Curing Performance of Monocomponent Polyurethane Porous Elastic Mixture

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Abstract. Polyurethane (PU) is a kind of clean material, which can be utilized as the binder for porous elastic mixture in pavement engineering. In this paper, curing performance of monocomponent polyurethane porous elastic mixture were investigated. Fourier Transform Infrared Spectrum (FTIR) and Marshall test were conducted to analysis the curing performance of monocomponent polyurethane and polyurethane porous elastic mixture (PPEM). The results show that PPEM-I and PPEM-II are nearly fully cured after 4 days curing. In terms of Marshall stability, PPEM-I and PPEM-II are nearly fully cured after 4 days curing. And the Marshall stability of PPEM-I is higher than that of PPEM-II under the same room curing condition. Meanwhile, water sprinkle method can be adopted to improve the curing speed, when the water-PPEM ratio is 2%, the Marshall stability of PPEM-I and PPEM-II is close to that of 4 days room curing conditioned sample.

1. Introduction
Polyurethane (PU) is a kind of clean material, which can be utilized as the binder for porous elastic mixture in pavement engineering [1]. Meanwhile, PU only need be heated to 60~80°C before mixing with aggregate [2]. However, as for bituminous binder, the mixing temperature is usually more than 120°C, which will consume more fuel for heating mixing facilities and lead to more air pollution in engineering [3].

There are two kinds of polyurethane binder, which are two component polyurethane and monocomponent polyurethane respectively [4]. In terms of two component polyurethane, the binder is the production of reaction between polyol and isocyanat [5]. The curing speed of two component polyurethane is so fast that the viscosity of PU binder will be more than 3000 mPa.s after about 40 minutes’ curing [6~7]. However, there is usually one mixing station every 10~20 km to fabricate mixtures for highway paving in China, and the maximum transport time (from mixing station to paving field) is usually more than 2 hours[8]. It indicates that the two component polyurethane can hardly be used for highway paving in China because of its fast curing speed. As for monocomponent polyurethane, its workability is much better than two component polyurethane. Specifically, the viscosity of monocomponent polyurethane can be controlled by heating/cooling condition during highway paving[9]. So monocomponent polyurethane were usually adopted as the binder for mixture in highway pavement, especially for highway porous elastic pavement.
In terms of curing performance of polyurethane, even though the curing performance of monocomponent polyurethane is significant for starting the transport service, it was seldom investigated in existed researches [10]. Dong et al. [11] analyzed the polyurethane acrylate films with various curing conditions under dual curing system by FT-IR, Raman and DSC for chemical structure characterization, as well as uniaxial tensile tests. Das et al. [12] studied the curing characteristics of polyurethane and its nanocomposite, specifically the curing properties were determined in terms of “dry to touch” and “dry to hard” time. Meanwhile, two dynamic methods were used to carry out the cure reaction kinetics to calculate the activation energy for the polyurethane formation[13].

As for porous elastic mixture, it is composed of polyurethane binder, basalt aggregate and rubber aggregate [14]. However, former researchers mainly focused on the mechanical performance of porous elastic mixture bonded by two component polyurethane, instead of curing performance of monocomponent polyurethane [15]. Wang et al. [16] fabricated poroelastic road surface (PERS) by two component polyurethane and rubber aggregate, and the absorption coefficients of PERS was investigated by acoustic experiment. Li et al. [17] compared the mechanical, functional and mesosscopic properties of polyurethane bounded pervious mixture with porous asphalt mixture. Meanwhile, the suitability of PERS for urban roads in cold regions regarding mechanical and functional performances was investigated by means of experiments and numerical simulation [18].

In order to investigate the curing performance of monocomponent polyurethane porous elastic mixture (PPEM), the current study is conducted. FTIR test was conducted to analysis the curing performance of monocomponent polyurethane. Marshall test was adopted to study the stability of PPEM in different curing conditions.

2. Fourier Transform Infrared Spectrum (FTIR)

Monocomponent polyurethane is the production of reaction between isocyanate (-NCO) and moisture (H₂O) in the air. Specifically, the isocyanate reacts with moisture in the air to produce carbamate (-NH-CO-OH) first. Then the carbamate is easy to be decomposed into amic (-NH₂) and carbon dioxide (CO₂), as is shown in chemical reaction equation (1). The produced amic can continue reacting with isocyanate to produce urea (-NH-CO-NH-), as is shown in chemical reaction equation (2)[19].

\[ R\text{-}NCO+H_2O \rightarrow R\text{-}NH\text{-}CO\text{-}OH-R \rightarrow R\text{-}NH_2+CO_2 \uparrow \]  
\[ R\text{-}NCO+R\text{-}NH \rightarrow R\text{-}NH\text{-}CO\text{-}NH-R \]  

According to equation (1) and (2), the content of isocyanate and urea can be utilized to characterize the curing degree of monocomponent polyurethane. Meanwhile, FTIR was adopted to measure the absorbance of key functional groups in monocomponent polyurethane after different curing time. Moreover, Isocyanate Index and Urea Index were calculated by peak area ratio method [20] according to the equation (3) and equation (4). Specifically, the benzene group (1599 cm⁻¹) was adopted as the reference group because it would not participate in reaction for monocomponent polyurethane curing, and the wavenumber for isocyanate group and urea group are 2265 cm⁻¹ and 1642 cm⁻¹ respectively. Furthermore, the maximum curing time for monocomponent polyurethane was 7 days, and the temperature and humidity data of the 7 curing days (average temperature: 16.2 °C; average humidity: 40.9 %) were shown in Fig. 1. The FTIR results of monocomponent polyurethane after different curing time is shown in Fig. 2.

\[ \text{Isocyanate Index} = \frac{A_{\text{NCO}}}{A_{\text{Benzene}}} \]  
\[ \text{Urea Index} = \frac{A_{\text{NH\text{-}CO\text{-}NH\text{-}}} }{A_{\text{Benzene}}} \]
According to Fig. 2, the Isocyanate Index of PU-I and PU-II decreases with the increase of curing time, while the Urea Index have the opposite trend. Meanwhile, both the Isocyanate Index and Urea Index of PU-I and PU-II are stable after 4 days curing, indicating that PU-I and PU-II are nearly fully cured after 4 days curing.

3. Marshall Stability Test for PPEM under Different Curing condition

3.1. Room curing condition
According to the mixing and compacting temperature of PU-I and PU-II, PPEM Marshall specimens were fabricated. Specifically, basalt aggregate, rubber aggregate, PU-I and PU-II were adopted as the binder for PPEM mixture, which were named as PPEM-I and PPEM-II respectively. Meanwhile, the gradation of PPEM is shown in Table 1. After fabricated the PPEM Marshall specimens, Marshall stability test was conducted, and the results are shown in Fig. 3. Specifically, the temperature and humidity data of the 7 curing days were same as the curing condition for FTIR.
Tab.1 Gradation of PPEM

| Aggregate Type | Basalt Aggregate | Rubber Aggregate | Optimum Asphalt Content (%) |
|---------------|------------------|------------------|-----------------------------|
| Sieve size (mm) | 13.2 9.5 4.75 2.36 1.18 |                 | 4.5                         |
| Percentage by weight (%) | 5.9 27.1 55.4 6.5 5.1 |                 |                             |

According to Fig. 3, there is a significant positive correlation between Marshall stability and curing time for PPEM-I and PPEM-II. Specifically, the Marshall specimen could not demold when curing in room condition for 1 day, because the PPEM would lose directly. Meanwhile, the Marshall stability of PPEM-I and PPEM-II is higher than 3.5kN (the criterion of OGFC-13 in JTG F40-2004 [24]), after 2 days room curing. Moreover, after 4 days curing, the Marshall stability of PPEM-I and PPEM-II is stable, and the coefficients of variation are 0.064 and 0.037 respectively. It indicates that PPEM-I and PPEM-II are nearly fully cured after 4 days curing. Furthermore, the Marshall stability of PPEM-I is higher than that of PPEM-II under the same room curing condition.

3.2. Fast Curing Condition

According to the Marshall stability of PPEM under room curing condition, the curing speed of PPEM is not fast enough, which will lead to the delay for transport service. Because monocomponent polyurethane is the production of reaction between isocyanate and moisture in the air, water sprinkle method can be adopted to improve the curing speed for PPEM in pavement engineering. In order to shorten the curing time for PPEM, water sprinkle method was adopted as the fast curing condition. Specifically, after fabricated PPEM Marshall specimens, water were sprinkled to the top and bottom side of cylinder, which is shown in Fig. 4. Meanwhile, the water-PPEM ratios are 0.5%, 1%, 1.5% and 2% by weight respectively. After sprinkled water, PPEM Marshall specimens were cured under room environment for 1 day, and Marshall test was conducted to measure their Marshall stability. The results are shown in Fig. 5.
Fig 4. Water Sprinkle Method for PPEM

According to Fig. 5, the Marshall stability of PPEM-I and PPEM-II increases with fast curing conditioning. Meanwhile, the Marshall stability of PPEM-I is higher than that of PPEM-II under the same fast curing condition. Moreover, when the water-PPEM ratio is 2%, the Marshall stability of PPEM-I and PPEM-II is close to that of 4 days room curing conditioned sample, indicating that PPEM-I and PPEM-II are nearly fully cured. So in the following specimen fabrication for PPEM, water sprinkle method was adopted to improve the curing speed, and the water-PPEM ratio was 2%.

4. Conclusion
In this paper, curing performance of monocomponent polyurethane porous elastic mixture were investigated. FTIR and Marshall test were conducted to analysis the curing performance of monocomponent polyurethane and PPEM. Conclusions can be summarized as follows:

1) Both the Isocyanate Index and Urea Index of PU-I and PU-II are stable after 4 days curing. Moreover, after 4 days curing, the Marshall stability of PPEM-I and PPEM-II is stable. It indicates that PPEM-I and PPEM-II are nearly fully cured after 4 days curing.

2) PPEM-I and PPEM-II are nearly fully cured after 4 days curing. And the Marshall stability of PPEM-I is higher than that of PPEM-II under the same room curing condition.

3) When the water-PPEM ratio is 2%, the Marshall stability of PPEM-I and PPEM-II is close to that of 4 days room curing conditioned sample. Meanwhile, water sprinkle method can be adopted to improve the curing speed.

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