Innovative Use of Polyurethane Precursor to Facilitate the Reaction-Rejuvenation of Aged SBS Modified Asphalt

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ABSTRACT

The high-quality reutilization of waste SBS modified asphalt (SBSMA) mixtures has been a focus area for researchers in recent times. Commonly used rejuvenators are not satisfactory to fully restore their overall properties as it has no effect on the SBS modifier in aged binder. A significant research gap still exists regarding the restoration of the molecular structure and properties of aged SBS to instigate the high-performance recovery of aged SBSMA binders which will concurrently lead to enhancement of mixture performance. On this basis, this study considered the adoption of reactive organic materials, namely polyurethane (PU) precursor and 1, 4-butanediol diglycide ether (BUDGE) for the investigation of the reaction-rejuvenation of aged SBSMA binders and mixtures. For the binder study, conventional rheological tests such as softening point, penetration, ductility, and infrared spectra spectroscopy were employed to evaluate the rejuvenation of the collective use of PU precursor and BUDGE on aged SBSMA binder. For the mixture study, two rejuvenator addition approaches, namely carrier-free method and carrier-support method were applied for aged SBSMA mixtures, and the high-temperature property, moisture-induced damage resistance, and low-temperature crack resistance were comparatively analyzed. The results indicated that PU precursor contributes to improving the softening temperature of aged SBSMA binder, and in combination with BUDGE, increased low-temperature ductility and flexibility can be attained. From the mixture performance results, the carrier-supported rejuvenation method can recover the permanent deformation resistance of the rejuvenated SBSMA mixture to similar levels as that of the fresh SBSMA mixture. Additionally, it can also effectively improve the moisture-induced damage resistance of the aged SBSMA mixture, as well as shows a more superior resistance to low-temperature cracking compared to the carrier-free rejuvenation method.

Keywords: aged SBS modified bitumen; reaction-rejuvenation; polyurethane precursor; 1, 4-butanediol diglycide ether; carrier-supported rejuvenation method

INTRODUCTION

SBS is a triblock-structure thermoplastic elastomer which is commonly used to modify asphalt binder to improve its resistances to high-temperature deformation and low-temperature cracking (Cao et al., 2020; Xu et al., 2020). After being subjected to the impacts of natural environment, such as ultraviolet light, heat, oxygen, SBS modified asphalt (SBSMA) pavements will deteriorate in performance after long-term service (Ghabchi and Pereira Castro, 2021; Xing et al., 2020). Ultimately, these end-of-life mixtures are generally reclaimed and disposed of at landfills and stockpiles (Asadi et al., 2021; Cong et al., 2020; Rivera et al., 2021) leading to environmental contaminants and waste of valuable resources (Azahar et al., 2016; Cao et al., 2019; Viscione et al., 2021).

A major reason for the performance deterioration of SBSMA mixtures after service is binder aging which includes not only the aging of virgin binder, but also the oxidative degradation of SBS (Kamboozia et al., 2021; Sonibare et al., 2021; Zhou et al., 2022). As of now, most studies have mainly focused on the use of conventional rejuvenation methods to recycle SBSMA based on binder and mixture characterizations methods (Xu et al., 2022). For example, Lin et al. (2021) adopted a self-made industrial rejuvenator (REJ-A) that contains rich aromatics to rejuvenate the aged SBSMA binder and reported that the partial engineering properties of aged binder, including fatigue characteristic can be improved after rejuvenation. But its resistance to deformation is poor and not to the level as that of aged and fresh binder. Wang et al. (2017) used three different kinds of rejuvenators to recycle reclaimed SBS modified asphalt pavement (RSMAP) materials and suggested that the rejuvenators benefit to improve the water stability and low-temperature crack resistance of aged mixtures with high RSMAP content at varying degrees. As mentioned above, the conventional rejuvenation methods are not entirely intended to fully improve the performance properties of aged SBSMA binders and mixtures, because their effects are mainly for the chemical components of aged virgin binder

(Arabzadeh et al., 2021; Eltwati et al., 2022; Zahoor et al., 2021).

To simultaneously obtain the performance improvement of aged bitumen and aged SBS, novel approaches have recently emerged that suggests the utilization of a physicochemical rejuvenation technique to reach the high-quality rejuvenation of aged SBSMA binders and mixtures. For instance, Wei et al. (2020) used a new catalytic-reactive rejuvenator containing epoxidized soybean oil (ESO) and triphenyl phosphine (TPP) to recycle aged SBSMA binder, and reported that the softening point, viscoelastic properties, and low-temperature flexibility of aged binder could be improved as well as the damaged network structure of SBS. Xu, S. et al. (2017) found that the developed epoxidized reactive rejuvenator was capable of improving the overall properties of aged SBSMA binder, including the low-temperature ductility, through the chemical interaction between degraded SBS and rejuvenator. From the limited literature available, it has been demonstrated that the reaction-rejuvenation methods can effectively improve the overall properties of aged SBSMA binders and mixtures. Based on several studies, it can be understood that the selection of reactive chemicals is definitely a crucial topic for the purpose of high-quality rejuvenation of aged SBSMA mixtures. Therefore, future studies are still very important to support and identify this approach for aged SBSMA mixtures, in order to give strong evidence for field use.

Polyurethane (PU) precursor, as one of the representatives of reactive materials, with high active isocyanate groups (-NCO) has strong reaction capability with -OH and -COOH based functional groups at mild conditions. For example, Lu et al. (2019) reported that PU precursor can react with the surrounding -OH based functional groups including molecular water to enhance the bonding characteristic, permeability, and mechanical properties of pervious asphalt pavement. Zhang et al. (2020) found that PU precursors resulted in asphalt mixtures with a more excellent high-temperature stability, low-temperature flexibility, moisture-resistant characteristic, and fatigue resistance. Li et al. (2022) employed a PU precursor-based reactive modifier

(PRM) for asphalt modification, and stated that appropriate amounts of PRM could result in a crosslinking polymerization reaction and improve the low-temperature properties of asphalt binder, while its excess would promote the asphalt binder to be more susceptible to deformations. From these various evidence, it can be summarized that PU precursor could be used as modifier to improve the performance of asphalt pavement materials through chemical reactions. However, its rejuvenation application for aged SBSMA materials has not yet been investigated in order to check its viability to address the general issue of the decreased high-temperature deformation resistance of commonly rejuvenated asphalt mixtures.

To fill this knowledge gap, this study aims to use PU precursor and BUDGE as reactive materials to chemically recycle aged SBSMA binder and mixture based on the reaction-rejuvenation mechanism. For the binder study, the softening point, penetration, ductility, and infrared spectroscopy tests will be conducted to assess the synergistic rejuvenation of PU precursor and BUDGE on aged SBSMA binder. As for the mixture study, two recycling approaches, namely carrier-free method (direct-throw way) and carrier-support method (indirect-throw way) will be designed and used for aged SBSMA mixture, while the high-temperature stability, moisture-induced damage resistance, and low-temperature crack resistance will be comparatively studied. Hereby, it is worthwhile noting that the selected carrier is the virgin binder. The research flowchart of this study is displayed in Figure 1.

Fig.1 Research flowchart of this study

Materials and Methodology

Raw Materials

Asphalt Binder

SBSMA binder and virgin asphalt binder were both provided by local suppliers. Virgin asphalt was the binder with penetration grade of 70, which was used as the carrier of rejuvenators or rejuvenating component

for aged SBSMA mixtures. The basic physical properties of the used asphalt binders are shown in Table 1.

Polyurethane (PU) Precursor

PU precursor used in this study was purchased from the BASF polyurethane special products (China) Co, Ltd., of which its general chemical structure and physical nature are displayed in Figure 2. The relevant physical properties are listed in Table 2. It is a single-component polyurethane containing isocyanate groups (-NCO) that can react with active groups such as -OH, -COOH, etc. This study adopted PU precursor to mainly repair the molecular structure of SBS degradation products in aged binder with the aim of reducing the loss of high-temperature properties of SBS based RAP binder when rejuvenated.

Fig.2 General chemical structure (a) and physical status (b) of PU precursor

1, 4-Butanediol Diglycidyl Ether (BUDGE)

BUDGE is a chemical owning epoxy-based flexible structures, which can potentially react with the materials containing groups such as -OH and -COOH at certain conditions. It was used in this study as a reactive low-temperature performance enhancer for aged SBSMA binder and mixture. Some measured results of relevant technical indexes are shown in Table 3.

Aggregates

Natural limestone aggregates, including mineral powder, were used in this study for preparing asphalt mixtures and its technical details are presented in Table 4.

Experimental Process

Preparation of Aged SBSMA binder

According to ASTM D6521, the thermo-oxidative aging method was adopted to prepare aged SBSMA binders. Prior to aging, the fresh SBSMA binder was heated to 170°C and poured into the standard steel plates with a weight of approximately 50g. Subsequently, these plates were shifted to an oven and conditioned at 163°C for 48h. Lastly, the aged SBSMA binder binders were obtained and collected into containers for further

use. The flowchart showing the thermal aging procedure of SBSMA binder is displayed in Figure 3.

Fig.3 Flowchart showing the thermal aging procedure of SBSMA binder

Preparation of Rejuvenated SBSMA Binder

For the first rejuvenation process, PU precursor at 0.5%, 1.0%, and 1.5% by weight was added to and blended with aged SBSMA binder for 5 min after the binder was heated to 170°C. The optimum addition of PU precursor and its rejuvenated binder (PU/aged SBSMA binder) were confirmed by evaluating some basic physical properties such as penetration, ductility and softening point. Then BUDGE, at different dosages of 1.0%, 2.0%, 3.0%, and 4.0%, was added to and mixed with the binder at the same temperature for 5min to prepare the collectively rejuvenated binders (PU/BUDGE/ aged SBSMA binder). To fully comprehend the rejuvenation process of aged SBSMA binder is presented in Figure 4, and the rejuvenated binders are also denoted in Table 5.

Fig.4 Brief rejuvenation process of aged SBSMA binder

Preparation of SBSMA Mixtures

This study adopted AC-13 as the target gradation of rejuvenated SBSMA mixture, and its gradation curve is shown in Figure 5. According to Marshall design method, five asphalt-aggregate ratios of 3.5%, 4.0%, 4.5%, 5.0%, and 5.5% were selected to prepare standard Marshall specimens. Through the measurement of volume parameters and Marshall stability test, the optimum asphalt-aggregate ratio of SBSMA mixture was determined as 4.8%. Based on this, target SBSMA mixtures for different tests were thus fabricated at 170°C following the same mixing procedures.

Fig.5 AC-13 gradation curve for the job mix of target asphalt mixtures

Preparation of Aged and Rejuvenated SBSMA Mixtures

The short-term and long-term aging of SBSMA mixture were conducted at 135°C for 4h and at 85°C for

5d, respectively, to simulate the aging process during the blending/paving and service period. After aging, the residual asphalt content was obtained through a combustion method, and then the incorporating content of reactive rejuvenators, namely PU and BUDGE, were determined accordingly. Subsequently, virgin asphalt (Pen. 70) was also supplemented for the same mixing proportion of oil component used in fresh SBSMA mixtures.

Based on the above, this study designed two rejuvenation methods: (1) carrier-free method, direct addition of PU, BUDGE, and virgin binder to aged SBSMA mixture; and (2) carrier-supported method, use virgin bitumen as carrier, first addition of PU and BUDGE to virgin bitumen and then to SBSMA mixtures after stirring evenly. During their mixing, both methods were controlled at 170°C for around 90s.

Experimental Methods

Physical Properties Test

According to ASTM D5, ASTM D113, and ASTM D36, the penetration at 25°C, ductility at 5°C, and softening point of fresh, aged, and rejuvenated SBSMA binders were measured, respectively. These tests were used to comprehensively assess the rejuvenation quality of aged SBSMA binders.

Fourier Transform Infrared Spectroscopy (FTIR) Test

FTIR test was used to examine the changes in molecular structure of SBSMA binder after aging and rejuvenation. Before testing, fresh, aged and rejuvenated SBSMA binder samples were dissolved in carbon disulfide to form a uniform solution. Subsequently, the solutions were dripped onto kalium bromatum (KBr) thin plate, and then placed in an infrared oven at 60℃ for 20 minutes to ensure that the carbon disulfide was completely volatilized, so that the sample formed a uniform and light-transmitting film on the kalium bromatum thin plate and then was tested by infrared. The test conditions are set as follows: resolution of 4 cm^{-1}, scanning times of 64, and the wavenumber range of 400 ~ 4000 cm^{-1}.

Performance Tests for Mixtures

High-temperature Rut Deformation Resistance

According to AASHTO TP63-05, the rut specimens with size of 300mm×300mm×50mm were first fabricated and then tested under conditions of 60°C. Through this test, the high-temperature resistance of SBSMA mixtures to rut deformation before and after aging and rejuvenation were characterized. Furthermore, the dynamic stability (DS), calculated following the Equation (1), as well as rut depth, were used to evaluate the high-temperature behavior of target mixtures.

$$DS = \frac{(t_2 - t_1) \times N}{d_2 - d_1} \times C_1 \times C_2 \quad (1)$$

where, DS refers to dynamic stability of asphalt mixture, cycles/mm; d_1 and d_2 refer to the rut depths at 45min (t_1) and 60min (t_2), respectively; C_1 and C_2 refer to the respective coefficient of device type and specimen, normally 1.0; and N refers to the round-trip wheel speed, 42 cycles/min.

Moisture-induced Damage Resistance

This study applied the Marshall test and indirect tensile test to evaluate the moisture-induced damage resistance of target mixtures. For Marshall test, the specimens were kept in a 60°C-water bath for 0.5h, immersion Marshall test needs to be kept in a 60°C-water bath for 48h. After conditioning, the residual Marshall load ratio of target mixtures was obtained following the Equation (2)

$$MS_0 = \frac{MS_1}{MS} \times 100\% \quad (2)$$

where, MS_0 refers to the residual Marshall load ratio of asphalt mixture, %; MS_1 refers to the residual Marshall load of asphalt mixture after moisture-immersion for 48h, kN; and MS refers to the initial Marshall load of asphalt mixture after moisture-immersion for 0.5h, kN.

According to AASHTO T 283, the specimens were conditioned under the vacuum degree was 730mmHg for 15min, placed in water for 0.5h, frozen in a -18°C constant temperature refrigerator for 16 hours, placed in a

60°C-water bath for 24 hours, and placed in a 25°C constant temperature sink for no less than 2 hours prior to the test. Afterwards, the specimens were taken out for the indirect tensile test to collect the load values. The splitting tensile strength of target mixtures before and after one freeze-thaw cycle and the corresponding tensile strength ratio (TSR) were calculated by Equations 3, 4 and 5.

$$R_{T1} = 0.006287 P_{T1}/h_1 \quad (3)$$

$$R_{T2} = 0.006287 P_{T2}/h_2 \quad (4)$$

where, R_{T1} refers to the splitting tensile strength of the specimen before the freeze-thaw cycle, MPa; R_{T2} refers to the splitting tensile strength of the specimen subjected to the freeze-thaw cycle, MPa; P_{T1} refers to the peak load value of the specimen before the freeze-thaw cycle, N; P_{T2} refers to the peak load value of the specimen after the freeze-thaw cycle, N; h_1 refers to the height of the specimen before the freeze-thaw cycle, mm; and h_2 refers to the height of the specimen after the freeze-thaw cycle, mm.

$$TSR = \frac{\bar{R}_{T2}}{\bar{R}_{T1}} \times 100\% \quad (5)$$

where, *TSR* refers to the freeze-thaw splitting strength ratio of the specimen, %; $\bar{R}_{T1}$ refers to the average splitting tensile strength of the specimen before the freeze-thaw cycle, MPa; and $\bar{R}_{T2}$ refers to the average splitting tensile strength of the specimen after the freeze-thaw cycle, MPa.

Low-temperature Crack Resistance

According to AASHTO T321, the trabecular bending test was carried out in this study to evaluate the influence of two used rejuvenation methods on low-temperature crack resistance of target asphalt mixture. Before the test, the trabecular prisms with the dimension of 250mm×30mm×35mm and the span of 200mm±0.5mm were placed to universal testing machine (UTM) and insulated for 5h at -10°C. After insulation, trabecular prism was put across two fulcrums with a span of 200mm and tested at a loading rate of 50mm/min. Finally, the relevant parameters of the trabecula, including flexural tensile strength (R_B), maximum

flexural strain (ε_B), and flexural stiffness modulus (S_B) were calculated respectively according to Equations 6, 7 and 8.

$$R_B = \frac{3 \times L \times P_B}{2 \times b \times h^2} \quad (6)$$

$$\varepsilon_B = \frac{6 \times h \times d}{L^2} \quad (7)$$

$$S_B = \frac{R_B}{\varepsilon_B} \quad (8)$$

where, R_B refers to the flexural and tensile strength of the specimen at failure, MPa; ε_B refers to the flexural and tensile strain of specimens at failure, με; S_B refers to the modulus of bending stiffness when specimen is broken, MPa; b refers to the across the width of the interrupt interview piece, mm; h refers to the across the interrupt interview document height, mm; L refers to the span of the specimen, mm; P_B refers to the maximum load at failure of specimen, N; and d refers to the mid-span deflection of the specimen at failure, mm.

Results and Discussion

Effects of Reaction-rejuvenation on Physical Properties of Aged SBSMA Binder

Figure 6 illustrates the effect of PU precursor on physical properties of aged SBSMA binder. It is clear that the penetration and ductility of fresh SBSMA binder after aging decreases from 48dmm to 26dmm and 41.5cm to 1.1cm, respectively, indicating the aging has a significant impact to cause the hardening and plasticity of SBSMA binder. Meanwhile, the softening point of fresh SBSMA binder increases from 60.4°C to 70.3°C after aging, indicating the aging improves the high temperature resistance of SBSMA binder. As PU precursor is increasingly added to aged binder from 0.5% to 1.0% and then to 1.5%, by weight of the total binder, the penetration and ductility showed decreasing trend, reducing to 23dmm, 21dmm, 18dmm and 0.9cm, 0.6cm, 0.4cm, respectively, while the softening point presents a remarkably increasing trend and increases to 73.8°C, 76.5°C, and 79.2°C, respectively. The results indicated that PU precursor helps continuously enhance the resistance of aged binder to the high-temperature effects but makes no significant contributions to the flexibility

240 improvement of aged binder. This depends upon that the newly-formed polymer structure to be easily reformed
241 through chemical interactions between -NCO and -OH/-COOH groups from the PU precursor and SBS
242 degradation products, leading to the decreasing structural flexibility of rejuvenated binder due to the
243 introduction of benzenes. As per the comprehensive consideration of these results and other cost related
244 concerns, PU precursor was determined as 1% by weight for the rest of the studies.

245 Fig.6 Effects of PU precursor on physical properties of aged SBSMA binder

246 To optimize the overall performance of rejuvenated binder, BUDGE was used to improve the flexibility-
247 related performances of 1PU/aged SBSMA binder. Figure 7 illustrates the effect of BUDGE on physical
248 properties of 1PU/ aged SBSMA binder. As BUDGE is increasingly added to 1PU/ aged SBSMA binder at 1%,
249 2%, 3%, and 4%, the penetration and ductility are both raised from 21dmm to 26dmm, 32dmm, 37dmm, and
250 43dmm, as well as from 0.6cm to 8.3cm, 16.5cm, 24.2cm, and 32.1cm, respectively, while the softening point
251 is correspondingly reduced from 76.5°C to 72.4°C, 69.1°C, 67.5°C, and 65.9°C, respectively. These results
252 implied that as the BUDGE addition increases, the low-temperature ductility and flexibility of 1PU/aged
253 SBSMA binder can be gradually improved at a relatively high rate, and the corresponding high-temperature stability
254 will also be decreased to some extent. It is worth noting that the softening point of 1PU/4BUDGE/aged SBSMA
255 binder still remains at a high level reaching up to 65.9°C, owing to the contributing effect of PU precursor.
256 Accordingly, 1%PU precursor and 4%BUDGE are overall considered to reach an optimal reaction-rejuvenation
257 of aged binder.

258 Fig.7 Effects of BUDGE on physical properties of 1PU/ aged SBSMA binder

259 **Effect of Reaction-rejuvenation on Molecular Structures of Aged SBSMA Binder**

260 Some previous studies have shown that BUDGE molecules are able to chemically react with the functional
261 groups such as -OH and -COOH from the SBS degradation products of aged binder while mixing at evaluated

262 temperatures (Xu, X. et al., 2017a; Xu, X. et al., 2017b). Thus, this section will importantly discuss if PU
263 precursor can still react with those functional groups on the molecular structure of SBS degradation products in
264 aged SBSMA binder.

265 FTIR spectra demonstrating the rejuvenation effect of PU precursor on the molecular structure of aged
266 SBSMA binder are shown in Figure 8 and chemical attributions of the corresponding main infrared
267 characteristic bands are listed in Table 6. From Figure 10a, it is very clear that PU precursor has a strong peak
268 signal located at 2250cm^{-1}, which is attributed to the stretching vibration characteristic from -NCO groups. As
269 observed from Figure 10b, in terms of fresh SBSMA binder after aging, the peak signal at 1260cm^{-1}, attributed
270 to the C-H bending vibration of -CH_2=CH_2-, gets significantly weakened, and a new peak signal at 1697cm^{-1},
271 attributed to the C=O stretching vibration appears. Meanwhile, with the incorporation of 1% PU precursor into
272 aged SBSMA binder, the strong peak signal of -NCO groups at 2250cm^{-1} cannot be found and a newly-formed
273 peak signal at 880cm^{-1} attributed to C-N stretching vibration slightly appears. These spectra information
274 indicated that 1% PU precursor can be completely consumed through the mutual chemical interactions with the
275 characteristic oxygen-containing groups in aged SBSMA binder, and implies that a small amount of PU
276 molecules can fix the damaged molecular structure of SBS degradation products in aged binder.

277 Fig.8 Rejuvenation effect of PU precursor on molecular structure of aged SBSMA binder: infrared spectra of (a) PU
278 precursor and (b) fresh, aged and rejuvenated binders

279 **Effect of Reaction-rejuvenation on the High-temperature Performance of Aged SBSMA**
280 **Mixture**

281 Fitted curves showing the effect of reaction-rejuvenation on rut depth of aged SBSMA mixture at 60°C are
282 displayed in Figure 9 and the fitted curve equations of rutting depth at 60°C are correspondingly presented in
283 Table 7. The obtained correlation coefficients (R^2) of the fitted curve equations are all above 0.98, indicating
284 that the fitted results can truly reflect the rut deformation resistance of target mixtures. As observed, the rut

depth of fresh SBSMA mixture decreases to some extent after aging, while the rejuvenations promote the rut depth of aged SBSMA mixture to a varying extent. By contrast to the carrier-free rejuvenation method, the carrier-supported rejuvenation method allows the rut depth of aged SBSMA mixture to reach close levels to that of the fresh mix. These results indicate that compared to the carrier-free rejuvenation method, the carrier-supported rejuvenation method will cause the permanent deformation resistance of rejuvenated SBSMA mixture to more easily approach towards that of fresh mixes. The main reason for that is that 4% BUDGE and 1% PU embedded in the carrier of asphalt binder can be more effectively migrated into and activate aged binder adhered to the aggregates, contributing to improving the flexible component of the rejuvenated mixture.

Fig.9 Fitted curves showing the effect of reaction-rejuvenation methods on the rut depth of aged SBSMA mixture at 60°C

Based on the rut depth results of target mixtures, the rut depths at 45min and 60min and the DS values are presented in Table 8. It can be found that when subjected to aging the Δd value of fresh SBSMA mixture decreases from 0.129mm to 0.089mm, while its DS value increases from 4883 cycles/mm to 7078 cycles/mm. As the carrier-supported and carrier-free rejuvenation methods are used, the Δd value changes to 0.116 mm and 0.107 mm, respectively, and the DS value goes to 5431 cycles/mm and 6387 cycles/mm, respectively. These results suggest that these two rejuvenated mixtures show higher resistances to permanent deformation as compared to the fresh mixtures, and for the carrier-supported method, it can promote the anti-rutting level of aged mixture approaching towards that of the fresh mixture. It indicates that the carrier-supported method works well to allow the reactive molecules which are embedded in the asphalt carrier to better meet the molecular fragments from aged SBS in binder for reaction rejuvenation at elevated temperatures, whereas the carrier-free method cannot be responsible for the full rejuvenation of aged mixtures due to the local rapid reactions between reactive molecules and aged binder molecules.

Effect of Reaction-rejuvenation on the Moisture-induced Damage Resistance of Aged

SBSMA Mixture

Residual Marshall Stability

Figure 10 shows the influence of reaction-rejuvenation methods on the Marshall load of aged SBSMA mixtures, before and after immersion. It was found that the MS and MS_1 values of fresh SBSMA mixtures after aging decreased from 16.16kN to 13.69kN and from 15.09kN to 10.24kN, respectively. After carrier-supported rejuvenation, their values were 16.04kN and 14.50kN, respectively, while for a carrier-free rejuvenation, they were15.20kN and 12.42kN, respectively. From these results, it is believed that these two rejuvenation methods both show good rejuvenation performances to recover the Marshall loads to levels as that of the fresh mixtures before and after immersion. Nevertheless, it should be noted that the carrier-supported method works more significantly.

Fig.10 Influence of reaction-rejuvenation methods on the Marshall load of aged SBSMA mixture before and after immersion

With respect to the changes of target mixtures in the MS0 value, the results are calculated and presented in Figure 11. It is clear that the fresh SBSMA mixture decreases dramatically from 93.4% to 74.8% after experiencing aging and it is successfully rehabilitated to 90.4% and 81.7% as the carrier-supported and carrier-free methods are used respectively. The results obtained demonstrated that these rejuvenation methods are both effective to allow the improvement of the moisture-induced damage resistance of aged SBSMA mixtures, but by contrast, the carrier-supported method shows a more significant effect. This can be mainly attributed to the fact that the reactive rejuvenators in the asphalt carrier can easily move into aged binder and react with SBS degradation products at high temperatures for chemically enhance the moisture adhesion of rejuvenated binder to aggregates, when it is added directly into the aged mixtures, the integral fixation of the aged binder cannot be realized due to its dispersion limitation.

Fig.11 Effects of reaction-rejuvenation methods on the residual Marshall load ratio of aged SBSMA mixture

Freezing-thawing Splitting Strength Ratio (TSR)

Figure 12 illustrates the effects of reaction-rejuvenation methods on the splitting tensile strength of aged SBSMA mixture before and after one freeze-thaw cycle. It indicates that the splitting strength of fresh mixtures after aging decreases from 1.999MPa to 1.817MPa, which is recovered to 1.948MPa and 1.925MPa when rejuvenated by carrier-supported rejuvenation method and carrier-free rejuvenation method, respectively. Correspondingly, when experiencing one freeze-thaw cycle, the splitting strength of fresh mixture after aging decreases from 1.828MPa to 1.45MPa and then increases to 1.74MPa and 1.599MPa after using carrier-supported rejuvenation and carrier-free rejuvenation, respectively. The results obtained illustrates that these two rejuvenation methods can both contribute to improving the resistance of aged SBSMA mixture to the freeze-thaw moisture-induced damage, in which the carrier-supported method exhibits a more superior performance.

Fig.12 Effects of reaction-rejuvenation methods on the splitting tensile strength of aged SBSMA mixture before and after one freeze-thaw cycle

Figure 13 shows the effects of reaction-rejuvenation methods on TSR of aged SBSMA mixture after one freeze-thaw cycle. From the results, the TSR value of fresh mixture decreases from 91.5% to 79.8%, and after carrier-supported and carrier-free rejuvenations, it recovers to 89.3% and 83.1%, respectively. It is worth noting that the TSR value of the carrier-supported rejuvenated mixture is close to that of the fresh mixture. The results indicated that the carrier-supported rejuvenated mixture can undergo a more serious freeze-thaw environmental impact in comparison with the carrier-free rejuvenated one. This is because the carrier can carry the reactive rejuvenators successfully to aged binder adhered to aggregates at high temperatures and reach an in-situ chemical interaction to enhance the interfacial strength between rejuvenated binder and aggregates, but without the carrier, these directly added rejuvenators will just only reach a limited rejuvenation for aged mixtures during the short-term mixing period.

Fig.13 Effects of reaction-rejuvenation methods on TSR of aged SBSMA mixture after one freeze-thaw cycle

Effect of Reaction-rejuvenation on the Low-temperature Cracking Resistance of Aged

SBSMA Mixture

Flexural Strength

Figure 14 shows the effects of reaction-rejuvenation methods on the flexural strength of aged SBSMA mixtures at -10°C. The results show that the low-temperature flexural strength of fresh mixtures presented a remarkable decrease from 13.21MPa to 8.66MPa after subjecting to aging, and is recovered to 12.41MPa and 10.46MPa with the use of the carrier-supported and carrier-free rejuvenation methods are respectively used. The results demonstrated that regardless of rejuvenation methods, the low-temperature crack resistance of aged mixture can be well restored to some extent after rejuvenations. When comparing the two methods, the carrier-supported rejuvenated mixture shows a more superior resistance to the flexural failure at low temperature, approaching close to that of the fresh mixture. The main reason for this is that the flexible component (BUDGE) in the carrier can more easily contact the aged binder and react with the molecular pieces of SBS degradation products at high temperature and reassemble soft molecular structure which contributes to the effective flexibility recovery of aged mixture (Xu, X. et al., 2017a; Xu, X. et al., 2017b).

Fig.14 Effects of reaction-rejuvenation methods on the flexural strength of aged SBSMA mixture at -10°C

Flexural Strain at Break

Figure 15 shows the effects of reaction-rejuvenation methods on the flexural strain of aged SBSMA mixture at break at -10°C. It is found that the flexural strain at break for fresh mixture after aging decreases from 3935με to 2122με, failing to satisfy the minimum requirement of 2500με. After carrier-supported and carrier-free rejuvenation methods, the flexural strains at break for aged mixtures is increased to 3584με and 2962με respectively. This indicated that these two rejuvenation methods have good capacity to improve the flexural strain of aged mixture at break to resist the low-temperature loading damage, in which the carrier-supported rejuvenation method works better.

Fig.15 Effects of reaction-rejuvenation methods on the flexural strain of aged SBSMA mixture at break at -10°C

Figure 16 illustrates the effects of reaction-rejuvenation methods on the stiffness modulus of aged SBSMA mixtures at -10°C. The stiffness modulus of fresh mixture after aging increases from 3357MPa to 4081MPa and then decreases to 3462MPa after carrier-supported rejuvenation and to 3531MPa after carrier-free rejuvenation, respectively. It is worthwhile noting that the stiffness modulus values of rejuvenated mixtures are close to that of the fresh mixture. These results revealed that the aging will provide the fresh mixture a better deformation resistance to the external loads at low temperature, and the reaction rejuvenations will slightly decrease the stiffness of aged mixture towards that of the fresh one. With the flexural strength and breaking strain results, it is overall concluded that the carrier-supported rejuvenation method exhibits a more effective improvement in low-temperature properties of aged mixture by contrast to carrier-free rejuvenation method. The result obtained is related to the flexibility contributions from the introduction of BUDGE molecules to aged mixture, which is detailed in analysis in flexural strength section.

Fig.16 Effects of reaction-rejuvenation methods on the stiffness modulus of aged SBSMA mixture at -10°C

Concluding Remarks and Suggestions

This study considered using PU precursor and BUDGE as reactive rejuvenators to chemically rejuvenate aged SBSMA mixtures, based on the molecular structure reconstruction of SBS degradation products in aged binder. Through physical properties and infrared spectra characterization, the matching proportion of PU precursor and BUDGE was determined. Subsequently, the designed carrier-supported and carrier-free rejuvenation methods were systematically evaluated through characterizing the engineering performance of rejuvenated SBSMA mixtures. Main conclusions can be drawn as follows:

(1) Physical properties results demonstrated that PU precursor contributes to improving the softening temperature of aged SBSMA binder, and in combination with BUDGE, increased low-temperature ductility and flexibility can be reached. Optimally, the comprehensive use of 1% PU precursor and 4% BUDGE, by weight

of virgin binder, is recommended for the highest rejuvenation of the aged binder.

(2) FTIR analysis indicated that 1% PU precursor can be completely consumed to react with characteristic groups in aged SBSMA binder, especially the active oxygen-containing groups such as -OH and -COOH from degradation products of SBS.

(3) Rutting test results specified that both rejuvenation methods will not cause the high-temperature deformation resistance of aged mixtures to be lower than that of fresh mixtures, in which the carrier-supported method promotes the anti-rutting characteristic of aged mixtures closest to that of fresh mixtures.

(4) Moisture-induced damage resistance results obtained revealed that compared to the carrier-free rejuvenation method, the carrier-supported rejuvenation method shows a better improvement in the moisture-induced damage resistance of aged SBSMA mixture, even under a serious freeze-thaw condition.

(5) Low-temperature property test results implied that compared to the carrier-free rejuvenation method, the carrier-supported rejuvenation method provides a more superior resistance of aged mixture to the flexural failure at low temperature, which leads to the performance of rejuvenated mixture close to that of the fresh mixtures.

Overall, the collaborative use of PU precursor and BUDGE can vastly improve the performance properties of aged SBSMA mixtures. The carrier-supported and carrier-free rejuvenation methods are suitable to be used for the high-quality rejuvenation of waste SBSMA mixtures. Future studies are recommended to focus on more advanced rheological characterization at the binder level using as well as the durability analysis of these rejuvenated SBSMA mixtures.

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488

489 Table 1 Basic physical properties of the used asphalt binders

Test item	SBSMA binder	Virgin bitumen	Reference standard
Penetration at 25°C/dmm	41	78	ASTM D5
Ductility /cm	41.5 (5°C)	≥100 (15°C)	ASTM D113
Softening point/°C	60.4	47.6	ASTM D36
Brookfield viscosity at 135°C /mPa·s	1220	400	ASTM D4402

490

491 Table 2 Relevant physical properties of PU precursor

Item	Test result/status
Appearance	Brown liquid
Density/(g/cm^3)	1.22
Boiling point/°C	330
Viscosity at 25°C /mPa·s	170
Flash point/°C	204

492

493 Table 3 Results of relevant technical indexes of BUDGE

Item	Result/Status	Standard value
Appearance	Transparent liquid	-
Density /(g/cm^3)	1.1	-
Boiling point /°C	266	≥210
Flash point /°C	>230	-
Rotational viscosity at 25°C /mPa·s	17	10-25
Epoxy value /(eq/100g)	0.772	0.74-0.78
Water content /%	0.06	≤0.1

494

Table 4 Technical index results of the used aggregates

Category	Test item	Test result	Standard requirement
Coarse aggregate	Apparent relative density	2.864	≥2.60
	Water absorption /%	1.71	≤2.0
	Crushing value /%	16.2	≤26
	Firmness /%	3.2	≤12
Fine aggregate	Apparent relative density	2.749	≥2.50
	Firmness /%	3.2	≤12
	Firmness /%	2.6	≤12
	Sand equivalent /%	83.3	≥60
Mineral powder	Apparent density	2.627	≥2.50
	Water content /%	0.13	≤1
	Appearance	No agglomeration	No agglomeration
	Hydrophilic coefficient	0.51	＜1

497 Table 5 Abbreviations of rejuvenated SBSMA binders

Test samples	Abbreviation
0.5%PU+ aged SBSMA binder	0.5PU/ aged SBSMA binder
1.0%PU+ aged SBSMA binder	1PU/ aged SBSMA binder
1.5%PU+ aged SBSMA binder	1.5PU/ aged SBSMA binder
1.0%PU+1.0%BUDGE+ aged SBSMA binder	1PU/1BUDGE/ aged SBSMA binder
1.0%PU+2.0%BUDGE+ aged SBSMA binder	1PU/2BUDGE/ aged SBSMA binder
1.0%PU+3.0%BUDGE+ aged SBSMA binder	1PU/3BUDGE/ aged SBSMA binder
1.0%PU+4.0%BUDGE+ aged SBSMA binder	1PU/4BUDGE/ aged SBSMA binder

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499 Table 6 Chemical attributions of the main infrared characteristic bands

Wavenumber/(cm^{-1})	**Group/Chemical bond**	**Vibration type**
2250	-NCO	-N=C=O asymmetric stretching
1697	C=O	C=O stretching
1580, 1542, 1436	Benzene ring	C=C stretching (skeleton)
1260	$-CH_2=CH_2-$	C-H bending
880	$-CH_2-NH-$	C-N stretching

500

501 Table 7 Fitted curve equations of rut depth of target mixtures with rolling time at 60°C

Sample	Fitted equation	R^2
a	$y=-1.410e^{(-x/941.474)}+1.370$	0.992
b	$y=-0.975e^{(-x/1112.831)}+0.979$	0.993
c	$y=-1.367e^{(-x/897.747)}+1.349$	0.993
d	$y=-1.117e^{(-x/941.474)}+1.119$	0.989

502

503 Table 8 Rut depth and DS values of target mixtures

Sample	d_1/mm	d_2/mm	Δd/mm	DS/(cycles/mm)
a	1.283	1.412	0.129	4883
b	0.891	0.980	0.089	7078
c	1.274	1.390	0.116	5431
d	1.048	1.155	0.107	6387

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