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Influencing factors of reserve time and the rheological properties of thermosetting polyurethane-modified asphalt

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Abstract: Thermosetting polyurethane-modified asphalt (PUMA) undergoes an irreversible curing reaction, which means any improper handling during construction cannot be corrected. This study investigates the effects of hard segment content, isocyanate index, polyurethane (PU) content, and temperature on the viscosity of PUMA and proposes a method for regulating its reserve time. Based on viscosity-temperature profiles, a viscosity growth model was established to predict the evolution of PUMA viscosity with temperature and time. The results indicate that temperature exerts the most pronounced effect on the reserve time of thermosetting PUMA. Moreover, the developed viscosity growth model under different temperatures enables the prediction of PUMA reserve time. As PU content increases, the microstructure of PUMA evolves from a dispersed to a continuous phase. When the PU content exceeds 30%, a continuous crosslinked network forms, imparting excellent thermal resistance and elastic recovery at high temperatures. Furthermore, high PU content enhances the low-temperature flexibility of PUMA. These findings provide valuable insights for optimizing the application of PUMA materials in pavement engineering.

Key words: road engineering; polyurethan-modified asphalt; viscosity; reserve time; rheological performance

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In recent years, polyurethane (PU) has attracted considerable attention as an asphalt modifier in pavement engineering. Structurally, PU is composed of alternating soft segments (oligomers) and hard segments (isocyanates and crosslinkers), which collectively impart excellent mechanical properties, flexibility, and chemical stability[1-3]. When the PU content exceeds 20%, a crosslinked network gradually forms, and polyurethane-modified asphalt (PUMA) transitions from thermoplastic to thermosetting behavior, thereby significantly enhancing its road performance[4-5]. However, as a thermosetting material, PUMA exhibits a continuous increase in viscosity during the crosslinking reaction and ultimately loses construction workability. Consequently, clarifying the viscosity evolution of PUMA during curing is crucial for its design and field application.

Multiple chemical reactions occur during the PU modification process. When the PU modifier content in PUMA reaches 50%, a crosslinked network structure similar to that of neat PU is formed[6]. Compared with traditional epoxy asphalt, this composite exhibits superior mechanical properties, flexibility, and storage stability while offering cost advantages[7-8]. Other researchers have explored the optimal content and preparation methods of various modifiers and analyzed the impact of PU on asphalt rheological properties[9-10]. By adjusting the soft-to-hard segment ratio in PU, its properties can be precisely tuned, thereby affecting its distribution within the base asphalt and enabling tailored modification effects[11]. Existing research primarily focuses on the advantages of PUMA in terms of mechanical properties and high-temperature stability. However, thermosetting PUMA undergoes an irreversible curing reaction during the modification process. As PU curing proceeds, the viscosity of the PUMA system progressively increases[12-13]. To prevent thermosetting PUMA from losing its processability during construction, it is therefore necessary to investigate the factors that govern its reserve time.

The construction reserve time is a critical technical parameter that determines the overall quality of pavement construction. Although existing studies have attempted to explore the viscosity evolution of PUMA, most remain limited to phenomenological descriptions under single-factor conditions[14-15]. Systematic investigations

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into the synergistic effects among hard-segment content, isocyanate index, and construction temperature are still lacking, which obscures the distinctiveness and practical importance of regulating reserve time[16-17]. Several researchers have predicted the allowable reserve time of epoxy asphalt during construction and recommended maintaining the mixing temperature of epoxy asphalt mixtures within 110-130 ℃[18-20]. They have also analyzed the effects of factors such as temperature and epoxy asphalt content on reserve time, as well as evaluated the paving performance of epoxy asphalt mixtures[21-22]. Collectively, these studies provide a fundamental basis for regulating the reserve time of thermosetting modified asphalts. However, compared with epoxy asphalt, research on the reserve time of PUMA involves more complex influencing factors, which represents a key current research gap.

Therefore, this study systematically varies the hard-segment content, isocyanate index, PU content, and reaction temperature to elucidate the intrinsic correlation between viscosity evolution and microstructure, thereby enabling effective prediction and control of the construction reserve time. In addition, the rheological properties of PUMA under different conditions are investigated to provide both theoretical guidance and practical insights for its engineering application.

1 Materials and Methods

1.1 Raw materials

Donghai 60/70# penetration grade asphalt and 4.5% (mass fraction) styrene-butadiene-styrene (SBS)-modified asphalt were used in this study. The basic properties of the asphalt are listed in Table 1. Hexamethylene diisocyanate (HDI) trimer was supplied by Wanhua Chemical Group Co., Ltd. The oligomeric polyol, polytetrahydrofuran diol (PTMEG), and the chain extender, 1,4-butanediol (BDO), were obtained from the Macklin reagent platform. The physical properties of the raw materials are summarized in Table 2.

Table 1 Property indicators of the asphalt

Properties	60/70# asphalt	4.5% SBS
Penetration (25 ℃)/0.1 mm	68.9	51.8
Ductility (10 ℃)/cm	18.1	54
Softening point/℃	48.05	69.5
SHRP PG	PG 64-22	PG 76-22

1.2 Preparation

PUMA was prepared using a two-component reactive system, similar to that of epoxy asphalt. Component A consisted of base asphalt, PTMEG, and BDO, while Component B was the HDI trimer. The calculation formulas for the raw materials and the preparation process are based on the authors' previous research[23].

Table 2 Physical properties of PU raw materials

Properties	HDI trimer	PTMEG	BDO
—NCO content/%	23.28		
Molecular weight	333.43	2 000	90.12
Viscosity/(mPa·s)	1 252	950-1 450	
Hydroxyl/(mg KOH·g^{-1})		55.7	
Melting point/℃		32	19-21

1.3 Test methods

The viscosity variation of PUMA was investigated using a Brookfield rotational viscometer with a No. 27 spindle at a rotational speed of 20 r/min. Additionally, the microtopography and structural changes of PUMA were observed via an OLYMPUS-BX41 fluorescence microscope and Fourier transform infrared (FTIR) spectroscopy. Finally, a dynamic shear rheometer and a bending beam rheometer were employed to comprehensively evaluate its rheological properties[14-15].

2 Results and Discussion

2.1 Analysis of different influencing factors

2.1.1 Hard segment content

The hard segments typically influence the softening or melting temperature of the polymer, as well as its high-temperature properties. A high content of hard segments generally enhances the mechanical properties. Moreover, the hard segment content in PU significantly affects its curing process. Therefore, the viscosity-time behavior of PUMA with varying hard segment contents (ω_H=10%-50%) was investigated. The calculation formulas for the formulations are based on the authors' previous research[23], and the experimental results are shown in Fig. 1.

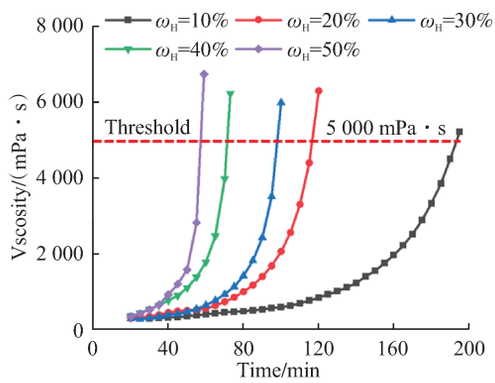

Fig. 1 Viscosity-time profiles for PUMA with varying hard segment contents

According to the General Specifications of Epoxy Asphalt Materials for Paving Roads and Bridges (GB/T 30598—2014), the reserve time is defined as the time required for the viscosity to reach 5 000 mPa·s. This is

widely recognized as a critical threshold marking the transition of thermosetting modified asphalt from a workable to a non-workable state. As shown in Fig. 1, the viscosity growth rate of PUMA increases and the reserve time decreases with increased hard-segment content, indicating the significant influence of hard segments in PU on the viscosity evolution of PUMA. This behavior is attributable to the formation of rigid hard segments through hydrogen bonding and microphase separation between the HDI trimer and BDO. These rigid domains restrict the mobility of the soft-segment chains. An increase in hard-segment content directly raises the crosslinking density and decreases the relative proportion of soft segments. Consequently, an increased number of chemical crosslinking sites form per unit volume, accelerating network formation and curing. This substantially limits chain mobility, causing the viscosity of PUMA to reach its critical threshold rapidly. Reducing the hard-segment content can effectively extend the reserve time of PUMA. However, excessively low hard-segment content may lead to undesirable effects. For example, PUMA with a hard-segment content of only 10% shows high molecular mobility; however, the resulting crosslinked network is sparse and contains insufficient effective crosslinking points. This leads to inadequate structural strength and stiffness. Although the viscosity increases slowly in this case, such behavior indicates incomplete crosslinking or an extremely slow curing process, preventing the formation of a robust three-dimensional network.

Adjusting the hard-segment content provides an effective means to precisely control the reserve time of PUMA. An ω_H above 20% is recommended to achieve a balance between reserve time and mechanical intensity, while practical formulation design requires a trade-off between reserve time and mechanical performance.

2.1.2 Isocyanate index

An excessive proportion of —NCO groups in the formulation results in incomplete curing, leading to a hard PU structure, while an excessive proportion of —OH groups reduces PU cohesion. This study investigates the viscosity-time behavior of PUMA at varying isocyanate indices (the molar ratio of NCO to OH R=0.8-1.2). The calculation formulas for the formulation are based on the authors' previous research[23], and the experimental results are shown in Fig. 2.

The component ratio of the two-component PU system can be adjusted within a certain range, providing flexibility in formulation. As shown in Fig. 2, an increase in the isocyanate index R leads to a rapid viscosity increase. When R increases from 0.8 to 1.2, the number of —NCO groups available for chemical crosslinking increases, resulting in a high crosslink density. The accelerated formation of the network structure rapidly restricts chain mobility, thereby increasing the viscosity growth rate

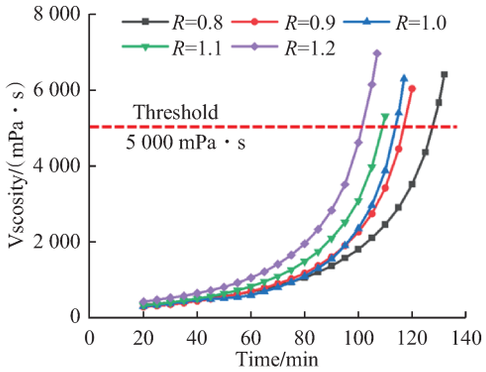

Fig. 2 Viscosity-time profiles for PUMA with varying isocyanate indices

and shortening the reserve time of PUMA. When R < 1.0 (e.g., R = 0.8), excess —OH groups are present in the system. Some —NCO groups are rapidly consumed during the early stage; however, owing to insufficient —NCO content, not all —OH groups on long-chain PTMEG and BDO can be effectively linked. Consequently, an under-crosslinked and loosely connected network forms, containing a substantial number of hydroxyl-terminated flexible chains. This incomplete network exhibits weak curing kinetics, leading to the slowest viscosity increase. When R > 1.0 (e.g., R = 1.2), the system contains an excess of —NCO groups. This accelerates the curing rate during the rapid viscosity-growth stage and increases the initial viscosity owing to an intensified early-stage reaction. Moreover, small coagulated particles may form during asphalt modification because the locally high —NCO concentration promotes localized reactions. The highly reactive —NCO groups can react not only with hydroxyl groups but also, at later stages, with moisture in the air or undergo self-reactions such as biuret or allophanate formation. These competing reaction pathways lead to a chaotic and accelerated crosslinking process, causing an overly restricted network structure to form prematurely. Consequently, molecular mobility becomes severely limited, and the viscosity rises rapidly, significantly reducing the reserve time of PUMA.

Therefore, the isocyanate index must be controlled within an appropriate range when designing PUMA formulations. An R value between 0.9 and 1.1 is recommended, as it provides a balanced correlation between reaction kinetics and material uniformity. In addition, the influence of the component formulation on the mechanical properties should be considered to achieve optimal overall properties.

2.1.3 PU content

Variations in PU content affect both the mechanical and construction properties of the material by regulating molecular structure, crosslinking density, and interfacial adhesion in a complex manner. The viscosity-time corre-

lations of PUMA with varying PU contents (10%-50%) were analyzed under identical PU molecular structures and preparation conditions. The calculation formulas for the formulation are based on the authors' previous research[23], and the experimental results are shown in Fig. 3.

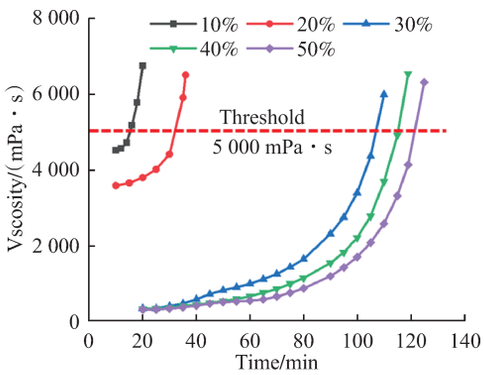

Fig. 3 Viscosity-time profiles for PUMA with varying PU contents

The effect of the PU content on the viscosity of the PUMA system essentially arises from changes in the continuous phase and the evolution of the micromorphology. As shown in the subsequent microstructural investigation, the morphology transitions from "microsphere dispersion" to "two-phase dispersion" and eventually to a "crosslinked network." At the macroscopic level, this process manifests as a competitive mechanism involving an initial decrease in viscosity followed by a subsequent viscosity build-up, as shown in Fig. 3. At 10% PU, the asphalt behaves as a supercooled liquid with limited free volume, and the small amount of PU dispersed as microspheres within the asphalt increases the flow resistance. Therefore, the initial viscosity is relatively high. At 20% PU, the number of PU microspheres increases, leading to a distinct two-phase structure. In this case, the PU soft segments exert a diluting and plasticizing effect on the asphalt, thereby reducing the initial viscosity. When the PU content exceeds 30%, a large quantity of low-viscosity reactants (e.g., PTMEG) disrupts the originally continuous asphalt phase and redistributes it within the PU phase, causing a further decrease in the initial viscosity. As the reaction proceeds, the hard segments gradually become enriched. Through hydrogen bonding and microphase separation, a three-dimensional crosslinked network is formed. This markedly restricts chain mobility, resulting in a rapid increase in viscosity during the later stage of reserve time and a pronounced viscosity-building effect.

Overall, as the PU content increases, the processing window of the modified asphalt gradually widens. According to the requirements for thermosetting resin materials in GB/T 30598—2014, the reserve time should be no less than 40 min. Therefore, the PU content in thermosetting PUMA systems should be greater than 30%.

2.1.4 Reaction temperature

The initial reaction temperature of PU affects the structural regularity of its molecular architecture, while the reaction temperature also strongly influences the curing rate of PU. As the temperature increases, the reaction rate between isocyanate groups and active hydrogen-containing compounds is markedly accelerated. Therefore, it is essential to investigate the influence of temperature on the PU curing process. To this end, the viscosity-time behavior of PUMA with identical PU molecular structure and content was examined at different temperatures. The raw material mass ratio of PUMA was m(asphalt):m(HDI trimer):m(PTMEG):m(BDO) = 100:18.89:80:1.11, and the experiments were conducted at temperatures of 95, 100, 105, 110, 115, and 120 ℃. The results are shown in Fig. 4.

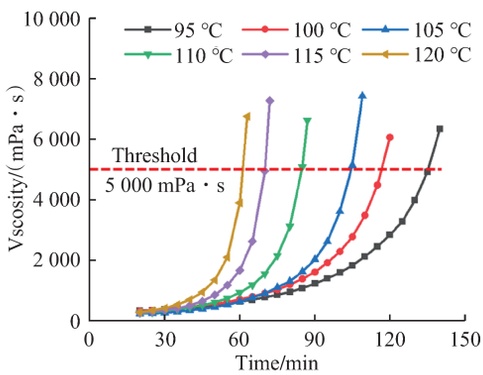

Fig. 4 Viscosity-time profiles for PUMA with varying temperatures

As shown in Fig. 4, curing temperature has a significant impact on the viscosity evolution of PUMA, with its processing time varying by more than twofold at different temperatures. In the initial stage, the viscosity of PUMA with the same molecular structure remains <1 000 mPa·s. Higher reaction temperatures correspond to lower initial viscosities, which can be attributed to the weakening of intermolecular interactions in the asphalt at elevated temperatures. This effect increases intermolecular distance, enhances fluidity, and lowers viscosity. At this stage, only a limited number of PU molecules participate in the curing reaction, resulting in relatively low overall viscosity. As the reaction progresses, the PU components gradually cure, leading to a moderate viscosity increase during the slow-growth stage. Once sufficient contact occurs between PU monomers, the curing reaction accelerates, entering the rapid-growth stage. When the temperature exceeds 110 ℃, the viscosity of PUMA increases exponentially, while at temperatures near 100 ℃, viscosity increases follow an almost linear trend. Additionally, with increasing temperature, the durations of the initial and slow-growth stages gradually shorten. Overall, the viscosity of thermosetting PUMA increases with tempera-

ture in accordance with the Arrhenius law, as the chemical reaction rate increases exponentially. Consequently, chain mobility accelerates, facilitating the rapid formation and interconnection of crosslinking points, leading to rapid viscosity growth.

Thus, regulating temperature significantly influences the curing kinetics and molecular interactions in PUMA. In practical engineering applications, an optimal processing temperature ensures effective dispersion and mixing of the reactants without significantly accelerating the curing rate. Therefore, the optimal mixing temperature for thermosetting PUMA should be maintained between 100 and 105 ℃. This range effectively balances reaction kinetics and viscosity control while ensuring material properties and processing feasibility.

2.1.5 Viscosity model

Currently, the Roller model, which integrates the absolute reaction rate theory and the Arrhenius law, has been widely applied in thermosetting asphalt materials[24-25]. Herein, the model was further refined and employed to analyze the evolution of viscosity-temperature curves of thermosetting PUMA. At a given absolute temperature T, the correlation between the viscosity $\eta(t, T)$ of the PUMA system and time t is expressed as follows:

$$\eta(t,T)=\eta_{t0}(T)\exp(k(T)t) \tag{1}$$

where $\eta_{t0}(T)$ is the initial viscosity (unit: Pa·s); $k(T)$ is the rate of reaction, which is a function of the absolute temperature T (unit: K).

Over the past decade, researchers have proposed numerous expressions for $k(T)$, among which the Arrhenius equation has been widely accepted and applied. The correlations between initial viscosity $\eta_{t0}(T)$ and reaction rate $k(T)$ with temperature T can all be considered to conform to the Arrhenius law[25], expressed as follows:

$$\eta(t,T)=\eta_{t\infty}\exp(E_\eta/(RT)) \tag{2}$$

$$k(T)=K_0\exp(-E_a/(RT)) \tag{3}$$

where $\eta_{t\infty}$ is the Arrhenius prefactor (unit: Pa·s), representing the lowest viscosity of the thermosetting system under the ideal condition of zero curing degree; E_η is the flow activation energy (unit: kJ·mol^{-1}); R is the gas constant (8.314 J/(K·mol^{-1}); K_0 and E_a are the pre-exponential factor (unit: s^{-1}) and the reaction activation energy (unit: kJ/mol), respectively, which are considered independent of T.

In the reaction described above, E_η and E_a are intrinsic to the system and do not vary with external conditions such as temperature or pressure. By substituting Eqs. (2) and (3) into Eq. (1), the following expression can be derived:

$$\eta(t,T)=\eta_{t\infty}\exp(E_\eta/(RT))\cdot \exp(K_0\exp(-E_a/(RT))t) \tag{4}$$

Under isothermal curing conditions at a constant temperature, taking the natural logarithm of both sides of Eq. (4) yields the expression for $\eta(t, T)$ as follows:

$$\ln\eta(t,T)=\ln\eta_{t\infty}+E_\eta/(RT)+K_0t\exp(-E_a/(RT)) \tag{5}$$

For non-isothermal curing conditions, Eq. (5) can be solved by integrating over temperature. As shown in Eq. (5), at a specific curing temperature, the logarithm of the system viscosity $\ln\eta(t, T)$ is a linear function of the curing reaction time t. Thus, Eq. (5) can be reformulated as follows:

$$\ln\eta(t,T)=a+bt$$
$$a=\ln\eta_{t\infty}+E_\eta/(RT),\quad b=K_0\exp(-E_a/(RT)) \tag{6}$$

To validate whether the correlation between $\ln\eta(t, T)$ and reaction time t can be effectively modeled using Eq. (6), we first derived fitting parameters using viscosity-time curves obtained at 95 and 100 ℃. The fitting results are illustrated in Fig. 5. Through linear regression, the intercept a and slope b of the linearized curve were determined, corresponding to the parameters a and b in Eq. (6). Based on these values, the optimal parameters for Eq. (5) were calculated, as summarized in Table 3. Substituting these parameters into Eq. (4) then yields the expression for $\eta(t, T)$:

$$\eta(t,T)=0.014\,5\exp(3\,503.8/T+664\,800t\cdot \exp(-4\,811.16/T)) \tag{7}$$

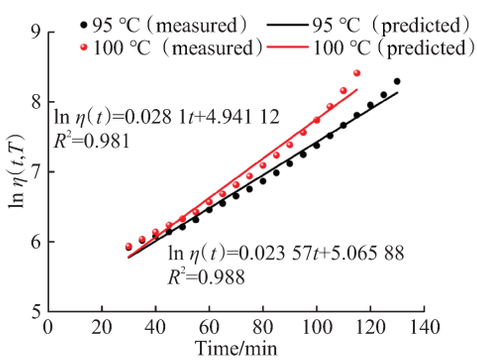

Fig. 5 Evolution of logarithmic viscosity with reserve time for PUMA

Table 3 Parameters of PUMA used for viscosity prediction

$\eta_{t\infty}$/(Pa·s)	E_η/(kJ·mol^{-1})	K_0/s^{-1}	E_a/(kJ·mol^{-1})
0.014 5	28.5	11 080	40.0

Using the method described in Eq. (7), the predicted viscosity models of PUMA at different temperatures were calculated and are presented in Table 4. The corresponding curves were plotted for comparison with the experimental data, as shown in Fig. 6. The results indicate that the predicted values closely coincide with the experimental measurements.

Table 4 Predictive modeling of PUMA

Celsius/℃	Thermodynamic temperature/K	Prediction model
95	368.15	$\eta(t,T) = \exp(0.023\,6t + 5.065\,9)$
100	373.15	$\eta(t,T) = \exp(0.028\,1t + 4.941\,1)$
105	378.15	$\eta(t,T) = \exp(0.036\,7t + 4.390\,9)$
110	383.15	$\eta(t,T) = \exp(0.044\,5t + 4.354\,0)$
115	388.15	$\eta(t,T) = \exp(0.053\,5t + 4.307\,3)$
120	393.15	$\eta(t,T) = \exp(0.062\,6t + 4.230\,1)$

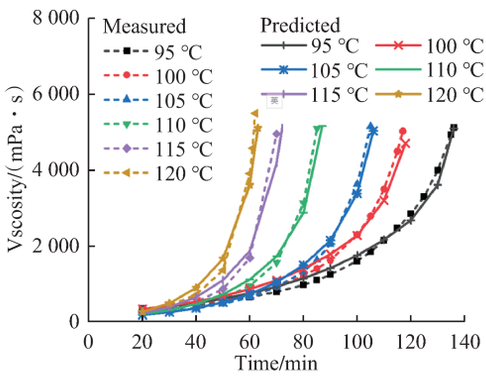

Fig. 6 Measured and predicted viscosity-reserve time relationship of PUMA

These findings demonstrate that the viscosity growth model for thermosetting PUMA, established using the dual Arrhenius equations, exhibits excellent applicability. By employing this model, it becomes feasible to estimate the allowable construction reserve time, providing critical guidance for forecasting construction reserve times in practical engineering applications.

2.1.6 Comparison of different influencing factors

To quantitatively evaluate the relative influence of these factors, a range analysis was conducted to compare their impacts. The results of this analysis are presented in Table 5.

Table 5 Comparison of different influencing factors

Factor	Hard segments	Isocyanate index	PU content	Temperature
Time/min	58-117	103-127	108-123	62-136

Among these factors, temperature has the most pronounced effect. Within the range of 95-120 ℃, the reserve time can be extended by about 74 min, corresponding to an increase of about 3 min per 1 ℃ rise. This highlights the importance of precise temperature control during preparation. In addition, adjustments to hard segment content, isocyanate index, and PU content can further modulate reserve time; however, these parameters must be carefully balanced against their effects on mechanical properties. High values generally enhance stiffness but accelerate crosslinking, thereby reducing reserve time. For the isocyanate index, an optimal range of 0.9-1.1 balances reaction kinetics and material homogeneity. Similarly, increasing PU content increases the crosslinking density of PUMA but may compromise its workability. This multifactor analysis underscores the necessity of a holistic approach to formulation design, ensuring both sufficient reserve time for construction and optimal mechanical properties in service.

2.2 Micromorphology

The phase morphology of PUMA is determined by the PU concentration and its structural interactions with asphalt. The distribution and morphological evolution of PU in the modified asphalt system can be observed using fluorescence microscopy (FM), as shown in Fig. 7.

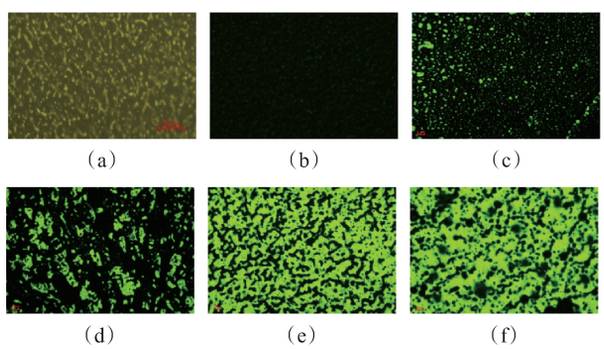

Fig. 7 FM images of PUMA. (a) 4.5% SBS; (b) 10%; (c) 20%; (d) 30%; (e) 40%; (f) 50%

At low PU contents (<20%), asphalt serves as the continuous phase, while PU is dispersed as microspheres, resembling the morphology observed in SBS-modified asphalt, as shown in Figs. 7(b) and (c). At higher PU contents (>30%), PU branches interconnect to form a crosslinked network structure within the asphalt matrix. Within the 20%-30% range, a critical phase inversion occurs, where PUMA transitions from a dispersed PU phase to a continuous PU phase. In this state, asphalt becomes the dispersed component within the polymer matrix, as shown in Figs. 7(c) and (d). These observations corroborate previous findings, confirming that within the 20%-30% PU range, PUMA gradually shifts from thermoplastic to thermosetting behavior. This demonstrates that the FM characterization approach employed in this study can effectively capture the overall evolution of the PU network structure, thereby avoiding the potential bias associated with surface observations alone.

2.3 Chemical characteristics

To analyze functional group changes during the curing process of PUMA, the variations of characteristic peaks were monitored via FTIR spectroscopy. The results are shown in Fig. 8.

The characteristic peak of isocyanate (—NCO) groups appears at 2 270 cm^{-1}, a signature functional group of PU. In the initial stage, a strong —NCO absorption peak

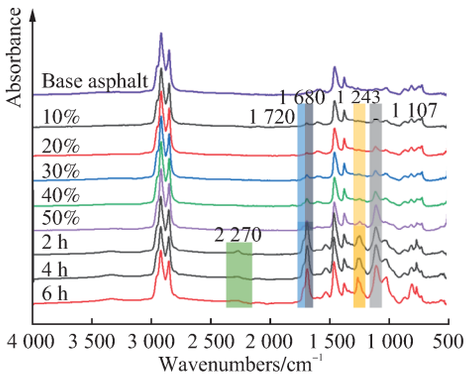

Fig. 8 Infrared spectra of different PUMA

at 2 270 cm^{-1} is observed owing to the multiple —NCO groups present in the HDI trimer. This —NCO peak gradually diminishes as the —NCO groups react with —OH groups from PTMEG and BDO, forming urethane bonds (—NHCOO—). The stretching vibration of urethane C═O appears in the 1 680-1 730 cm^{-1} range, confirming successful PU synthesis. After 6 h, the —NCO peak disappears, confirming the complete reaction of —NCO groups with —OH groups. The absorption peak positions of PUMA with varying PU contents are nearly identical. However, as the PU content increases, the peak intensities at specific wavenumbers gradually strengthen: 1 107 cm^{-1} corresponds to the ether bond C—O—C from PTMEG; 1 243 cm^{-1} represents the asymmetric stretching vibration of C—O—C in —NHCOO—; 1 680-1 720 cm^{-1} corresponds to the carbonyl C═O stretching vibrations of urethane groups. These trends indicate the increasing dominance of PU interactions within the modified asphalt system.

2.4 High-temperature properties

2.4.1 Temperature sweep

The high-temperature rheological properties of different PUMA were analyzed using the temperature sweep mode and compared with those of SBS-modified asphalt. The results are shown in Fig. 9.

As shown in Fig. 9, the incorporation of PU improved the rutting resistance of asphalt, with higher PU content corresponding to greater rutting factors. By contrast, the rutting factor of SBS-modified asphalt gradually decreased with increasing temperature, reflecting the typical viscoelastic behavior. PUMA containing 10% and 20% PU shows rutting factor and phase angle trends comparable to those of SBS-modified asphalt, indicating viscoelastic behavior. However, when the PU content exceeded 30%, the rutting factor of PUMA gradually increased with rising temperature, deviating from conventional viscoelastic behavior. Significant differences in high-temperature performance were observed among PUMA with different PU contents. As the temperature increased, the phase angle of low-PU-content PUMA and SBS-modified asphalt decreased gradually. These results indicate that high-content PUMA exhibits superior resistance to high-temperature deformation, markedly outperforming both low-PU-content PUMA and SBS-modified asphalt. When PU content increased from 20% to 30%, a crosslinked PU network with mechanical strength formed within the asphalt. Consequently, for PU contents above 30%, thermosetting PUMA exhibited pronounced elasticity at high temperatures, with higher PU content providing greater elastic performance.

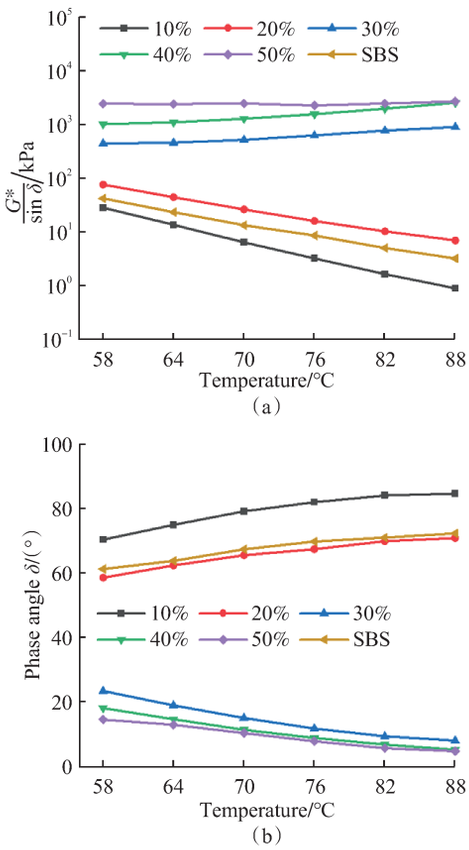

Fig. 9 High-temperature rheological properties of different PUMA. (a) Rutting factor; (b) Phase angle

2.4.2 Multiple stress creep and recovery

The high-temperature elastic recovery performance of different PUMA samples was evaluated using the multiple stress creep recovery test and compared with SBS-modified asphalt. The results are shown in Fig. 10.

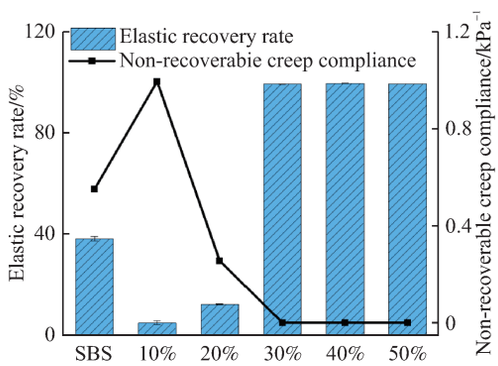

Fig. 10 Creep and recovery behavior of different PUMA

As shown in Fig. 10, the elastic recovery rate of PUMA gradually increases with increasing PU content. When the PU content is less than 30%, the elastic recovery rate of PUMA is slightly lower than that of SBS-modified asphalt, showing performance similar to that of thermoplastic materials. This is because low PU content has not initiated the formation of a crosslinked network structure of PUMA. When the PU content exceeds 30%, thermosetting PUMA exhibits excellent high-temperature elastic recovery performance, with an elastic recovery rate exceeding 99%. As PU content increases, the irreversible creep compliance of PUMA gradually decreases. When the PU content exceeds 30%, the irreversible creep compliance of thermosetting PUMA approaches zero. These results indicate that thermosetting PUMA exhibits outstanding high-temperature elastic recovery performance.

2.5 Low-temperature properties

The low-temperature cracking performance of different modified asphalt samples was evaluated using a bending creep test and compared with that of SBS-modified asphalt. The test results are shown in Fig. 11.

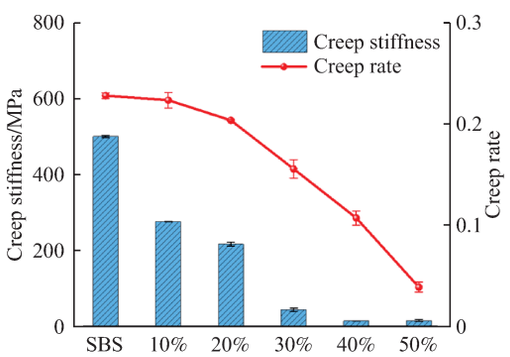

Fig. 11 Low-temperature creep properties of different PUMA

As shown in Fig. 11, the $S(t)$ value of SBS-modified asphalt is significantly higher than that of PUMA, indicating greater hardness and brittleness at low temperatures. When the PU content exceeds 40%, the variation in creep stiffness becomes minimal, indicating a stable low-temperature response. With increasing PU content, the creep rate of PUMA gradually decreases. Remarkably, when the hard segment content is 20%, the isocyanate index is 1, and the PU content exceeds 30%, the creep rate of PUMA is significantly lower than that of SBS-modified asphalt. These results indicate that PU can effectively reduce the stiffness modulus and the accumulation of low-temperature stress in PUMA, thereby significantly enhancing the low-temperature cracking resistance of asphalt.

3 Conclusions

(1) Temperature has the greatest impact on reserve time: within the range of 95-120 ℃, the reserve time varies by up to 74 min. A viscosity evolution model for PUMA was developed based on the dual Arrhenius equation.

(2) With a hard segment content of 20%, an isocyanate index of 1.0, a temperature of 100-105 ℃, and a PU content of 50%, PUMA achieves an optimal balance between extended reserve time and excellent mechanical properties.

(3) At 100 ℃, the reaction of PU in asphalt is nearly complete after 6 h. PUMA gradually forms an interconnected network structure, exhibiting significant elastic recovery performance at high temperatures.

(4) As PU content increases, the high- and low-temperature performances of thermosetting PUMA gradually improve. When PU content exceeds 30%, both high- and low-temperature performances are significantly enhanced.

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热固性聚氨酯改性沥青容留时间影响因素及流变性能研究

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摘要: 热固性聚氨酯改性沥青(PUMA)会产生不可逆的固化反应,导致施工过程中的任何不当操作都无法修正。本文研究了硬段含量、异氰酸酯指数、聚氨酯(PU)掺量和温度对PUMA黏度的影响,并提出调节容留时间的方法。基于黏度-温度曲线,建立了用于预测PUMA黏度随温度和时间变化的黏度增长模型。结果表明,温度对热固性PUMA容留时间的影响最为显著。通过建立不同温度下的黏度增长模型,实现了对PUMA容留时间的预测。随着PU掺量的增加,PUMA的微观结构由分散相演变为连续相。当PU掺量超过30%时,形成连续的交联网状结构,且具有优异的高温和弹性恢复性能。此外,较高的PU掺量提高了PUMA的低温柔韧性。这些发现为优化PUMA材料在路面工程中的应用提供了有益的指导。

关键词: 道路工程;聚氨酯改性沥青;黏度;容留时间;流变性能

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