



Preparation, properties and modification mechanism of polyurethane modified emulsified asphalt

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HIGHLIGHTS

- New PU modified emulsified asphalt is prepared using developed prepolymer method.
- PU modified emulsified asphalt process includes physical and chemical modifications.
- PU modified emulsified asphalt shows satisfactory mechanical and thermal properties.
- PU forms compact interpenetrating network of molecular chains in emulsified asphalt.
- A suitable PU content of 6% has been proposed to prepare modified emulsified asphalt.

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ABSTRACT

To prepare new polyurethane (PU) modified emulsified asphalt (EA), and further understand modification mechanism of PU to EA, effects of PU on basic engineering performances, chemical composition compatibility, morphology and element compositions, thermal properties, phase microstructures of EA were discussed. The results indicate that basic properties of PU modified EA firstly meet relevant requirements of technical specifications. Improvement effects of PU with a suitable content on penetration and ductility is better than that of styrene butadiene styrene (SBS), but their softening points are similar. Secondly, PU modified EA process includes physical and chemical modifications. PU is dispersed uniformly in evaporation residues of EA when PU content is less than 6%, and meta-stable two-phase interface transition layers are formed between PU and asphalt binder, forming a uniform dispersion system and interpenetrating network structures in modified EA. The compatibility between PU and EA is satisfactory, forming a stable multiphase structure in modified EA. This is conducive to improve high-temperature stability and low-temperature ductility of modified EA. Thirdly, the contents of such main chemical elements as carbon (C), oxygen (O) and sulfur (S) in evaporation residues of EA show no obvious changes before and after modified by PU, indicating that physical modification is main method during the preparation of PU modified EA. Fourthly, PU is difficult to form a continuous crystalline phase in EA. However, the molecular chain spacing and microcrystalline size of PU modified EA are decreased at a suitable PU content, generating more compact interpenetrating network of molecular chains. Motions of asphalt molecules are limited, improving thermal stability and mechanical properties of EA. Finally, a suitable PU content of 6% is proposed to prepare modified EA.

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1. Introduction

Many distresses such as loose, crack and rutting were often found on asphalt pavement due to the continuous increase in asphalt aging, traffic volume, overloading, and canalized traffic in China [1]. It is necessary to maintain and restore the distressed

pavement surface performance. Currently, the commonly used pavement maintenance materials are emulsified asphalt (EA). However, since EA is a kind of water-emulsion materials, EA performance mainly depends on technical properties of evaporation residues after the moisture is evaporation [2]. Further, it is difficult for EA to meet traffic and environmental requirements of asphalt pavement before it is modified. Therefore, the modifier selection to modify first and then emulsify asphalt binder has been paid more attention, improving the durability of maintenance materials of asphalt pavement [3].

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In general, the modifiers of asphalt binder are classified into three categories according to their chemical structures and properties, including elastomers, plastomers and polymeric materials with reactive groups [4]. Among them, such thermoplastic elastomers as SBS and styrene-isoprene styrene (SIS) block copolymers are most commonly used. Their microstructures are generally made up of elastomers and plastic incompatible macromolecules or segments, forming a two-phase system to absorb light components of asphalt binder. Thus it is swelled to form a cross-linked network structure, which facilitates asphalt binder to show plasticity, elasticity and ductility [5]. Behnood et al. [6] found that SBS modifier could improve the high-temperature properties of asphalt binder, but SBS had not significantly effects on its low-temperature performance. Nciri et al. [7] reported effects of SBS modifier on physical and chemical properties of asphalt binder, and found SBS modification results strongly depended on asphalt component and SBS contents.

Additionally, other modifiers also utilized to modify asphalt binder. Liang et al. [8] optimized molecular structural parameters of ethylene vinyl acetate copolymer (EVA) to use as modifier of asphalt binder. EVA improved the high-temperature stability and low-temperature anti-cracking performance, and balanced the viscoelasticity and thermal stability of asphalt binder. Gama et al. [9] modified asphalt binder using elastomer polymers, high-density polyethylene, and polyphosphoric acid, increasing the elastic properties to lower the permanent deformation of asphalt pavement. Han et al. [10] used rubber powder and nanosilica to modify asphalt binder for improving the high-temperature stability and elastic recovery rate, but the low-temperature ductility was slightly decreased.

Compared with the elastomer modifier, reactive polymers provide a different modification method for asphalt binder. The reactive ethylene ternary copolymer was utilized as bulking agent between polyolefin and other polymers [11]. These copolymers could be theoretically used as asphalt modifiers or compatibilizers between asphalt binder and conventional polymers. However, this application in asphalt industry is actually very limited, and there are a few studies on these asphalt modifiers [12].

At present, in general, the commonly used polymer modifiers are physically blended with asphalt binder, and no obvious chemical changes occur [13]. In addition, there are some differences between asphalt binder and polymer modifiers in molecular weight, density, structure and other properties. It is difficult to form a stable thermodynamic system between polymer modifiers and asphalt binder so that their compatibility is limited, leading to delamination and segregation without continuous stirring at high temperature [13]. Therefore, several commonly used polymer modified EA has some deficiencies in production, storage, economical efficiency, and performance. For example, SBS modified asphalt binder is difficult to emulsify because its viscosity is so large. Also, the high-temperature stability of SBR modified asphalt is dissatisfactory and current epoxy resin is so expensive [14]. Therefore, it is necessary to find a new modifier and modified method to prepare modified EA.

More recently, PU, as a new type of modifier, has attracted more attention. PU is a kind of block carbamate polymer, which is usually synthesized by using long chain polyols (e.g. polyester and polyether) to react with isocyanate and chain extender [15]. PU properties greatly depend on microstructures of soft and hard segment phases, in which the soft segment phase provides the elasticity and low-temperature ductility of PU materials [16]. On the other hand, the hard segment phase provides the softening temperature, melting temperature, adhesivity, high-temperature stability, and mechanical properties [17]. Because PU has dual advantages of rubber and plastic, it has been applied in automobile

industry, construction, household, petroleum industry, intelligent packaging, textiles, biomedicine, etc [18].

Singh et al. [19] used PU prepolymer to modify asphalt binder, and found the glass transition temperature and moisture permeability of prepared modified asphalt binder were lowered. The waterproofing and sealing effects were limited due to the lack of flexibility at low temperature. Carrera et al. [20] studied the feasibility of preparing PU modified EA, and pointed out the modifier concentration was key factor to affect its storage stability and rheological properties. Xia et al. [21] reported that PU modifier improved the resistance to deformation and mechanical properties of asphalt binder due to the chemical modification process. Yu et al. [22] modified asphalt binder using nanoscale PU emulsion, and found the PU emulsion was uniformly dispersed in modified asphalt binder, enhancing the storage stability of the modified asphalt system.

It is notes that although PU has been applied in different fields, it is seldom used as EA modifier to prepare maintenance materials of asphalt pavement. The preparing method of PU modified EA was rarely discussed and it is still uncertain whether PU has satisfactory influences on properties of EA to better meet technical requirements of related engineering standards. Also, the modification mechanism of PU on EA is not very clear. The objectives of this study is to prepare a new PU modified EA using the developed prepolymer method, and to further understand modification mechanism of PU to EA, and thus propose a suitable PU content to modify EA, improving various properties of EA.

In this study, asphalt binder was first modified by PU using the developed pre-polymer method, and then chain extension and emulsification were performed to prepare PU modified EA. Synchronously, SBS modified EA was prepared to used as a control sample. Then basic performances of prepared modified EA with different PU contents were tested to confirm whether they can meet relevant technical requirements. After that, Fourier transform infrared spectroscopy (FTIR) was used to characterize effects of PU on chemical compositions and functional groups of EA, discussing the compatibility between EA and PU with different contents.

Also, influences of PU with different contents on morphology and element compositions of evaporation residues of EA were studied by environmental scanning electron microscope (ESEM) and energy dispersive spectrometer (EDS). Additionally, influences of PU contents on thermal stability, endothermic and exothermic reactions of EA samples were analyzed using a differential scanning calorimeter (DSC). Finally, effects of different PU contents on the phase microstructures and network structure of modified EA were investigated by X-ray diffraction (XRD), revealing the modification mechanism of PU to EA. As a result, a suitable PU content was proposed to modify EA and the modification mechanism of PU to EA was further understood.

2. Experiment and method

2.1. Materials

Polytetrahydrofuran ether glycol (PTMG, Aladdin Reagent Co., Ltd., Shanghai, China. Mn = 2000) was selected as soft segments in PU because its melting temperature is lower. Thus PTMG was used to synthesize PU with a lower glass transition temperature (T_g).

The 2, 4-toluene diisocyanate (TDI, TCI Chemical Industry Development Co., Ltd., Shanghai, China.) was used as hard segments in PU due to its relatively regular microstructures so that the prepared PU has more obvious phase separation.

The 1, 4-butanediol (BDO, Sinopharm Group Chemical Reagent Co., Ltd., Shanghai, China.) was applied as chain extender to improve molecular chain regularity of hard segments, increase crystallinity and phase separation in PU, and elevate strength and modulus of PU.

SK-70[#] asphalt binder was obtained from Diansheng Industrial Co., Ltd., Jiangxi, China. Cationic asphalt emulsifier was bought from Duxiu Highway Maintenance Technology Co., Ltd., Shandong, China. Anhydrous calcium chloride (CaCl₂) was bought from Jiuyi Chemical Reagent Co., Ltd., Shanghai, China. Polyvinyl alcohol (PVA) was bought from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. SBS modifier of linear type was obtained from Lucky Gold Chemical Co., Ltd., Tianjin, China.

2.2. Developed preparation method of PU modified EA

In this study, PU modified EA was prepared by three steps. PU pre-polymer was first synthesized, and then asphalt binder is modified using PU pre-polymer, and BDO was added for chain extension in asphalt binder. Finally, PU modified asphalt binder was emulsified.

2.2.1. Synthesis of PU pre-polymer

The calculated amount of PTMG was first placed in a three-necked flask equipped with a thermometer, a mechanical stirrer, and a vacuum connecting pipe. The temperature was increased to 110 °C and the dehydration was performed under a vacuum degree of 0.10 MPa for 1.5 h. Then, the temperature was lowered to 80 °C and the dehydrated TDI in vacuum was added to react with PTMG for 1.5 h under the stirring conditions. As a result, PU pre-polymer was synthesized.

2.2.2. Preparation of PU modified asphalt binder

The calculated amount of asphalt binder was heated to 130 °C, and then was fully mixed with PU pre-polymer for 30 min using a high-speed shear instrument at 1500 rpm. After that, the required amount of BDO was added into the above mixture for chain extension, and the shear mixing was continued for another 30 min to obtain PU modified asphalt binder. Then it was placed in an oven for sufficient reaction development at 105 °C for 2 h. According to the same preparing procedure, PU modified asphalt binder samples containing PU contents of 2%, 4%, 6% and 8% by weight were prepared, respectively.

2.2.3. Preparation of PU modified EA

Firstly, the calculated amount of distilled water was heated to 75 °C on an electric furnace. Then the required amount of PVA was dissolved in the hot water. The aqueous solution was fully stirred until its color was changed from turbid to transparent. Secondly, the aqueous solution was cooled to 60 °C, and then CaCl₂ and emulsifier were added and the mixture was stirred at 1500 rpm for 1 min to obtain a soap solution.

Thirdly, the stirrer speed was increased to 4000 rpm, and hot PU modified asphalt binder was slowly and uniformly injected into the soap solution. Then the stirrer speed was increased from 4000 rpm to 7500 rpm at an increasing rate of 500 rpm until the emulsion was stirred to become uniform. Thus PU modified EA was obtained, and prepared samples with different PU contents were marked as EA, 2%PU/EA, 4%PU/EA, 6%PU/EA and 8%PU/EA, respectively. In addition, because SBS modified asphalt binder with the content of 4% is widely used and studied in China, the SBS content of 4% was used to prepare modified EA as a control sample according to the same emulsifying procedure, which was marked as SBS/EA.

2.3. Characterization methods

2.3.1. Basic performance tests

There are no specific engineering technical requirements for PU modified EA since it is a new type of modified EA. In this study, basic properties of prepared modified EA were tested, including residue content on sieve, evaporation residue content, and penetration, softening point and ductility of evaporation residues according to technical requirements of polymer modified EA in Technical Specifications for Construction of Highway Asphalt Pavements (JTG F40-2004) in China. Test methods of modified EA samples were based on Standard Test Methods of Bitumen and Bituminous Mixtures for Highway Engineering (JTG E20-2011) in China.

2.3.2. FTIR test

In order to study effects of PU modifier on chemical compositions and functional groups of EA, FTIR tests were performed using a FTIR spectrometer (Vector 22 type, Bruker, Germany) to discuss the compatibility between EA and PU with different contents. Each sample was prepared by casting film onto a potassium bromide (KBr) thin plate. The spectra were collected in the wave number range from 4000 cm⁻¹ to 500 cm⁻¹ at a resolution of 4 cm⁻¹.

2.3.3. ESEM and EDS tests

To characterize visually the compatibility between PU modifier and asphalt binder, ESEM (Quanta 2000 type, FEI, America) equipped with an EDS was used to observe microscopic morphology characteristics and identify chemical composition changes of evaporation residues of PU modified EA samples, respectively. Samples were first fixed on an aluminum sample stub and sputtered with gold under vac-

uum conditions. Then the sample chamber was opened to place samples. Finally, the morphologies of the samples were observed using ESEM, and chemical compositions were detected using EDS, respectively.

2.3.4. DSC test

A DSC (204F1 type, Netzsch, Germany) was used to analyze effects of PU with different contents on thermal stability, endothermic and exothermic reactions of EA samples. Approximately 10 mg sample was heated from -70 °C to 100 °C at a heating rate of 20 °C/min. Subsequently, the sample was dropped to -70 °C with a cooling rate of 20 °C/min. This cyclic operation was to eliminate effects of the thermal history of materials. Once again, the sample was heated to 80 °C at a heating rate of 20 °C/min.

2.3.5. XRD test

A XRD (Ultima IV type, Rigaku, Japan) was used to investigate the influence of different PU contents on phase microstructures and molecular network of modified EA. XRD analyzer was with Cu-K α radiation ($\lambda = 0.15418$ nm). The accelerating voltage and applied current were 40 kV and 30 mA, respectively. XRD patterns were recorded in the 2θ range from 10° to 80° in the step scanning mode at a rate of 4°/min.

3. Results and discussion

3.1. PU effects on basic properties of EA

Effects of PU with different contents on basic properties of EA were tested as shown in Table 1.

As shown in Table 1, test results of prepared PU/EA samples can meet technical requirements of polymer modified EA in China. It is found that penetrations of evaporation residues are decreased first and then increased as PU content is increased from 0% to 8%. The penetration reaches the minimum when PU content is 6%. This is because that PU adsorbs the lightweight components in asphalt binder and swells to forms a stable three-dimensional network structure because of physical cross-linking effects [23]. As a result, penetrations of evaporation residues are gradually decreased. When PU content is further increased, the swelling PU reaches saturation and the evaporation residues gradually becomes soft so that the penetration value shows an increasing trend.

As shown in Table 1, softening point of evaporation residues shows a continuous increasing trend, and the increasing rate is gradually lowered as PU content is increased from 0% to 8%, tending to a stable value after PU content is up to 6%. The reason for this is that lightweight components in evaporation residues gradually penetrate and diffuse into PU molecular networks [24]. The free wax content in evaporation residues is significantly decreased, and evaporation residues with higher wax content are developed toward the sol-gel structures [25]. The temperature sensitivity of evaporation residues is lowered significantly, and softening point is increased. However, after PU content reaches 6%, the stable sol-gel structures have been formed so that the increase in softening point of evaporation residues is not obvious.

Finally, it is noted from Table 1 that the ductility of evaporation residues increases first and then decreases with the increase in PU content, and reaches the maximum when PU content is up to 6%. This is because PU absorbs lightweight components to swell, forming mutually embedding spatial network structures [26]. The parallel deformation easily occurs under the action of external load so that the stress is effectively dissipated, increasing the ductility of evaporation residues.

However, when PU content is further increased to 8%, the swelling PU reaches saturation and the excessive PU is freely dissociated in evaporation residues. Micro-regions and holes are formed after the evaporation residues are cured at low temperature. Cracks easily occur under the action of tensile stress, resulting in the decrease in ductility of evaporation residues.

From Table 1, it is also noted that the penetration of SBS/EA is higher by 14.3% than that of the minimum value of PU modified EA. The softening point of SBS/EA is higher by 7.8% than that of

Table 1
Test results of basic properties of EA and its evaporation residues (ER) with different PU contents.

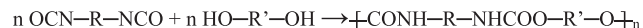
Samples	EA	2% PU/EA	4% PU/EA	6% PU/EA	8% PU/EA	SBS/EA	Technical Requirements
Residue content on sieve (%)	0	0	0.02	0.04	0.05	0.08	≤0.1
ER content (%)	62.2	63.6	61.4	64.8	63.1	65.0	≥50
Penetration of ER (0.1 mm)	88.3	74.0	72.1	65.4	74.6	76.3	40–120
Softening point of ER (°C)	50.2	52.1	56.3	58.7	59.1	63.7	≥50
Ductility (5 °C) of ER (cm)	2.6	21.3	22.2	26.3	22.7	23.5	≥20

the highest value of PU modified EA, but the ductility of SBS/EA at 5 °C is lower by 10.6% than that of the lowest value of PU modified EA. Therefore, according to the comparison of basic performances of EA and its evaporation residues with different PU contents, it is concluded that the penetration and ductility of modified EA with a suitable PU content are better than that of SBS/EA, while the softening point of PU modified EA is almost similar with that of SBS/EA [21].

3.2. Compatibility between PU and EA

FTIR was used to discuss effects of PU modifier on chemical compositions and functional groups of EA. FTIR test results of evaporation residues of PU and SBS modified EA are shown in Figs. 1 and 2, respectively.

From Fig. 1, it is observed that there are a few differences in FTIR spectra of EA between before and after modified by PU with different contents. There is a new absorption peak at the band of 1109 cm^{-1} on FTIR spectra of PU modified EA as shown in Fig. 2 (d)–(g), which is assigned to urethane group (–NH–COO–). It is usually derived from the reaction between isocyanates and alcohols. The schematic diagram of chemical reaction is shown as follows.



Another new peak at around 1750 cm^{-1} is attributed to carbonyl group of urethane in PU, and its peak strength is gradually increased as PU content is raised, but the increase in PU content is so small that the increase in signal strength is not obvious. All these indicate that PU is synthesized after the chain extension reaction of pre-polymer occurs due to the addition of chain extender of BDO. This belongs to physical modification for asphalt binder [27].

As shown in Fig. 1(a), it is found that the absorption peak at the band of 2255 cm^{-1} is attributed to the existence of isocyanate group (–NCO) in PU pre-polymer although the peak intensity is weak due to its low content. However, the band at 2255 cm^{-1} is not found on FTIR spectra of PU modified EA samples, indicating the –NCO group in the pre-polymer experience a chemical reaction. This is because the –NCO group reacts with BDO to generate PU. On the other hand, it also reacts with H_2O to produce carbamic acid which then is decomposed to generate CO_2 and amines. If the isocyanate is excessive, the generated amine continues to react with the isocyanate to generate substituted carbamido. The schematic diagram of chemical reactions is shown as follows.

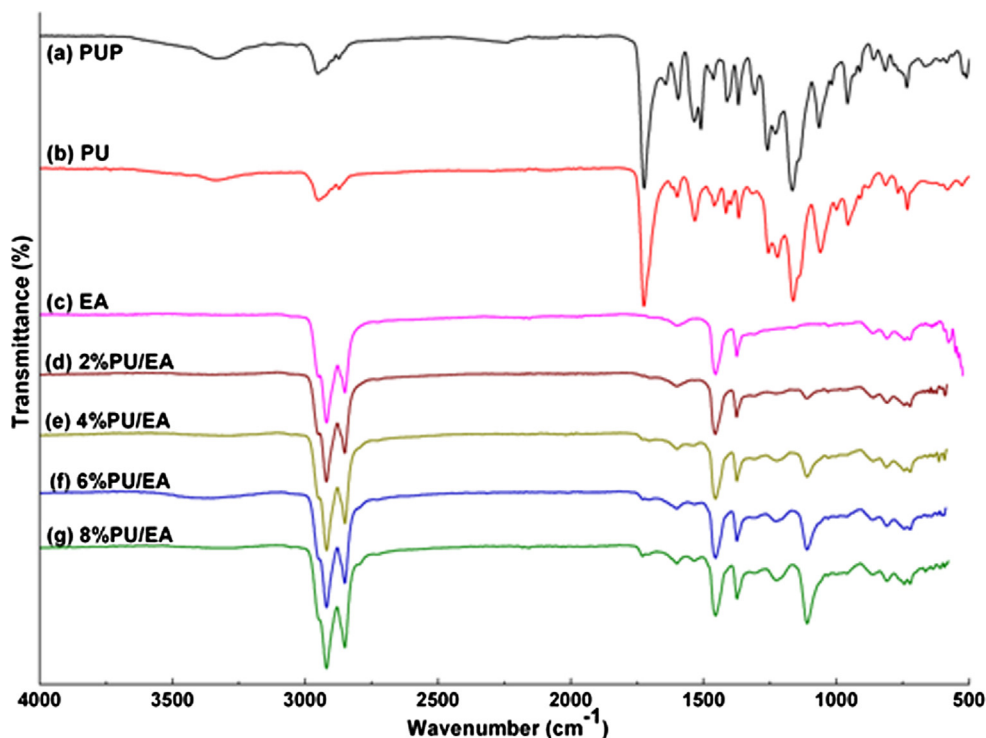
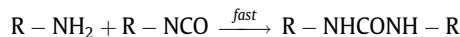


Fig. 1. FTIR spectra of evaporation residues of EA and modified EA with different PU contents.

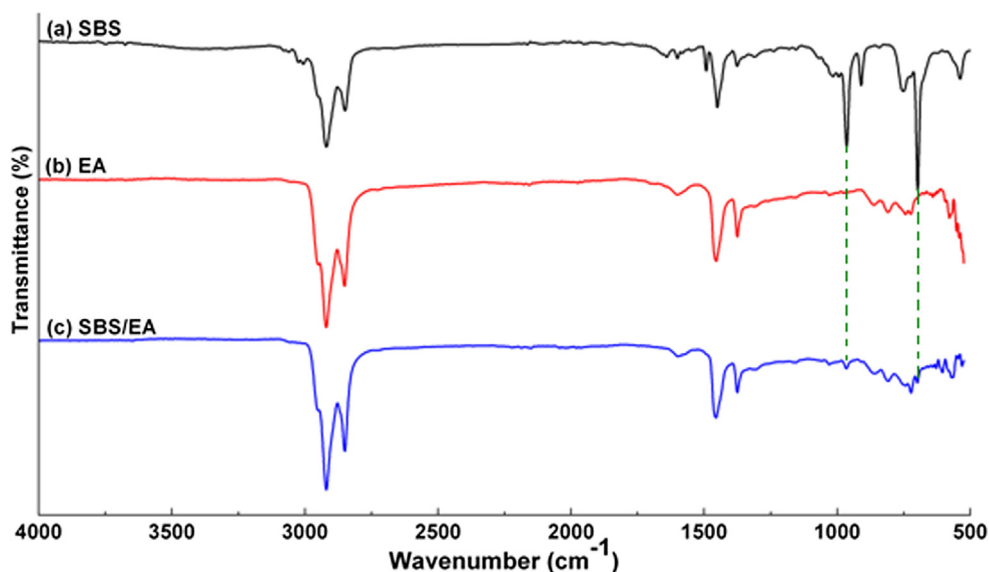


Fig. 2. FTIR spectra of evaporation residues of SBS, EA and SBS modified EA.

Carbamido can increase the elasticity of PU. This belongs to chemical modification for asphalt binder [19].

Additionally, from Fig. 1(c)–(f), it is noted that the absorption peak intensity of -NH-COO- group at around 1109 cm^{-1} gradually become stronger with the increase in PU content. This suggests that effects of PU on chemical compositions of asphalt binder is basically consistent with test results of basic performances of PU modified EA.

Comparatively speaking, as shown Fig. 2, two new absorption peaks are found at the band of 966 cm^{-1} and 699 cm^{-1} after asphalt binder is modified by SBS, but the peak intensity is weak because of its low content. The band at 966 cm^{-1} is the characteristic absorption peak of double bond in polybutadiene segments. The band at 699 cm^{-1} is due to out-plane wagging vibration of C–H bonds on the benzene rings in polystyrene segments. Compared with Fig. 2(a) and (b), the band of absorption peak in Fig. 2(c) is the same as that in Fig. 2(a) and (b), and only the peak intensity shows changes, indicating the absorption peak in Fig. 2(c) is the simple superposition of absorption peaks in Fig. 2(a) and (b). This suggests that there are no new chemical compositions or functional groups to generate. SBS modified asphalt binder belongs to physical modification without chemical reactions.

3.3. Morphology and chemical compositions

ESEM and EDS were used to visually discuss the compatibility between PU and SBS modifiers and EA. SEM images and EDS spectra of evaporation residues of EA and modified EA samples are shown in Figs. 3 and 4, respectively.

From Fig. 3(a), it is seen that the surface morphology of evaporation residues of EA is more compact, which is a homogeneous integral structure. Compared with Fig. 4(a), SEM images of evaporation residues of modified EA samples have obvious morphological characteristics as shown in Fig. 3(b)–(f). Both PU and SBS are white elastomers at room temperature, and the surface morphology of evaporation residues is almost uniform after PU and SBS are mixed with asphalt binder. As shown in Fig. 3(b), there are particle-like protrusions on the surface of evaporation residues of SBS modified EA.

However, as shown in Fig. 3(c)–(e), the surfaces of evaporation residues of PU modified EA are smoother and have a small number of floc-like protrusions. This is because PU modified EA includes

physical modification, and meta-stable two-phase interface transition layers are formed between PU modifier and asphalt binder. There is almost no boundary between PU modifier and asphalt binder. Additionally, the interface between SBS particles and asphalt binder is very ambiguous as shown in Fig. 4(b). All these indicate that the compatibility between the above two modifiers and EA are satisfactory, forming a stable multiphase structure in modified EA. This can greatly improve the anti-deformation capability of EA [7].

By contrast, it is seen from Fig. 3(c)–(f) that the surface morphology characteristics of evaporation residues of PU modified EA gradually become clearer with the increase in PU content from 2% to 6%, indicating that the modification effects of PU to EA are more obvious. Further, molecular chains in PU are interconnected through the interfacial layers, forming a dispersion system and interpenetrating network structures in evaporation residues of PU modified EA. When PU content reaches 8%, the white stripe morphology and a few cracks are observed as shown in Fig. 3(f) on the surface of evaporation residues of PU modified EA. The reason for this is that the excessive PU modifier causes its swelling to reach saturation and the excessive PU dissociates in asphalt binder to form agglomeration. Therefore, microzones, holes and even cracks are observed in evaporation residues of PU modified EA after the low-temperature curing [28].

Fig. 4 shows effects of PU and SBS modifiers on chemical element changes of evaporation residues of modified EA.

From Fig. 4, it is noted that such main chemical elements as C, O, S and Cl are found in evaporation residues of EA and modified EA. H element may also exist, but its molecular weight is too small to be detected, and it is not listed in Fig. 4. From the compositions of chemical elements, asphalt binder is a complicated mixture of hydrocarbons and their nonmetal derivatives of oxygen, sulfur, etc. PU is a kind of polymeric material containing the functional group of -NHCOO- in its molecular structures. Therefore, main chemical elements of C, O and S and their contents in evaporation residues of EA and modified EA show few changes before and after the modification of EA. Cl may be a residual element from stabilizer in soap solution while preparing EA.

C element content is decreased after PU is added in EA. This is because that the proportion of C element in asphalt binder is larger than that in PU. Further, as PU content is increased from 2% to 6%, C element content in evaporation residues of modified EA is still less than that of EA, but it shows a slight increasing trend. The reason is

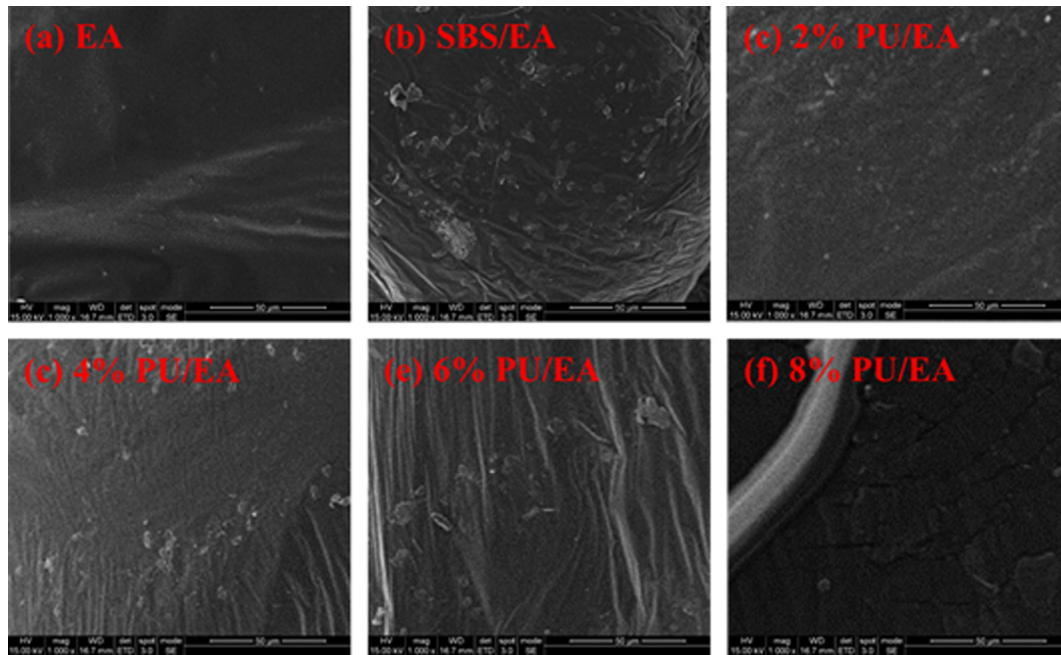


Fig. 3. SEM images of evaporation residues of EA and modified EA samples.

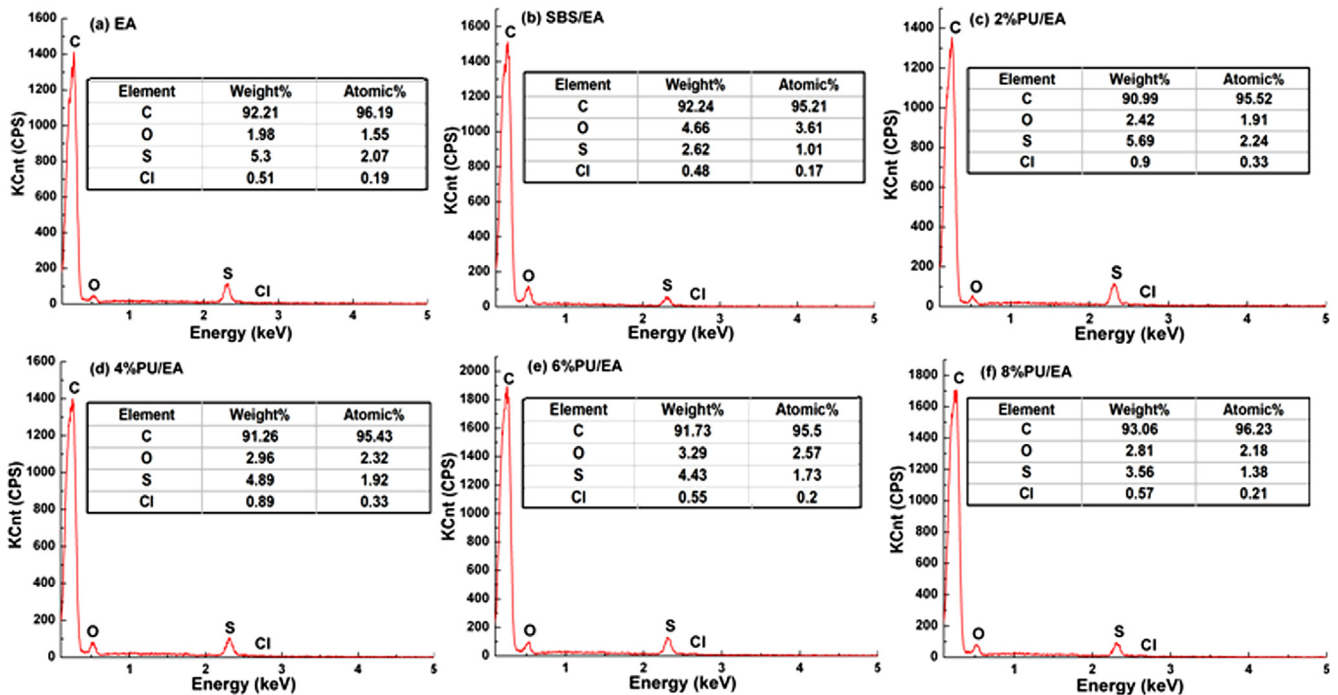


Fig. 4. EDS spectrograms and element contents of evaporation residues of PU and SBS modified EA samples.

that chemical reactions occur to generate the carbamido during the PU modification of EA, and C element content in carbamido is larger than that in urethane group. When PU content reaches 8%, C element content is increased. This may be due to uneven distribution of PU modifiers in evaporation residues of modified EA, leading to more C element in the scanning range of EDS.

As shown in Fig. 4, the oxygen content in evaporation residues of PU modified EA sample shows an increasing trend as PU content is increased from 0% to 6%. However, the oxygen content is lowered when PU content is up to 8%. This may be due to uneven distribution of PU modifier in evaporation residues of PU modified EA,

which causes the oxygen content to decrease in the scanning range of EDS. The sulfur content basically shows a decreasing trend. This is because sulfur element is only included in asphalt binder, and asphalt binder content is decreased as the PU content is increased in modified EA.

Therefore, according to the above SEM and EDS test results, it is concluded that the optimum PU content is about 6%. Also, main chemical element contents show no obvious changes before and after modified by PU. This suggests that physical modification is main method during the preparation of modified EA although chemical modification also occurs.

3.4. Thermal properties

DSC was used to discuss effects of PU contents on thermal properties of evaporation residues of EA, determining the glass transition temperature (T_g) and endothermic and exothermic reactions of evaporation residues. In this study, the middle point of the first step on DSC curves is regarded as T_g [29]. DSC curves are shown in Fig. 5, and test results are summarized in Table 2.

It is known that the evaporation residues of EA include many different components, and their microstructures are very complicated, and their properties are unstable. These components are changed during the heating. Therefore, several peaks are presented on DSC curves as shown in Fig. 5. Among them, PU shows an obvious endothermic peak in the temperature range of 20.7–32.2 °C. After the addition of SBS and PU modifiers, DSC curves of evaporation residues are similar, but endothermic peak intensity become weaker, indicating that endothermic reactions of evaporation residues of modified EA are decreased. As a result, thermal properties of modified EA become more stable.

Further, it is noted from Table 2 that endothermic amount of evaporation residues of modified EA are gradually lowered as the PU content is increased. This suggests that the thermal stability of modified EA is gradually improved. The main reasons for this are that PU and SBS are high-molecular-weight compounds, while asphalt binder is lower-molecular-weight mixtures, and the interaction force between molecules is smaller and molecular chains are not arrayed closely [30]. As a result, the heating causes a large change in molecular force, leading to the obvious motions of molecular segments. Therefore, the thermal stability becomes weaker on the macro level.

However, the molecular weights of PU and SBS modifier are larger, and molecular chains are intertwined each other so that the intermolecular force is larger. Molecular chains are arrayed closely to limit their relative motions, resulting in the decrease in temperature sensitivity of modified EA. In addition, some asphalt molecules are adsorbed on polymer molecular chains. This also lowers the total number of small molecules in PU modified EA. As a whole, the addition of PU and SBS limits the motions of molecule chains to a certain extent, thus the mobility of molecules is lowered, improving the thermal stability of modified EA [31].

It is also found from Table 2 that the T_g of evaporation residues is lowered when PU and SBS modifiers are used to modify EA. T_g is lowered first and then raised as PU content is increased, and T_g reaches the lowest temperature of –18.8 °C when PU content is 6%. T_g of evaporation residues of SBS modified EA is slightly higher than the lowest temperature. This indicates that both PU and SBS can improve the low-temperature performance of EA to a certain extent, which is also consistent with the ductility test result at 5 °C [32].

3.5. Phase structure analysis

XRD tests were conducted on PU and evaporation residues of EA and modified EA with different PU contents, respectively. The test results are illustrated in Fig. 6

It is seen from Fig. 6(a) that PU shows a broad diffused diffraction peak at $2\theta = 18.92^\circ$, suggesting that prepared PU is amorphous polymeric material, including a large number of amorphous phases or microcrystals in PU. The reasons for this are that the crystals in PU are usually microcrystalline structures, and their crystallite

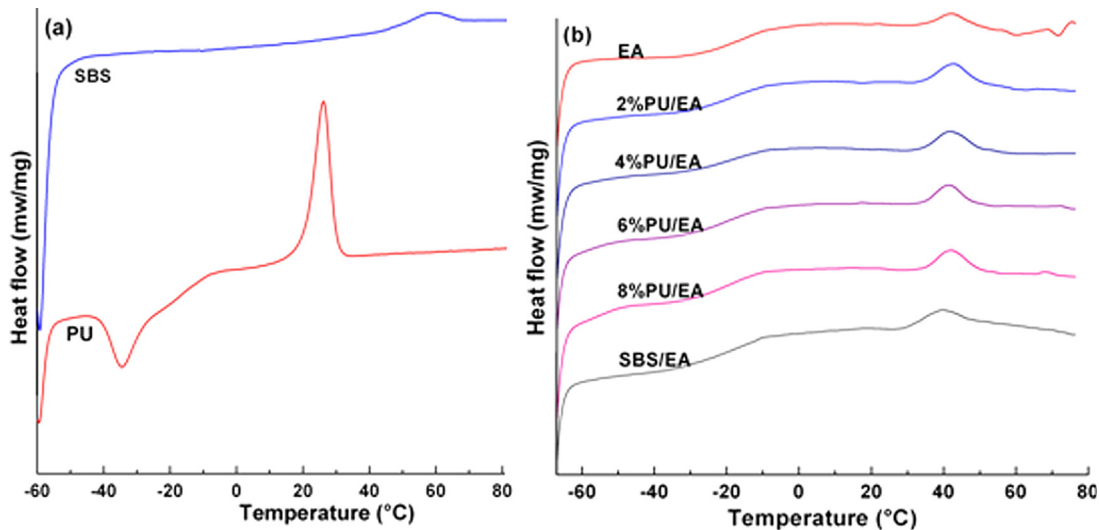


Fig. 5. DSC curves of modifiers and evaporation residues of modified EA with different PU contents.

Table 2

DSC test results of PU and evaporation residues of modified EA with different PU contents.

Sample	T_g (°C)	Endothermic temperature range		Enthalpy (J/g)
		Peak width (°C)	Peak temperature (°C)	
PU	–13.6	20.7–32.2	27.9	17.40
EA	–15.7	37.1–54.7	45.9	1.73
2% PU/EA	–16.5	36.8–54.3	44.5	1.62
4% PU/EA	–17.9	37.1–51.0	44.2	1.06
6% PU/EA	–18.8	32.7–51.1	42.1	0.95
8% PU/EA	–17.5	37.7–52.5	44.9	0.70
SBS/EA	–18.5	37.8–52.8	44.9	0.99

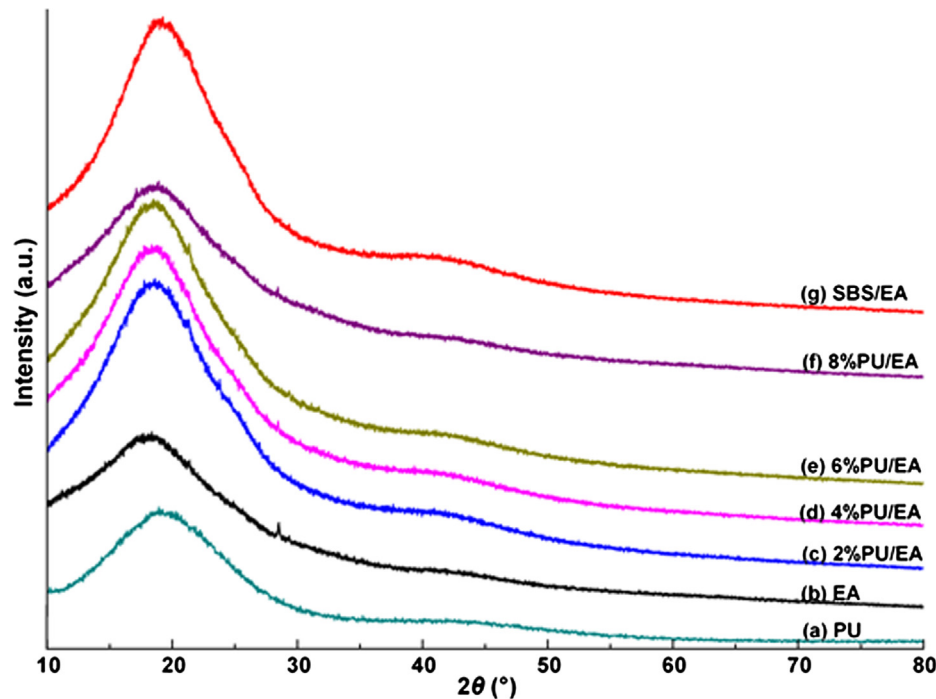


Fig. 6. RD patterns of PU and evaporation residues of EA and modified EA with different PU contents.

Table 3

XRD test results of PU and evaporation residues of EA and modified EA with different PU contents.

Samples	2θ (°)	FWHM (°)	Spacing (Å)	Crystallite size (Å)
PU	18.92	0.566	4.6875	145
EA	18.37	0.390	4.8248	213
2%PU/EA	18.62	0.655	4.7618	124
4%PU/EA	18.78	0.711	4.7210	114
6%PU/EA	18.94	0.717	4.6816	113
8%PU/EA	18.89	0.493	4.6922	167
SBS/EA	18.74	0.948	4.7307	85

sizes are small [29]. The aggregation of soft segments of PTMG due to microphase separation in PU also results in the broad diffused diffraction peak. This indicates that reactions between soft segments of PTMG and hard segments of TDI is difficult to form a continuous crystalline phase [33]. The reason for this is when PTMG is selected as soft segments in PU, the compatibility between the two phases is larger. The interaction lowers the system separation degree, causing PU is more difficult to crystallize.

As shown in Fig. 6(b), there is a broad diffused diffraction peak at $2\theta = 18.37^\circ$, which is attributed to the aliphatic layer, aliphatic chains, or saturated rings in evaporation residues of EA [7]. From Fig. 6(c)–(g), it is found that XRD patterns of evaporation residues of EA and modified EA are similar, but microcrystalline diffraction peaks of evaporation residues of modified EA become higher and narrower after modified by PU and SBS. This suggests that the microcrystalline content in evaporation residues of modified EA is increased. According to Bragg and the Scherrer formulas, the molecular chain spacing and microcrystalline size of evaporation residues of EA and modified EA are calculated, respectively [29]. The XRD analysis results are shown in Table 3.

It is noted from Table 3 that the molecular chain spacing and microcrystalline size are decreased first and then increased as PU content is increased from 0% to 8%. In particular, the molecular chain spacing and microcrystalline size reaches the minimum when PU content is 6%. This indicates that network structures of molecular chains in PU modified EA are more compact, and the

elasticity of PU modified EA is significantly increased at low temperature, and the thermal stability is greatly improved.

However, when PU content is up to 8%, the molecular chain spacing and microcrystalline size become larger. The probable reasons are that the saturated PU modifier forms aggregations in evaporation residues of PU modified EA, leading to the increase in molecular chain spacing and microcrystalline size. The microzones are formed in evaporation residues of PU modified EA after low-temperature curing, which damages the original network structures. Therefore, the low-temperature brittleness is increased, resulting in the decrease in anti-cracking performance of PU modified EA. Also, from Table 3, it is seen that a dense network structure is formed in evaporation residues of SBS modified EA. This improves the thermal stability of EA [34]. The above analysis is consistent with DSC test results.

4. Conclusions

In this study, PU modified EA samples are successfully prepared by the developed preparation method, and their various properties are characterized and discussed. The main conclusions are obtained as follows.

- (1) Basic properties of PU modified EA meet relevant requirements of technical specifications. When PU content is 6%, penetration, softening point and ductility of PU modified

EA are better improved. Improvement effects of PU on penetration and ductility is better than that of SBS, but PU effects on softening point is similar with that of SBS.

- (2) Wave-numbers and intensities of characteristic peaks of evaporation residues of PU modified EA indicate that there are both physical and chemical modifications in the preparation process of PU modified EA, improving its high-temperature stability and elasticity. By contrast, the preparation process of SBS modified EA mainly includes physical modification.
- (3) PU modifier is dispersed uniformly in evaporation residues of EA when PU content is less than 6%, and the meta-stable two-phase interface transition layers and interpenetrating network structure are formed in PU modified EA. The compatibility between PU and SBS modifiers and EA are satisfactory, forming a stable multiphase structure in modified EA.
- (4) Main chemical elements as C, O, S and Cl are found in evaporation residues of EA and modified EA, and their contents show no obvious changes before and after modified by PU. This suggests that physical modification is main method during the preparation of modified EA although chemical modification also occurs.
- (5) Endothermic and exothermic reactions of EA and PU modified EA are similar, but enthalpy changes are decreased with the increase in PU content. High-temperature stability and low-temperature ductility of PU modified EA are improved. Asphalt molecules are adsorbed on PU molecular chains and network to improve the thermal stability of modified EA.
- (6) PU modifier is difficult to form a continuous crystalline phase in modified EA. However, the molecular chain spacing and microcrystalline size of PU modified EA are decreased at a suitable PU content of 6%, forming more compact interpenetrating network structures of molecular chains. Thermal stability and mechanical properties of EA are improved. A suitable PU content of 6% is proposed to prepare modified EA.

Declarations of interest

None.

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