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Performance assessment of self-healing polyurethane elastomer as an additive in modified asphalt†

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Since the development of polymer-modified asphalt, its functionality and preparation process have been continuously optimized, thus improving driving comfort and extending the service life of asphalt pavements. However, traditional polymer-modified asphalt is faced with certain limitations in terms of production and storage. To address these issues and enhance the storage stability of modified asphalt materials, a novel polyurethane (PU) elastomer with high elasticity and self-healing properties, named S-PU, was developed using dynamic covalent bond reversible technology. S-PU was applied as a modifier for asphalt modification. Through conventional performance and fluorescence microscopy (FM) tests, the optimal dosage of S-PU for asphalt modification was determined. The best asphalt modification effect was achieved when the S-PU content was 10%. Furthermore, atomic force microscopy (AFM) and Fourier transform infrared spectroscopy (FT-IR) were employed to analyze the micromorphology and modification mechanism of S-PU-modified asphalt. The results reveal an increase in the size of the "bee-like" structures after asphalt modification, along with chemical crosslinking between S-PU and asphalt molecules. This study introduces a novel approach for preparing self-healing asphalt through the utilization of dynamic covalent chemistry, offering new perspectives in the field.

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Sustainability spotlight

A novel polyurethane elastomer with high elasticity and self-healing properties has been synthesized and was used as a modifier to modify asphalt. This study provides a new approach to further explore the advantages of PU and fully utilize them to meet the urgent demand for high-performance asphalt pavement.

1. Introduction

Asphalt is widely used in pavement engineering as a bonding material due to its flat surface, absence of joints, comfortable driving experience, and short construction period.¹ However, during the use of asphalt pavement, various external factors, such as driving load, temperature, and moisture, can lead to issues such as rutting, cracking, gravel spalling, and potholes.^{2,3} These problems significantly affect the road's service level and the safety of vehicle driving. With increasing traffic volumes and vehicle loads, the demand for higher pavement performance has increased. Ordinary asphalt is increasingly unable to meet the requirements of transportation development for road surfaces, and therefore, engineers are seeking high-quality modified asphalt.⁴ Researchers have been modifying asphalt by adding polymers to enhance its road performance.^{5,6} While

rubber has been used as an asphalt modifier, an increasing number of polymers (such as SBS and SBR) are being employed in the field of modified asphalt.^{1,7} These polymers exhibit different properties and have varying effects on asphalt modification. However, the production, storage, and performance of traditional polymer-modified asphalt are still unsatisfactory.

Recently, a new type of material called self-healing asphalt has been proposed, drawing inspiration from the biological mechanism of self-healing after damage. Applying this material to asphalt pavement can extend the road's service life and optimize its functionality.⁸ The repair principle of self-healing asphalt can be categorized into two types: external self-healing material and intrinsic self-healing material. External self-healing material is developed by implanting microcapsules or microvessels containing healing agents into the polymer. When the polymer is damaged by external forces, the healing agents are released from the microcapsules or microvessels, promoting the repair process.⁹ However, external self-healing materials can only be repaired once or several times, and their preparation process is complex, limiting their application.^{10,11} Lehn *et al.*¹² (2005) proposed the concept of dynamic polymers, which

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broadened researchers' perspectives and led to a focus on self-healing materials containing dynamic bonds. Intrinsic self-healing materials containing reversible dynamic bonds have become the main research focus due to their simple preparation and multiple repair capabilities.^{13,14} Currently, the synthesis of intrinsic self-healing materials mainly involves reversible covalent bonds and reversible non-covalent bonds. Reversible covalent bonds include disulfide bonds, D-A bonds, borate bonds, acylhydrazone bonds, and others, while reversible non-covalent bonds include hydrogen bonding, π - π stacking, metal coordination, and host-guest interactions.¹⁵ These reversible dynamic bonds have different mechanisms of action but effectively enhance the self-healing ability of polymers.

Polyurethane (PU) is widely used in various fields owing to its inherent structural advantages, such as flexibility, high strength, and high modulus. Notably, PU can easily introduce dynamic bonds during the synthesis process by adjusting the hard and soft segments.^{16,17} When the surface of PU is damaged, the dynamic bonds are broken. However, with the movement of molecular chains and appropriate external stimuli, the reversible dynamic bonds at the damaged area can recombine, achieving self-healing of the damaged region.¹⁸ This characteristic sets it apart from commonly used polymer asphalt modifiers in the current market. PU-modified materials have yielded promising results in the construction of self-healing roads. For example, Li *et al.*¹⁹ prepared a PU-modified asphalt binder using an *in situ* synthesis method, providing a new type of PU-modified asphalt binder. Their investigation of the high and low-temperature properties, mechanical properties, and water stability of PU-modified asphalt binder revealed its good resistance to high-temperature deformation and low-temperature cracking. Fang *et al.*²⁰ modified base asphalt with thermoplastic polyurethane elastomer (TPU) as a modifier, resulting in PU-modified asphalt (APU) with high stability and tensile elongation. Qi *et al.*²¹ developed a PU-modified asphalt suitable for steel bridge decks, exhibiting high flexural strength, high high-temperature stability, low-temperature cracking resistance, fatigue cracking resistance, and aging resistance.

This modified asphalt significantly extends the service life of the road surface. Liang *et al.*²² analyzed the performance of asphalt mixture specimens repaired with different PU content filling materials. Their research showed that PU joint filling materials greatly improved the repair of asphalt pavement cracks, with higher PU content leading to significant improvements in low-temperature crack resistance, low-temperature tensile performance, and water stability. Chen *et al.*²³ designed a mixture of PU-modified asphalt and conducted various tests, including small beam bending, rutting, and freeze-thaw splitting tests at different cold zone temperatures. The experimental results indicated that PU substantially improved the basic performance indicators of asphalt mixtures and enhanced their low-temperature performance in cold regions, suggesting good prospects for PU in pavement applications in cold regions. However, it is unfortunate that most of the literature research mentioned above, both domestically and internationally, in the past decade focused on optimizing the preparation process of PU-modified asphalt and designing mixture proportions. While some progress has been made, there has been limited exploration of the correlation between macroscopic performance and microstructure.^{24,25}

Building upon this background, this study employed reversible dynamic covalent bond self-healing technology to introduce multiple dynamic covalent bonds into the main chain of PU, forming a crosslinked network structure inside the PU.²⁶ As a result, a novel PU material with excellent mechanical properties, referred to as S-PU, was obtained. Experimental results indicated that the original tensile strength of the prepared S-PU material was as high as 52.08 MPa, with an elongation at a break of 1269.37%. Furthermore, the S-PU material exhibited scratch self-healing capabilities in water environments. The experimental findings indicated that the temperature required for healing in a water environment was the lowest within the same duration (12 h, 70 °C), and the mechanical properties were well restored after fracture healing. Additionally, S-PU, which possesses high ductility and self-healing properties, was added to the base asphalt. Conventional performance tests of asphalt and FM

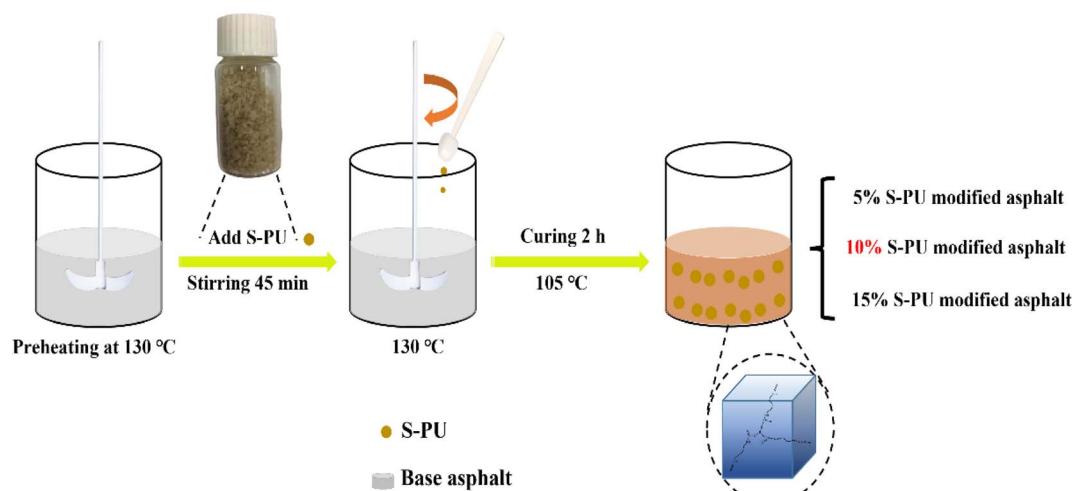


Fig. 1 Preparation process of S-PU modified asphalt.



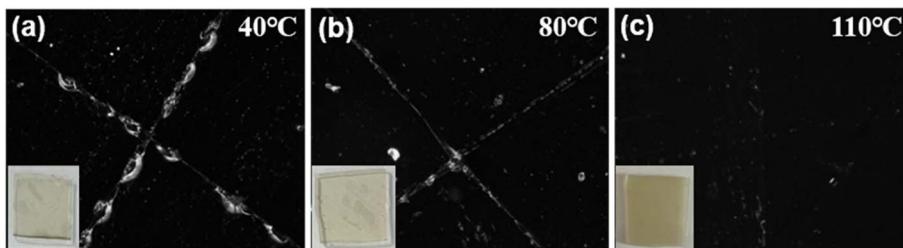


Fig. 2 Optical microscope images of the self-healing performance for the S-PU under different temperature changes (12 h) ((a) 40 °C; (b) 80 °C; (c) 110 °C) (the illustration shows the color change of S-PU film).

revealed that the asphalt modified with 10% S-PU content had the most superior characteristics. The changes in microstructure before and after asphalt modification were analyzed using FT-IR and AFM.²⁷ This study provides a new approach to further explore the advantages of PU and fully utilize them to meet the urgent demand for high-performance asphalt pavement.

2. Experimental section

2.1 Raw materials

Poly-1,4-butanediol adipic acid (PBA-2000), isophorone diisocyanate (IPDI), dibutyltin dilaurate (DBTDL), 4,4-diaminodiphenyl sulfide (DTDA), and boric acid (BA) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. High-purity nitrogen gas was supplied by Shandong Deyang Gas Co., Ltd. Acetone reagent was used after anhydrous treatment.

2.2 Synthesis of S-PU

Firstly, 20 g of PBA-2000 was added to a three-necked flask, and the reaction was continued at 110 °C for 2 hours. Then, 4.45 g of IPDI and 0.01 g of DBTDL were added after lowering the temperature to 80 °C, and the mixture was stirred for 3 hours. Subsequently, 1.19 g of DTDA dissolved in 5 mL of acetone was added to the reaction and stirred for 2 hours. Finally, 0.30 g of BA (in a 10 mL acetone solution) was added to the reactor, and the stirring was continued for 10 minutes before turning off the heating. The reaction solution was poured into a petri dish, and any bubbles were removed in a vacuum drying oven at 80 °C for approximately 12 hours. This process resulted in the formation of the PU elastomer referred to as S-PU,^{28,29} as shown in Fig. S1.† The entire reaction process was carried out under a nitrogen gas atmosphere.

2.3 Preparation of S-PU-modified asphalt

The base asphalt A-70, provided by Shandong Hi-Speed Construction Materials, Jinan, China, was used in this research. Table S1† presents the physical properties of this asphalt, and its relevant property indicators were determined according to the JTGE20-2011 'Standard Test Methods of Bitumen and Bituminous Mixtures for Highway Engineering'.³⁰ A high-speed shear machine was employed for preparing the modified asphalt. Thin films with the same thickness were prepared and aged in ovens at different temperatures for 12 hours. The morphological changes

in the S-PU films at different temperatures were compared, and 130 °C was selected as the mixing shear temperature for asphalt mixture, as shown in Fig. S2.† The detailed preparation process is as follows: firstly, the A-70 base asphalt was heated to a flowing state (~130 °C) in an iron chamber. Then, a predetermined amount of S-PU (5%, 10%, and 15% by weight) was accurately weighed and added to the flowing asphalt, which was subsequently stirred by a high-shear mixer at 1500 rpm. To ensure uniform dispersion, the S-PU was gradually added to the asphalt. Once the S-PU was added, the mixture was sheared at 1500 rpm for 45 minutes. After the shearing process was completed, the mixture was maintained at 105 °C for 2 hours. This procedure allowed the preparation of S-PU-modified base asphalt with different doping ratios. Fig. 1 depicts a flowchart illustrating the process used for preparing the S-PU-modified asphalt.

2.4 Self-healing properties

The standard dumbbell-shaped specimens were cut with a sharp knife from the middle; subsequently, the cut surfaces of the broken samples were placed in full contact at 120 °C under a small force (approximately 10 N) and allowed to set for 30 min, 1 h, 3 h, 6 h, 12 h, and 24 h before mechanical testing. The self-healing efficiency (η) was evaluated by calculating the recovery of tensile strength using the following equation:

$$\eta = \frac{\sigma_{\text{healed}} - \sigma_{\text{cut}}}{\sigma_{\text{original}} - \sigma_{\text{cut}}} \quad (1)$$

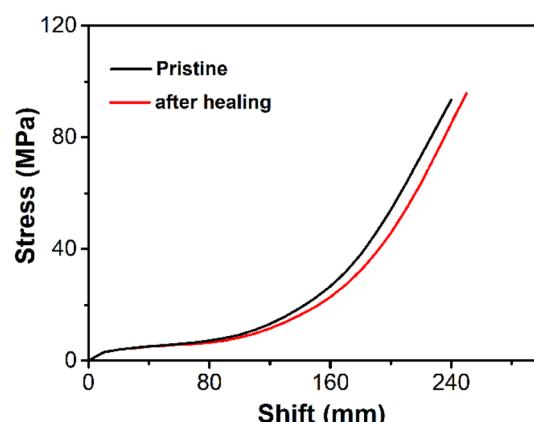


Fig. 3 Stress-strain curve of pristine and post-healing S-PU at 110 °C.



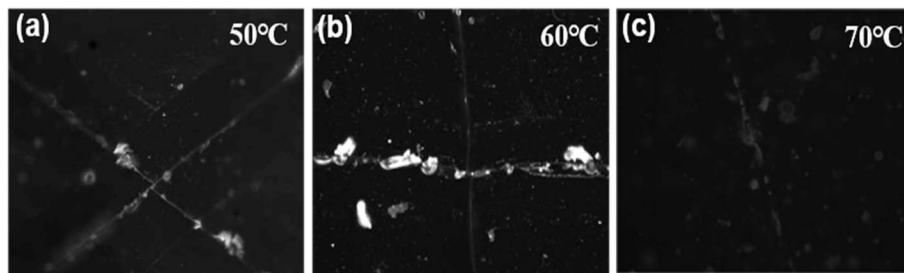


Fig. 4 Optical microscope images of the self-healing performance for the S-PU in freshwater environments at different temperatures (a) 50 °C; (b) 60 °C; (c) 70 °C.

where σ_{healed} denotes the tensile strength of the healed samples, σ_{cut} denotes the tensile strength of the unhealed cut samples, and σ_{original} denotes the tensile strength of original sample.³¹

2.5 Characterization methods

The chemical properties and microstructure of the base asphalt and S-PU-modified asphalt were characterized through FT-IR, fluorescence microscopy, and AFM. FT-IR absorption spectroscopy was employed to observe the functional groups in the base and S-PU-modified asphalt and was performed using a Nicolet iS10 instrument from Thermo Fisher Scientific. The scan range was from 4000 to 400 cm^{-1} . Prior to acquiring the FT-IR spectra, all samples were ground with potassium bromide powder, and KBr pellets were prepared. The morphology of all asphalt samples was examined using a Bruker Nano AFM Multimode 8 with nanoscope software. AFM samples were prepared by hot-casting, which involved dipping a glass rod into melted asphalt and dropping the asphalt onto a glass slide ($10 \times 10 \times 1 \text{ mm}^3$). The glass slide with the asphalt was then tilted at approximately 30 °C above the horizontal position in an oven at 130 °C for 15 minutes to allow the asphalt to flow and spread on the surface of the glass slide under the influence of gravity.^{32,33} Finally, the asphalt films were collected once they reached ambient temperature.

3. Results and discussion

3.1 Self-healing property of S-PU

To evaluate the self-healing ability of S-PU, a representative specimen was intentionally scratched with a sharp blade to create cracks. The cracked sample was then subjected to heating at temperatures of 40 °C, 80 °C and 110 °C, as shown in Fig. 2a–c. After cooling down, the self-healed sample was observed under an optical microscope to examine the recovery of the scratches. The results demonstrate that as the temperature increases, the scratches gradually become shallower.³⁴ When the temperature reaches 110 °C, the scratches on the sample surface almost disappear, leaving only slight healing traces. This improvement can be attributed to the high steric hindrance of IPDI and the activation of reversible effects of hydrogen and disulfide bonds, promoting molecular flow and enhancing the self-healing ability of the S-PU material. For comparison, the morphology of S-PU at 25 °C after scratching

was also examined using an optical microscope, as shown in Fig. S3.† The images revealed the presence of scratches on the surface of the sample.

To quantitatively assess the self-healing efficiency, uniaxial tensile tests were conducted to determine the mechanical properties of the original S-PU and the self-healed S-PU at 110 °C. The original S-PU material exhibited excellent mechanical properties, with a high tensile strength of 52.08 MPa and an elongation at break of 1269.37% (Fig. 3). After heating for 12 h at 110 °C, the self-healed S-PU material demonstrated a tensile strength of 47.72 MPa and an elongation at break of 1219.35%, resulting in a remarkable self-healing efficiency of 91.62%.

To investigate the potential applications of the S-PU material, the self-healing properties of S-PU scratch samples were examined in freshwater environments at different temperatures for a duration of 12 hours. An optical microscope was used to analyze the samples, and the experimental findings revealed an increasing self-healing effect as the temperature rose in freshwater environments. Notably, the scratches completely disappeared at 70 °C, as illustrated in Fig. 4(a–c). This improvement can be attributed to the simultaneous activation of reversible reactions involving hydrogen and disulfide bonds, as well as the activation of borate ester bonds in water

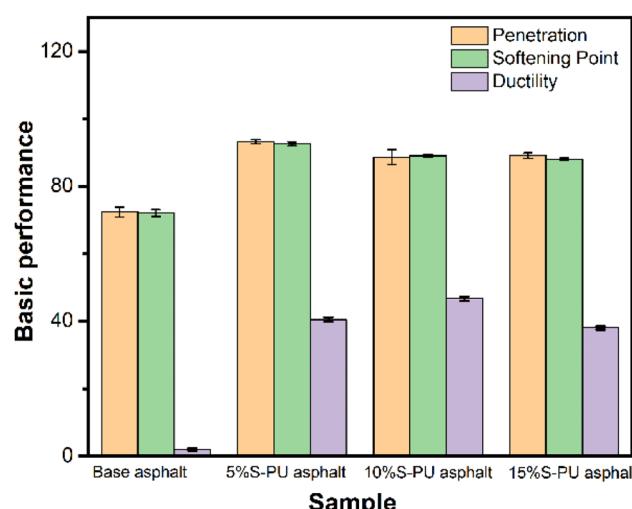


Fig. 5 Conventional properties test results of base asphalt and S-PU-modified asphalt.



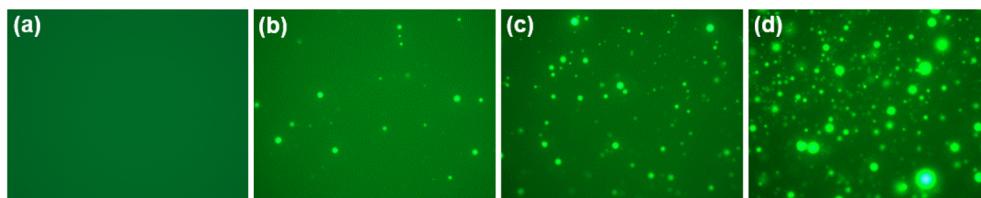


Fig. 6 FM images of four types of bitumen: (a) base asphalt; (b) 5% S-PU modified asphalt; (c) 10% S-PU modified asphalt; (d) 15% S-PU modified asphalt.

mediums, which further enhanced the mobility of the molecular chains.^{35,36} In addition, the contact angle measurements of the S-PU indicated that S-PU possesses a certain degree of hydrophobicity (Fig. S4†).

3.2 Analysis of results for optimum process parameters

3.2.1 Conventional performance of asphalt testing. In this study, a PU elastomer called S-PU, with high elasticity and a three-dimensional network structure with self-healing properties, was selected as an additive to investigate its influence on the performance of base asphalt. The conventional performance of S-PU-modified asphalt was evaluated according to the relevant regulations and standards. Penetration, softening point, and 5 °C ductility of base asphalt and S-PU-modified asphalt with different ratios (5%, 10%, and 15%) were compared. As illustrated in Fig. 5, unlike the base asphalt, the penetration and ductility at 5 °C initially increased and then decreased with increasing PU content. Conversely, the softening point first decreased and then increased. Experimental data indicated that the optimal modification performance was achieved when the PU content was 10%, particularly in terms of improving ductility performance at 5 °C.

3.2.2 FM performance of asphalt. Fluorescence microscopy (FM) was employed to observe the distribution of S-PU in asphalt, as shown in Fig. 6.³⁷ The base asphalt exhibited minimal fluorescence reflection, while the S-PU-modified asphalt at different dosages (5%, 10%, and 15%) exhibited fluorescence points, with each point corresponding to an S-PU particle. When the dosage was 5%, the S-PU particles were small and unevenly dispersed. At a dosage of 10%, the S-PU particles were small and uniformly dispersed. However, at a dosage of 15%, the S-PU particles became larger and aggregated. This phenomenon can be attributed to the high viscosity of asphalt at 130 °C. These observations indicated that the compatibility and dispersibility of S-PU-modified asphalt are improved when the dosage is 10%.

3.3 Microscopic mechanism analysis

3.3.1 FT-IR spectrum analysis. Fourier transform infrared spectroscopy (FT-IR) was utilized to analyze the functional group changes in S-PU-modified asphalt (Fig. 7). First, two typical characteristic peaks occurred at 1735 cm^{-1} , and 3366 cm^{-1} , corresponding to stretching vibration absorption of RCOOH and N-H, respectively, in the FT-IR spectra of S-PU. Subtle changes were indicated by the infrared spectra of base

asphalt and S-PU-modified asphalt. A prominent bulge peak attributed to the stretching vibration absorption of C=O in S-PU appeared in the range of 1620–1890 cm^{-1} , which was absent in the FT-IR spectrum of base asphalt. These results indicated chemical crosslinking between S-PU and asphalt molecules during the modification process.

3.3.2 AFM analysis. Atomic force microscopy (AFM) was employed to examine the mechanism of the PU modification of asphalt. The AFM images (Fig. 8) indicated morphological differences between base asphalt and S-PU-modified asphalt. The “bee” structures in base asphalt were smaller and less numerous (Fig. 8a), whereas the “bee” structures in S-PU modified asphalt were larger and more abundant (Fig. 8b). Studies have suggested that these structures are associated with the presence of asphaltenes in asphalt.^{38,39} Asphaltenes with strong polarity are expected to adsorb onto the hard segments of the PU molecule when PU is added to asphalt, leading to larger bee structures. Notably, in the atomic force microscopy images of polyurethane, the soft segment was a dark area,^{40,41} and the soft segments around the hard segment affected observation. The findings of this study confirmed that the interaction between PU and asphalt molecules is more complex than simple physical blending.⁴² In addition, FT-IR experiments revealed chemical crosslinking between S-PU and asphalt molecules during the modification process. Thus, modifying asphalt with polyurethane does not result in mere physical blending but a complex interaction between polyurethane and asphalt molecules.

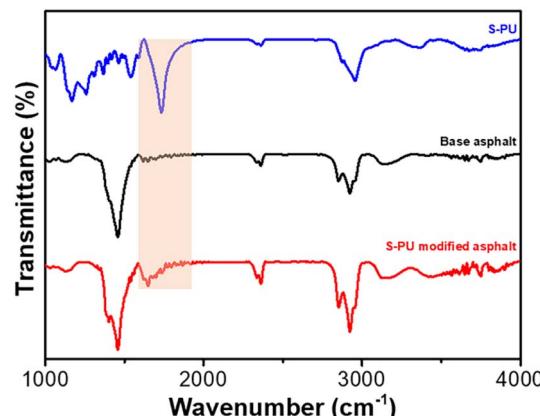


Fig. 7 FT-IR spectrum of the as-prepared S-PU, base asphalt, and S-PU modified asphalt.



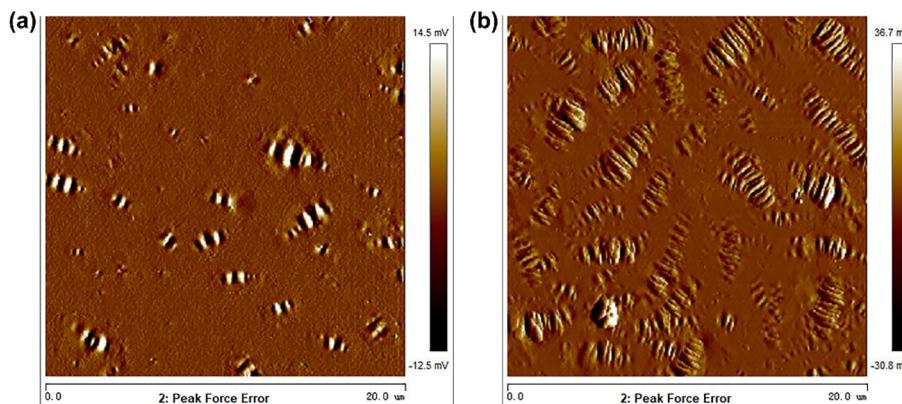


Fig. 8 AFM micrographs of (a) base asphalt, (b) S-PU modified asphalt.

4. Conclusions

This study synthesized a PU elastomer, referred to as S-PU, with a crosslinked network structure. The S-PU exhibited excellent mechanical properties and demonstrated superior self-healing ability in a water environment. The self-healing technology employed in this study introduced multiple reversible dynamic covalent bonds into the main chain of PU. Conventional performance tests on asphalt and FM revealed that the optimal S-PU content after asphalt modification was 10%, resulting in improved ductility. Furthermore, AFM and FT-IR were utilized to investigate the micro-morphology and internal mechanism of self-healing PU-modified asphalt. The experimental data indicated an increase in the size of the bee-like structures during the asphalt modification process, along with the occurrence of chemical crosslinking between S-PU and asphalt molecules. The findings of this study contribute to a deeper understanding of the self-healing mechanism of self-healing PU-modified asphalt materials and offer valuable guidance for future studies.

Data availability

The authors declare that the data supporting the findings of this study are available within the paper and its ESI.†

Author contributions

Writing—original draft and writing—review & editing, Y.-l. Wu; investigation, Q.-y. Luo, and X.-d. Wang; data curation and supervision, K.-x. Xu, H. Li, and Y.-t. Wu; resources, X.-l. Zheng, and X. Li, funding acquisition, J. Li. All authors have read and agreed to the published version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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