



Article Mechanism of Polyurethane Binder Curing Reaction and Evaluation of Polyurethane Mixture Properties

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Abstract: This study focuses on analyzing the curing reaction mechanism of polyurethane (PU) binders and comprehensively evaluating the PU mixture's properties. The former was investigated by conducting a Fourier transform infrared spectroscopy (FTIR) test on PU binders with different curing times. The volume change characteristics, construction operation time, and strength formation law were clarified through the splitting tensile test of PU mixtures under different environmental conditions. The optimal PU mixture stacking time and curing time under different environmental conditions were determined. The properties of the PU mixture and asphalt mixture were evaluated and compared through a rutting test, low-temperature bending test, freeze-thaw splitting test, and four-point bending fatigue test. The results show that the physical and chemical curing of the PU binder occurred within the first 24 h of curing, and the reaction speed gradually accelerated to form a polyurea structure 24 h later. It is recommended to stack the PU mixture for 4 h before compaction and to cure it for 2 days before opening under the conditions of 50% humidity and 15-40 °C surrounding temperature. The PU mixture shows better temperature stability and fatigue resistance than the asphalt mixture, and the splitting tensile strength of the PU mixture before and after the freeze-thaw splitting test is also higher. It is clear that the PU mixture is a green road building material with good performance.

Keywords: PU binder; curing reaction mechanism; PU mixture; properties; stacking time; curing time

1. Introduction

Asphalt pavement is widely used owing to its low cost, in addition to its characteristics of low noise and good driving quality; nearly 90% of the roads worldwide comprise asphalt mixtures [1]. In recent years, severe loads and extreme temperatures have occurred frequently; therefore, special roads—such as long and wide longitudinal slope highways, port area highways, port special roads, heavy-duty bridge deck pavement, and airport runways—have higher requirements for pavement materials [2]. However, asphalt is a temperature-sensitive material, which makes asphalt mixtures prone to rutting, cracks, water damage, and other forms of damage that can affect their service life [2]. Furthermore, hot-mix asphalt mixtures consume significant amounts of fuel to heat mineral aggregates and asphalt during the production process [3]. A large amount of carbon dioxide, sulfur dioxide, PM2.5 dust, and smoke are also emitted into the atmosphere during the construction process, which imposes a significant burden on the surrounding environment [1,3]. Therefore, new energy-saving and emission-reducing green pavement construction materials are required for the aforementioned special types of road [4]. To mitigate these



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). problems, scholars have proposed the concept of polyurethane (PU) mixture pavement, where high molecular weight polymer PU is used to replace asphalt as the binder for pavements [5]. Since the end of the 1970s, researchers have begun to use one- or two-component PU to replace asphalt as the binder for functional pavement [6–23], pavement structural

layers [24–26], bridge deck pavement [27], etc. The PU mixture can be prepared, transported, and compacted at room temperature, save energy and emission, and has good temperature stability and durability, which can greatly reduce the frequency and cost of road maintenance. The active end -NCO group of the PU binder reacts with the water adsorbed on the substrate surface and the active hydrogen, such as -OH species, on the surface to form urea bonds and promote crosslinking and curing, gradually increasing the strength [28]. During the formation of the PU mixture, the environmental conditions affect the curing reaction of the PU binder [29]. When the ambient temperature is high, the functional group reaction is vigorous, and the opening time of the PU binder is short, which affects the construction operable time of the mixture [30]. When the ambient humidity is high, the curing reaction rate is accelerated, and carbon dioxide (CO₂) is released during the reaction which leads to PU mixture volume expansion [30]. After the formation of the PU mixture, water immersion can easily cause the plasticization and hydrolysis of PU, and the temperature will further accelerate its oxidation, plasticization, and hydrolysis [31]. Wang et al. [5,17,18] determined the strength and modulus of a PU macadam mixture based on the cube unconfined compression test and rectangular beam bending test, investigating the strength characteristics and failure mechanisms of porous PU mixtures (PPMs) based on the load stress test. Wang et al. designed porous elastic road surfaces (PERSs) based on PU binders, which not only showed good noise-reduction performance, but also high low-temperature tensile performance, polishing resistance, and rutting resistance [7,8]. Cong et al. [4] analyzed the impact of water immersion damage on the mixture and found that, in comparison to traditional porous asphalt mixtures, an open-graded mixture designed with PU instead of asphalt can obtain a higher effective void ratio (greater than 20%). The mechanical, functional, and mesoscopic properties of a high-performance PU bounded pervious mixture (PUPM) were further clarified by Li et al., who found that PUPM exhibits excellent ant-stripping performance, and has a larger equivalent radius, effective void fraction, and tortuosity [12]. Hong et al. [32] studied the evolution law of the performance of the PU binder under ultraviolet (UV) aging by using a UV aging chamber to simulate the natural aging process; the tensile properties and viscoelasticity were taken as the evaluation indexes, and the PU dense-graded concrete prepared using the vacuum-assisted resin transfer molding technology was evaluated [33]. However, current research mainly focuses on the mixture composition and performance evaluation of PU mixtures [34]. Research on the main reaction types and key group transformations of different PU binder curing reaction stages has not been conducted in-depth. The strength formation mechanism of polyurethane mixture is not clear, which affects the determination of composition design index of polyurethane mixture, thus the mixture with the best performance cannot be obtained. Furthermore, the influence law of environmental factors on the strength formation law and volume change characteristics of PU mixtures needs to be further investigated. As the basis for guiding the connection time of mixing, paving, compaction, and other processes in the construction of polyurethane mixture, guide the construction of polyurethane mixture pavement. The temperature stability, water stability, and fatigue resistance of PU mixtures require more accurate quantitative characterization to comprehensively evaluate the specific applicable working conditions.

Therefore, this study aims to explore the curing reaction mechanism, strength formation law, and performance of PU mixtures. The curing reaction mechanism of PU binders was detected using Fourier transform infrared spectroscopy (FTIR). The strength formation law was clarified using the splitting tensile test of PU mixtures under different environmental conditions, and the curing and stacking time under these conditions was proposed. The properties of the PU mixture were evaluated through the rutting test, low-temperature bending test, freeze-thaw splitting test, and four-point bending fatigue test, etc. The PU binder curing mechanism and PU mixture strength formation mechanism provide basis for the composition design and construction process arrangement of PU mixture. The performance evaluation results of PU mixture help to determine the construction conditions of PU mixture and recommend PU pavement structure. This study's results provide a new idea for the research and development of high-performance road materials, and is conducive to the development of green construction technology in road engineering.

2. Materials and Methodology

2.1. Materials

2.1.1. Raw Material

The materials used herein mainly included PU, 70# matrix asphalt, styrene butadiene styrene (SBS) modified asphalt, and aggregates. The mineral aggregates were 0–3 mm, 3–5 mm, 5–10 mm, and 10–15 mm basalt aggregates and limestone mineral powder. The SBS modified asphalt and 70# matrix asphalt were produced by Shandong Huarui Road Materials Co., Ltd. (Zibo, China). The PU binder was a linear organic polymer embedded in soft and hard segments, produced by Wanhua Chemical Co., Ltd. (Yantai, China). The soft segment of PU was composed of polyol, and the hard segment was composed of the diphenylmethanc-4,4'-diisocyanate (MDI), carbamate, and urea groups. The specific technical indexes of PU binders are given in Table 1.

Table 1. Technical indexes of PU binder.

Technical Indicators		Unit	Technical Requirement
Surface drying time		min	40 ± 10
Tensile strength		MPa	≥ 15.0
Fracture elongation		%	≥ 100
Molecular weight		/	13,000–17,000
UV aging	Tensile strength	MPa	≥ 9.0
	Fracture elongation	%	≥ 40

2.1.2. Mixture Composition and Production

The composition design results for the PU mixture (SPU-13), SBS modified asphalt mixture with a skeleton dense structure (SMA-13), and suspended dense structure matrix asphalt mixture (AC-13) are summarized in Table 2.

Cumulative Passing Percentage of Each Sieve (%) Sieve size (mm) **SMA-13** AC-13 SPU-13 16 100 100 100 13.2 81.8 99.4 95.9 9.5 61.2 88.1 67.8 4.75 24.2 74.1 31 2.3619.9 41.9 21.41.18 16.8 33.5 16.724.511.50.6 14.50.3 17.9 12.4 8.6 0.15 10.9 11.7 6.1 0.075 10.1 7.7 2.4**Binder Content (%)** 5.9 4.84.4

 Table 2. Mineral aggregate gradation and binder content of mixtures.

The preparation of AC-13 and SMA-13 mixtures was carried out in accordance with the methods specified in "Standard Test Methods of Bitumen and Bituminous Mixtures for Highway Engineering" (JTG E20-2011) [35]. The SPU-13 mixture was prepared using an asphalt mixture mixer (BH-20, Cangzhou Huayun Experimental Instrument Co., Ltd.,

Cangzhou, China); however, the aggregates and binder were not heated before mixing. First, the specified proportion of aggregates were mixed in the mixing pot for 20–30 s. Next, the corresponding proportion of PU binder was added and mixed for 30–50 s. Finally, the corresponding proportion of mineral powder was added and mixed for 30–50 s, and the smoothness of the mixture was checked.

2.2. *Methodology*

2.2.1. Fourier Transform Infrared Spectroscopy Test for PU Binder

The EQUINOX-55 FTIR spectrometer (Bruker, Karlsruhe, Germany) was used to characterize the original, curing, and cured PU binder, and to identify chemical groups according to ASTM D5477. The PU binder was dried in a 120 °C vacuum oven (VO-60T, Shanghai Dengsheng Instrument Manufacturing Co., Ltd., Shanghai, China) for 1 h. The PU binder was coated on KBr sheet to prepare FTIR specimens. The specimens were cured at 20 °C and 50% ambient humidity for 0 h, 2 h, 4 h, 24 h, 72 h, and 168 h, following which FTIR tests were conducted. The scanning range was 4000–400 cm⁻¹ and the resolution was 4 cm⁻¹, with 32 scanning iterations.

2.2.2. Basic Performance Test Method for the Mixtures

The basic performance test of the mixtures was conducted in accordance with the methods specified in "Standard Test Methods of Bitumen and Bituminous Mixtures for Highway Engineering" (JTG E20-2011).

(1) Marshall specimen height test

The PU mixtures were stacked under different environmental conditions and were then compacted 50 times on each side to form a Marshall test piece. Then, the height of the test piece after curing for 3 h, 6 h, 12 h, 24 h, 36 h, 48 h, 72 h, and 168 h was measured. The stacking conditions and serial numbers are shown in Table 3.

Temperature (°C)	Humidity (%)	Stacking Time (h)	Serial Number
20	0.5	0	SPU-1
20	0.5	4	SPU-2
20	0.5	8	SPU-3
20	0.95	4	SPU-4
40	0.5	4	SPU-5

Table 3. Stacking conditions and serial numbers of PU mixtures.

(2) Splitting tensile test

The splitting tensile tests of the PU mixtures were carried out according to the provisions of T 0716-2011. The loading rate was 50 mm/min. There were three specimens in each group, and the average value was taken as the splitting strength.

(3) Rutting test

The rutting tests of the three mixtures were carried out according to the methods of T0719-2000. Each group had three parallel specimens with a size of $15 \text{ cm} \times 15 \text{ cm} \times 5 \text{ cm}$, with a test temperature of 60 °C, pressure conditions of 0.7 MPa, and a traveling speed of 42 cycles/min.

(4) Low-temperature bending test

To characterize the low-temperature crack resistance of the three mixtures, the bending tests were carried out in accordance with regulations of T0715-2011. Each group had three parallel specimens with a size of 250 mm \times 30 mm \times 35 mm [35], a loading speed of 50 mm/min, and a test temperature of -10 °C.

(5) Freeze–thaw splitting test

To characterize the water stability of the three mixtures, freeze–thaw splitting tests were carried out according to the methods in T0729-2000, and each group had three parallel specimens [35].

(6) Four-point bending fatigue test

Under the action of a standard load, the maximum tensile strain at the bottom of the pavement was between 300–600 $\mu\epsilon$. As an excellent pavement building material, PU mixtures have excellent fatigue resistance and self-healing properties; however, they are expensive [7,8]. Their use is suitable for special roads such as long and long longitudinal slope pavement, heavy load pavement, and long-life pavement [12–15]. The maximum tensile strain at the bottom of the surface layer of such sections is often greater than that for ordinary pavement [33]. At present, the SMA-13 mixture is mainly used for these special sections. Therefore, four-point bending fatigue tests on SMA-13 and SPU-13 mixtures with 600 $\mu\epsilon$, 800 $\mu\epsilon$, and 1000 $\mu\epsilon$ strain level were conducted. The fatigue tests were carried out according to the provisions of T0739-2011, the test temperature was 15 °C \pm 0.5 °C and the loading frequency was 10 Hz \pm 0.1 Hz [35]. Three parallel tests were carried out at the same strain level, and the size of the test piece was 380 mm \times 65 mm \times 50 mm.

3. Results and Discussion

3.1. Curing Reaction Mechanism of the PU Binder

3.1.1. Fourier Transform Infrared Spectroscopy Analysis of the Initial PU Binder

The infrared spectrum of the initial PU binder sample is shown in Figure 1. The infrared spectrum bands and the types of functional groups represented are summarized in Table 4. The C=O stretching vibration from the –NHCOO functional group appeared at about 1728.9 cm⁻¹, and there was an obvious characteristic band of the –N=C=O functional group at 2267.9 cm⁻¹, indicating that there was an unreacted –N=C=O functional group in the molecular structure of the initial PU sample [34]; further, there was a free ethoxy characteristic band at 1103.1 cm⁻¹, indicating that the PU binder was polyether PU, so the PU binder has good hydrolysis stability, good flexibility and elongation, and good low temperature resistance.



Figure 1. Infrared spectrum of the original PU binder.

Wave Bands (cm $^{-1}$)	Functional Group Category
2973.7, 2927.9, 2857.7	Telescopic vibration from $-CH_2$
2267.9	–N=C=O antisymmetric stretching vibration band
1732.2	C=O telescopic vibration from the –NHCOO functional group
1599.0	Bending vibration band from –NHCOO
1526.9	Bending vibration band from –NH
1454.5	Shear vibration from $-CH_2$
1413.1	-COO vibration band
1372.7	Symmetrical bending vibration from –CH ₃
1103.1	Free ether oxygen characteristic band
1017.7	-C-C absorption band

Table 4. Functional groups represented by the infrared spectrum bands of the PU binder [34].

3.1.2. Reaction Characteristics of PU Binder during Curing

The infrared spectrum test results of the original PU binder and that cured for 2 h, 4 h, 24 h, 72 h, and 168 h are shown in Figure 2.



Figure 2. Infrared spectrum of PU binder at different curing times.

When comparing the infrared spectra of the original and cured for 2 h, 4 h, and 24 h PU binders, it is clear that the –NH stretching vibration band appeared and strengthened near 3328.1 cm⁻¹ and increased with curing reaction time. The –NCO characteristic band near 2274.6 cm⁻¹ did not weaken significantly within the first 4 h of curing time; however, the band weakened significantly after 24 h of curing. The bending vibration band of NHCOO near 1599 cm⁻¹ exhibited a gradually increasing trend, indicating that the physical and chemical curing of the PU binder shown in Figure 3a occurred in the first curing 24 h. It is shown that Carbon dioxide (CO₂) was produced in the process of the chemical curing reaction, which could have caused the volume expansion of the PU mixture with a dense structure.

(a)
$$R-N=C=O+H_2O \xrightarrow{\text{slow}} [R-NH-COOH] \longrightarrow R-NH_2+CO_2^{\dagger}$$

(b)
$$R-N=C=O+R'-NH_2 \xrightarrow{quick} R-N=C \stackrel{OH}{\swarrow} R-NH-C-NH-R'$$

Figure 3. (a) Preliminary curing of PU binder. (b) Subsequent curing of PU binder.

The C=O stretching vibration band of urea appeared at 1654.1 cm^{-1} in the 24 h curing infrared spectrum; however, there was no such characteristic band in the 2 h and 4 h curing infrared spectrum, indicating that the reaction shown in Figure 3b began after 24 h of curing, and then gradually accelerated to form a polyurea structure. The polyurea bond structure had high strength and cohesion energy, resulting in a sharp increase in the bonding strength of the binder. It implied that the strength of polyurethane mixture increased greatly after 24 h of curing reaction.

3.1.3. Main Group Changes of the PU Binder during Curing

The vibrational absorption band of the NCO group was strong and sharp and therefore cannot be affected by the absorption of other chemical functional groups, the NCO group was taken as the research object to study the curing process of the PU binder [28,29]. The FTIR curves of the NCO group with different curing times are shown in Figure 4. It can be seen that the characteristic band of the NCO group weakened gradually with time, and the curing reaction rate over the first 72 h was significantly higher than that in the later stages. In the first 72 h, the NCO group band changed significantly, and the reaction rate then slowed down. It may be because the linear polymer chain increased with the progress of the reaction in the first 72 h, and then the reaction speed slowed down because some unreacted NCO groups were wrapped in the adhesive system, blocking the contact between NCO groups and water.



Figure 4. The FTIR curves of the NCO band.

The FTIR curves of the NH band are shown in Figure 5. It can be seen that the characteristic band of NH is not stable in the first 24 h of the curing reaction, while the NH band was practically stable after 72 h of curing. The characteristic band of the infrared spectrum moved from 3332.4 cm⁻¹ to 3295.8 cm⁻¹, indicating that the internal hydrogen bond of PU was still gradually enhanced in the later stages of chemical curing. Both the migration of NCO and the penetration of water need time. Therefore, in the later stages of curing, the bond strength of the binder increased slowly; this process usually lasted for a long time. The reaction created more hydrogen bonds between polar functional groups in the PU molecular structure and increased its linear polymer chains.



Figure 5. The FTIR curves of the NH band.

3.2. Volume Characteristics and Strength Formation Law of the PU Mixture 3.2.1. Volume Characteristics of the PU Mixture during Curing

The height of specimens during curing was also measured. The height differences of the specimens were obtained by subtracting the initial height of the specimens before curing and are shown in Figure 6.



Figure 6. Height difference of specimens during curing.

According to the SPU-1 curve, the Marshall specimen that was directly formed after the preparation of the PU mixture suffered from the issue of volume expansion, and the height differences of the specimen were basically stable and maintained at about 2.4 mm after 96 h of curing. However, the test curves of SPU-2, SPU-3, SPU-4, and SPU-5 showed that the volume of the specimens stabilized after 72 h of curing; the height differences of SPU-2, SPU-4, and SPU-5 specimens stabilized at about 0.5 mm; and the height differences of SPU-3 specimens stabilized at about 0.3 mm. This indicated that the proper stacking of the prepared PU mixture can effectively control the volume expansion of the PU mixture. This is because, after the preparation of the PU mixture, the PU binder reacts according to Figure 3a within the first 4 h, releasing CO_2 , and resulting in volume expansion. After stacking for 4 h or 8 h, compaction molding discharges CO_2 in the mixture, thus inhibiting the volume expansion of the mixture.

Within the first 24 h of curing, the height difference growth rate of the SPU-4 specimen was greater than that of SPU-2 and SPU-5. After 72 h of curing, the height difference of SPU-4 was 0.05 mm greater than that of SPU-2 and SPU-5, indicating that a high ambient humidity accelerates the curing reaction rate of the PU mixture and affects the subsequent reaction behavior, resulting in difference was greater than that of SPU-2; however, the sight difference of SPU-4 height difference was greater than that of SPU-2; however, the height difference of SPU-2 and SPU-4 was the same after 72 h of curing, indicating that the ambient temperature accelerated PU mixture curing reaction rate, but did not change the subsequent reaction behavior; the reaction endpoints of the two mixtures were the same. Therefore, it was suggested that the PU mixture was properly stacked after preparation to control the volume expansion of the PU mixture, and the stacking time is consistent with the transportation, paving, and other construction procedures.

3.2.2. Permissible Stacking Time of the PU Mixture

The PU binder gradually solidifies in the stacking process, it is necessary to study the influence of stacking time and ambient temperature on the permissible stacking time of the PU mixture. The prepared PU mixture was stacked at 50% humidity and 15 °C, 20 °C, 40 °C, 60 °C, and 80 °C ambient temperatures; then, the Marshall specimens were formed. The Marshall specimens were cured at 15 °C and 50% humidity for 4 days, and the splitting tensile strength was then tested. The results are shown in Figure 7.



Figure 7. Splitting tensile strength of the PU mixture at different stacking times.

According to Figure 7, the higher the natural stacking time, the lower the splitting tensile strength of the cured PU mixture. This is because, during the stacking process, the curing reaction of the PU binder occurred, the subsequent compaction destroyed the formed strength to a certain extent, resulting in a reduction in the splitting tensile strength. The higher the ambient temperature, the more obviously the splitting tensile strength

was affected by the stacking time. This is because, when the temperature was higher, the chemical condensation reaction of the PU mixture was more intense, leading to a higher strength during stacking. Taking an 80% reduction of the splitting strength as the standard for the construction operability of the PU mixture, the permissible stacking time of the PU mixture at the temperatures of 15 °C, 20 °C and 40 °C was 4 h, and the permissible stacking times of the PU mixture at the construction temperatures of 60 °C and 80 °C were 3 h and 2 h, respectively. Based on the volume expansion law, the permissible stacking time, and the plant mixing construction technology of the PU mixture under different environmental conditions, it was recommended to stack the PU mixture for 4 h before compaction, in an environment of 50% humidity and 15–40 °C temperature.

3.2.3. Strength Formation Law of the PU Mixture

The PU mixture was prepared at 20 $^{\circ}$ C and a humidity of 50%. The Marshall specimens were formed when the PU mixture was prepared and stacked for 4 h, which were then cured at 50% and 95% of air humidity. The splitting tensile strength of the specimens is shown in Figure 8.



Figure 8. Splitting strength of the PU mixture with different curing humidities.

It can be seen in Figure 8 that the splitting tensile strength of the PU mixture increased rapidly in the first 48 h and 72 h of curing in environments of 95% and 50% air humidity. After 96 h, the curing of the PU mixture was basically complete. The final splitting tensile strength of the PU mixture at the two humidities stabilized at about 3.5 MPa. The results showed that water was one of the key factors affecting the curing of the PU binder. The higher the air humidity, the higher the curing rate. Previous studies have shown that the splitting tensile strength of the AC-13 and SMA-13 mixture stabilized at about 1.1 MPa and 1.3 MPa, respectively [31,32]. According to the curves, the splitting tensile strength of the SPU-13 mixture with 48 h curing could meet this requirement. Therefore, it was recommended that the PU mixture be opened to traffic after curing for 48 h.

3.3. Basic Performance of the PU Mixture

3.3.1. Temperature Stability of the PU Mixture

The results of the 60 °C rutting test and low-temperature bending test of the three mixtures are shown in Figure 9. The dynamic stability of SPU-13 was 40.9 times and

10.7 times that of AC-13 and SMA-13, respectively, and the low-temperature bending strain of SPU-13 was 2.4 times and 1.8 times that of AC-13 and SMA-13, respectively, indicating that the PU mixture had good high- and low-temperature stability. This is because the PU binder reacted with the water in the air and the hydroxyl groups on the surface of aggregates to form a bonded network structure. In this process, the internal hydrogen bond of PU was gradually strengthened, gradually strengthening the PU mixture. Therefore, the PU mixture was less affected by high and low temperatures.



Figure 9. High- and low-temperature test results for the three mixtures.

3.3.2. Water Stability of the PU Mixture

The freeze–thaw splitting test results of different types of mixtures are shown in Figure 10. The freeze–thaw splitting strength ratio of the SPU-13 mixture was lower than that of the SMA-13 and AC-13 mixtures, which did not meet the provisions of the "Technical code for construction of highway asphalt pavement" (JTG F40-2004) [36]. However, the splitting tensile strength of the SPU-13 mixture before and after the freeze–thaw action was higher than that of the SMA-13 mixture. This indicated that, although the freeze–thaw cycle caused great damage to the PU mixture, the strength of the PU mixture after the freeze–thaw cycle could still meet the requirements of pavement materials. The reason for this was that, as a viscoelastic–plastic heterogeneous material, the weak points in the molecular chain (C–O bond, unsaturated C=C double bond, etc.) of the PU mixture could have led to chemical changes, such as bond breaking after freeze–thaw action, which affected the internal stress transmission and coordinated strain development of the PU mixture.

3.3.3. Fatigue Resistance of the PU Mixture

The bending stiffness modulus of the SPU-13 and SMA-13 mixtures during the fatigue test are shown in Figures 11 and 12, respectively. Taking the cyclic loading times corresponding to the attenuation of the bending stiffness modulus of the initial modulus, the fatigue life results of the two mixtures under different strain levels are shown in Figure 13.



Figure 10. Freeze-thaw splitting test results for different mixtures.



Figure 11. Bending stiffness modulus of the SPU-13 mixture.

Figures 11–13 show that the bending stiffness modulus of the two mixtures decreased sharply at the initial stages, and then increased slowly. The stiffness modulus curves gradually exhibited a stable trend until the bending stiffness modulus decreased to 50% of the initial modulus, and there was no inflection point in the stiffness modulus curves, implying that the fatigue failure of the two mixtures did not occur until the end of the test. Therefore, it was conservative to use the 50% reduction of the initial flexural tensile stiffness modulus of the mixture as the termination condition of the fatigue test and the determination standard for fatigue life.



Figure 12. Bending stiffness modulus of the SMA-13 mixture.



Figure 13. Fatigue life test results of the SPU-13 and SMA-13 mixtures.

For the same mixture, the higher the strain level, the faster the flexural tensile stiffness modulus decreases and the earlier the fatigue test terminates, indicating that the ability of the mixture to resist repeated loads at high strain levels was weak and the fatigue life was low. At the same strain level, the durations of the initial sharp decline stages of the two mixtures' flexural stiffness modulus curves were basically the same; however, the duration of the slow fatigue development stage of the SPU-13 mixture was longer than that of the SMA-13 mixture, and the flexural tensile stiffness modulus of the SPU-13 mixture decreased very slowly at this stage. This shows that the speed of fatigue damage of the SPU-13 mixture specimen under alternating loads was relatively slow, and the instances of the initiation and development of microcracks in the specimen were fewer. The fatigue lives

of the SPU-13 mixture under strain levels of 600 $\mu\epsilon$, 800 $\mu\epsilon$, and 1000 $\mu\epsilon$ were 2.93 times, 3.31 times, and 3.89 times that of the SMA-13 mixture, respectively, indicating that the PU mixture had a strong ability to resist repeated loading, which meets the needs of special pavement such as long longitudinal slopes, heavy load road, etc.

4. Conclusions

This study contributed to the comprehensive understanding of the curing reaction mechanism of PU binder, strength formation law and the properties of PU mixtures. The following conclusions can be drawn:

- 1. The internal hydrogen bond of PU was formed in the first 24 h, and then the reaction slowed down. The linear polymer chain increased with the progress of the reaction in the first 72 h, and then the reaction speed slowed down because some unreacted NCO groups were wrapped in the adhesive system, blocking the contact between-NCO groups and water.
- 2. It was recommended to stack the PU mixture for 4 h before compaction under conditions of 50% humidity and 15–40 °C temperature. Furthermore, it is recommended that the PU mixture be cured for 2 days before being opened to traffic.
- 3. The PU mixture has excellent high and low temperature stability and fatigue stability. Though the freeze-thaw stability is not good, the splitting strength of the PU mixture before after freeze-thaw can meet the requirements of pavement materials. Thus, the PU mixture can be applied in pavement materials to prolong the service life of pavement and reduce energy consumption and emission.
- 4. The freeze-thaw damage mechanism and its enhancement mechanism are still unclear. More meso and micro tests should be carried out to improve the freeze-thaw stability of PU mixture in the future so to apply it to more complex working conditions.

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