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A state-of-the-art review on cold binders for sustainable paving materials ☆

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ABSTRACT

Hot mix asphalt (HMA) has been widely used as a pavement material for decades because of its quick construction process and good engineering performance. However, its construction has to be performed at elevated temperature, causing significant energy consumption and hazardous emissions. Cold mix, which demands no heating in the construction process, is a cleaner and more environment-friendly paving technique. The cold mix binder, which bonds aggregates at ambient temperature, plays a key role in the environment-friendly cold mix pavement. However, in-depth understanding of the working mechanism and applications of cold mix binders is still lacking. To fill this gap, three different kinds of cold binders commonly used in pavement industry are extensively discussed, namely, the conventional bitumen emulsions, and the newly emerging epoxy resin and polyurethane.

Bitumen emulsions are by far the most widely used cold binder in pavement construction for surface dressing, tack coat and cold mix. However, bitumen emulsions are inferior to HMA in terms of early strength and mechanical properties, which limited them from been used in structural layers. To improve the performance of bitumen emulsion, polymer latexes, such as SBR latex and waterborne epoxy resin, are commonly used as modifiers to prepare polymer modified bitumen emulsions. The incorporation of polymer latexes can significantly improve the performance of bitumen emulsion, including high- and low-temperature performance, adhesion with aggregate, and fatigue performance.

Recently, polymer binders like epoxy resin and polyurethane have been introduced into the pavement industry. Epoxy resin and polyurethane are characterized as fast curing, remarkable mechanical strength, and strong adhesion with aggregate and substrates. However, there are still some shortcomings need to be addressed for the resin binders before they can be applied in large quantities, such as limited workability, insufficient resistance to weathering and high initial cost.

Abbreviations: HMA, Hot Mix Asphalt; WMA, Warm Mix Asphalt; HWMA, Half-Warm Mix Asphalt; CMA, Cold Mix Asphalt; SARA, Saturates, Aromatics, Resins, and Asphaltenes; PMB, Polymer Modified Asphalt Binder; PMBE, Polymer Modified Bitumen Emulsion; SBR, Styrene-Butadiene Rubber; NR, Natural Rubber; SBS, Styrene-Butadiene-Styrene; SIS, Styrene-Isoprene-Styrene; MSCR, Multiple Stress Creep and Recovery; CLSM, Confocal Laser Scanning Microscopy; WER, Waterborne Epoxy Resin; WEBER, Waterborne Epoxy Resin Modified Bitumen Emulsion Residue; RAP, Reclaimed Asphalt Pavements; ITS, Indirect Tensile Strength; ITSM, Indirect Tensile Stiffness Modulus; PC, Polymer Concrete; DGEBA, Diglycidyl Ether of Bisphenol-A; PA, Polyamide Amine; ALA, Alicyclic Amine; ARA, Aromatic Amine; AA, Aliphatic Amine; POA, Polyether Amine; PAA, Phenolic Aldehyde Amine; PU, Polyurethane; HS, Hard Segment; SS, Soft Segment; SMA, Stone Mastic Asphalt; GA, GussAsphalt; EAC, Epoxy Asphalt Concrete; PUM, PU Mixture; PERS, Poroelastic Road Surface; PUC, Polyurethane Concrete.

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This paper set out to provide a state-of-the-art review on the constitutions, properties, applications, and pros and cons of three cold binders, i.e., bitumen emulsion, epoxy resin and polyurethane, paving the way for future research and applications of these cleaner construction materials in pavement engineering.

1. Introduction

Over the last decades, Portland cement and asphalt materials have been extensively used as rigid and flexible pavement binders, respectively (Khay et al., 2010){Khay, 2010 #158;Lu, 2009 #91}. Due to its flexibility and wear-resistance, asphalt pavement now dominates in road transportation infrastructure (García-Morales et al., 2006). Asphalt binder, a residual product from petroleum distillation, is a viscoelastic material, which behaves like an elastic solid at low temperatures, while acts as a viscous liquid at elevated temperatures (Lesueur, 2009). Note that "asphalt binder" and "bitumen" both refer to the bonding material of asphalt concrete, and these two terms are used interchangeably in this review paper. Asphalt binder is generally heated to over 130 °C to ensure sufficient workability (Yang et al., 2013). However, concerns about the properties degradation and, particularly, environmental issues during the production and construction of Hot Mix Asphalt (HMA) are rising in recent years. When asphalt binder and aggregate are mixed at high temperatures, asphalt binder will inevitably undergo short-term aging (Airey, 2004){Navarro, 2009 #156;Airey, 2004 #157}. In addition, HMA produces significant amount of volatile organic compounds (VOC) and greenhouse gas (GHG) emissions such as carbon dioxide (CO_2) and sulfur dioxide (SO_2) (Capitão et al., 2012). These emissions dramatically increase the environmental burdens and affect human health. Furthermore, HMA consumes large amount of fossil fuels to reach the required temperature.

To implement greener and more sustainable approach of pavement construction, this industry has been seeking alternative techniques to produce asphalt mixture at lower temperature such as Warm Mix Asphalt (WMA, 100 ~ 140 °C), Half-Warm Mix Asphalt (HWMA, 60 ~ 100 °C), and even Cold Mix Asphalt (CMA, 0 ~ 40 °C) (Rubio et al., 2012, Leng et al., 2017). These techniques significantly reduce the consumption of fossil fuels and hazardous emissions (Jamshidi et al., 2016). It is reported that a 10 °C decrease in the production temperature of asphalt mixture contributes to the reduction of 1L fossil fuel consumption and 1 kg carbon dioxide emission per ton of asphalt mixture (Jamshidi et al., 2013). During the past decades, WMA has attracted extraordinary interests in pavement industry. Three main approaches have been applied to produce WMA, including: (1) organic additives, (2) chemical additives and, (3) water-based foaming processes (Anthonissen et al., 2016). Furthermore, to meet the increasingly stringent environmental controls, the utmost goal, however, is to produce and compact the pavement concrete at ambient temperature, which reduces the consumption of fossil fuels and emissions of VOC and GHG to a minimum level. Traditionally, bitumen emulsion and cutback asphalt are used as the binder of CMA because of their lower viscosity. Since cutback asphalt contains substantial amount of volatile solvent such as kerosene, which is harmful to environment and fire hazardous (Gorman et al., 2004), its application has become very limited and will not be included in this review paper. Similarly, Portland cement concrete was previously used for the construction of rigid pavement. However, the proportion of rigid pavement is now very low due to the following reasons, 1) significant GHG emissions (Barcelo et al., 2014), 2) long curing period (Long et al., 2024), and 3) difficulty in maintenance or rehabilitation (Liu et al., 2021b). Therefore, cement is also not included in this paper.

This paper aims to provide a state-of-the-art review on the conventional and newly emerging cold-mix binders in pavement industry, namely, bitumen emulsion, epoxy resin and polyurethane, paving the way for future research and applications of these cleaner construction materials in pavement engineering. The use of bitumen emulsion in pavement engineering can date back as early as to the beginning of the 20th century (Addae et al., 2023). Due to insufficient mechanical performance, polymers and/or polymer latexes modified bitumen emulsion with improved performance was developed in the last three decades (Takamura and Heckmann, 1999). In recent years, polymer concrete using resins, e.g., epoxy resin and polyurethane, as binder has been widely studied and applied in transportation infrastructures in replace of traditional cement concrete or asphalt concrete, due to superior mechanical performances, such as high abrasion resistance, impermeability to water and salts, outstanding bonding strength and corrosion resistance (Jung et al., 2015a). Since these binders, bitumen emulsion, epoxy resin, and polyurethane, can be applied at ambient temperature without heating, they are more environment-friendly, significantly reducing energy consumption and GHG emissions. To better understand these cold binders, their constitutions, properties, applications, and pros and cons are thoroughly reviewed and discussed in this review paper.

Fig. 1 shows a flow chart of this review paper. The rest of this paper is organized as follows. Section 2 details the materials constitutions, modification and application of bitumen emulsion. Section 3 introduces the material composition of epoxy resin based cold mix binder, and the properties of epoxy binder and mixture, representative applications in pavement are discussed. Section 4 describes the material composition of polyurethane based cold mix binder, and the properties of polyurethane binder and mixture, representative applications in pavement are presented. Section 5 shows the recommendations for future research regarding the three cold binders in consideration, and Section 6 presents the summary and conclusions.

2. Bitumen emulsion

Bitumen emulsion is one of the most widely used cold construction material in the pavement industry at present (Querol et al., 2019). The main applications include pavement surface treating, tack coat, cold recycling, and cold mixes (Raposeiras et al., 2016, Wang et al., 2018). Bitumen emulsion is mainly composed by bitumen, emulsifier, and water. With bitumen droplets dispersed in the aqueous phase, the viscosity of bitumen emulsion is low enough to achieve good workability at ambient temperature.

2.1. Constitutes of bitumen emulsion

2.1.1. Bitumen

Bitumen is a semi-solid viscoelastic material with an extremely high viscosity (~7000 Pa·s) at ambient temperature (Rodrıguez-Valverde et al., 2003). Owing to their pronounced waterproofing, adhesion, and rheological performance, bitumen is recognized as the most eligible materials for pavement construction currently. Bitumen is predominantly composed by carbon and hydrogen (> 90 wt%), and the rest elements are mainly sulfur, nitrogen, and oxygen (Lesueur, 2009). Generally, bitumen is divided into four fractions based on their polarity and aromaticity: saturates, aromatics, resins, and asphaltenes (SARA) (Corbett, 1969). The fractions with lower molecule weight: saturates, aromatics, and resins are defined as maltenes, while asphaltenes are the heaviest fraction in bitumen (Salou et al., 1998). It is generally recognized that the SARA fractions form the so-called 'colloid' structure (Lesueur, 2009), that the asphaltenes are surrounded by the maltenes, and the resins act as the interface layer between the solid-like asphaltenes and the liquid-like oily phase. Based on the contents of the SARA fractions, the bitumen can form the so-called sol structure and gel structure as shown in Fig. 2, and the colloid structure lies between the two, sol–gel structure, may also be formed (J. Read, 2015).

2.1.2. Emulsifiers

Typically, bitumen emulsion is characterized by high solid content (50 ∼ 70 %), and the average size of bitumen droplets generally falls in the range of 5–50 μm (Arenas-Calderon et al., 2014). As the highly-dispersed droplets possess enormous interfacial energy, bitumen emulsion is thermodynamically unstable (Firoozifar et al., 2010). Fig. 3 shows a microscopy image of bitumen emulsion, with the yellow particles represent bitumen particles and the dark continuous phase represents the aqueous water phase. The bitumen droplets tend to coalescence and form larger asphalt particles, inducing phase separation of the bitumen emulsion (Fang et al., 2016). To increase the bitumen emulsion stability, emulsifiers are essentially an indispensable part. In general, emulsifiers are surfactant molecules with a hydrophilic head and a hydrophobic backbone (Liu and McGrath, 2005). When producing bitumen emulsions, emulsifiers are normally applied as stabilizer, which will then diffuse from water to the interface of asphalt binder and water, thereby reducing the interfacial energy and increasing the stability (Jada et al., 2004). Based on the electric properties of the hydrophilic head, emulsifiers can be divided into three categories: cationic, anionic, and non-ionic (Ronald and Luis, 2016). As the non-ionic emulsifiers are rarely used in bitumen emulsion, only cationic and anionic emulsifiers are discussed here.

The cationic type emulsifiers are the most widely used emulsifiers in bitumen emulsions (Rodríguez-Valverde et al., 2008). They are mainly composed by the fatty amines, alkyl-amide polyamines or lignin derivatives (Banerjee et al., 2011). The cationic emulsifiers are activated in acid conditions (e.g., addition of chlorine hydride) (Gingras et al., 2005). These emulsifiers then arrange themselves around the bitumen droplets, thus making the bitumen droplets positively charged. As most aggregates are of electronegative nature, the cationic type emulsifiers can effectively absorb to a wide variety of mineral aggregates, resulting in strong bitumen-aggregate adhesion. This is the reason why the cationic emulsifiers are more favored in manufacturing bitumen emulsions (Al-Sabagh et al., 1997). The absorption of emulsifier on aggregate surface changes the aggregate from hydrophilic to hydrophobic, which becomes ideal for the wetting of bitumen. The physicochemical interactions between bitumen droplets and aggregate then initiate the bitumen emulsion breaking and the bitumen sets on aggregate. Possible stages in the setting process of a cationic emulsion are presented in Fig. 4. Furthermore, cationic emulsifiers are capable of reacting with both alkaline aggregates (e.g., limestone) and acid aggregates (e.g., basalt and granite). The salts (ammonium carbonates or ammonium silicates) formed following the chemical reaction can further enhance the adhesion between asphalt binder and aggregate (Ziyani et al., 2016).

The anionic emulsifier molecules consist a long hydrocarbon chain terminated with a negatively charged group, mostly carboxylate ($R\text{-}COO^-$) and sulfonate ($R\text{-}SO_3^-$) (Fang et al., 2016). The anionic bitumen emulsions can provide effective coating or bonding properties when mixed with alkaline aggregate such as calcium carbonate (Ronald and Luis, 2016). $R\text{-}COO^-$ or $R\text{-}SO_3^-$ anions can react with calcium ions and form organic salt at the bitumen-aggregate interface, which improves the interfacial adhesion. However, the weak adhesion with acid aggregates is the main drawback for anionic bitumen emulsions. Hydrogen ions (H^+) produced by acid aggregate will easily combine with anions and weaken the stability of bitumen emulsions (Ronald and Luis, 2016). As a result, the bitumen emulsions may break up before absorbing onto aggregate, leading to poor bonding between the residual emulsions and aggregate. Therefore, the application of anionic surfactants is more appropriate when the aggregate is of positive charge.

2.2. Modification of bitumen emulsion

2.2.1. Modification methods

The mechanical performance of bitumen emulsion is generally insufficient compared with hot mix asphalt, especially at early stage (Li et al., 2019b). To improve the performance of bitumen emulsion, polymers, including solid polymers and polymer latexes are used as modifiers to prepare polymer modified bitumen emulsion. In general, there are four methods in preparing the polymer modified bitumen emulsions (PMBEs), i.e., the preblending method, the comilling method, the soap prebatching method, and the postblending method (Mohammadi and Modarres, 2022) (Fig. 5). The preblending method indicates that the polymer is first blended with bitumen using a high shear mixer to produce the polymer modified bitumen (PMB), and the

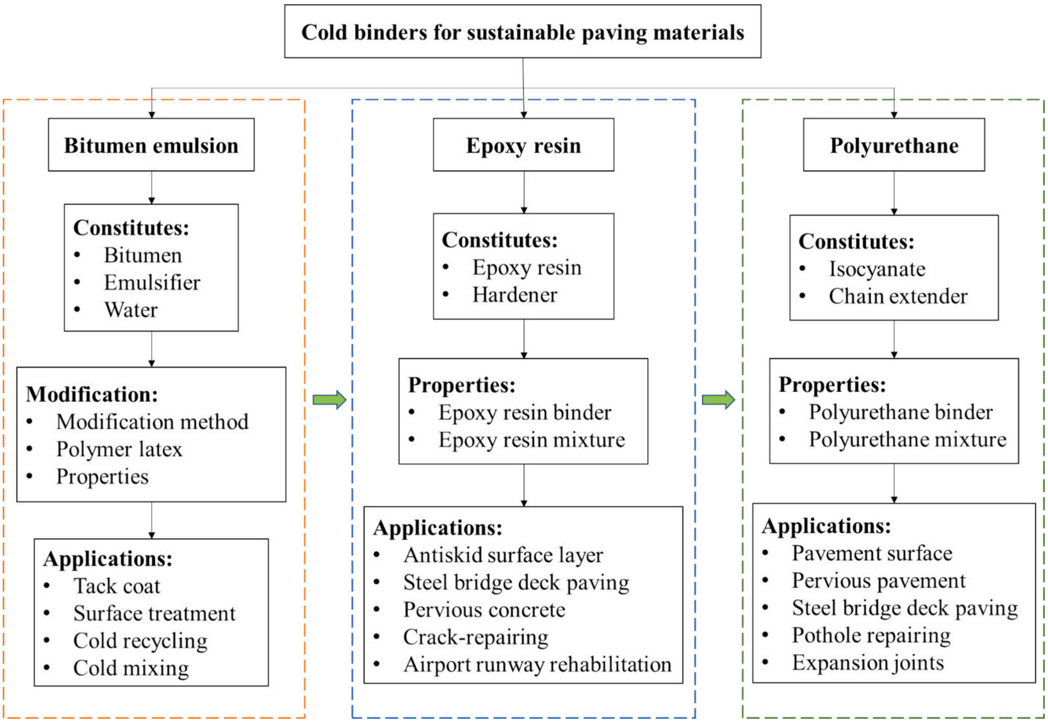


Fig. 1. Flow chart of this review paper.

PMB then undergoes the milling process with soap water to prepare PMBE. The comilling method indicates that the neat bitumen, polymer, emulsifier, acid and water are poured simultaneously into the colloid mill and the PMBE is obtained directly. The soap prebatching method indicates the polymer is first mixed with the soap water, and the soap-polymer mixture is milled with bitumen in a colloid mill. The post-blending method indicates the bitumen emulsion is first prepared, and the polymer is then mixed with the bitumen emulsion to prepare PMBE. The preblending method is more common for solid polymers. It involves the preparation of PMB at high temperature (up to 180 °C). However, the emulsification of PMB is difficult because of the high viscosity of PMB. In addition, it was also noted that the polymer pre-blending method may not form the continuous polymer network in the residue, which affects the final performance of the bitumen emulsion (Takamura, 2005). The other three methods can be used for polymer latex, which is more energy saving and convenient. However, the rating of these methods varies from study to study (Asadi Azadgoleh et al., 2021, Keymanesh et al., 2022, Ziari et al., 2022). Polymer latexes are water-based dispersion of polymers, and can be easily mixed with bitumen emulsion to prepare PMBE. Since bitumen emulsion can be prepared in advance and stored for a certain period of duration, it is readily available to be mixed with polymer latex before application simply by stirring, in a plant or on site. Thus, the postblending method is more favored considering its convenience and efficiency of handling.

2.2.2. *Polymer latexes*

Various polymer latexes have been used in preparing PMBEs, such as Styrene-Butadiene Rubber (SBR), natural rubber (NR), styrene–butadiene–styrene (SBS), styrene–isoprene-styrene (SIS), epoxy resin, polyurethane, and etc. (James, 2006a). Table 1 summarizes typical polymer latexes used in emulsion modification. It is reported by Forbes et al. (2001) that an introduction of 3 wt% of polymer latex into bitumen emulsion is able to form a continuous polymer-rich phase for the latex modified bitumen emulsion. In contrast, at least 6 ~ 7 wt% of solid polymers are needed in the PMB to form such polymer-rich continuous phase (Lesueur, 2009). SBR latex is the most popular latexes used to modify bitumen emulsion at present. In addition, water-borne epoxy resin has attracted increasing interest in recent years. Due

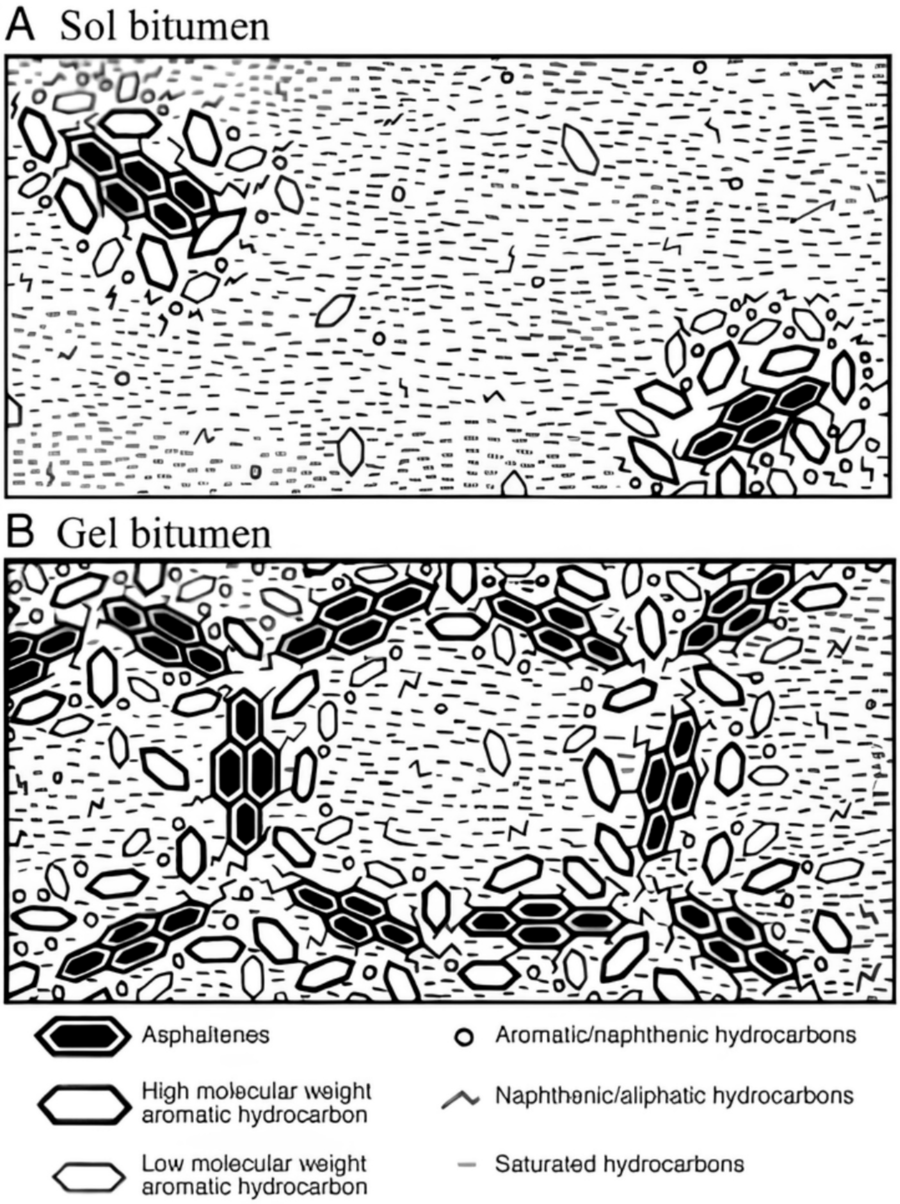


Fig. 2. Colloid structure of bitumen: sol and gel bitumen (J. Read, 2015).

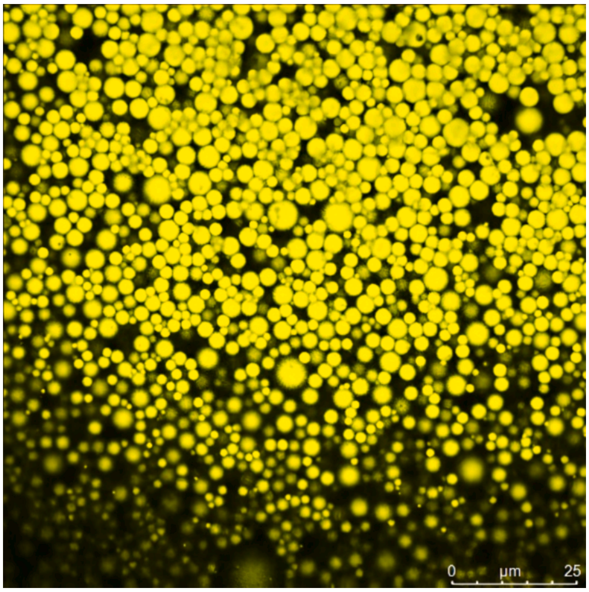


Fig. 3. Florescence microscopy image of bitumen emulsion (Li, 2021).

to length limitation, only these two polymer latexes are discussed detailly in this review paper.

2.2.3. SBR modified bitumen emulsion

(1) Properties of SBR latex

SBR is a random copolymer of styrene and butadiene, and SBR-latex is dispersions of evenly distributed micro SBR polymer particles in an aqueous solution. The basic properties of a typical SBR latex are shown in Table 2. Previous research has shown that SBR latex can effectively improve the high temperature performance, low temperature ductility, resistance to fatigue, adhesive ability of the emulsion residue (Khadivar and Kavussi, 2013, Mohammadi and Modarres, 2022).

(2) Microstructure of SBR modified bitumen emulsion

Takamura and Heckmann (1999) investigated detailly about the microstructure of SBR modified bitumen emulsion. As shown in Fig. 6, the SBR modified bitumen emulsion residue was treated with OsO, then the bitumen was extracted with MEK (methyl ethyl ketone). The treatment with OsO makes SBR polymer insoluble to the organic solvent and also improves the contrast for the scanning electron microscope observation. After removing of the asphalt by solvent, a honeycomb-like structure of the SBR polymer was then observed with a scanning electron microscope. Takamura (2002) further found that the SBR latex was dispersed in the aqueous phase at the initial stage when mixed with bitumen emulsion, which then formed a continuous polymer network around the bitumen particles upon curing of the emulsion (Fig. 7), and the formed polymer network remained intact even when reheated to “hot mix” temperatures.

(3) Conventional properties of SBR modified bitumen emulsion

The conventional properties of SBR modified bitumen emulsion were evaluated by Khadivar and Kavussi (2013), and the results are presented in Table 3. It can be seen that with the increase of the latex content, the softening point increases while the penetration decreases, indicating that the high-temperature performance was improved. Furthermore, it can be noticed that the ductility of the bitumen emulsion residue increases remarkably from 4.9 cm at 4 °C for the neat bitumen to 28.2 cm for the 5 wt% SBR modified bitumen emulsion residue. In addition, the penetration index also increased with larger content of SBR, indicating a decreased temperature susceptibility was achieved. Therefore, it can be inferred that SBR has significant positive effect on both the high and low temperature performance of emulsion residue.

(4) Adhesion between SBR modified bitumen emulsion and aggregate

Adhesion between bitumen emulsion and aggregate is rather important for its application. Abedini et al. (2017b) used Vialit test to

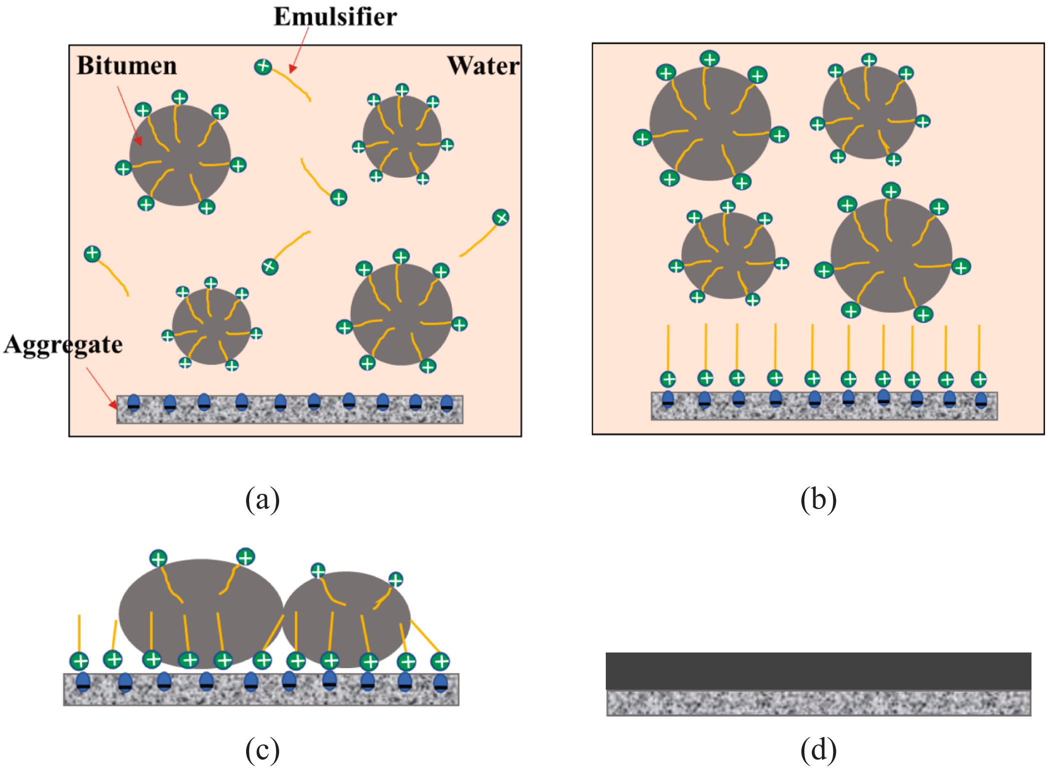


Fig. 4. Possible stages in the setting process of a cationic emulsion: (a) contact of emulsion with aggregate, (b) emulsifiers absorb on aggregate, (c) droplet coalescence, and (d) bitumen film formation (modified from (James, 2006b)).

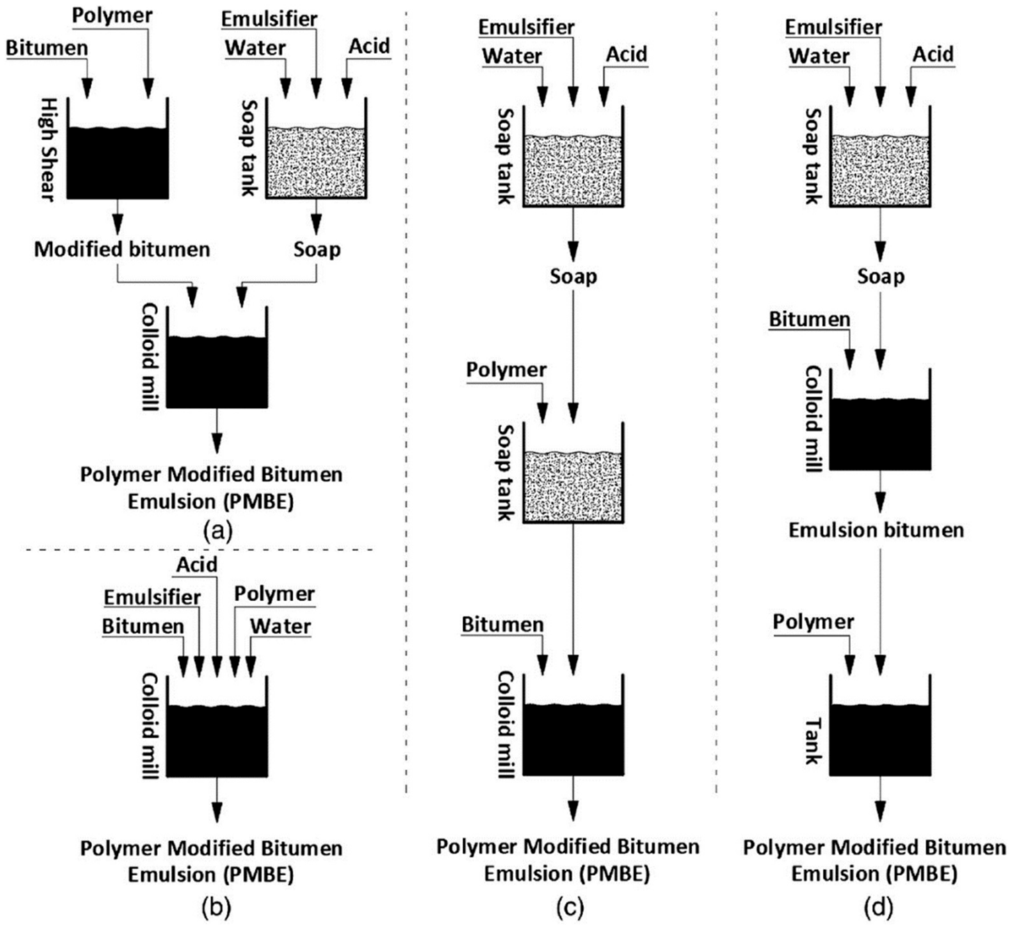


Fig. 5. Schematic of polymer bitumen emulsion production methods: (a) preblending; (b) comilling; (c) soap prebatching; and (d) postblending (Mohammadi and Modarres, 2022).

Table 1
Studies about polymer latex modified bitumen emulsion.

Polymer latex	Effects	References
SBR	Improved softening point and ductility, reduced penetration and temperature sensitivity, formation of polymer networking was achieved.	(Abedini et al., 2016), (Abedini et al., 2020), (Khadivar and Kavussi, 2013), (Ziari et al., 2022),(Ren et al., 2022)
NR	Increased softening point, decreased penetration and temperature sensitivity, no contribution on low temperature ductility.	(Abedini et al., 2017a), (Khadivar and Kavussi, 2013)
SBS	Increased softening point, ductility, and fatigue life, reduced penetration and temperature sensitivity.	(Cai et al., 2010), (He et al., 2020), (Wang et al., 2023a)
SIS	Increased softening point and ductility.	(Xia and Luo, 2017b)
Epoxy resin	Increased high temperature performance, adhesion with aggregate, fatigue performance, reduced low temperature performance.	(Li et al., 2019b), (Hu et al., 2019), (Wang et al., 2021a), (Fu et al., 2022), (Han et al., 2020)
Polyurethane	Increased softening point, reduced penetration.	(Shirkavand Hadavand et al., 2020), (Xu et al., 2021b)

evaluate the adhesion between SBR modified bitumen emulsion and aggregate, and the results are presented in Fig. 8. It can be seen that the addition of SBR into bitumen emulsion increased the adhesion with aggregate effectively, especially at lower temperatures. The aggregate loss rate for the 2 wt% SBR modified bitumen emulsion was only 27 % at −15 °C, which is less than half of that for the control emulsion. The difference of the aggregate loss rate declines as the temperature grows. Such finding is supported by the study of Pan et al. (2019), which indicates that the bonding strength between SBR modified bitumen emulsion and aggregate decreases with the increase of temperature. The reason may be that SBR networks softens at higher temperatures, and thus its reinforcing ability weakens. Furthermore, the increase of the bonding strength diminishes when the SBR concentration reached beyond 4 wt%, which indicates that after the formation of the SBR networks within the emulsion residue, the marginal gain of the bonding strength is minimum with further increasing of the polymer.

Table 2
Basic properties of a typical SBR latex.

Property	Value
State	Milky white liquid
Solid content	48.5 %
Mean particle size	0.15 μm
Density	1.01 g/cm^3
Viscosity	30 mPa·s
pH Value	7.5
Glass transition temperature (Tg)	−7 °C

(5) Rheological properties

Khadivar and Kavussi (2013) investigated the rheological properties of the bitumen emulsion residues containing different contents of SBR. Fig. 9 demonstrates the complex moduli and phase angle of SBR

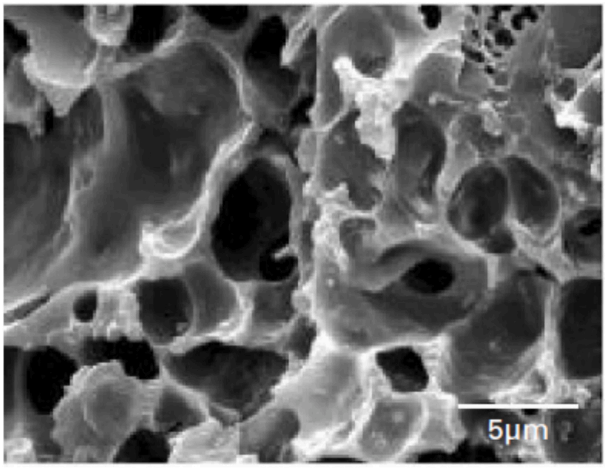


Fig. 6. Scanning electron microscope image of latex polymer structure (Takamura and Heckmann, 1999).

modified bitumen emulsion residues. It is clear that the complex moduli increased with larger content of latex modification, which is in line with the softening point increasing trend in Table 3. On the other hand, the phase angle of the emulsion residues shows a decreasing trend with larger content of SBR latexes. Indicating the elasticity of the emulsion residues was improved by the incorporation of SBR latex.

The creep recovery behavior of the emulsion residues was further evaluated using the multiple stress creep and recovery (MSCR) test in the study of Khadivar and Kavussi (2013). Fig. 10 demonstrates the percent recovery of SBR and NR modified bitumen emulsion residues at different temperatures, and Fig. 11 shows the non-recoverable creep compliance. Clearly, the percent recovery increased with larger SBR contents at both stress levels (0.1 kPa and 3.2 kPa), while the non-recoverable compliance decreased. Similar findings were also reported by (Abedini et al., 2017b). Lower creep compliance indicates improved resistance to rutting. Thus, it can be inferred that the incorporation of SBR demonstrates positive effect on the high temperature performance of the emulsion residue.

(6) Fatigue performance

The fatigue performance of SBR modified bitumen emulsion residues was investigated in a study by Carpani et al. (2021) using the linear amplitude sweep (LAS) test. Three different emulsion residues were compared, i.e., unmodified bitumen emulsion, SBR latex modified bitumen emulsion (post-blending), and SBS modified bitumen emulsion (pre-blending), denoted as EB, LMEB and EPMB. The shear stress measured as a function of shear strain is shown in Fig. 12. It can be seen that that the stress reaches the peak rapidly with increasing strain for EB, which then declines sharply. On the other hand, the stress for LMEB and EPMB only decreases gradually after reaching the peak. Such results indicate that the structure of conventional bitumen emulsion was damaged and failure occurs following the peak stress, while the polymer modified bitumen emulsion residues (LMEB and EPMB) can still withstand the test stress. The fatigue life was then calculated based on the viscoelastic continuum damage (VECD) model, and the results are presented in Fig. 12 (b). It is clear to see that the fatigue life for the polymer modified bitumen emulsion residues increased significantly compared with conventional EB at both strain levels (2.5 % and 5.0 %). The results demonstrate that the fatigue life of bitumen emulsion can be improved dramatically by the incorporation of polymers like SBR latex.

In summary, with the addition of SBR latex into bitumen emulsion, the SBR polymer networks can be formed in the emulsion residue, and the overall performance of bitumen emulsion can be improved, including high- and low-temperature performance, reduced temperature susceptibility, ductility, adhesion with aggregate, and resistance to fatigue damage.

2.2.4. *Waterborne epoxy resin modified bitumen emulsion*

(1) Properties of waterborne epoxy resin

The incorporation of waterborne epoxy resin (WER) into bitumen emulsion is a relatively new approach to modify bitumen emulsion. Waterborne epoxy resin is an epoxy in water emulsion, within which the epoxy resin is stabilized by surfactant. There are two components in waterborne epoxy resin, i.e., epoxy resin and curing agent, which are mixed together before application. The basic properties of typical waterborne epoxy resin and curing agent are shown in Table 4 and Table 5 (Liu et al., 2021a).

Table 3
Effect of SBR contents on the properties of bitumen emulsion residues (Khadivar and Kavussi, 2013).

Test item	Neat bitumen	SBR content (wt%)		
		3	4	5
Softening point (°C)	51.1	56.6	62.2	71.2
Penetration at 25 °C (0.1 mm)	65	59	57.5	57
Ductility at 4 °C (cm)	4.9	10.5	17.5	28.2
Penetration index	−0.286	0.75	1.83	3.38

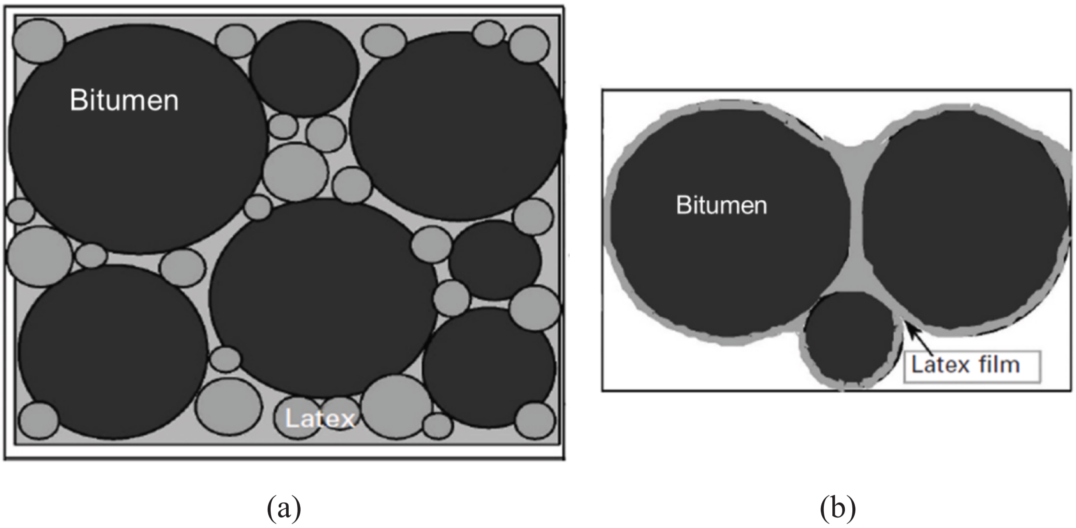


Fig. 7. Schematic diagrams of (a) latex-modified bitumen emulsion and (b) continuous latex polymer phase after breaking (Takamura, 2002).

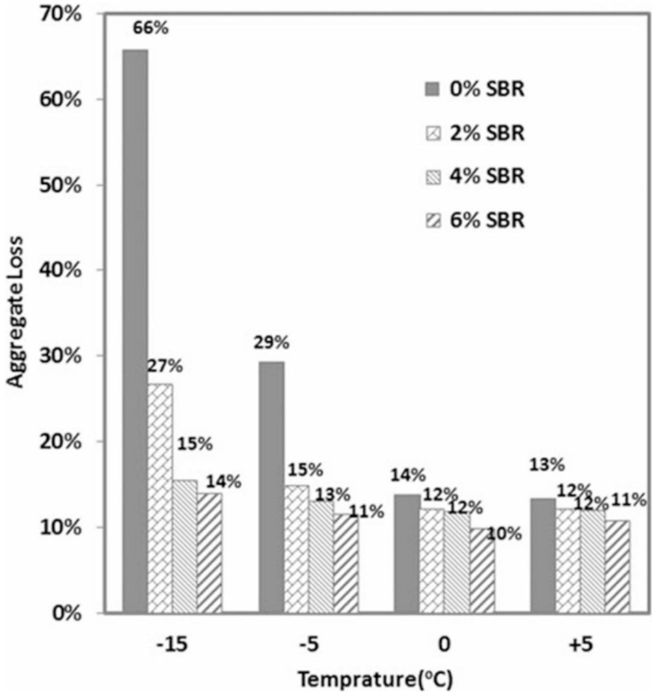


Fig. 8. Effect of SBR latex on the bitumen-aggregate adhesion at low temperatures (Abedini et al., 2017b).

(2) Microstructure of WER modified bitumen emulsion

The WER modified bitumen emulsion can be prepared by mixing WER with bitumen emulsion, in which the epoxy resin disperses in the aqueous phase. As water evaporates, the epoxy resin droplets coalesce, which initiates the curing reaction, resulting with the inter-connected polymer structure. Li et al. (2019b) synthesized a waterborne curing agent in laboratory, which can act as an emulsifier and a curing agent for epoxy resin at the same time. The WER prepared was then used to modify bitumen emulsion. The micro structures of the modified bitumen emulsion residues were first characterized (Fig. 13). Fig. 13 shows the confocal laser scanning microscopy (CLSM) images of waterborne epoxy resin modified bitumen emulsion residues (WEBER) with different concentrations of waterborne epoxy resin. In which, WEBER-0, WEBER-1, WEBER-3 and WEBER-5 represent the emulsion residues with 0 wt%, 1 wt%, 3 wt%, and 5 wt% of WER. It can be seen that when the concentration of WER reached 3 wt%, an interconnected polymer structure was formed in the residue. Another study by Gu et al. (2019) revealed that the WER forms an interconnected skeleton structure in the emulsion residue after curing. Fig. 14 demonstrates the microstructure of the WER modified bitumen emulsion residues, in which the bitumen phase has been removed using the "dissolving-evaporating" technique, and the remaining epoxy resin skeleton structure was shown.

(3) Conventional properties of WER modified bitumen emulsion

The conventional properties of softening point, ductility, and penetration of emulsion residues as a function of the WER content is shown in Fig. 15. It can be seen that the softening point increases with increasing WER content, while the penetration decreased, indicating that the high temperature performance of bitumen emulsion residue was improved by

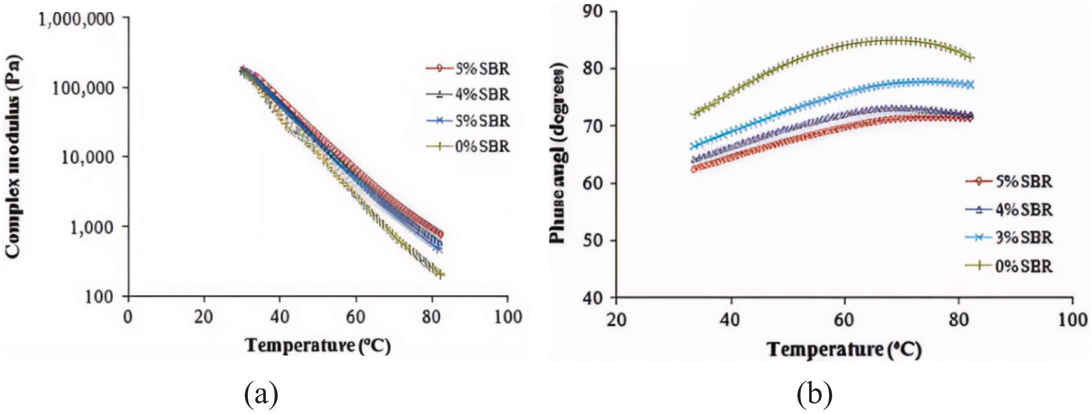


Fig. 9. Complex moduli (a) and phase angle (b) of SBR modified bitumen emulsion residue (Khadivar and Kavussi, 2013).

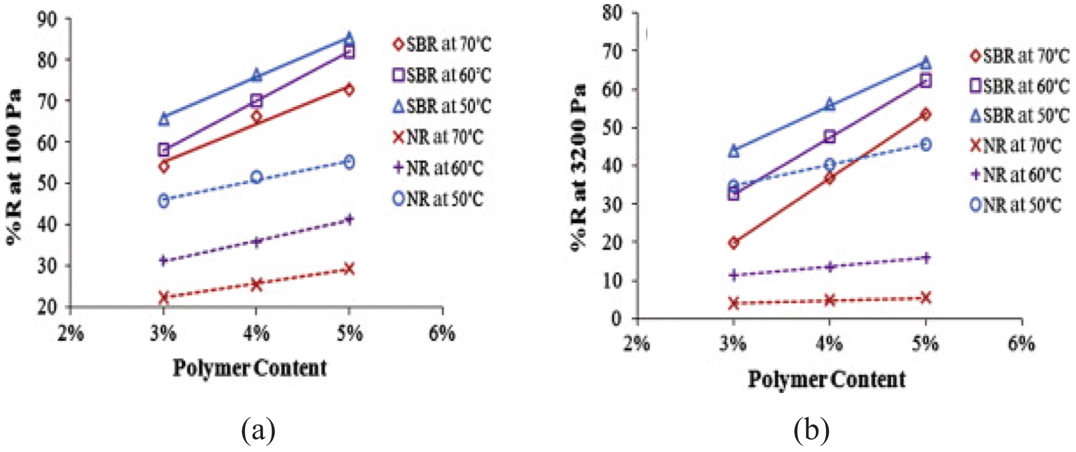
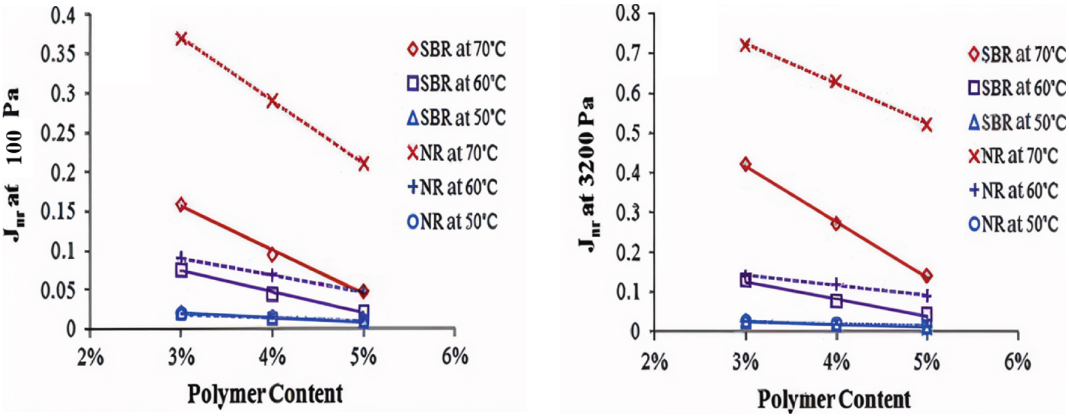
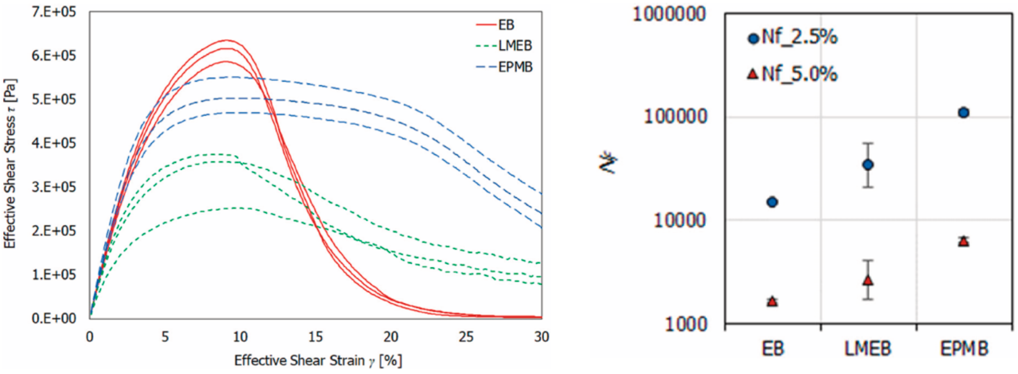


Fig. 10. Percent recovery of bitumen emulsion residues at (a) 0.1 kPa and (b) 3.2 kPa.



(a) (b)

Fig. 11. Non-recoverable creep compliance (J_{nr}) of emulsion residues at (a) 0.1 kPa and (b) 3.2 kPa.



(a) (b)

Fig. 12. LAS test and fatigue life, (a) stress vs strain curves and (b) fatigue life prediction (Carpani et al., 2021).

Table 4
Basic properties of waterborne epoxy resin.

Item	Appearance	Solid content/wt%	Density/ g·cm^{-3}	PH	Epoxy value/ mol/100 g
WER	Milky white liquid	56 ± 2	1.07 ± 0.03	6–8	0.221

Table 5
Basic properties of curing agent.

Item	Appearance	Solid content/ wt%	Density/ g·cm^{-3}	PH	Active hydrogen equivalent/ g·mol^{-1}
Curing agent	Light yellow liquid	58 ± 2	1.07 ± 0.03	7	242

WER. On the other hand, the low temperature ductility shows a decreasing trend for larger content of WER, which demonstrates that the low temperature performance was negatively affected by incorporation of WER. Epoxy resin is a thermosetting rigid material, and its flexibility and elongation ability are poor. As shown in Fig. 14, the WER forms the skeleton structure in the emulsion residue after curing. Thus, the addition of WER leads to increase of softening point and decrease of ductility.

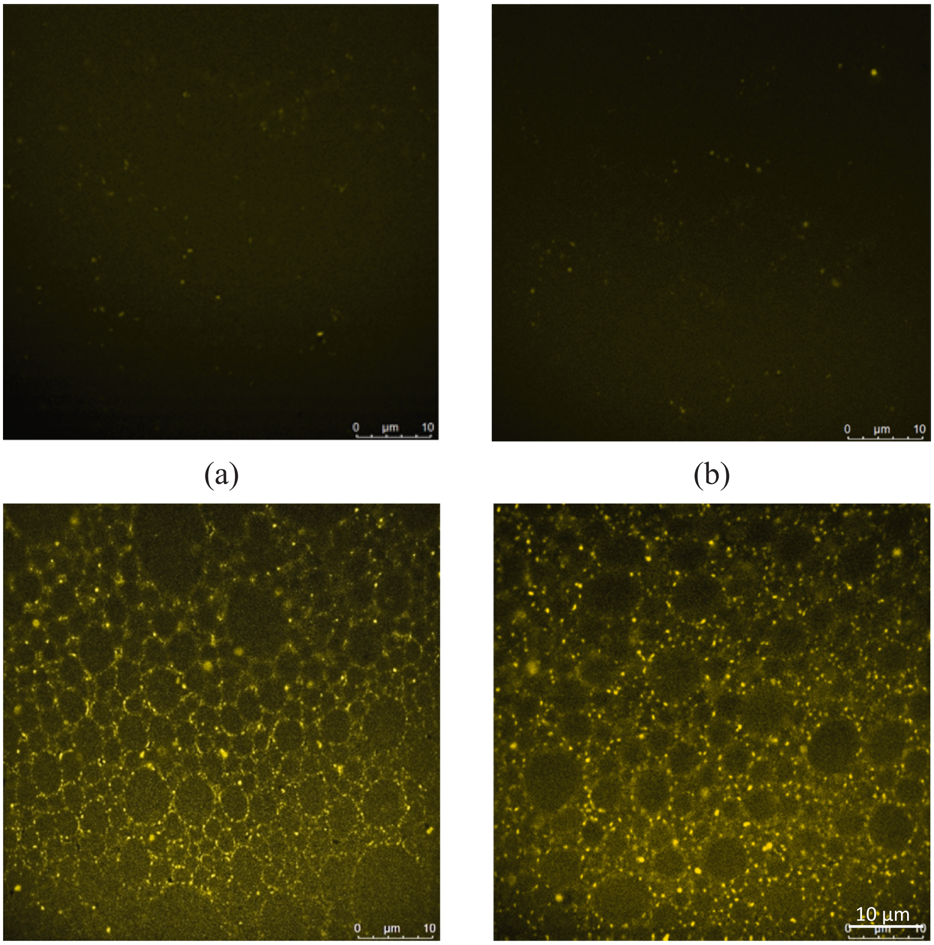
(4) Adhesion between WER modified bitumen emulsion and aggregate

The bond strength between WER modified bitumen emulsion with aggregate was evaluated by Li (2021) using binder bonding strength test (Fig. 16). It clearly demonstrates that the bond strength with aggregate increases with larger content of WER, which reached more than 3.0 MPa for WEBER-5 (5 wt% of WER). Furthermore, it is noticed that the bond strength decreased with growing temperature. The bond strength tested at 50 °C dropped more than 50 % in comparison with the 23 °C group.

The adhesion of WER modified bitumen emulsion with aggregate was further measured by the boiling water text. The prepared emulsion aggregate mixtures were conditioned at ambient room temperature for 24 h before the boiling water test. The images obtained after the boiling water test are shown in Fig. 17. The control mixture (0 wt% WER) had the largest boiling loss area (the bitumen removed area), and the boiling loss area decreases as the increase of the content of WER. No apparent stripping was observed when the WER content reached 3 wt% or above. From the boiling test results, it can be inferred that waterborne epoxy can significantly improve the adhesion between bitumen emulsion and aggregate. The cross-linked epoxy networks strengthened the bonding between the bitumen emulsion and aggregate in the curing process.

(5) Rheological properties

The rheological properties of WER modified bitumen emulsion were analysed and the master curves of complex moduli |G*| and phase angle were constructed in the study by Li et al. (2022) (Fig. 18). It is clear that the complex moduli |G*| increases and the phase angle decreases with larger content of WER especially at lower frequency, indicating an increased stiffness and elasticity of the modified emulsion residues with the incorporation of WER.



(a) (b) (c) (d)

Fig. 13. CLSM images of WEBERs (a) WEBER-0, (b) WEBER-1, (c) WEBER-3, and (d) WEBER-5 (Li et al., 2022).

The MSCR test was adopted to evaluate the high temperature performance of WEBERs. Fig. 19 shows the percent recovery of WEBERs, which demonstrates that the recovery ability increased dramatically for the emulsion residues with the incorporation of WER. The average percent recovery increased to more than 90 % when the content of WER reached 3 wt% at the stress level of 0.1 kPa. In addition, the non-recoverable compliance shows a decreasing trend with larger content of WER, indicating that the high temperature performance of the emulsion residues was improved substantially by WER (Fig. 20). Such results are supported by the microscopy structures of WEBERs in Fig. 13.

(6) Fatigue performance

The fatigue performance of the emulsion residues with different contents of WER was compared with the LAS test. Fig. 21 shows the relationships between the shear stress and shear strain for different binders. It can be seen that the shear stresses first increased with the shear strains and then declined progressively at higher strain levels. In addition, the peak stress increases with larger content of WER. It is also interesting to note that the stress decreasing rates varies significantly with different content of WER. With the increase of the WER content, the post-peak stress decreases at lower rates. Such outcome indicates the emulsion residues with WER can withstand higher level of stress before failure, and the epoxy resin skeleton improved the resilience of the emulsion residues.

Table 6 presents the predicted fatigue lives (N_f) at the strain levels of 2.5 % and 5.0 % based on the VECD model. The results indicate that with the increase of WER, the predicted fatigue life increased, especially at the lower strain of 2.5 %, while the difference of fatigue life diminishes with the larger strain of 5.0 %. As shown in Fig. 13, WER forms interconnected polymer structure in the emulsion residue. The polymer structure contributed to the fatigue life improvement at the lower strain of 2.5 %. However, due to the low flexibility and deformability of the networks, no significant improvement of fatigue life was observed at the strain of 5.0 %.

In summary, the incorporation of WER in bitumen emulsion leads to positive effects on the performance of bitumen emulsion, such as increased high-temperature performance, better adhesion with aggregate, improved resistance to fatigue damage. However, due to rigidity of epoxy resin, the ductility of WER modified emulsion residue was decreased.

2.2.5. *Other polymer latexes modified bitumen emulsion*

Other polymer latexes, including SBS, SIS, and polyurethane, were less investigated and used. He et al. (2020b) studied the effect of SBS latex on the properties of bitumen emulsion. The results indicated that the softening point increases substantially with larger SBS content, which reached 77.4 °C at a 6.0 wt% SBS latex concentration. The ductility at 5 °C also shows a growing trend with increasing SBS latex content. Thus, the incorporation of SBS latex can both improve the high and low temperature performance of the emulsion residues. Xia and Luo (2017a) synthesized a SIS latex, which was then used to modify bitumen emulsion. Their results showed that with an incorporation of 5 wt% of SIS latex, the emulsion residue showed a significant increase in complex modulus at high temperature and a significant decrease in loss tangent, and the ductility at 5 °C also increased to some degree. Shirkavand

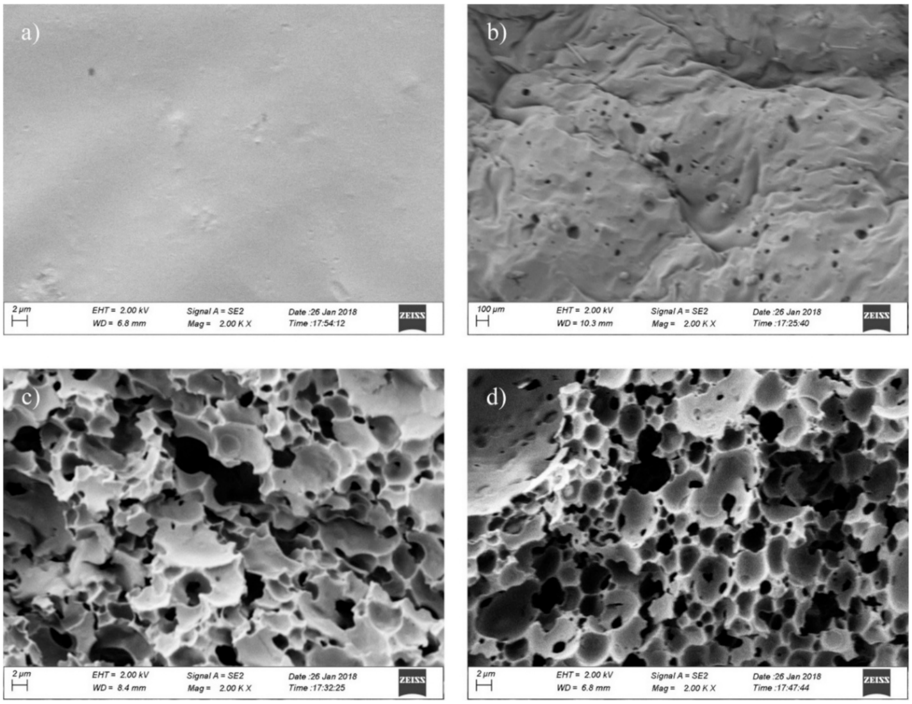


Fig. 14. Variation of skeleton structure of cured emulsion residues after "dissolving-evaporating" process with increasing contents of WER: a) 0 wt% of WER; b) 10 wt% of WER; c) 20 wt% of WER; d) 30 wt% of WER (Gu et al., 2019).

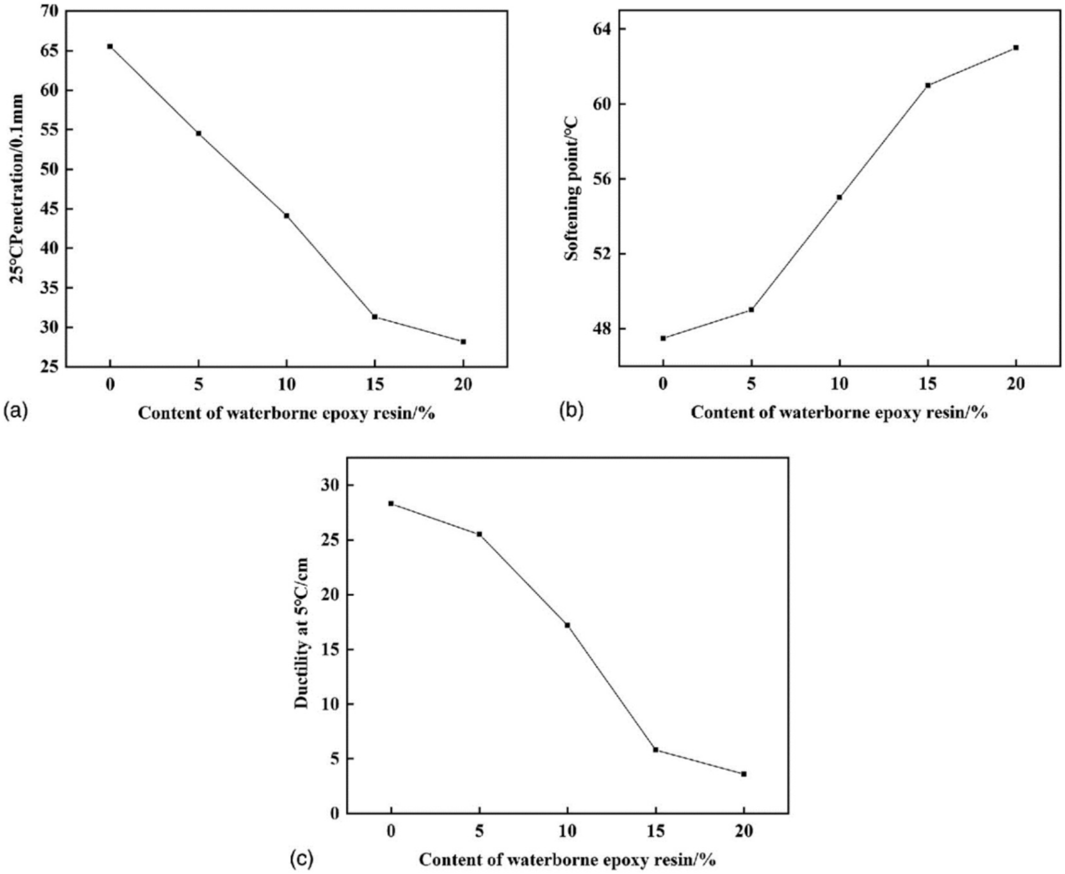


Fig. 15. Effect of WER on conventional properties of emulsified asphalt: (a) penetration; (b) softening point; and (c) ductility at 5 °C. (He et al., 2023).

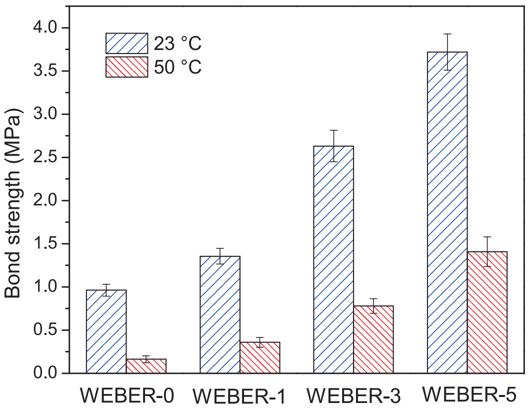


Fig. 16. Bond strength of different WEBERs (Li, 2021).

Hadavand et al. (2020) demonstrated that both the softening point and ductility of bitumen emulsion can be improved by polyurethane latex, while the penetration was decreased.

These studies indicated that the polymer latexes can be dispersed in the aqueous phase of bitumen emulsion, and a continuous polymer-rich network will be formed at a relatively small content of polymer latexes. Such continuous polymer-rich structure provides the residual binders with improved performances, such as increased stiffness, increased adhesion, decreased temperature sensitivity, improved fatigue life, and enhanced elastic recovery.

2.3. Application of bitumen emulsion in pavement

Conventionally, bitumen emulsion was used in non-structural layers or low-traffic roads due to their weak strength, such as tack coat, surface treating, cold recycling or cold mixes (Khadivar and Kavussi, 2013, Takamura and James, 2015).

(1) Tack coat

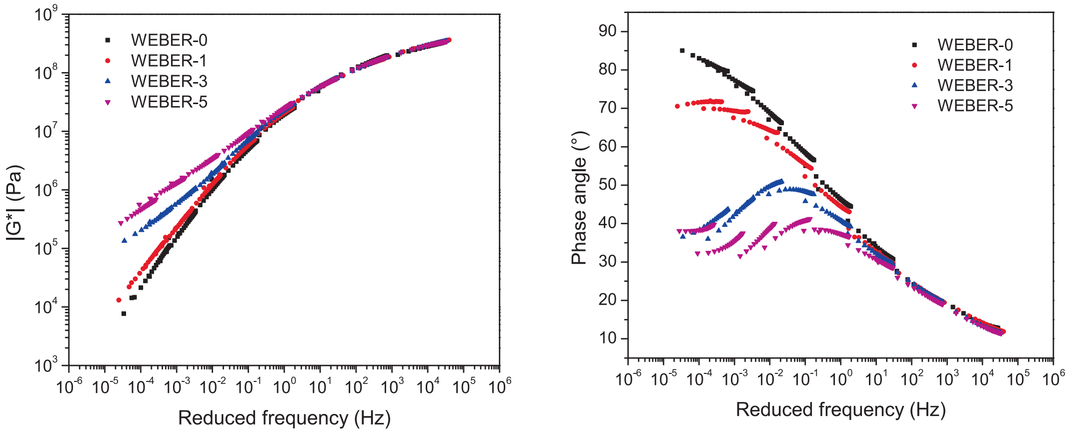
Weak interlayer bonding of different pavement layers usually leads to distresses like slippage (Zhang, 2017), especially at areas of frequent braking and accelerating (Hachiya et al., 1997). Tack coat is generally used to enhance the interlayer bonding of different pavement layers (Raposeiras et al., 2013). A survey conducted by Mohammad et al. (2008) shows that bitumen emulsion is the most commonly used material for tack coat. Collop et al. (2011) found that bitumen emulsion can generally improve the shear strength of different pavement layers. Diakhaté et al. (2011) compared the bonding fatigue performance of two asphalt concrete layers with and without tack coat, and the result indicated that bitumen emulsion tack coat increased the fatigue performance substantially. From these studies, it is concluded that the interlayer bonding strength of different pavement layers is rather important to reduce premature distresses, and bitumen emulsion plays a crucial role in improving the interlayer bonding.

(2) Surface treatment

Due to the impact of weathering and repeated vehicle loadings (Cuadri et al., 2016), many different kinds of premature distresses will occur on asphalt pavements during their service life. These distresses, like rutting, cracking, and loss of friction, must be treated in time to prevent further deterioration. To preserve pavement quality and functional performance, maintenance is necessary (Wang and Wang, 2013). Previous research has found that maintenance could minimize the development of distresses, leading to an extended service life, reduced life cycle cost (Gong et al., 2015, Broughton et al., 2012), and lower environmental impact (Pellecuer et al., 2014). Chip seal, slurry seal, fog seal, micro-surfacing and etc. have been proven to be effective

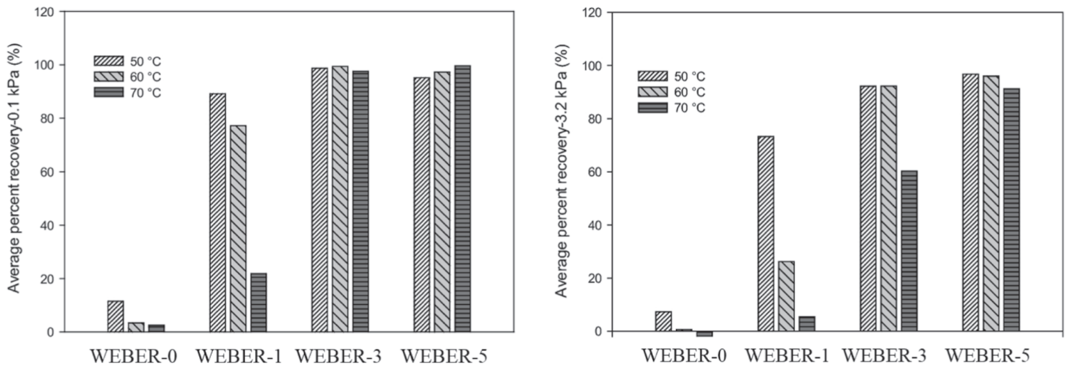
0 wt% WER 1 wt% WER 3 wt% WER 5 wt% WER

Fig. 17. Images of WER modified bitumen emulsion mixture after boiling (Li et al., 2019b).



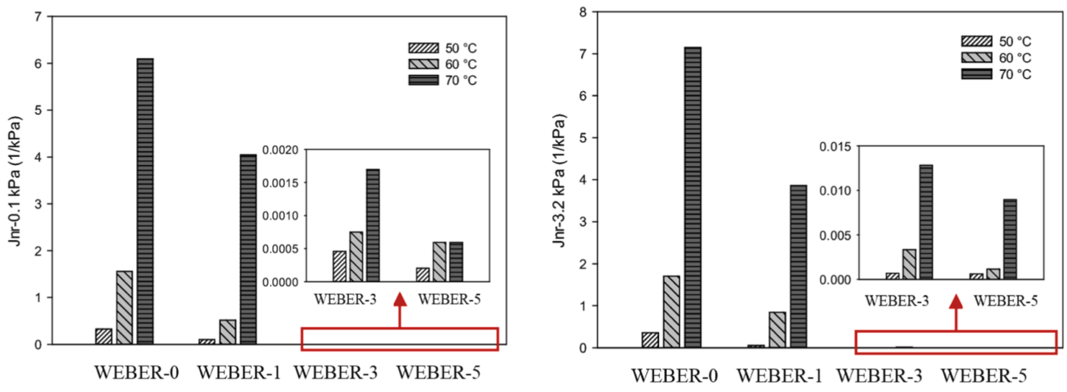
(a) (b)

Fig. 18. Master curves of WER modified bitumen emulsion: (a) complex moduli and (b) phase angles at the reference temperature of 10 °C (Li et al., 2022).



(a) (b)

Fig. 19. Percent recovery of WEBERs at (a) 0.1 kPa, (b) 3.2 kPa (Li et al., 2019b).



(a) (b)

Fig. 20. Non-recoverable creep compliance (J_{nr}) of MSCR test (a)0.1 kPa, (b)3.2 kPa (Li et al., 2019b).

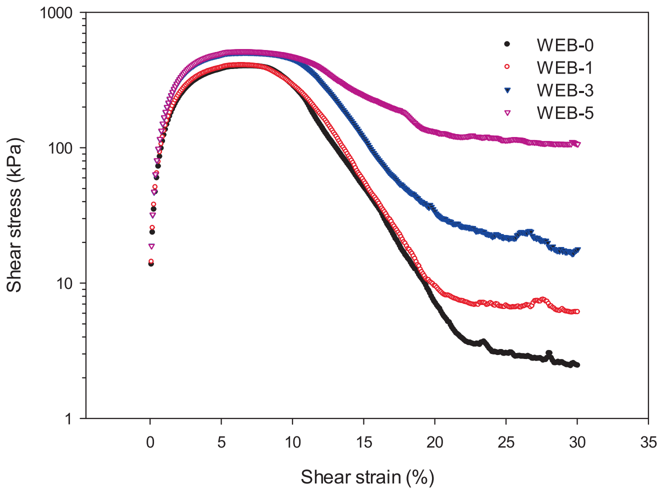


Fig. 21. Stress–strain curves of different bitumen binders (Li et al., 2019b).

Table 6
Fatigue life prediction based on VECD model.

Binder type	N_f (2.5 %)	N_f (5.0 %)
WEBER-0	6,516	676
WEBER-1	7,162	766
WEBER-3	14,067	836
WEBER-5	59,717	1,231

maintenance methods (Mamlouk and Dosa, 2014, Simões et al., 2017). However, it is worth noting that one maintenance method may not be universally applicable for all kinds of distresses. To determine the optimum maintenance method, the pavement conditions and climate must be carefully considered (Simões et al., 2017). Bitumen emulsion is the major type of material used in pavement maintenance for ease of application, environmental benefits, and cost-effectiveness (Giustozzi et al., 2012). Table 7 lists various surface treatment methods for different pavement distresses using (polymer modified) bitumen emulsion.

(3) Cold recycling

Recycling of the reclaimed asphalt pavements (RAP) is becoming increasingly important for the sustainability of pavement industry. The aggregate and asphalt binder in RAP materials are still valuable resources which can partially replace the virgin aggregate and binder (Yang et al., 2015a), no matter it is used in hot recycling (Roja et al., 2021) or cold recycling (Yuliestyan et al., 2018). The recycling of RAP brings various benefits, like reduced energy consumption, less GHG emissions and lower costs (Aurangzeb et al., 2014). Cold recycling can further reduce the environmental footprint in comparison with other rehabilitation techniques as it is conducted at ambient temperature (Aker and Ozer, 2025). Both foamed asphalt and bitumen emulsion have been evaluated in cold recycling to bond RAP materials (Kim et al., 2011, Algraiti and Kavussi, 2023). However, bitumen emulsion can be more successfully applied than foamed asphalt especially in wet conditions (Mills-Beale and You, 2010). One concern of cold recycling of

Table 7
Comparison between different surface treatment methods for pavement (Wang and Wang, 2013).

Distress	Treatments					
	Crack seal	Fog seal	Slurry seal	Cape seal	Chip seal	Micro-surfacing
Roughness (not associated with stability)				✓		✓
Rutting						✓
Fatigue cracking (low severity)		✓	✓	✓	✓	✓
Longitudinal and transverse cracking	✓		✓	✓	✓	✓
Asphalt binder exudation					✓	✓
Ravelling	✓	✓	✓	✓	✓	✓

RAP lies in the slow strength development at early age. Li et al. (2024) found that the early strength of cold recycling RAP materials depends strongly on the moisture evaporation, which generally takes 28 days or more to be stabilized. To improve the performance of cold recycled materials, Chen et al. (2025a) has explored the possibility of waterborne epoxy resin modified bitumen emulsion as the binder for RAP, which indicates that the inclusion of waterborne epoxy resin significantly improved the high- and low-temperature performances, and resistance to moisture damage.

(4) Cold mixing

Bitumen emulsion cold-mix asphalt (CMA) is considered as an eco-friendly paving material due to its low environment impacts. It is reported that HMA consumes 275MJ/t of energy during production, while CMA consumes only 14 MJ/t, representing a 95 % reduction of energy consumption in the production phase for CMA compared with HMA (J. Chehovits, 2010). Until now, the application of CMA is mostly limited to pavement maintenance works and low-volume roads (Liu et al., 2024), primarily due to the low early strength, high air voids and insufficient resistance to cracking. It is found by previous research that the presence of water negatively affects the adhesive and cohesive properties of CMA, which resulting the aforementioned limitations (Fang et al., 2016). To improve the performance of CMA, use of active fillers such as cement, lime, fly ash, and ground granulated blast furnace slag, have been investigated (Prasad et al., 2024). The chemical hydration of these active fillers can consume part of the water and accelerate the bitumen emulsion breaking (Fang et al., 2016), leading to rapid strength development of CMA. A 1 ~ 3 wt% incorporation of cement increases the mechanical performance of CMA to a level comparable or larger than normal dense-graded HMA (García et al., 2013). Due to the application of theses additives, CMA has been further used in middle and lower layers of highways, e.g., pavement base and subbase (Liu et al., 2024). Similar with bitumen emulsion cold recycling, the early strength of CMA increases with curing time. Li et al. (2020) found that the Marshall stability, indirect tensile strength (ITS) and indirect tensile stiffness modulus (ITSM) grow rapidly in the first 7 days, which then increase slowly until day 28 (Fig. 22). In addition, cement plays a significant role in improving the early strength of CMA.

2.4. Benefits and drawbacks

Since bitumen emulsions are used at ambient temperatures, the mixing and construction process will not produce volatile hazardous emissions. This is environment friendly, energy effective and poses no harm to field workers. Besides, bitumen emulsions can be manufactured in advance and stored in containers, which are readily available when in need. Though the mechanical performance of pure bitumen emulsion is

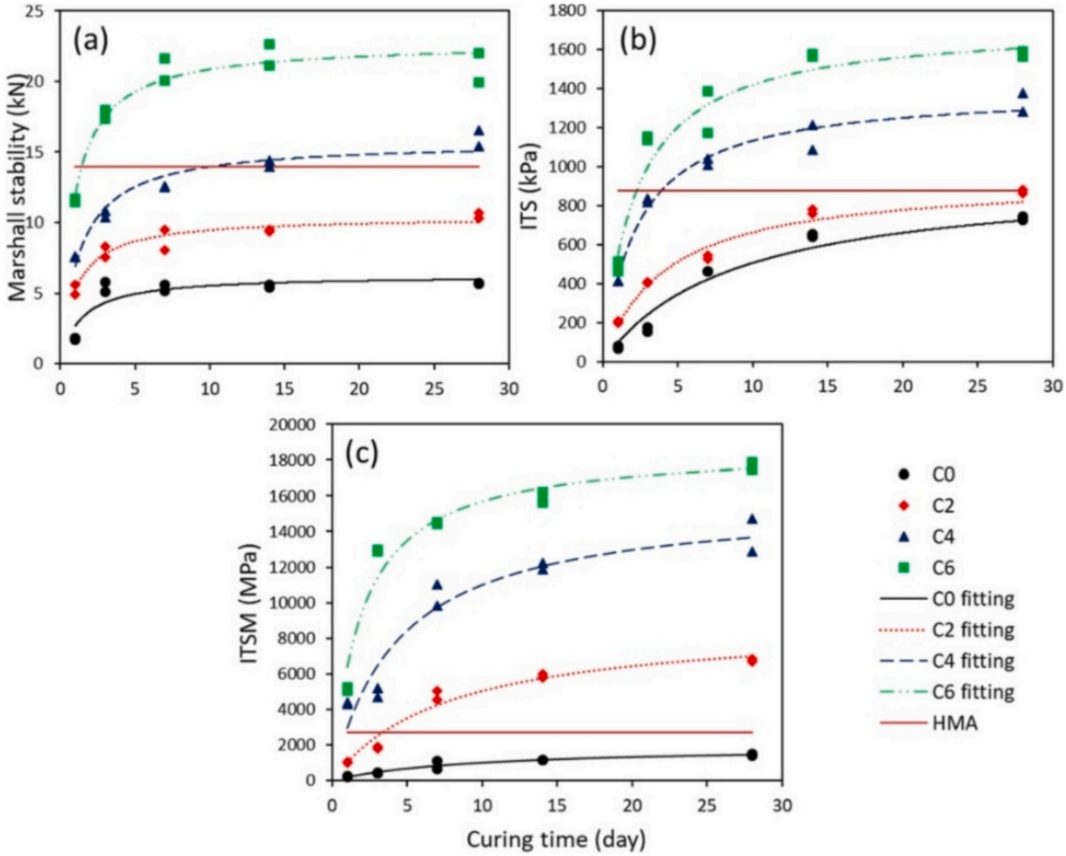


Fig. 22. Development of CMA mechanical performance with different amounts of cement: (a) Marshall stability, (b) ITS and (c) ITSM (Li et al., 2020).

low, addition of polymers or polymer latexes can significantly improve its overall performance. Furthermore, bitumen emulsions can be used in certain conditions when it is difficulty for HMA, such as in cold or moist weather.

Bitumen emulsions, however, also possess some drawbacks. As bitumen emulsions are quite vulnerable, they tend to destabilize after manufacturing, e.g., droplets sedimentation, flocculation and coalescence (Ronald and Luis, 2016). Therefore, bitumen emulsions must be handled appropriately, otherwise failure may occur during or after construction (Boucard et al., 2015, Ronald and Luis, 2016). Another defect of bitumen emulsions lies in the weak early strength and insufficient mechanical properties, thus their applications in structural layers are strictly limited (Al Nageim et al., 2012).

3. Epoxy resin based cold mix binder

Conventionally, cement and asphalt are used as the main construction materials of roads and runways for their many desirable properties. However, they also pose some deficiencies. Cement concrete is deemed to be insufficient regarding tensile and flexural strength, and high drying shrinkage (Toufigh et al., 2016). On the other hand, asphalt is sensitive to temperature variations and must be heated to high-temperatures for good workability. As a result, alternative materials such as polymer concrete (PC) have been explored as potential substitutes for pavement construction. PC is a concrete in which aggregates are bonded by polymer materials (Reis et al., 2003). Considerable research on the use of PC has been conducted, which demonstrates a wide variety of excellent properties in construction industry. The advantages of PC are represented by fast curing, low curing shrinkage, outstanding mechanical strength, strong adhesion properties, chemical resistance and good durability (Zhang et al., 2015, Toufigh et al., 2016). Due to its relatively high cost and unique properties, PC is mostly used for repair, adhesion and surface-treating purpose (Saribiyik et al., 2013). As PC is generally mixed without heating, from this respect of view, the polymers (mainly thermosetting polymers (Dębska and Lichołai, 2016)) that bond aggregates can also be viewed as cold binders.

Epoxy resin is one of the most important thermosetting polymers. It becomes amorphous and highly-crosslinked after curing reaction with hardeners. This structure results in many useful properties, such as high strength, high adhesive ability and low creep (Hsieh et al., 2010). Therefore, epoxy resin is widely used as adhesives and matrix for composite materials (Zamanian et al., 2013). In pavement engineering, the application of epoxy resin as the binder of aggregates has been extensively investigated in recent years (Oh et al., 2015). The resulting epoxy resin concrete exhibits extraordinary mechanical and chemical properties (Ferdous et al., 2016).

3.1. Materials and chemical reaction

Epoxy resin is a material that contains two or more epoxy groups (oxiranes) in the molecule structure. The epoxy groups are chemically active and can react with curing agents or hardeners, such as amines, amides, carboxy groups or anhydrides. After curing reaction, a three-dimensional cross-linked polymer structure can be formed. The cured epoxy resin will not dissolve in solvent or fuse at elevated temperature.

The diglycidyl ether of bisphenol-A (DGEBA)-based epoxy resins (E-44 and E-51) are most commonly used in pavement engineering at present (Fig. 23). Epoxy resins can be cured with different types of hardeners to produce products with different mechanical properties (Mustafa et al., 2014). During the curing process, the crosslink density increases and the epoxy-hardener system experiences gelation and vitrification stages, which leads to higher glass transition temperature (Tg) and mechanical properties (Ghaemy et al., 2004). Amines are a group of hardeners capable of reacting with epoxy resins at ambient temperature with relatively fast curing rate, and thus amines are frequently utilized to form composites with epoxy resin. In other words, the epoxy/amine system can be used as cold binder for aggregate.

The crosslink polymerization reaction between epoxy resin and amines involves a series of complicated processes illustrated in Fig. 24. The epoxy resin group first goes through ring-opening process and amino alcohols are formed subsequently (Fig. 24 (a)); the secondary amine then reacts with another epoxy group (Fig. 24 (b)); at the final stage, hydroxyl groups react with epoxy to form a three-dimensional inter-connected structure (Fig. 24 (c)) (Dębska and Lichołai, 2016). It is found that the hydroxyl groups obtained in the first stage can catalyze the curing reaction, which is typically an autocatalytic chemical reaction (Ramírez et al., 2008). Epoxy resin curing reaction is characterized as polyaddition or ion polymerization and will not produce low-molecular weight by-products. This is quite important for the manufacturing of high-performance epoxy end products (Dębska and Lichołai, 2016).

Fig. 25 demonstrates the FTIR spectra of epoxy resin (AL-3040) and polyamide 650 (curing agent) before and after curing. The peak at 909 cm^{-1} ascribes to epoxy group in epoxy resin, and the bands in at 3296 ~ 3347 cm^{-1} correspond to –NH (amine) stretching vibrations. The peaks at 1550 and 1640 cm^{-1} are associated with the bending vibrations of the primary and secondary amines. It can be seen that the epoxy peak almost disappeared in the spectra of the cured epoxy resin (Fig. 25), and the bands ascribe to amine groups weakened substantially. Such phenomenon agrees with the ring-opening crosslink reaction between epoxy resin with curing agent, as shown in Fig. 24.

It is worth noting that the curing of epoxy resin is environment sensitive, i.e., the curing is affected by temperature and moisture, especially low temperature and high humidity. Savvilotidou et al. (2017) conditioned the epoxy resin at 13 °C and 21 °C for up to 350 days, and found that the curing of epoxy resin is significantly delayed at low temperature. The Tg of the 13 °C cured epoxy resin was around

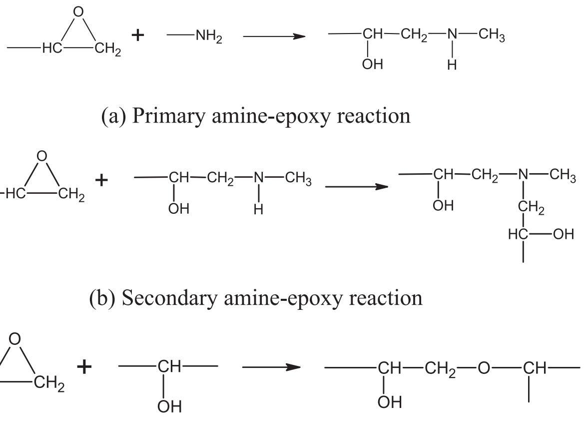


Fig. 24. Curing reaction process of epoxy resin and amine.

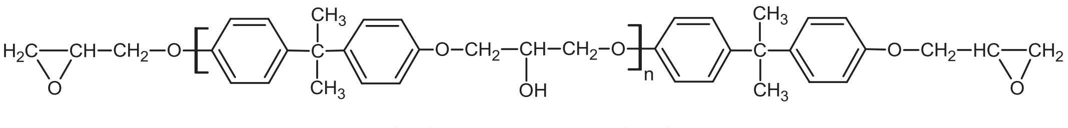


Fig. 23. Molecule structure of DGEBA-based epoxy resin.

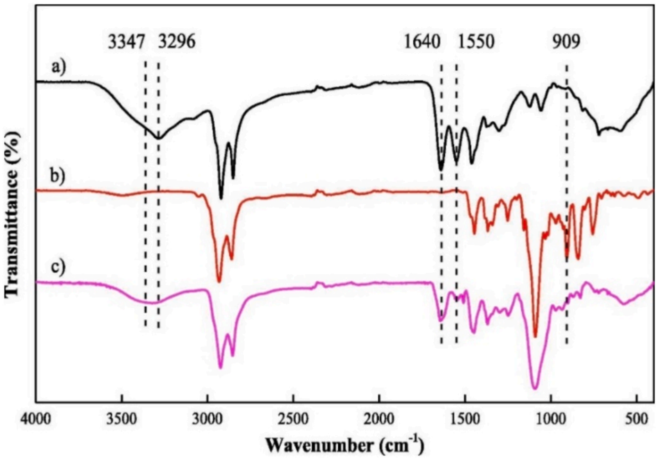


Fig. 25. FTIR spectra of a) Polyamide 650, b) AL-3040, and c) fully cured Epoxy resin (Wang et al., 2021b).

50 °C at the end of the conditioned stage, while the Tg of 21 °C cured group reached about 55 °C, which are lower than the Tg of fully cured epoxy resin (65 °C). Due to the delay of crosslink reaction at low temperature, a full degree of curing can hardly be achieved when epoxy resin is cured at low temperature (Maljaee et al., 2017). Furthermore, Vertuccio et al. (2013) evaluated the moisture effect on curing of epoxy resin. The epoxy resins were conditioned at dry and water immersed environment at 13 °C for up to 433 days in the curing stage. It was found that both the dry and water immersed epoxy resins reached a curing degree of 0.97–0.98. Though the curing degree was not affected by moisture, the Tg and modulus was decreased due to immersion. As the water uptake leads to plasticization of epoxy resin, thus resulting in a reduction of the Tg and modulus (Shi et al., 2014).

3.2. Properties of epoxy resin and mixture

3.2.1. Properties of epoxy resin binder

In the curing process of epoxy resin, its viscosity will increase. The viscosity increasing rate is significantly influenced by temperature. As shown in Fig. 26, the viscosity increases with time after mixing of the two parts, and higher temperature leads to more rapid increasing of the viscosity. The viscosity at the initial stage is closely related to its workability of the resin mixture.

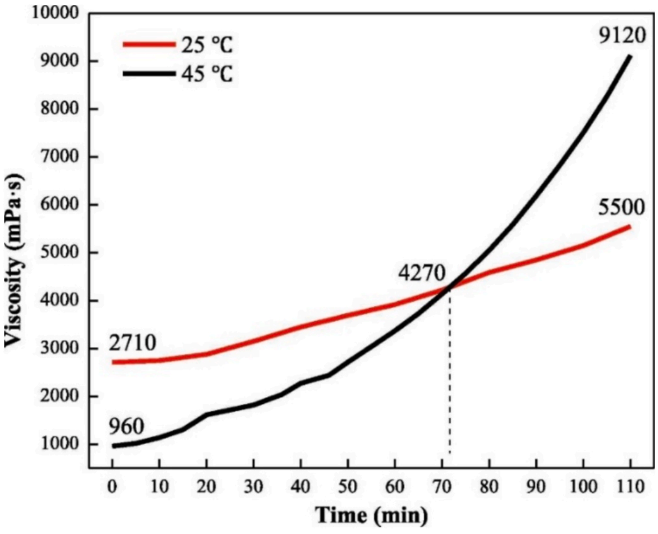


Fig. 26. Viscosity-time curves of typical epoxy binders (Wang et al., 2021b).

The mechanical properties of the cured epoxy resin is significantly affected by the types of hardeners. Wang et al. (2019) compared the mechanical performance of six kinds of epoxy resin cured by different hardeners, i.e., aliphatic amine (AA), polyamide (PA), Alicyclic amine (ALA), aromatic amine (ARA), polyether amine (POA), phenolic aldehyde amine (PAA). The result shows that generally the former three types of hardeners demonstrate superior overall mechanical performance based on tensile and bending test (Fig. 27).

Generally, epoxy resin is characterized as a stiff material, which is prone to cracking. Thus, increasing the toughness is important for the durability of epoxy resin. It can be seen from Fig. 28 that the tensile stress increases almost linearly before reaching the peak, and then a sharp fall was observed, which indicates rigid failure of epoxy resin. To increase the toughness of epoxy resin, Wang et al. (2021b) used a long-chain fatty acids as a toughener, and the tensile test result indicates that with the increase content of toughener, the tensile strength decreases while the elongation at break increases (Fig. 29).

Shi et al. (2024) inspected the fractured surface of epoxy resin with and without toughening agent using scanning electrical microscopy (SEM). It can be seen from Fig. 30 that the fractured surface of epoxy resin without toughening agent is relatively smooth, demonstrating typical brittle failure. On the other hand, the fracture surface of toughened epoxy resin is much rougher. In addition, the cavitation is observed on the surface of the toughened epoxy resin, which can dissipate more energy (Lu et al., 2025). Such difference is directly related to the presence of toughening agent in epoxy resin, which plays a critical role in retarding the crack propagation. Therefore, the toughened epoxy resin exhibits plastic deformation which increased the elongation at break.

The aging resistance of epoxy resin is further investigated by Ma et al. (2022). The cured epoxy resin samples were conditioned in an oven at 60 °C for 168 h, and the tensile test was then conducted. Fig. 31 shows that the mechanical properties of epoxy resin decreased after aging, with the tensile strength and elongation at break dropped to 85.2 % and 76.8 % of the unaged epoxy resin, respectively. Another study by Yang et al. (2015b) conditioned epoxy resin at much harsh conditions, at 130 ~ 160 °C for up to 30 days. The results indicate that the thermal aging at high temperature leads to oxidation in the surface of epoxy resin, while the bulk epoxy resin was not significantly affected. In terms of the mechanical performance, the flexural strength showed little change during the aging process, while the flexural strain decreased 25 ~ 50 % after 30 days of high temperature aging. Such results indicate that the aging degree of epoxy resin is closely related to the aging conditions.

In addition, ultraviolet (UV) aging also plays an important role in the degradation of epoxy resin, particularly when epoxy resin is exposed to outdoor environment. Zhang et al. (2024a) investigated the UV aging on the properties of epoxy resin. In their study, UV radiation lamps with a wavelength of 365 nm was used to irradiate the epoxy resin samples for 252 h, which equivalents to 3 years of environmental aging in Nanjing, China. Fig. 32 demonstrates the effect of UV aging on the impact strength of epoxy resin, in which the “neat” represents neat epoxy resin, and the rest represent epoxy resins with different contents of anti-UV additive (zinc oxide). It can be seen that the impact strength of neat epoxy decreased to a level of about 33 % of the unaged epoxy, while the retained strength increased significantly with the addition of zinc oxide. The results indicate that epoxy resin would degrade substantially when exposed to UV aging, and the addition of anti-UV additive can improve the UV-aging resistance.

Furthermore, prolonged exposure to high humidity can lead to properties decrease of epoxy resin, especially when it was combined with high temperature, i.e., hygrothermal aging. Wang et al. (2021c) soaked epoxy resin samples in distilled water at 40 °C for a duration of 180 days. The mechanical test results showed that the tensile strength decreased from 55 MPa to 43 MPa, and the elongation at break decreased from 3.2 % to 2.4 %. Wang et al. (2016b) immersed the cured epoxy resin samples in water at 60 °C for up to 28 days, and it was found

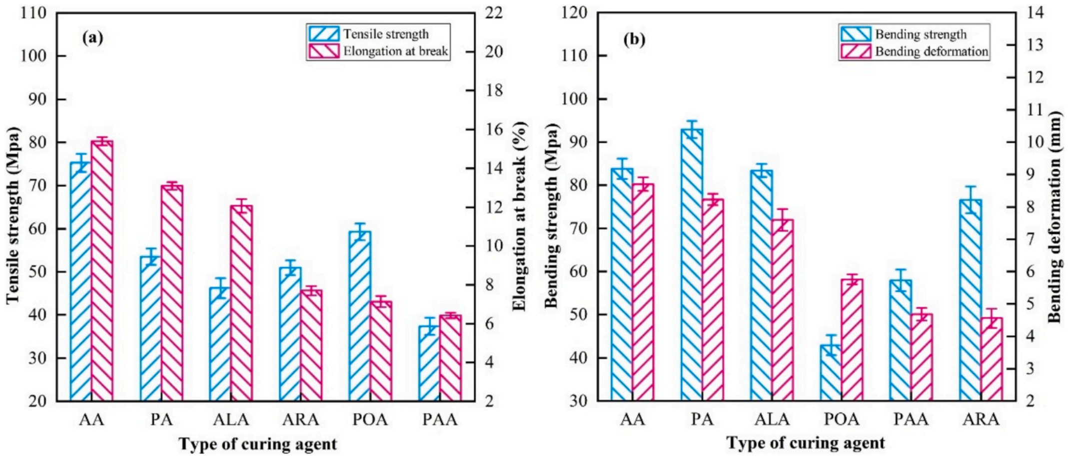


Fig. 27. Tensile and bending properties of epoxy resins cured by different hardeners (Wang et al., 2019).

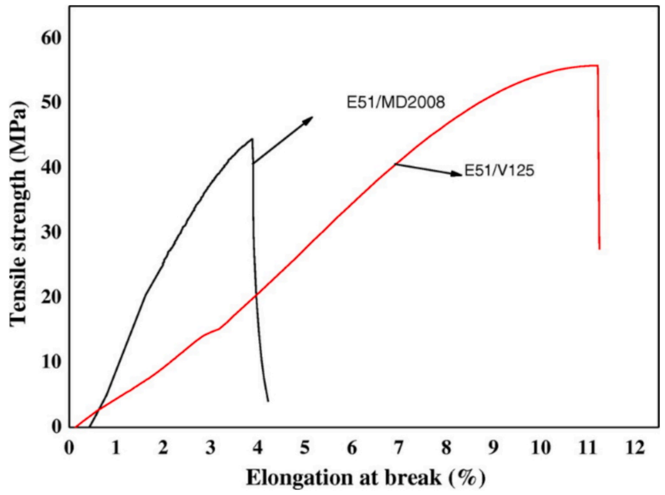


Fig. 28. Typical tensile stress–strain curves of epoxy resin (Wang et al., 2021b).

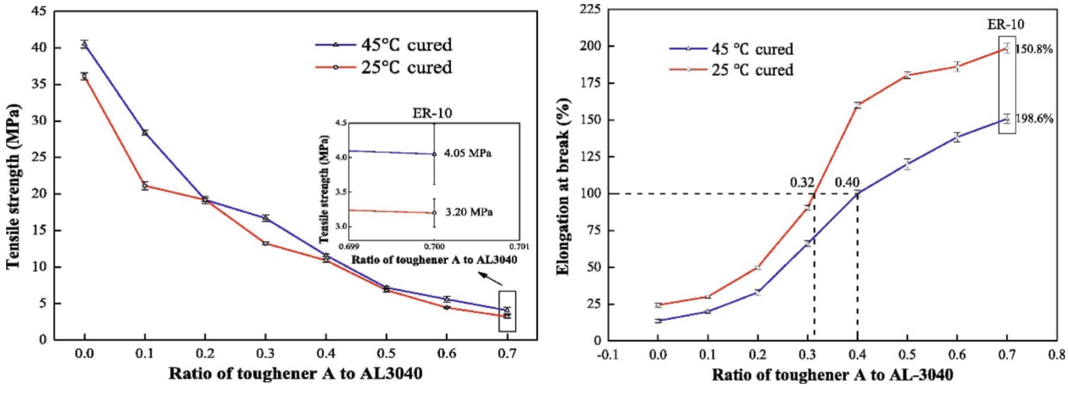
that retained tensile strength after aging decreased to 65 % of its original value, while the Tg decreased from 169 °C to 144 °C. Two main categories of reactions in hygrothermal aging were discovered: the first is the post curing process, which leads to a higher crosslinking density and a reduced interior stress; while the other is the plasticization and deterioration of epoxy resin attributed to moisture ingress.

3.2.2. *Properties of epoxy resin mixture*

The workability of epoxy mixture is important for mixing and compaction of this material. Similar with hot-mix epoxy asphalt, cold-mix epoxy mixture becomes difficult to be compacted after certain curing time. Zhang et al. (2020) compared the workability of cold-mix epoxy mixture (Z15-G2) with hot-mix epoxy asphalts, i.e., Japan epoxy asphalt and US epoxy asphalt. The Japan epoxy asphalt was produced by KINDAI KASEI Co., Ltd (Japan). It is constituted by two components, with component A as the epoxy resin and component B as the curing agent. The US epoxy asphalt was produced by ChemCo Systems Ltd (California, the United States), which is composed by two parts, in which part A is epoxy resin, and part B is a mixture of bitumen and curing agent. The epoxy mixtures were first prepared and conditioned at the specified temperatures for different durations, which were then compacted and the porosities were measured. Note that the epoxy mixture studied was a dense-graded mixture with a binder-aggregate mass ratio of 7.5 %. It can be seen from Fig. 33 that though the porosity of the cold-mix epoxy mixture increases with conditioning time, the porosity is still lower than 3.0 % even after 2.5 h, providing sufficient time for the handling of this mixture in construction.

After preparation, the mechanical performance of epoxy mixtures develops over time. As shown in Fig. 34, the uniaxial compressive strength of epoxy mixture grows rapidly at the initial stage, and reaches the plateau after 19 days of curing at ambient temperature.

The mechanical performance of epoxy mixtrue is significantly affected by binder-aggregate ratio (Fig. 35). It can be seen that the dynamic stability by rutting test peaks at a 5 wt% binder-aggregate ratio, which then decreases with further increasing of binder content.



(a) (b)

Fig. 29. Direct tensile strength and elongation at break, (a) Tensile strength, and (b) Elongation at break(Wang et al., 2021b).

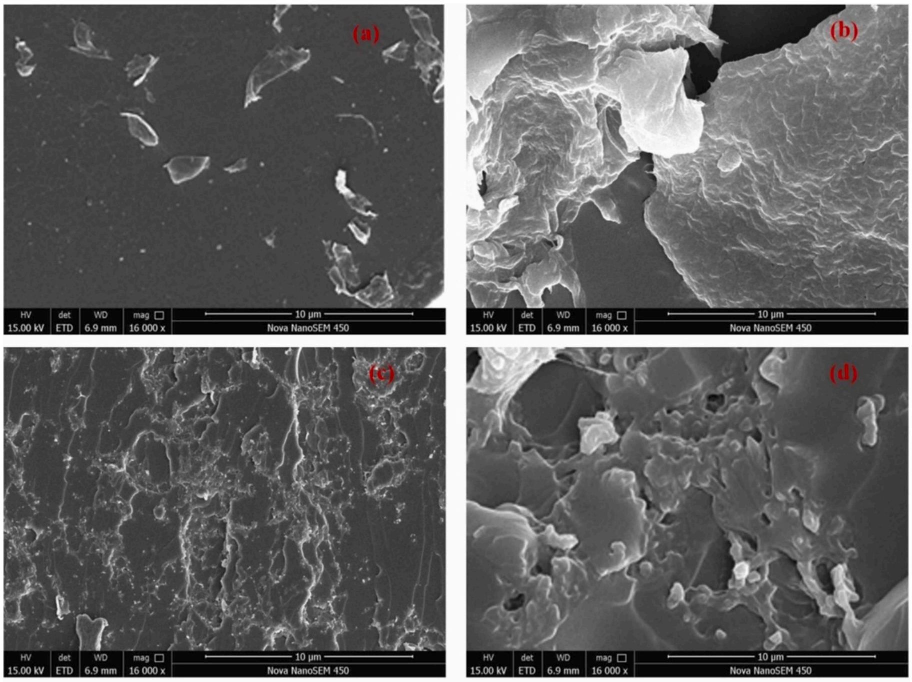


Fig. 30. SEM images of epoxy resin (a) without toughen (1000 ×); (b) without toughen (16,000 ×); (c) with toughen (1000 ×); (d) with toughen (16,000 ×) (Shi et al., 2024).

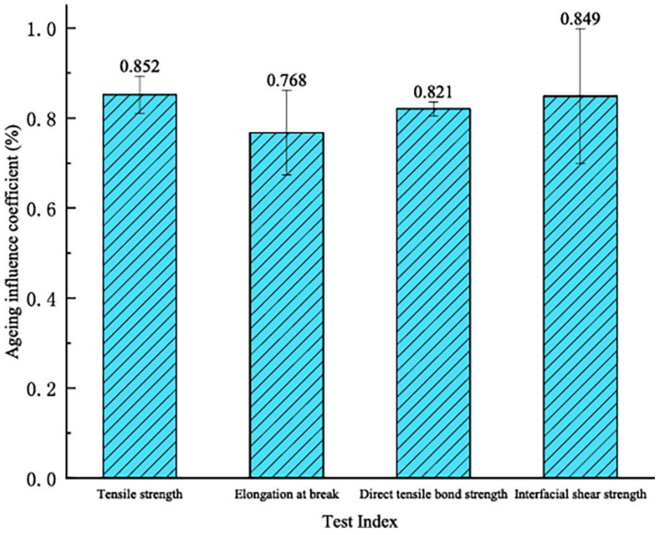


Fig. 31. Tensile test of epoxy resin after aging (Ma et al., 2022).

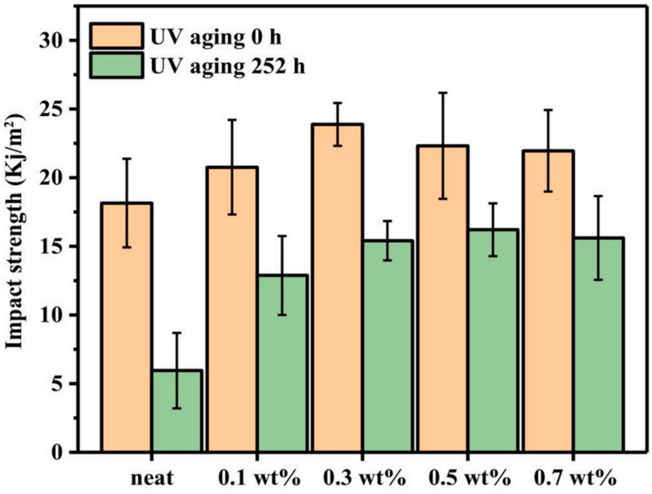


Fig. 32. Effect of UV aging on impact strength of epoxy resin (Zhang et al., 2024a).

However, the dynamic stability at binder content from 4 wt% to 6 wt% are all significantly larger than polymer modified asphalt concrete (AC-13). In addition, it is observed from Fig. 35 that the bending tensile strength and flexural strain increases with larger epoxy content, indicating that larger binder-aggregate ratio has positive effect on the flexibility of epoxy mixture.

Previous research has indicated that epoxy mixture possesses outstanding overall mechanical performances. As shown in Fig. 36, the Marshall stability and dynamic stability of cold-mix epoxy concrete (Z15-G1, Z15-G2) are comparable with hot-mix epoxy asphalt, indicating strong resistance to rutting at high temperature. In addition, the low-temperature flexural tensile strain lies between 5000 ~ 8000 με, which was even larger than that of hot-mix epoxy asphalt. Another study by Wang et al. (2021b) demonstrated that the low-temperature flexural tensile strain of cold-mix epoxy concrete is well above the value of dense-graded SBS modified asphalt concrete. Furthermore, the resistance to moisture-induced damage was characterized, and it is observed that residual stability and freeze–thaw splitting strength ratio were close to those of the hot-mix epoxy asphalt. The fatigue performance of cold-mix epoxy concrete was also investigated by Zhang et al. (2020), in which the four-point bending fatigue test was employed. Table 8 shows the fatigue performance of the epoxy concrete at different strain levels ranging from 400 με to 2000 με. It can be seen that the fatigue life N_f is larger than 1×10^6 cycles even at the strain level of 1600 με, demonstrating outstanding fatigue performance.

Overall, from the above analysis, it can be concluded that epoxy resin has many advantages as a cold paving binder, such as fast curing, resistance to rutting, good bonding ability with aggregate, resistance to fatigue. However, epoxy resin is prone to degradation when exposed to outdoor environment for long term, which should be considered in

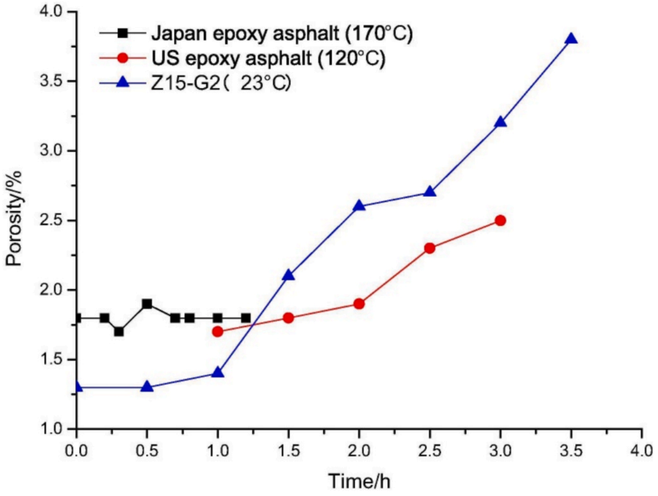


Fig. 33. Workability of cold-mix epoxy mixture and hot-mix epoxy asphalt (Zhang et al., 2020).

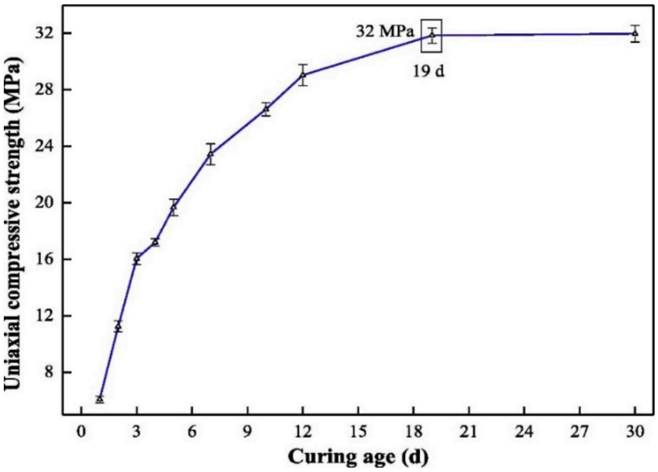


Fig. 34. Development of uniaxial compressive strength of epoxy mixture at different curing age (Wang et al., 2021b).

application.

3.3. Application of epoxy resin cold binder in pavement

Once cured, epoxy resin transforms into three-dimensional networks, which endows epoxy resin with exceptional mechanical properties. In addition, epoxy resin cures fast when mixed with hardener, achieving high strength in short time. Due to these advantages, cold-mix epoxy resin has found applications in pavement engineering for various purposes. Table 9 lists the representative applications of cold-mix epoxy resin, including antiskid surface layer, steel bridge deck paving, pervious concrete, pavement joint filling, etc.

(1) Antiskid surface layer

Liu et al. (2021c) developed an epoxy resin-based ultra-thin antiskid surface layer for epoxy asphalt pavement in steel bridge deck, and it was found that the epoxy resin-based ultra-thin antiskid surface layer has excellent high-temperature rutting resistance, low-temperature cracking resistance and interlayer bonding stability and was feasible to be used in epoxy asphalt pavement maintenance in steel bridge deck. To improve the flexibility and durability, Wang et al. (2019) prepared a polyurethane prepolymer modified epoxy resin, which was used to construct a colorful anti-skid surface of pavement. The results showed that the modified epoxy resin can significantly improve the durability and mechanical performance of the anti-skid layer. In addition, the epoxy binder also demonstrates superior resistance to corrosion conditions like acid, alkali, and oil.

(2) Steel bridge deck paving

To reduce the fatigue cracking in orthotropic steel deck pavements, Zhang et al. (2020) developed a new-generation, cold-mix, high-toughness epoxy resin for steel deck pavements by introducing a flexible chain into the molecular structure of epoxy resin based on the principle of action of a simultaneous interpenetrating polymer network. The results indicate that the cold-mix high toughness epoxy resin concrete can satisfy the requirements of steel deck pavement, and the fatigue life is much longer than that of normal epoxy asphalt mixture.

(3) Pervious concrete.

Tabatabaeian et al. (2019) investigated the application of epoxy resin in pervious concrete. It is found that the usage of epoxy resin significantly enhances the durability and mechanical properties. The increase in the resin content leads to higher strengths in compressive, tensile, and flexural strength, whereas, an increase in the size of coarse aggregate decreases the strengths. Xu et al. (2023b) used epoxy resin as the binder of porous pavement mixture in replace of asphalt binder. The results indicated that the epoxy resin porous mixture has higher strength, better deformation coordination ability, excellent permeability and rapid drainage in comparison with conventional porous asphalt mixture.

(4) Crack-repairing material

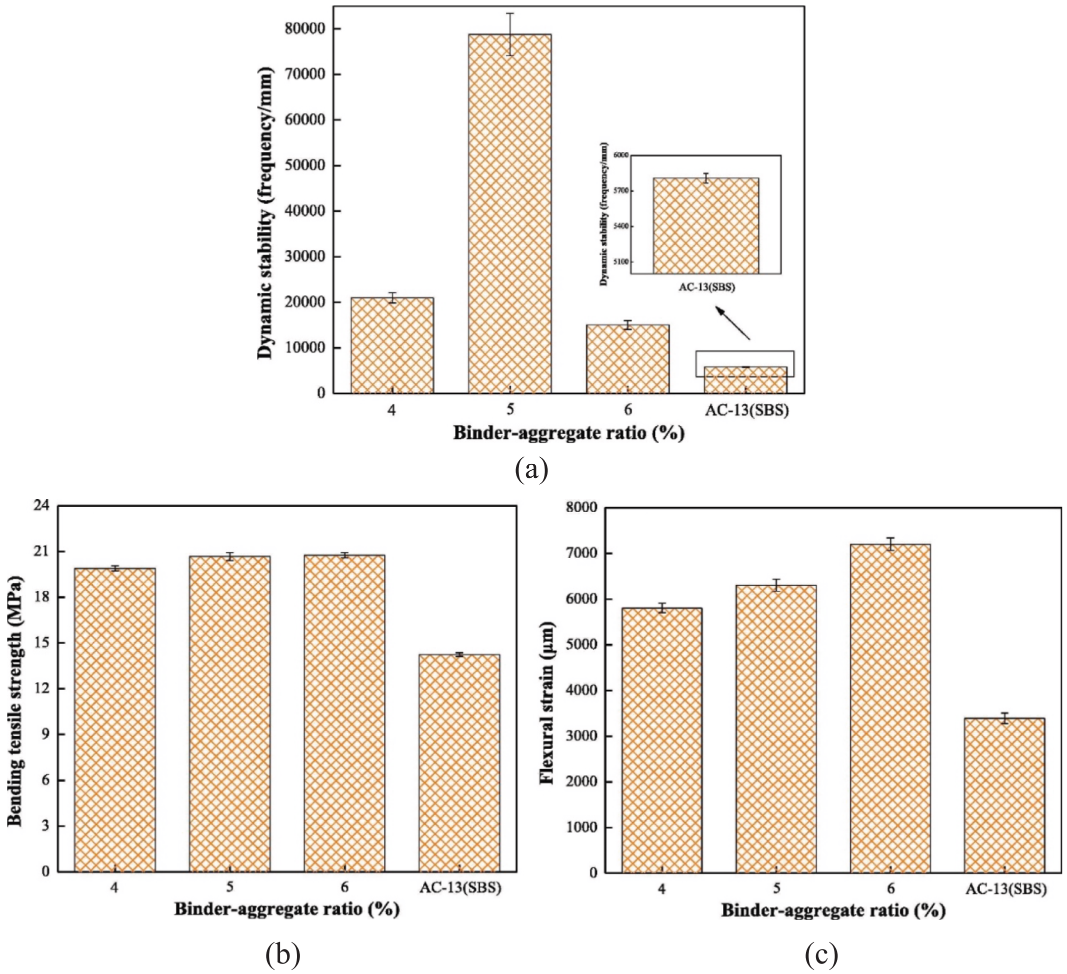
Ma et al. (2022) used epoxy resin as a crack-repairing material, consisting of epoxy resin and powder curing agent, for asphalt pavement, and the results indicated that epoxy-based cracking-repairing material exhibited good tensile bond performance, shear resistance, and water stability. Another study by Xu et al. (2023a) demonstrated that the epoxy resin sealant can recover up to 68.1 %, 67.8 %, and 70.5 % of the tensile strength, flexural strength, and oblique shear strength of the cracked asphalt pavement compared with undamaged asphalt pavement, which are better than conventional materials, e.g., SBS modified asphalt, silicone sealant, and polyurethane sealant.

(5) Airport runway rehabilitation

The favorable properties of epoxy concrete have also led to its growing application in airport runway rehabilitation. Portland cement concrete, the main construction material of runways, is cost effective and mechanically strong. Unfortunately, runways are exposed to a variety of adverse conditions, typically represented by chemical erosion, aircraft dynamic loads, and engine heat (Jung et al., 2014). These factors lead to failure of runways in the long run. However, it is impracticable to use cement concrete as the repairing material, due to its high drying shrinkage and long curing time to reach full strength (Jung et al., 2015b). On the contrary, epoxy resin has the advantages of low curing shrinkage, rapid hardening and strong adhesion to aggregates as well as existing cement concrete substrate (Toufigh et al., 2013), making it an ideal repairing material for runways.

3.4. Benefits and drawbacks

After curing reaction, epoxy resin turns into a highly-crosslinked polymer. This structure provides the material with many useful properties, such as high strength, high adhesive ability and low creep. However, because of their high cross-link density, cured epoxy resins are relatively brittle (Ruiz-Pérez et al., 2008), leading to weak resistance to crack initiation and propagation. Therefore, epoxy resins prone to fracture under impact loading. When such epoxy resins are used as binders, the epoxy concrete tends to be brittle, which influences the pavement driving comfortability and durability. Furthermore, epoxy resin is thermal-setting, thus the cured epoxy resin becomes difficult to be broken. How to handle the epoxy concrete at the end-of-life is a major challenge for its application in pavement. In addition, epoxy resin is more expensive than asphalt binder and cement, mainly because of the raw material costs, which hinders its wide application in pavement



(a)

(b)

(c)

Fig. 35. Influence of binder-aggregate ratio on mechanical performance of epoxy mixture: (a) dynamic stability, (b) bending tensile strength, (c) flexural strain (Wang et al., 2021b).

industry.

4. Polyurethane based cold mix binder

Polyurethane (PU) is one of the most important polymeric materials that have found wide applications in many areas. They represent an extraordinary versatile family of polymers (Sardon et al., 2013). The applications of PUs cover a broad spectrum of industrial fields and sectors, including coatings, adhesives, composites, biomedical devices, foam padding and high-performance structures (Koti Reddy and Shailaja, 2015, Špírková et al., 2011). PUs are generally produced from diisocyanates, macrodiols and short diol or diamine chain extenders. The diisocyanates and chain extenders form the hard segments (HS), while macrodiols form the soft segments (SS) (see Fig. 37). The HS and SS are characterized by high Tg (Tg above room temperature) and low Tg (Tg below ambient temperature) (Zhang et al., 2014), respectively. Therefore, at ambient temperature, the hard segments are glassy or crystalline, while the soft segments are in a rubbery state (Fragiadakis and Runt, 2013). The content of HS and SS greatly influences the properties of PU. Higher content of HS leads to higher stiffness and strength, while higher content of SS results better ductility and flexibility (Fragiadakis and Runt, 2013).

4.1. Materials and chemical reaction

PUs are named due to the presence of urethane linkage (–NH-COO-) in the molecules backbone, which is formed by isocyanates and diols. Generally, isocyanate groups can react with chain extenders containing active hydrogen and result with addition products. For example, isocyanate groups react with hydroxyl compounds or amines to form urethane (Fig. 38 (a)) or urea (Fig. 38 (b)), respectively (Chattopadhyay and Raju, 2007).

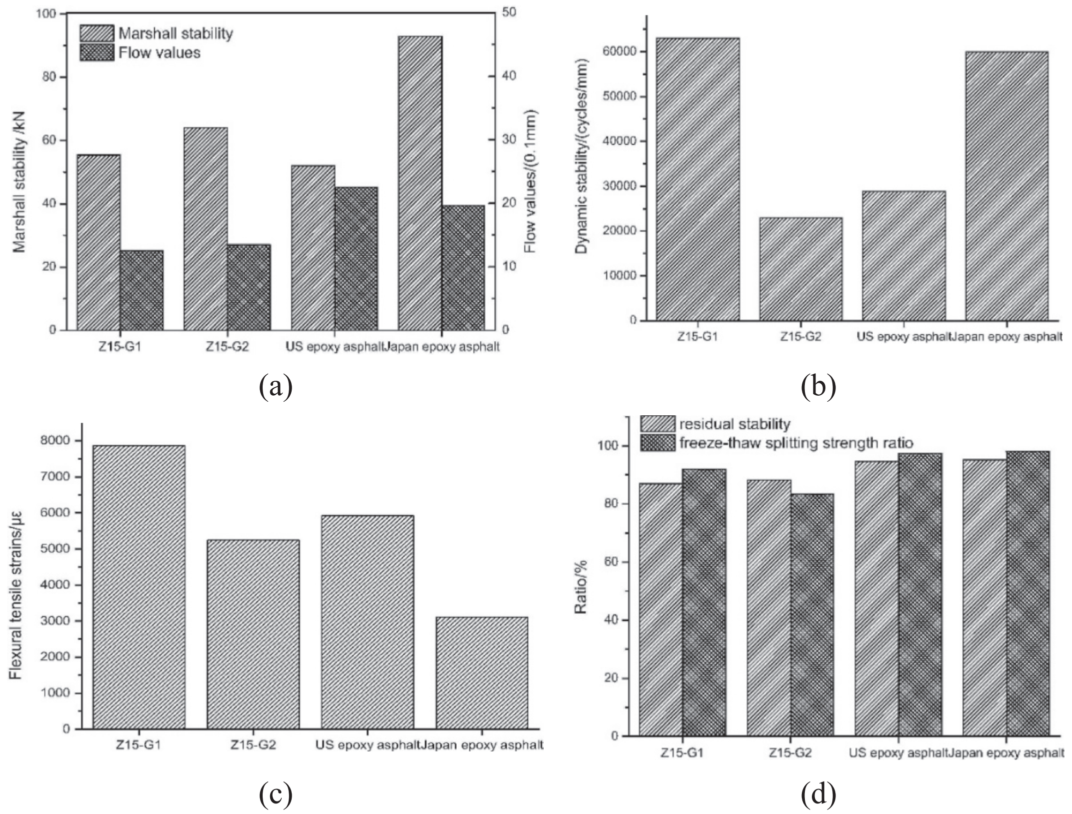
During the chemical reaction process, the isocyanate group in PU prepolymer reacts with chain extenders. The band assignment is shown in Table 10. Infrared spectra measurement shows that the peak at 2250 cm^{-1} ascribing to isocyanate group (–NCO) weakened in this process, indicating the isocyanate group has reacted (Fig. 39). The decrease of the peak strength at 1525 cm^{-1} attributed to N-H bending also confirms the chemical reaction.

4.2. Properties of polyurethane binder and mixture

4.2.1. Properties of polyurethane binder

The mechanical performance of PU is significantly influenced by the isocyanate content, as isocyanate mainly forms the hard segment in polyurethane. Therefore, it is found that the strength (tensile strength and tearing strength) and hardness of the PU increases with larger isocyanate content, while the elongation at break decreases (Fig. 40). Table 11 shows the basic mechanical properties of typical PUs, and it can be seen that the tensile strength generally shows a positive correlation with the modulus, while it demonstrates a negative correlation with tensile strain.

The mechanical performance of PU develops over time after the two components of PU are mixed together. The chain extending reaction is



(a) (b)

(c) (d)

Fig. 36. Mechanical performances of epoxy resin mixture: (a) Marshall stability, (b) dynamic stability, (c) flexural tensile strain, and (d) moisture susceptibility (Zhang et al., 2020).

Table 8

Fatigue performance of epoxy concrete at different strain levels (Zhang et al., 2020).

Strain level (με)	Mean fatigue life N_f (cycles)	Accumulated dissipated energy (J/m^3)
400	$>1 \times 10^6$	670
800	$>1 \times 10^6$	1243
1200	$>1 \times 10^6$	6313
1600	$>1 \times 10^6$	9056
2000	1100	120

Table 9

Representative applications of cold-mix epoxy resin in pavement.

Application	Epoxy resin system	References
Antiskid surface layer	Bisphenol A-type epoxy resin/ Amine curing agent	(Liu et al., 2021c), (Wang et al., 2019)
Steel bridge deck paving	E51/polyurethane/allyl glycidylethe/modified aliphatic amine curing agent	(Zhang et al., 2020)
Pervious concrete	Bisphenol A-type epoxy Resin/ Aliphatic amine; Bisphenol A-type epoxy resin E44/ Trimercaptopropionate	(Tabatabaeian et al., 2019), (Xu et al., 2023b)
Pavement crack repairing	Bisphenol A-type epoxy Resin/ Amine curing agent/polyurethane toughening agent/diluent	(Fang et al., 2021), (Xu et al., 2023a)
Airport runway rehabilitation	Epoxy resin (YD-128)/hardener (KH-891)	(Jung et al., 2014), (Jung et al., 2015b)
Others: Pavement joint filling; Cold patching; Epoxy resin bonded spreading material	Epoxy resin/curing agent/ toughening agent/ accelerator; Epoxy resin, toughening agent, diluent, curing agent, accelerator; NA	(Fang et al., 2022); (Wang et al., 2023b); (Wang et al., 2016a)

strongly affected by the reaction temperature. Higher temperature initiates more rapid reaction, and thus the mechanical performance grows faster (Fig. 41).

Similar with epoxy resin, PU is susceptible to aging in environment. Zhang et al. (2024b) evaluated the thermal-oxidative aging on the mechanical performance of PU. The samples were conditioned at 60 °C for 50 days, and it was found that the tensile strength declined 25.1 %, while the elongation at break showed a sharp 96 % drop. Burelo et al. (2025) compared the thermal aging effect on two types of PUs: one with saturated C–C bonds (SPU) and another with unsaturated C=C bonds (UPU). Both types of PUs underwent thermal aging for 30 days at 150 °C in an air atmosphere. The results indicated that the thermal degradation resulted in mass losses of approximately 5 % for SPU and 10 % for UPU. In addition, the mechanical performance experienced a large decline for both PUs, as shown in Fig. 42. The mechanical performance degradation after 15 days of aging is not significant for both PUs. However, after aging for 30 days, the mechanical properties decreased remarkably, with the tensile strength dropped 43 % and 51 %, and the elongation at break dropped 50 % and 64 %, for SPU and UPU, respectively.

To evaluate the anti-ultraviolet aging performance of polyurethane, Xiong et al. (2024) conditioned the polyurethane in UV environment for up to 14 days and the tensile test was performed during the process. It can be seen from Fig. 43 that the tensile strength increases with the increase of UV aging time, while the elongation at break decreases slightly. Such phenomenon may be attributed to that PU become hardened during the UV aging process, and thus the tensile strength increased while the ductility decreases.

Furthermore, long-term exposure to moisture also leads to degradation of PU. Zhang et al. (2024b) conditioned PU samples in a water bath at 25 °C for a duration of 18 days. It was found that the tensile

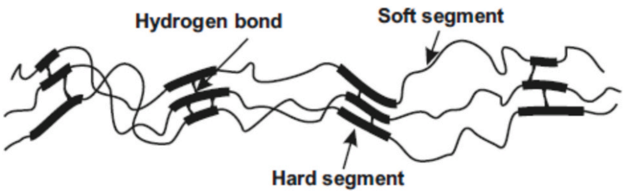
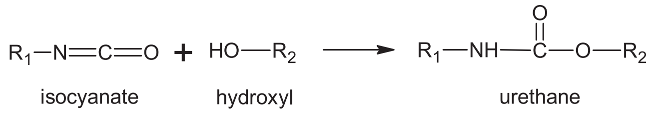
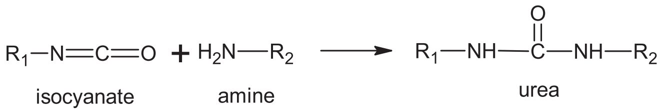


Fig. 37. PUs alternating hard segment-soft segment structure (Prisacariu,-cariu, 2011).



$$R_1{-}N{=}C{=}O + HO{-}R_2 \longrightarrow R_1{-}NH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}R_2$$

(a) Isocyanate-hydroxyl reaction



$$R_1{-}N{=}C{=}O + H_2N{-}R_2 \longrightarrow R_1{-}NH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH{-}R_2$$

(b) Isocyanate-amine reaction

Fig. 38. Isocyanate reaction with hydroxyl and amine.

Table 10
Typical band assignment of PU.

Wavenumber (cm^{-1})	Band assignment
1050	C–O–C symmetric stretching
1157	C–O–C asymmetric stretching
1525	N-H bending
1725	C=O stretching (amide)
2250	N=C=O stretching
2873, 2927	C–H stretching
3366	N-H stretching

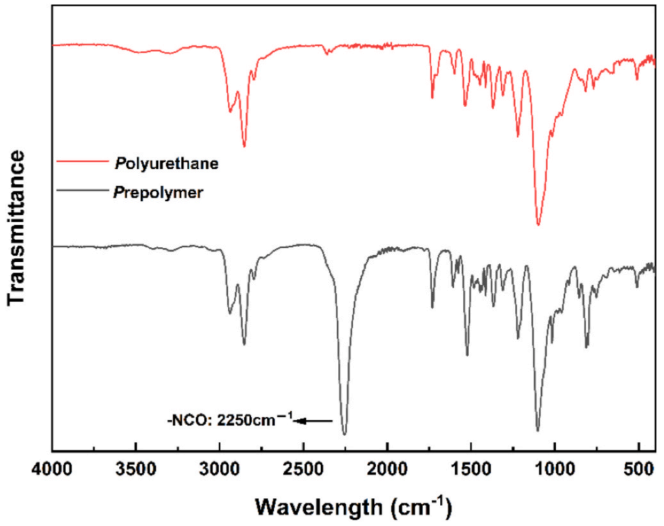


Fig. 39. FT-IR spectra of the PU binders in chemical reaction process (Liu et al., 2022).

strength and elongation at break demonstrate a reduction of 19.9 % and 87.7 %, respectively. In the study by Wang et al. (2025), PU was immersed in water for 7 days at 80 °C. It was found that tensile strength dropped 23.2 % after the hygrothermal aging. In addtion, the Tg decreased from −12.8 to −23.6 °C, which results from water penetration that caused swelling and plasticization of the resin matrix, increasing free volume and disrupting intermolecular hydrogen bonding. Tian et al. (2016) found that hygrothermal aging of polyruethane shortens the polyurethane chains with increasing humidity and aging time, and the decrease of molecular weight of the polyurethane chains caused a decrease of Tg.

4.2.2. *Properties of polyurethane mixture*

Similar with epoxy mixture, the binder content also influences the mechanical performance of polyurethane mixture. It can be seen from Fig. 44 that the compressive strength increases rapidly from binder content of 8 wt% to 10 wt%, and then grows gradually with further increasing of binder content. Considering the cost of polyurethane binder, it is suggested that a 10 wt% of binder content to be appropriate for the dense-graded mixture.

PU mixture generally demonstrates superior mechanical performance compared with conventional asphalt mixture. The study by Jiang et al. (Jiang et al., 2022) shows that the dynamic stability of PU mixture is significantly larger than SMA (stone mastic asphalt), GA (gussasphalt), EAC (epoxy asphalt concrete) (Fig. 45). In addition, the low-temperature bending performance between PU mixture (PUM) and SMA was compared in another study (Min et al., 2019), which clearly demonstrates that the low-temperature bending strain of PUM is more than double of that of SMA (Fig. 46).

However, as a polymer binder, polyurethane is susceptible to moisture. Hong et al. (2021) evaluated the moisture effect on both Marshall stability and tensile splitting strength (Fig. 47). It is clear to see that after moisture conditioning, both Marshall stability and splitting strength decreases, while the splitting strength shows larger degree of deterioration, possibility due to severer freeze–thaw conditioning.

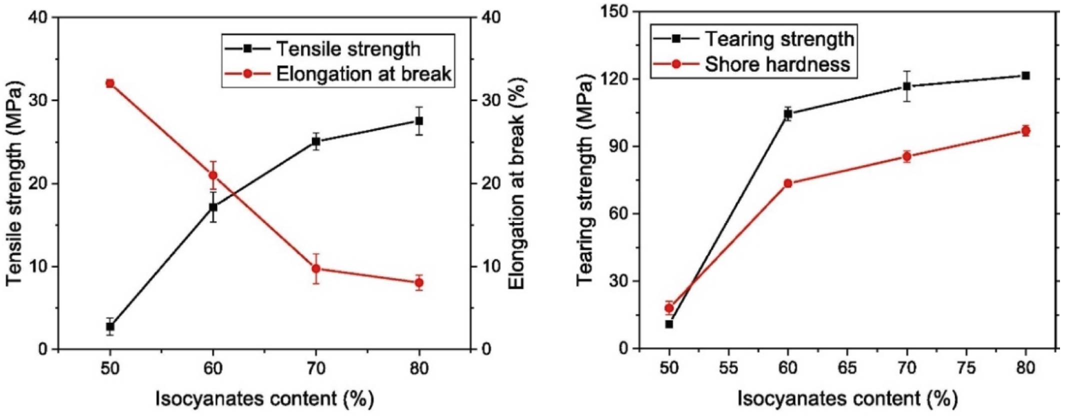
The fatigue performance of PUM was investigated by Zhuang et al. (2023) using four-point bending fatigue test. The stress-controlled fatigue results of PUM with conventional asphalt concrete (AC-20 and AC-25) and stone mastic asphalt (SMA-13) are presented and compared in Fig. 48. It is clear to see that when the stress level of SMA-13, AC-20, and AC-25 mixtures increases to 0.5, the fatigue life was only 1000 ~ 2000 cycles, while the fatigue life of the PUM-20 and PUM-25 was significantly higher, reaching more than 45,000 cycles at the same stress level. The fatigue life of PUM is more than 25 times that of the SMA-13, AC-20, and AC-25 mixtures at the stress level of 0.5, indicating that the PU mixture has a strong ability to resist fatigue load.

4.3. *Application of polyurethane cold binder in pavement*

Due to their exceptional elasticity and flexibility, PUs demonstrate excellent resistance to expansion and shrinkage, high tensile and compressive strength, and fatigue performance (Vennapusa et al., 2016). The application of PUs as an alternative binder in place of asphalt binder has also been explored recently. The advanced properties of PUs have attracted researchers to evaluate its performance in pavement. Some typical applications of PUs in pavement are summarized in Table 12.

(1) Pavement surface.

Due to its high cost, polyurethane is now used in pavement surface layer for some special necessities. One such application is the deicing/anti-icing pavement. Chen et al. (2018a) investigated the deicing and anti-icing performance of an innovative pavement surface layer that replaces asphalt binder with polyurethane. The deicing and anti-icing performance of polyurethane concrete at different freezing time was compared to the traditional asphalt concrete. It was found that polyurethane concrete has similar thermal conductivity but much greater specific heat in comparison with asphalt concrete. Compared to asphalt concrete, polyurethane concrete can significantly retard the ice-formation time. The pull-off strength and interface shear strength at the interface of ice and polyurethane concrete is about 50 % and 55 % of those at the interface of ice and asphalt concrete. The work of rupture to



(a)

(b)

Fig. 40. Mechanical properties of polyurethane binder as a function of isocyanate content: (a) Tensile strength and elongation at break; (b) Tearing strength and Shore hardness (Xu et al., 2022).

Table 11
Mechanical properties of polyurethane resin.

Polyurethane	Tensile strength (MPa)	Tensile strain (%)	Bonding strength (MPa)	Elastic modulus (MPa)	Compression strength (MPa)	Reference
1	25.7 ± 0.7	56 ± 3.5	NA	420 ± 35	30.5 ± 1.3	(Jiang et al., 2022)
2	8.2	315	3.3	NA	NA	(Xu et al., 2023c)
3	15.7	34	NA	NA	NA	(Niu et al., 2022)
4	2.45	485	NA	NA	NA	(Liu et al., 2019)
5	42.30 ± 2.26	9.43 ± 2.31	NA	942.11 ± 43.92	NA	(Hong et al., 2021)
6	23.32 ± 0.85	35.26 ± 1.60	NA	482.17 ± 38.96	NA	
7	17.84 ± 1.89	57.25 ± 8.46	NA	99.13 ± 5.50	NA	

break ice layer on polyurethane concrete is only about 50 % of the work required on asphalt concrete with the same ice layer thickness. The findings demonstrate the potential application of polyurethane concrete on roadways in cold regions to provide better anti-icing and deicing performance and enhance traffic safety at winter seasons.

Polyurethane has also been used in road tunnel paving. To mitigate the hazardous asphalt fume generated during pavement construction in tunnel, Hong et al. (2021) investigated PU mixture as tunnel paving material. Two aggregate gradations were evaluated as ultra-thin friction courses, i.e., open-graded friction courses (PU/OGFC-10) and dense-graded PU concrete (PU/AC-10), and the results indicated that both mixtures demonstrated excellent functional performances, such as skid resistance, noise absorption performance, and flame-retardant property. However, the resistance to moisture damage was poor, with the Marshall stability dropping 16 ~ 48 % after water immersion, and the indirect tensile strength decreasing 40 ~ 66 % after freeze-thawing.

(2) Pervious pavement.

Porous asphalt is widely used to for the purpose of fast water drainage (Kabir et al., 2024). Due to its large air voids, the contact area between the aggregates is relatively small. Thus, the bonding between the aggregates is not sufficient, leading to premature distresses like raveling in porous asphalt (Li et al., 2024). To solve this problem, polyurethan has been explored as a novel binder for porous pavement.

Cong et al. (2018) found that the porous polyurethane mixtures demonstrate excellent overall performance, which can potentially be used to substitute conventional porous pavement. Owing to its high strength after curing, polyurethane binder improves the mechanical bonding at the aggregate-aggregate contact point, which effectively enhances the service performance of porous pavement (Wang et al., 2022b). In addition, Chen et al. (2018b) reported that porous polyurethane mixture reduced the surface temperature and enhanced the anti-clogging performance of porous pavement.

Derived from porous asphalt, poroelastic road surface (PERS) was invented in Sweden to further reduce the tyre-road noise. Typically, PERS constitutes tyre rubber granules, aggregates, and polyurethane binder. PERS shows even larger air void (up to 40 %) in comparison with conventional porous asphalt. Wang et al. (2017b) evaluated the use of polyurethane as a cold binder for crumb rubber and quartz sand to prepare PERS, which had an air void content of 30 % to 35 %. The results indicated that the polyurethane binder leads to improved raveling resistance and rutting as well as better noise absorption. They also found that polyurethane PERS poses superior tensile strength at lower temperature than normal asphalt-based porous pavement and is suitable to be used in cold regions (Wang et al., 2017a). These pioneer works confirmed the possibility of using polyurethane as an alternative binder for porous pavement.

(3) Steel bridge deck paving.

Recently, PU-based concrete has found alternative applications as pavement for steel deck bridges. Conventional pavement materials like stone mastic asphalt and gussasphalt still have some limitations due to temperature susceptibility of asphalt binder. Epoxy asphalt concrete has good performances but also has fatigue problems stemming from their inherent chemical structures, which, in some cases, led to short service life. Therefore, polyurethane concrete (PUC) has been explored as alternative paving material for steel bridge decks. It was found that PUC composites demonstrate good resistance to rutting at high temperature and low-temperature cracking (Jiang et al., 2022). Xu et al. (2020) investigated the aging resistance of PUC for bridge deck pavement using indoor accelerated aging test. The mechanical performance before and after aging were measured, and the results indicated that though the mechanical performance declines to some extent after aging, it was still better than that of SBS modified asphalt mixture.

(4) Pothole repairing

Potholes are common distresses in asphalt pavement due to traffic loading or weathering. Timely repairing of such distress is important to retard further deterioration of pavement condition. Conventionally,

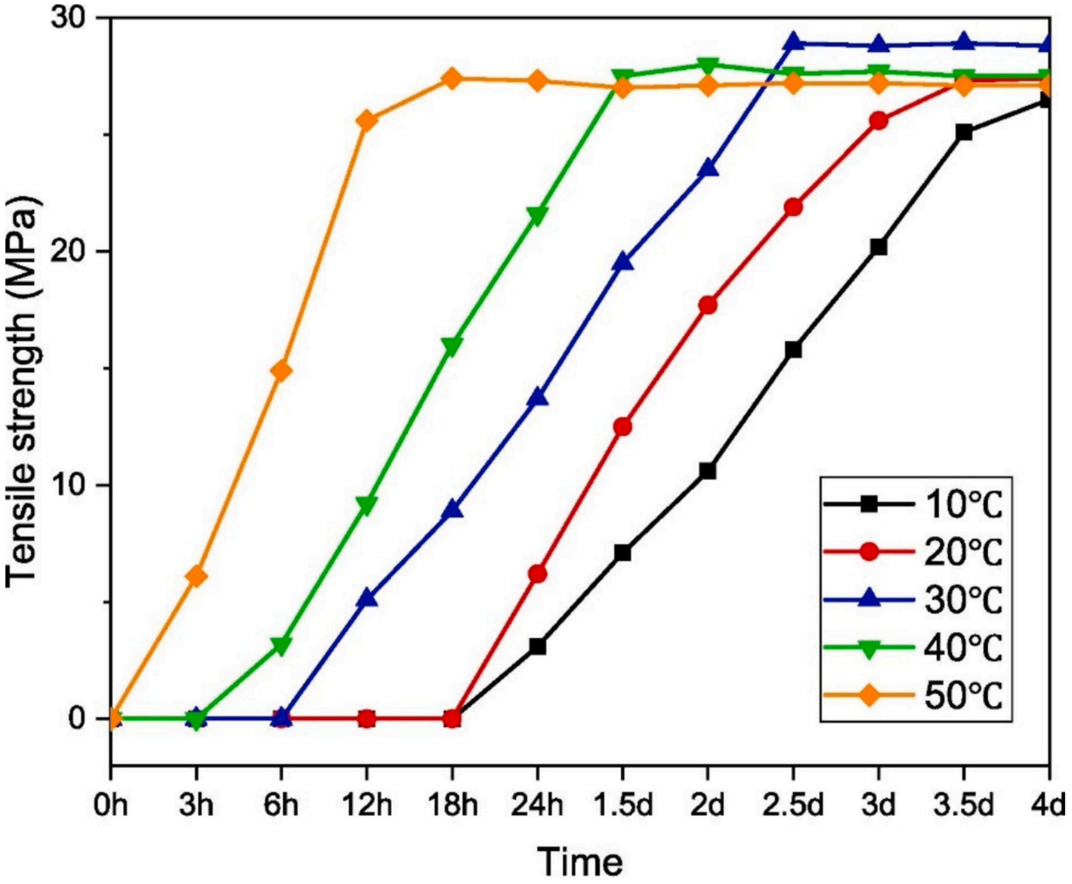
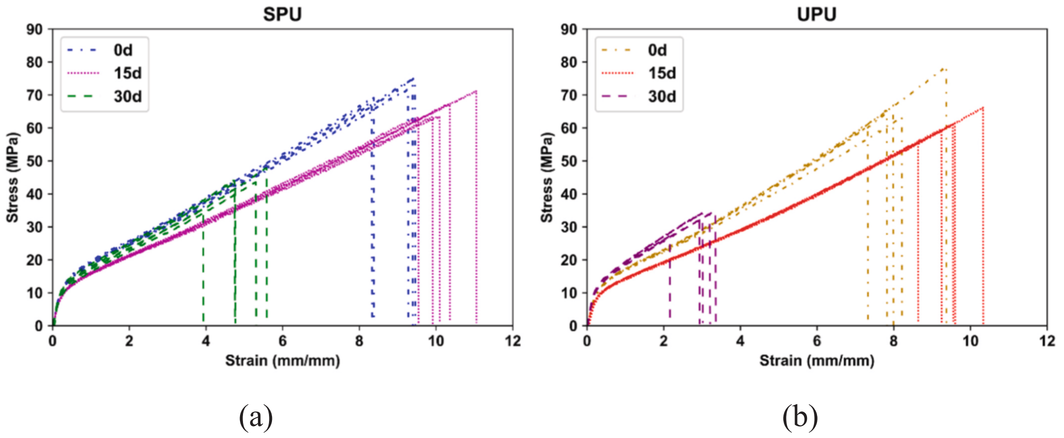


Fig. 41. Tensile strength changing of polyurethane binder at various temperatures (Xu et al., 2022).



(a)

(b)

Fig. 42. Stress–strain curves of PUs after thermal aging: (a) SPU, (b) UPU (Burelo et al., 2025).

asphalt based repairing materials are used. However, the durability of these repairing materials is generally poor. Polyurethane based repairing materials are attracting increasing interest in recent years. Liu et al. (2019) compared polyurethane patching material with emulsified asphalt and cutback asphalt, and it was found that polyurethane performs significantly better regarding shear strength and bonding strength. In addition, polyurethane patches showed improved resistance to shoving and freeze–thaw cycling in comparison with emulsified asphalt and cutback asphalt. Furthermore, polyurethane patches demonstrate good performance after more than one year of field inspection.

(5) Expansion joints

Bridge expansion joints are important components of bridge design. They go through a series of movement caused by temperature change, expansion and shrinkage, vehicle loads and humidity (Malla et al., 2011). From this point of view, expansion joints are the weak point of bridges. It is estimated that the maintenance cost of expansion joints accounts for 7 ~ 25 % of global maintenance costs of bridges (Marques Lima and de Brito, 2009). Traditionally, bituminous materials are used in flexible expansion joints for their low initial investment, ease of installation and maintenance (Mo et al., 2012). However, bitumen-based materials are sensitive to temperature variations, and thus failures are likely to occur under low temperatures or repeated deformation. Afterwards, the leakage of water or corrosive materials will

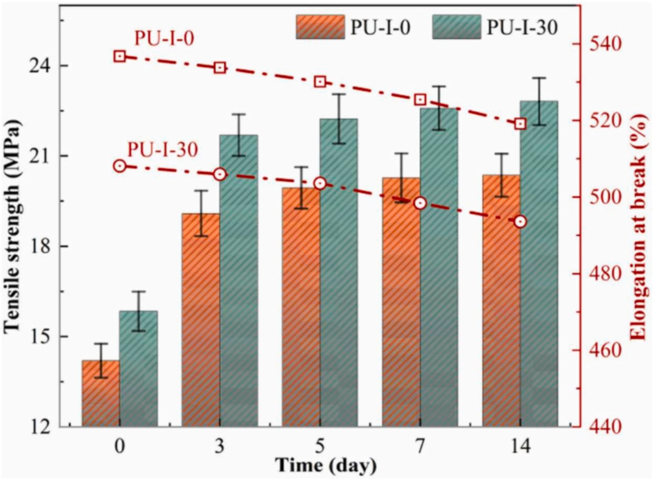


Fig. 43. Effect of UV aging on tensile properties (Xiong et al., 2024).

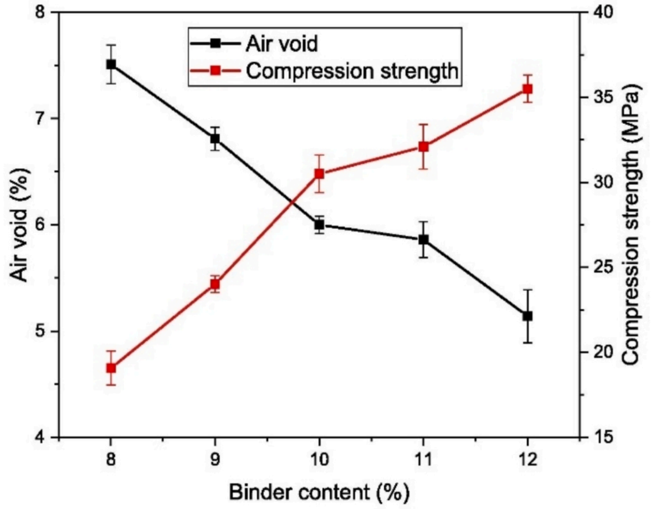


Fig. 44. Compressive strength of polyurethane-bonded mixtures with different binder contents (Xu et al., 2022).

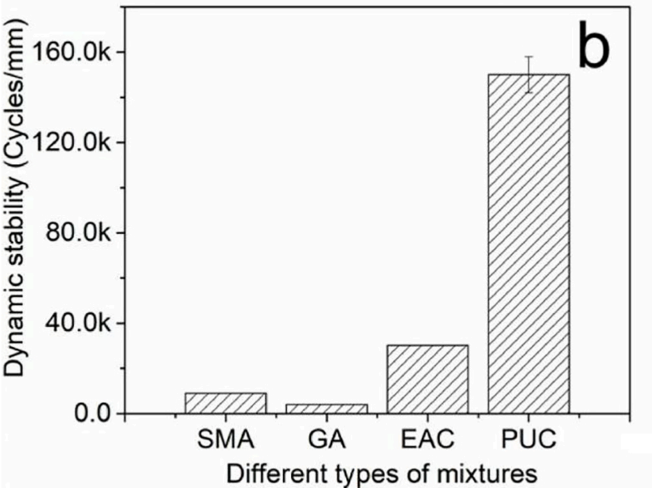


Fig. 45. Rutting test results of several mixtures (Jiang et al., 2022).

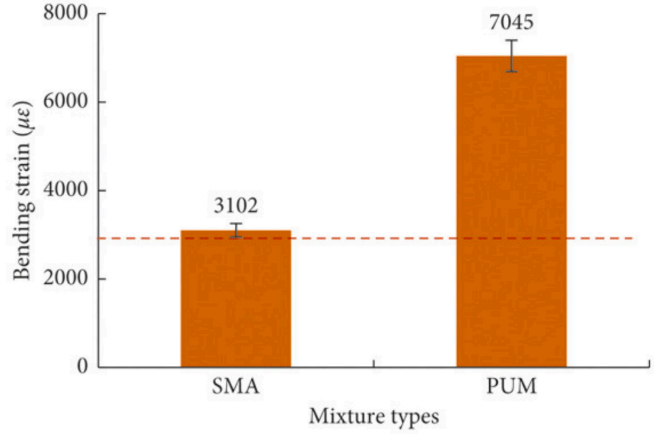


Fig. 46. Comparision between PUM and SMA regarding low-temperature bending (Min et al., 2019).

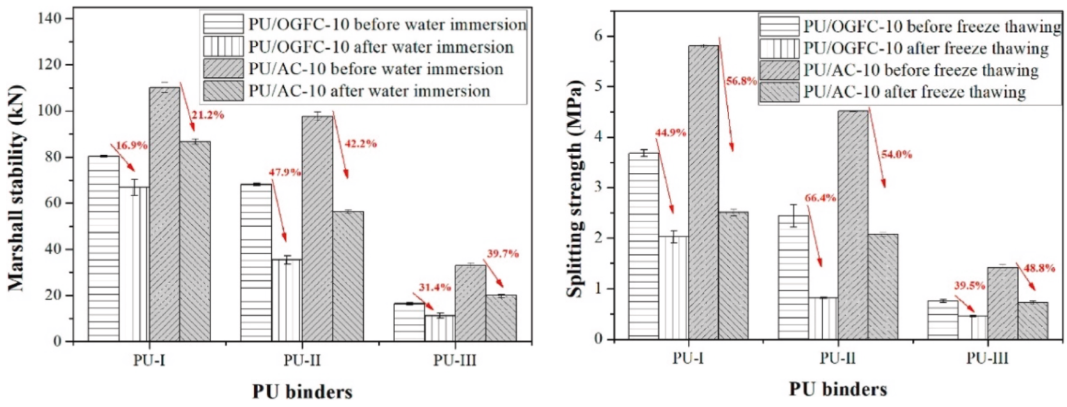
accelerate the damage of expansion joints, which in turn reduce the service life of bridge. On the contrary, polyurethane-based materials function well between −50 ℃ to 70 ℃ (Randall and Lee, 2002). Meanwhile, the exceptional elasticity of PU provides the expansion joints with good deformation ability. Therefore, polyurethane-based expansion joints prove to be durable, watertight, resistant to rutting and chemicals (Gallai, 2016).

4.4. Benefits and drawbacks

PUs are widely used in many industries. Due to their unique molecular structures, a variety of properties can be achieved via variations in chemical composition and synthesis routes. The use of PUs in pavement is relatively new, however, the exciting prospective has attracted great research interest. They have been successfully used in various applications in pavement engineering, demonstrating high tensile and compressive strength as well as resistance to deterioration caused by repeated deformation and load cycles. Nevertheless, some drawbacks of PUs should not be overlooked. For example, PUs are sensitive to environmental aging, and thus the durability of polyurethane should be considered when exposed to high temperature, UV light, and high humidity. In addition, the higher cost of PU in comparison with asphalt binder is an important factor which hinders its application.

5. Recommendations for future research

As environment standards for construction are becoming higher in recent years, cold binders are increasingly used. In this review paper, three major cold paving binders were extensively reviewed, i.e., bitumen emulsion, epoxy resin, and polyurethane. Based on the above analysis, these three cold binders are compared with conventional hot mix bituminous binder in Table 13. The handling temperature all decreased compared with asphalt binder, thus the GHG emission during construction phase also decreased. The mechanical performance of bitumen emulsion is generally lower in comparison with bitumen due to the presence of moisture, and when polymer latex is added the performance can be comparable with hot mix bitumen or polymer modified bitumen. The resin type of binders, including epoxy resin and PU, demonstrate increased mechanical performance, including high- and low-temperature performance, adhesion with aggregate, resistance to moisture, and fatigue performance. Furthermore, the cost and environmental impact were also evaluated. In terms of the material cost of the binders, the cost of conventional asphalt binder is about 570 USD/t, and the cost of bitumen emulsion is about 420 USD/t (Yi et al., 2023). Furthermore, the cost of epoxy resin and PU is about 3500 USD/t and 2000 USD/t, respectively (Shi et al., 2022b, Xiong et al., 2024),



(a) (b)

Fig. 47. Moisture sueceptibility of PUC: (a) Marshall stability, and (b) Spliting strength (Hong et al., 2021).

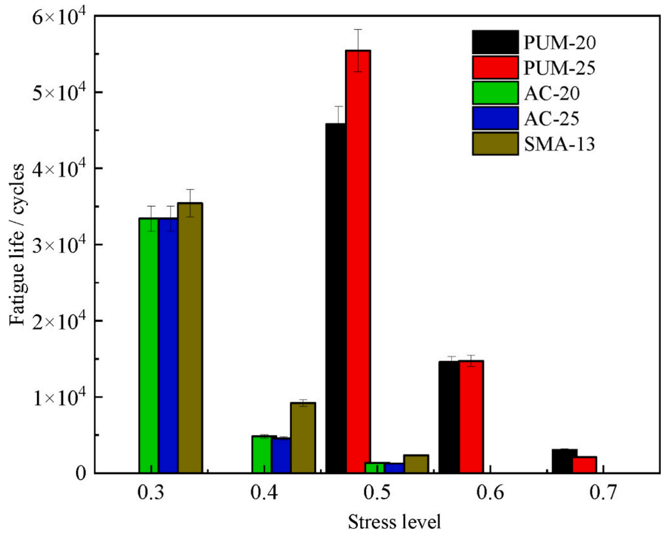


Fig. 48. Fatigue life comparison between PUM, AC and SMA (Zhuang et al., 2023).

significantly higher than that of asphalt binder. In addition, the carbon footprint can be effectively reduced by using cold binders in pavement construction. Anthonissen et al. (2015) demonstrated that the environmental impact of bitumen emulsion cold mix asphalt dropped more than 40 % compared with hot-mix asphalt based on life cycle analysis, and Xiao et al. (2018) pointed out that the GHG emissions lowered as much as 52 % using bitumen emulsion-based cold mixing technology in comparison with traditional hot-mix asphalt. Similarly, previous research found that the GHG emission of the cold mixture bonded by both epoxy resin and PU during construction phase reduced more than 50 % compared with traditional hot-mix asphalt (Chen et al., 2025b, Lu et al., 2019a).

Despite of the aforementioned advantages, the application of these cold binders is still limited due to some shortcomings which needs future research.

(1) Bitumen emulsion

The early strength and overall mechanical performance of bitumen emulsion need to be improved. Use of polymer latexes seems to be a feasible approach to improve the performance of bitumen emulsion. When developing polymer latexes modified bitumen emulsion, compatibility between the latexes and bitumen emulsion, and balanced mechanical performance, should be considered.

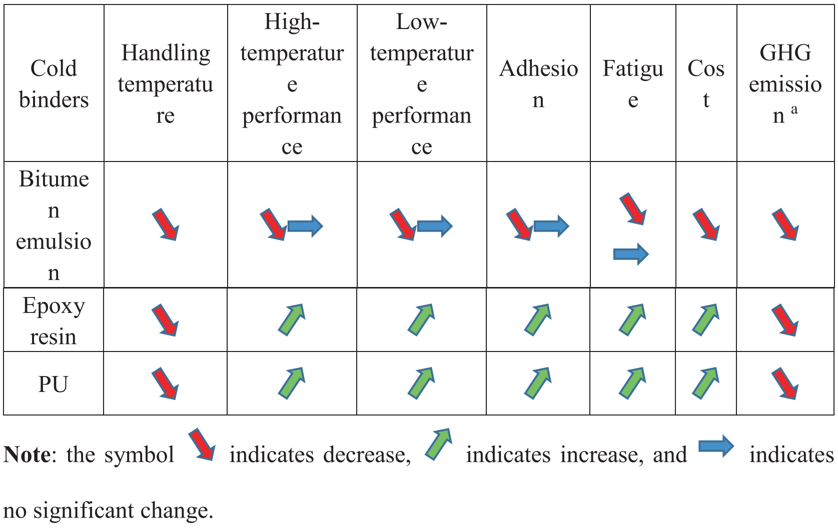
(2) Epoxy resin

Table 12
Representative applications of PUs in pavement.

Application	Polyurethane system	References
Pavement surface layer	Polyol component: (Elastopave® C 6551/202 C-A), and isocyanate component (ElastoCoast® C 6551 C–B)	(Hong et al., 2021), (Chen et al., 2018a)
Pervious pavement	One-component polyether polyurethane; Two-component isocyanate and polyol	(Xu et al., 2023c), (Lu et al., 2019b)
Bridge deck paving	Polycarbonate diol, HDI isocyanate, glycerin and the catalyst DBTL; Polyester polyurethane binder; Polyurethane and polyether polyol	(Jiang et al., 2022), (Niu et al., 2022), (Li and Yu, 2022)
Pothole repairing	Polyurethane prepolymer and dimethylol propionic acid; Diphenylmethane diisocyanate and polyether polyols; Polymethylene polyphenylene isocyanate and polyol	(Liu et al., 2019), (Jiang et al., 2021)
Pavement expansion joints/Joint filler	2, 4-diisocyanate toluene ester and polyadipate-1, 4-butane-diol ester diol	(Xu et al., 2021a), (Shi et al., 2022a)
Others: Pavement coating; Unbound pavement base materials; Grouting material	MDI polyether type polyurethane prepolymer and amino terminated polyether; NA; Isocyanate and polyether polyol	(Chen et al., 2023), (Peng et al., 2023), (Li et al., 2019a), (Zhong et al., 2023), (Liu et al., 2023)

Epoxy resin cold mix binder has found wide applications in pavement due to its high strength. However, epoxy resin is too stiff, leading to insufficient durability. Therefore, enhancement of toughness for epoxy resin is important for its successful application in pavement. Furthermore, epoxy resin is also susceptible to environment aging, resulting in premature degradation which influence its long-term durability. As a result, development and application of anti-aging additives for epoxy resin is recommended. In addition, the thermosetting epoxy resin cannot be melted like asphalt binder at elevated temperature, the recyclability of epoxy resin at the end-of-life is another issue. Currently, there are three different methods to recycle epoxy resins: mechanical degradation, thermal degradation, and chemical degradation (Oliveux et al., 2015). Thus, it is possible to recycle epoxy resin in the future. Furthermore, new research on epoxy resin is emerging, such as bio-based epoxy resin (Jin et al., 2023) and self-healing epoxy resin (Wang et al., 2022a), which may further reduce the environmental impact and increase the durability of epoxy resin.

Table 13
Comparison of different cold binders with hot-mix bitumen.



Cold binders	Handling temperature	High-temperature performance	Low-temperature performance	Adhesion	Fatigue	Cost	GHG emission [a]
Bitumen emulsion	↘	↘➡	↘➡	↘➡	↘ ➡	↘	↘
Epoxy resin	↘	↗	↗	↗	↗	↗	↘
PU	↘	↗	↗	↗	↗	↗	↘

Note: the symbol ↘ indicates decrease, ↗ indicates increase, and ➡ indicates no significant change.

[a] Construction phase.

(3) Polyurethane

Use of polyurethane as cold mix binder in pavement just emerged in recent years. The versatile selection of the raw materials to produce polyurethane with specific properties is one major advantage over other polymers. Nevertheless, there are still some concerns need to be addressed before polyurethane can be applied with meaningful quantities in pavement. Firstly, isocyanate reacts fast with polyols or moisture, making it difficult to handle the material in construction. Secondly, polyurethane is sensitive to environmental aging, and thus the durability of polyurethane should be considered especially when it is used in the surface course. Thirdly, the higher cost of polyurethane in comparison with asphalt binder is an important factor which hinders its application.

6. Summary and conclusions

HMA has been extensively used to in pavement industry, while the VOC, GHG and other hazards produced in the mixing and paving process affect the environment and human health adversely. With ever increasing environmental requirement, this industry is now exploring cleaner materials for pavement construction. Though warm mix asphalts can reduce the mixing temperature to some extent, the most promising and fundamental advancement lies in cold mixing. This novel approach has various benefits, including no/low VOC and GHG, and lower energy consumption. The cold mix binder, which bonds aggregates together at ambient temperature, plays a key role in the environment-friendly cold mixing technique. In this article, three different cold binders in pavement industry were reviewed, including the conventional bitumen emulsion, and the newly emerged epoxy resin and polyurethane.

Bitumen emulsions are commonly used in road engineering. Their applications primarily include surface treating, tack coat and cold recycling. However, bitumen emulsions are inferior to HMA in terms of early strength and mechanical properties, which limited them from been used in structural layers. It is therefore recommended to further modify bitumen emulsions and overcome this weakness. To improve the performance of bitumen emulsion, polymer latexes, such as SBR, NR, SBS, waterborne epoxy resin, etc., are used as modifiers to prepare polymer modified bitumen emulsions. It is found that the incorporation of polymer latexes can form an interconnected polymer structure in the emulsion residues upon curing, and thus the mechanical performance of bitumen emulsion, including high- and low-temperature performance, adhesion with aggregate, and fatigue performance.

Recently, polymers like epoxy resin and polyurethane have been introduced into the pavement industry. Both polymers can react with certain chemicals at ambient temperature, which allows for mixing with aggregates without external heating. Epoxy resin and polyurethane are characterized as fast curing, remarkable mechanical strength, strong adhesion with aggregate and substrates, and superior chemical resistance. However, there are still some shortcomings need to be addressed for the resin binders before they can be applied in large quantities, such as limited workability, insufficient resistance to weathering under high temperature, moisture, UV light, and high initial cost.

CRediT authorship contribution statement

Rui Li: Writing – review & editing, Writing – original draft, Methodology, Funding acquisition, Formal analysis, Conceptualization. **Xinyue Ma:** Writing – original draft, Validation, Investigation, Data curation. **Junheng Chen:** Writing – original draft, Investigation, Data curation. **Zhongchen Pan:** Writing – original draft, Data curation. **Zhen Leng:** Writing – review & editing, Investigation, Conceptualization. **Haopeng Wang:** Writing – review & editing, Investigation. **Manfred N. Partl:** Writing – review & editing, Investigation. **Xiong Xu:** Writing – original draft, Investigation. **Naipeng Tang:** Writing – original draft, Investigation. **Chunxiang Huang:** Writing – original draft, Investigation. **Hongzhou Zhu:** Writing – review & editing, Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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