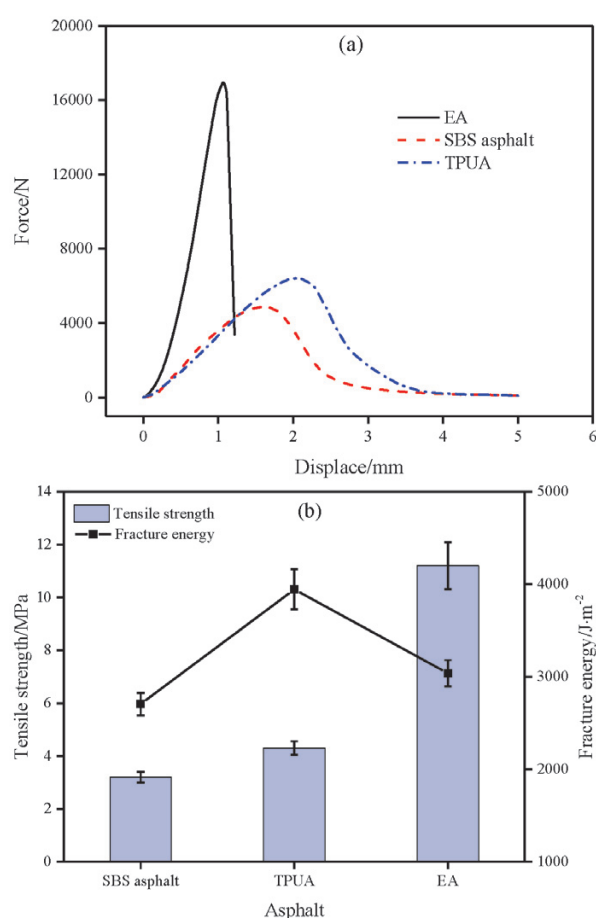


Figure 9: SCB test results: a) force-displacement curve, b) tensile mechanical properties

high stiffness due to the epoxy resin modifier's high crosslinking density and rigid structures containing benzene rings in the molecules. **Figure 9b** shows that the tensile strength of the TPUA mixture is between those of the SBS asphalt mixture and the EA mixture. However, the fracture energy of the TPUA mixture is significantly greater than those of the other two mixtures. Therefore, the TPUA mixture has excellent crack resistance performance.

3.2.5 Low-temperature flexibility

Traditional asphalt pavement materials gradually lose their viscosity and toughness at low temperatures and exhibit the brittleness and hardness of elastic materials, significantly increasing the risk of cracking.³⁸ A bridge deck pavement, especially a steel deck pavement, will experience significant deformation under load and environmental factors. At low temperatures, a steel bridge deck pavement is more at risk of cracking. A bending creep test was used to study the low-temperature flexibility (-10°C) of the TPUA mixture and control groups, and each group included 4 samples. The results are shown in **Figure 10**.

As shown in **Figure 10**, the bending stiffness modulus of EA, SBS asphalt and TPUA mixtures is 8.71×10^3 MPa,

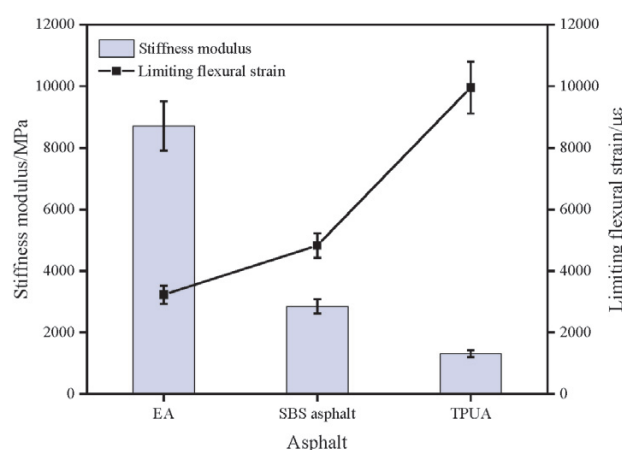


Figure 10: Low-temperature stability test results

2.85×10^3 MPa, and 1.31×10^3 MPa, respectively, which is consistent with the test results from Section 2.2. As the molecular structure of the epoxy resin modifier in the EA binder contains more benzene rings, the stiffness modulus of the EA mixture is much higher than those of the other two mixtures, reducing the low-temperature flexibility of the binder. The research by Han and Qian et al.^{36,39} also indicates that the low-temperature flexibility of epoxy asphalt mixtures is lower than that of traditional SBS asphalt mixtures. In addition, GB/T 30598-2014 requires that the low-temperature requirement for an epoxy asphalt mixture is also relatively low, not less than $2000 \mu\epsilon$. The stiffness modulus of the TPUA mixture is much lower than those of the other two mixtures because there are more flexible chain segments (PTMG) in the thermosetting polyurethane modifier, which can maintain the flexibility even at lower temperatures. From **Figure 10**, it can also be seen that the TPUA mixture exhibits excellent low-temperature crack resistance performance. The ultimate bending and tensile strains of EA, SBS asphalt and TPUA mixture are $3.23 \times 10^3 \mu\epsilon$, $4.82 \times 10^3 \mu\epsilon$ and $9.95 \times 10^3 \mu\epsilon$, respectively. The crack resistance of the TPUA mixture is more than three times that of the EA mixture and more than two times that of the SBS asphalt mixture. The reason is that the thermosetting PU modifier has a lower glass transition temperature and still has good ductility at low temperatures. The thermosetting PU modifier can significantly improve the low-temperature stability of its modified asphalt mixture.

4 CONCLUSIONS

We studied the high-temperature deformation resistance, low-temperature flexibility and mechanical properties of the TPUA binder. We comprehensively evaluated the pavement performance of the TPUA mixture by comparing it with traditional bridge deck paving materials. The conclusions are as follows:

(1) The traditional rutting factor index is unsuitable for evaluating the thermosetting resin modified asphalt

binder. TPUA and EA binders gradually exhibit the characteristics of elastic materials under high-temperature conditions and have excellent high-temperature deformation resistance.

(2) The TPUA mixture has excellent mechanical properties. The Marshall stability and splitting strength of the TPUA mixture are five times and more than three times that of the SBS asphalt mixture, respectively. Its dynamic stability also exceeds that of the SBS asphalt mixture by one order of magnitude and it has excellent high-temperature deformation resistance. The moisture stability of the TPUA mixture is between those of the SBS asphalt mixture and the EA mixture, which is much higher than the standard requirements.

(3) Under low-temperature conditions, the TPUA mixture has excellent low-temperature crack resistance performance; its fracture energy is more than three times that of the EA mixture and more than two times that of the SBS asphalt mixture.

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