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Investigation of Polyurethane Modified Cold Bitumen for Fast Cold In-Place Recycling

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Abstract

Cold in-place recycling is gaining more attention worldwide because of its lower energy consumption, while the normally used asphalt emulsion and foamed asphalt cannot meet this requirement of short traffic disturbance and road performance of the surface layer. In this research, a polyurethane-modified cold binder (PMCB) was designed and investigated for the fast and high-quality cold in-place recycling of reclaimed asphalt. For the first step, functional group analysis and fluorescent microscopy were used to reveal the curing process and the modification mechanism of the PMCB. Then a series of rheological tests were used to comprehensively evaluate the viscoelastic properties of the PMCB at different curing stages. Finally, the mechanical performance of the PMCB mortar sample was evaluated with the monotonic tensile test and tensile fatigue test. The results indicated that the polymerization reaction in the PMCB consisted of three reactions, and the urethane/urea linkage led to the formation of the polymeric network. The polyurethane polymeric network led to a significant increase in the complex modulus and a decrease of the phase angle. The PMCB also exhibits suitable viscosity at environmental temperatures, good relaxation properties at low temperatures, and less temperature sensitivity. Compared to the base asphalt and styrene butadiene styrene polymer modified bitumen mortar samples, the PMCB mortar samples showed significant advantages in tensile strength, dissipation energy, and tensile fatigue properties. Furthermore, the polyurethane-modified cold asphalt mixture (PMCM) showed better indirect tensile strength than the porous asphalt mixture with fresh aggregate and fresh asphalt binder when the curing time of the PMCM reached 6 h.

Keywords

infrastructure, construction, project delivery methods, cold recycling, materials, binders, asphalt binder modifiers, rheological properties

Nowadays, considering the current global interest to deploy pavement recycling with less traffic disturbance and lower energy consumption, cold in-place recycling is gaining more attention worldwide (1, 2). The strength gain speed of pavements in cold in-place recycling is relatively slow, which is seriously influenced by the environmental condition in the field (temperature, humidity, and wind), especially in the Netherlands. As the interruption of traffic may lead to increased traffic flow problems, the available time window for the roadway may often be as short as 4 h. The normally used asphalt emulsion and foamed asphalt cannot meet this requirement, which may lead to long-time traffic disturbance and result in rutting disease before fully hardening of the mixture. For these reasons, proper binder selection and reasonable mixing process design are necessary to develop

a fast, reliable, high-quality, environmentally friendly, and financially attractive cold in-place recycling and maintenance technology.

The polyurethane-modified bituminous mixture has received increasing attention because of its excellent

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performance as a new type of pavement material (3–5). The polyurethane-modified bituminous binder is a two-phase chemical system in which the thermosetting polyurethane is the dispersed phase and bitumen is the continuous phase. The tensile strength of the bituminous binder was enhanced when the polyurethane was uniformly distributed in the bituminous material. Previous research showed that the polyurethane-modified bituminous mixture has excellent road performance and has been used successfully in many porous pavements (6–8). The problem is that polyurethane-modified bitumen (PMB) needs to be used at 120–140°C, which does not meet the requirement of cold in-place recycling.

To address this problem, a three-component polyurethane-modified cold binder (PMCB) was designed in the lab at the Delft University of Technology for the quick in-place recycling of reclaimed asphalt pavement (RAP) materials. The main difference between PMB and PMCB is that the PMB is in a solid state, while the PMCB is in a liquid state at environmental temperature. The three individual components of the PMCB are in the liquid state with low viscosity at environmental temperature and can be stored for more than three months without deterioration. During application, the three components of the PMCB can be mixed at the designed ratio at atmospheric temperature in the field (5–35°C) to trigger the condensation reaction of polyisocyanate and polyol, which is similar to the reaction that occurred in the PMB (5, 9). Another difference between the PMCB and the PMB is that the polyurethane content in the PMCB (>30%) is much higher than that in the PMB, which ensures a high level of performance even when the PMCB is applied at atmospheric temperatures.

After homogeneous mixing, the polymerization reaction of the PMCB started, and the initial viscosity ensures the workability for mixing, paving, and compaction. After compaction, the cold recycling mixture will gradually gain strength, and the curing speed is determined by the environmental temperature. The main objective of this study is to investigate the reaction mechanism, curing process, and comprehensive evaluation of this new type of cold binder for cold in-place recycling.

Materials and Methods

Materials and Preparation

Materials. A three-component PMCB was designed for the quick in-place recycling of reclaimed asphalt. The three-component PMCB can be mixed at the designed ratio at room temperature in the field (5–35°C), as the viscosity of the PMCB is not strongly affected by temperature. After homogeneous mixing, the polymerization reaction started, and the PMCB transformed from the

Table 1. Basic Physical Properties of Binder Samples

Properties	Measurement
Base bitumen	
Penetration at 25°C, 100 g, 5 s (0.1 mm)	76
Softening point (°C)	50.2
PG-grade	PG 64-16
Viscosity @ 130°C	0.54
SBS modified bitumen (SMB)	
Penetration at 25°C, 100 g, 5 s (0.1 mm)	52
Softening point (°C)	68.2
PG-grade	PG 70-22
Viscosity @ 130°C	1.865
Polyurethane modified cold bitumen (PMCB)	
Viscosity at beginning @ 15°C (Pa.s)	1.62
Viscosity at beginning @ 25°C (Pa.s)	1.58

Note: SBS = styrene butadiene styrene; PG = Performance Grade.

liquid state to the solid state in the following hours. Meanwhile, base bitumen and SBS (styrene butadiene styrene) polymer modified bitumen (SMB) were used for comparison. Detailed information on the base bitumen, PMCB, and SMB can be seen in Table 1.

Sample Preparation. In this research, the hardening processes and rheological and mechanical properties of the PMCB were evaluated at the binder, mortar, and mixture levels. In the application of the PMCB, component A was first mixed with component B using a high-speed mixer at 500 rpm for about 60 s until the mix reached a homogenous state. Then, component C is added to the homogeneous mixture obtained in the previous step and mixed with a high-speed mixer at 500 rpm for another 120 s until a homogeneous mixture is achieved. As the reaction begins after mixing and the viscosity of the PMCB increases gradually, it is suggested to use the mixed PMCB within 30 min.

The asphalt mortar is the first decentralized system of an asphalt mixture and represents the matrix of the asphalt mixture between the aggregates. To characterize the mechanical property of the PMCB at the mortar level, PMCB mortar samples were prepared with the following procedures. Firstly, the newly mixed PMCB was mixed with fine aggregates (0–2 mm) in the ratio of 1:2. The ratio was chosen because, according to the gradation analysis of the RAP, there is almost no filler in the RAP and the ratio between the binder and fine aggregate (0–2 mm) is about 1:2. Secondly, the mixed mortar was poured into a designed silicon-rubber mold (see Figure 1a). Finally, after 24 h of curing, the PMCB mortar samples were used to conduct the direct tensile test and tensile fatigue test with Universal Testing Machine UTM-25 (see Figure 1c) to characterize the tensile strength and tensile fatigue performance, respectively.

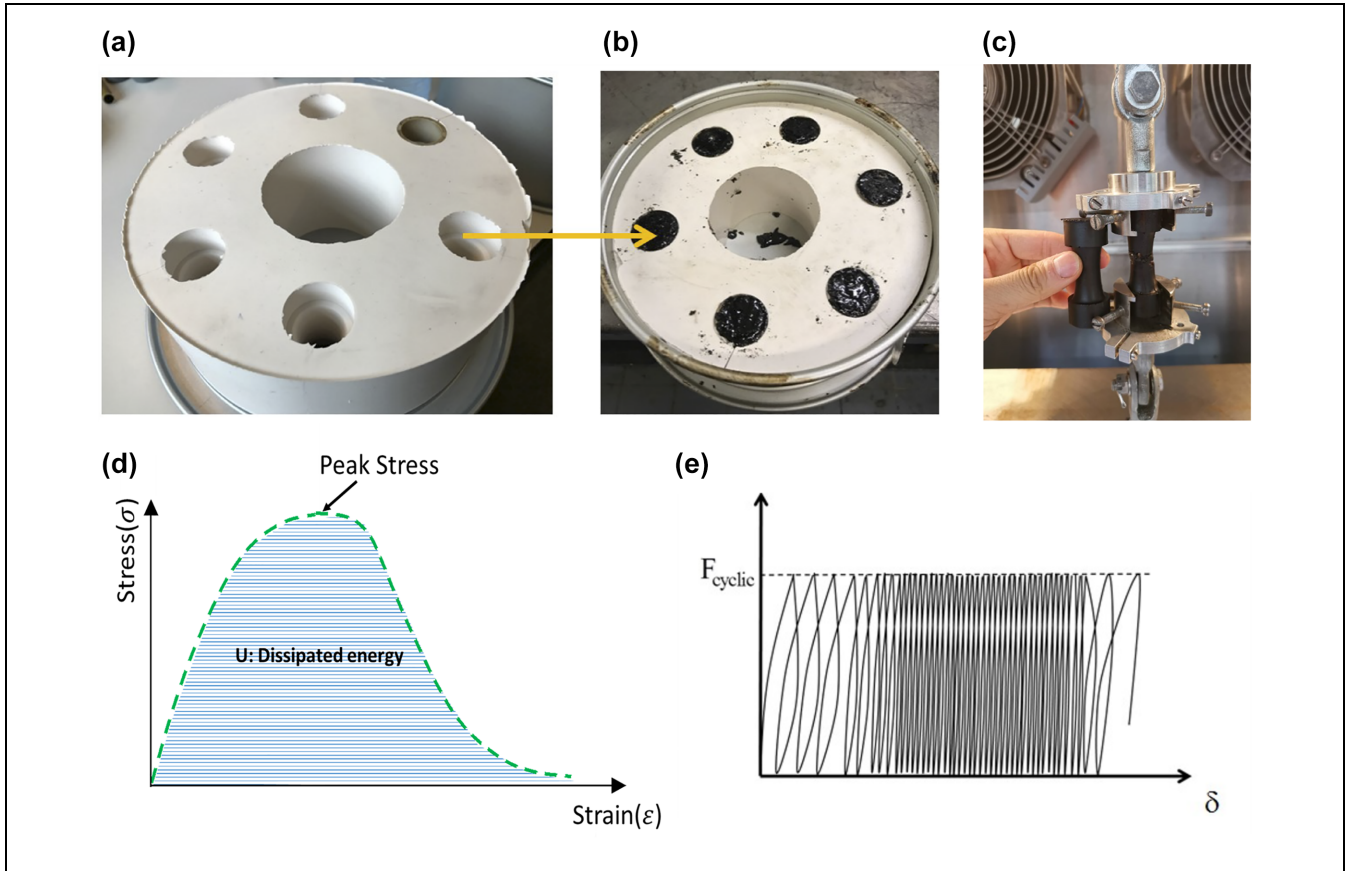


Figure 1. Mortar sample preparation and test method: (a) sample mold, (b) sampling, (c) loading device, (d) direct tensile $\sigma - \epsilon$ curve, and (e) fatigue loading spectrum.

Table 2. Sieve Passing Rate of the Polyurethane-modified Cold Asphalt Mixture

Asphalt mixture	Quality percentage of passing following sieves (mm [%])						
	22	16	11.2	8	5.6	2	0.063
PA-16	100	96.5	77.5	42.5	22.5	15	6

To evaluate the performance of the PMCB at the mixture level, polyurethane-modified cold asphalt mixture (PMCM) cylindrical specimens with a height of 50 mm and diameter of 100 mm were prepared with a Superpave Gyrotory Compactor (SGC). The porous asphalt with nominal maximum particle sizes of 16 mm (PA-16) was selected as the mixture structure, as PA-16 is most widely applied in the Netherlands. The gradation of PA-16 mixture specimens follows the mid-value of recommended gradation in the specification (RAW-2015), as shown in Table 2. RAP materials were collected and sieved for PMCM specimen preparation. Meanwhile, 5.2% was selected as the binder content for PMCM specimen preparation, as 5.2% is the minimum binder content for durable porous asphalt in the Dutch specification (RAW-2015). As a benchmark, the standard porous asphalt

mixture specimens were prepared with base bitumen and fresh aggregate with the same PA-16 gradation, coded as Base-PA16. The objective of selecting RAP and fresh aggregate for different specimens was to compare the performance of the PMCM with the most widely used porous asphalt mixture in the Netherlands.

Test Methods

Attenuated Total Reflection Fourier Transform Infrared Spectroscopy. Functional group distribution can be used to characterize the polymerization reaction of polyurethane in the PMCB. In this research, the hardening process of the PMCB was detected by an attenuated total reflection Fourier transform infrared (ATR-FTIR) spectrometer from PerkinElmer with a single-point ATR fixture. The

scanning range of the wavenumber was from 600 to 4000 cm^{-1} . The number of scan cycles was 12, and the instrument resolution was 4 cm^{-1} . The FTIR tests were conducted with three repetitions for each binder sample.

Fluorescent Microscopy. Fluorescence microscopy is one of the most widely used methods to research the morphology of PMB, which can characterize the binder's miscibility (3). In this research, the fluorescence microscopy test was performed using an Olympus microscope to track the evolution of the morphology of the PMCB during the hardening process.

Viscosity Test. To investigate workability evolution and the hardening process of the PMCB, the Brookfield rotational viscometer (THERMOSEL, BROOKFIELD, Stoughton, MA, U.S.A.) was used to determine the rotation viscosity at different curing times, according to the NEN-EN 13302 standard. At each temperature, the viscosity tests were firstly conducted at a shear rate of 20 rpm to get initial viscosity (rotation viscosity of binder before hardening) to evaluate the workability of the PMCBs. The viscosity test was then performed at 0.1 r/min at isothermal conditions until the viscosity of the PMCB reached the Brookfield viscometer limit (20,000 Pa.s). The evolution of the viscosity and the curing time at different temperature conditions will be used to describe the hardening process of the PMCBs. The viscosity test was conducted with three repetitions for each binder sample.

Temperature Sweep Test. To investigate the evolution of rheological properties, the PMCB samples were characterized using a dynamic shear rheometer (DSR, Anton Paar, EC Twist 502). The PMCB sample will become a stiff solid state after curing, which cannot be loaded on the DSR device. Thus, the PMCB samples were loaded in a liquid state after mixing, and the curing process occurs in the DSR. In all rheological tests performed with the DSR, 25-mm plate and 1-mm thickness were chosen to prevent the runoff of the PMCB. Viscoelastic characteristics, such as the complex modulus and phase angle, were used as reliable indicators for describing the mechanical properties of the PMCBs. The sample was placed onto the bottom plate at the desired test temperature ($\pm 0.1^\circ\text{C}$), and then isothermal temperature sweep measurements were performed at frequencies of 10 rad/s at temperature steps of 2°C from 0°C to 80°C . For each PMCB sample, three replication of the temperature sweep test was conducted.

Frequency Sweep Test. As a viscoelastic material, the rheological behavior of bitumen depends on time and temperature. Complex modulus and phase angle master

curves were constructed to assess the rejuvenation effect. Frequency sweep tests between 0.01 and 10 Hz were performed at 0°C , 20°C , 30°C , 40°C , 60°C , and 80°C in the DSR. As the PMCB samples can only be loaded in the liquid state, 25-mm plate and 1-mm thickness were chosen to prevent the runoff of the PMCB. In this research, the reference temperature for the master curves was 30°C , and the strain amplitude was within the linear viscoelastic (LVE) range. For each PMCB sample, three replications of the frequency sweep test were conducted.

The complex modulus master curves were constructed using the sigmoidal model and non-linear least-squares regression optimization with the Microsoft Excel Spreadsheet Solver function (10,11). The sigmoidal model is defined as follows:

$$a(T) = \frac{\omega_r}{\omega} \quad (1)$$

$$\log |G^*| = \nu + \frac{\alpha}{1 + e^{(\beta + \gamma \log f_r)}} \quad (2)$$

where $a(T)$ is the shift factor at the reference temperature T , ω_r is the reduced angular frequency at the reference temperature (rad/s), ω is the angular frequency at the tested temperature (rad/s), $|G^*|$ is the complex modulus (Pa), f_r is the reduced frequency, and α , β , γ are coefficients.

Relaxation Test. The relaxation test was conducted to evaluate the relaxation ability of the PMCB at low temperatures. As the PMCB can only be loaded in the liquid state before fully curing, 25-mm plates and a 1-mm gap were selected for the relaxation test to prevent the runoff of the PMCB. The relaxation tests were performed by increasing the strain to 1% in 0.1 s, followed by a relaxation period of 100 s while keeping the strain constant. The frequency of data collection was 100 Hz. The relaxation test was repeated three times for each binder sample.

Direct Tensile Test and Tensile Fatigue Test for the PMCB Mortar Sample. To compare the tensile strength and tensile fatigue properties of the PMCB mortar samples, the direct tensile strength of mortar samples was evaluated with the UTM-25 under controlled isothermal temperature conditions. To reduce undesired eccentricities, the specimens were carefully positioned in specially designed steel hinges (see Figure 1c). Furthermore, to control the crack/failure position, the conductive asphalt mortar specimens have been made in a parabolic geometry shape, with a height of 34 mm for the parabolic part and a thickness of 16.5 mm in the middle (12).

The mortar sample was loaded in tension with a displacement-controlled speed of 0.1 mm/s. The result of the monotonic tensile test is a series of force–

displacement data, as shown in Figure 1*d*. The tensile strength was calculated on the basis of the sample geometric configuration, and the calculated value can be used for further comparison. The force–displacement data can be converted to stress–strain data by the following formula:

$$\sigma = \frac{F}{0.25 \cdot \pi d^2} \quad (3)$$

where d is taken by the smallest diameter (16.5 mm) of the sample that is located in the middle of the specimen; the result is called engineering stress, and the corresponding strain is defined by the following:

$$\varepsilon = \frac{\Delta l}{l_0} \quad (4)$$

in which Δl is the displacement of the specimen recorded in the test, and l_0 (34 mm), which is the initial height of the specimen. These results then are post-processed to build the stress–strain curve.

Finally, the peak stress and the total amount of dissipated energy of the test can be determined. The term “energy” is obtained by integrating the total area under the stress–strain curve and simply explained by the following equation:

$$U = \int_0^{\varepsilon} \sigma d\varepsilon \quad (5)$$

Afterward, the fatigue tests are carried at -10°C with a loading frequency of 10 Hz, and the load level is determined by 35% of the peak load (Figure 1*d*) in the monotonic test results. The fatigue loading spectrum is shown schematically in Figure 1*e*. The goal here is to observe the influence of polyurethane on the fatigue performance of a mortar mix. Fatigue life is determined as the maximum cycle in which the sample develops significant deformation (response degradation).

Indirect Tensile Test for the PMCM. To evaluate the indirect tensile strength (ITS) for PMCM samples, an indirect tensile test (ITT) was conducted according to the specification (NEN-EN 12697-23). The ITS is used to evaluate the cracking resistance of the asphalt mixture, and the calculation is given in Equation 6:

$$ITS = \frac{2P}{\pi DH} * 1000 \quad (6)$$

where ITS is the ITS, expressed in kilopascals (kPa), rounded to three significant figures; P is the peak load, expressed in newtons (N), rounded to a whole number; D is the diameter of the specimen, expressed in millimeters (mm), to one decimal place; H is the height of the

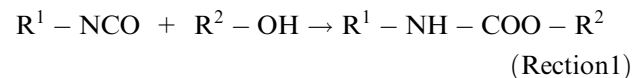
specimen, expressed in millimeters (mm), to one decimal place.

Results and Discussion

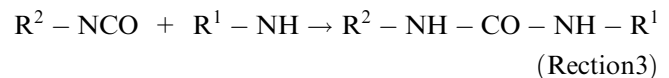
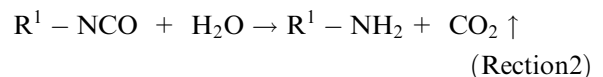
Chemical and Morphology Properties of the Binder

Functional Group Analysis. During the curing of the PMCB, there are complex polymerization reactions among polyol components, isocyanate groups, hydroxy groups in bitumen, and air moisture (i.e., water in the environment) (2, 13, 14). These complex reactions not only influence the functional groups but also are closely linked to the morphology and rheological and viscoelastic properties of the PMCB. Thus, FTIR tests were used to analyze the evolution of functional groups of the PMCB at different curing times to investigate the curing process and the modification mechanism of the PMCB.

Figure 2 depicts the FTIR results of the base bitumen, SMB, and PMCBs at different curing times. As shown in Figure 2*a*, the reaction led to a significant decrease in the $-\text{NCO}$ group (peak at 2250 cm^{-1}) and a significant increase in the $-\text{C}=\text{O}$ group (peak at 1725 cm^{-1}). The reactions started after mixing and continued for 20 days until the $-\text{NCO}$ peak totally disappeared. The reaction in the PMCB is mainly between the $-\text{NCO}$ group (peak at 2250 cm^{-1}) in isocyanate and the $-\text{OH}$ group in polyol, and the product is the $-\text{C}=\text{O}$ group (peak at 1725 cm^{-1}) in the polyurethane (15, 16). The reaction can be described as follows:



Meanwhile, there is a significant increase in the peak at 1604 cm^{-1} , which corresponds to the formation of urea (17, 18). The reaction can be described as follows:



Thus, the chemical modification mechanism of the PMCB can be described as three steps. Firstly, the polyol and the isocyanate reaction lead to the formation of urethane bonds between polymer and hydroxide groups in bitumen (mainly present in asphaltene, resin, and aromatics). Secondly, the isocyanate component available in the binder reacts with water from the environment and yields unstable carbamic acid. The unstable carbamic acid decomposes into amine and carbon dioxide (Reaction 2). Finally, the active amine reacts with

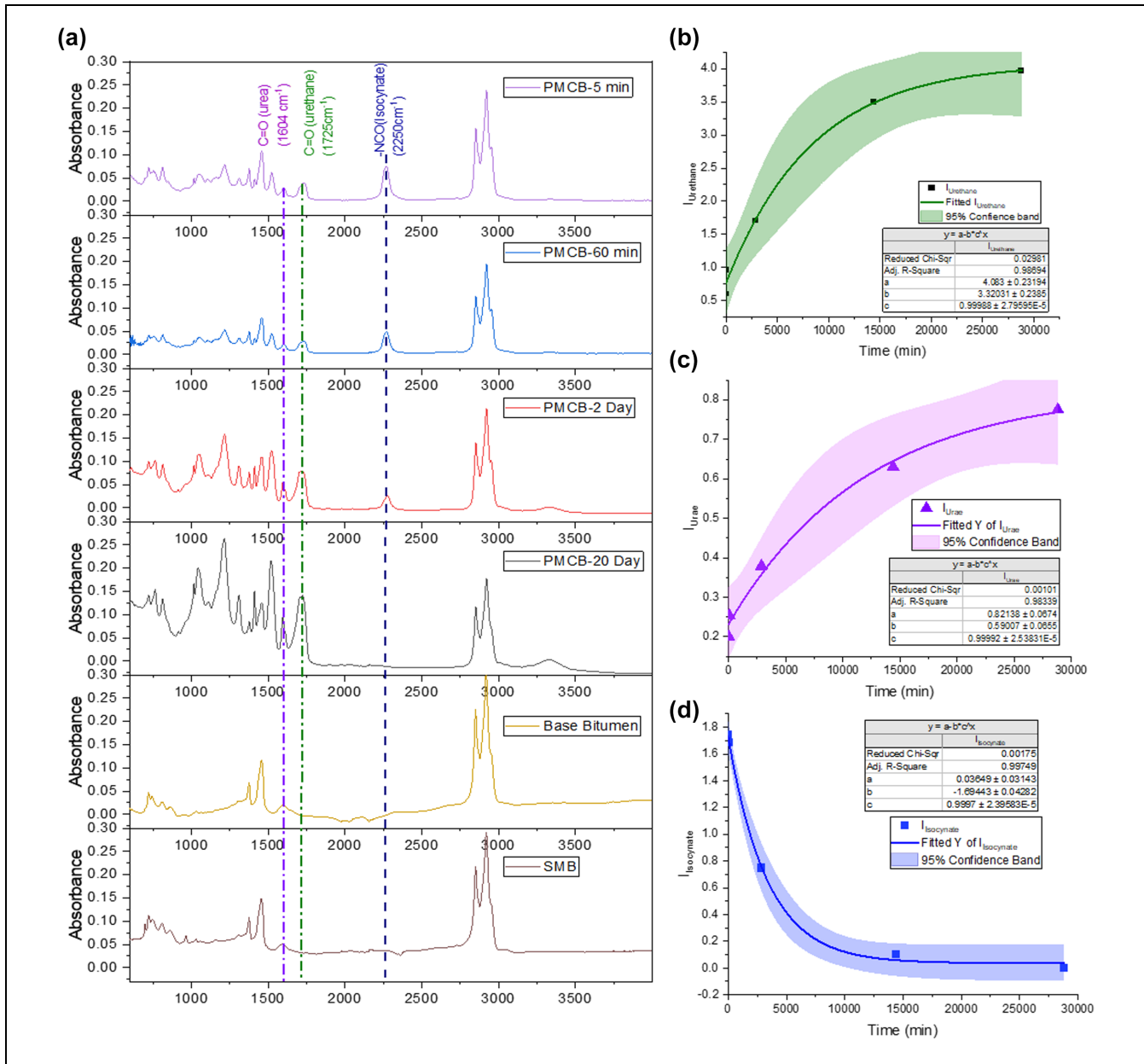


Figure 2. Fourier transform infrared (FTIR) spectroscopy results: (a) FTIR spectra of the polyurethane modified cold binder (PMCB), base bitumen, and styrene butadiene styrene polymer modified bitumen (SMB), (b) evolution of $I_{urethane}$ with curing time, (c) evolution of I_{urea} with curing time, and (d) evolution of $I_{isocyanate}$ with curing time.

isocyanate groups left in the binder with the formation of urea groups (19) (Reaction 3).

To quantitatively assess the complex chemical reaction in the PMCB, the urethane index $I_{urethane}$, urea index I_{urea} , and isocyanate index $I_{isocyanate}$ are proposed, which are calculated as follows.

Urethane index :

$$I_{urethane} = \frac{A_{1725}}{A_{1460} + A_{1375}} \quad (7)$$

Urea index :

$$I_{urea} = \frac{A_{1604}}{A_{1460} + A_{1375}} \quad (8)$$

Isocyanate index :

$$I_{isocyanate} = \frac{A_{2250}}{A_{1460} + A_{1375}} \quad (9)$$

The evolution of $I_{urethane}$, I_{urea} , and $I_{isocyanate}$ with curing time can be seen in Figure 2, b–d. As demonstrated in

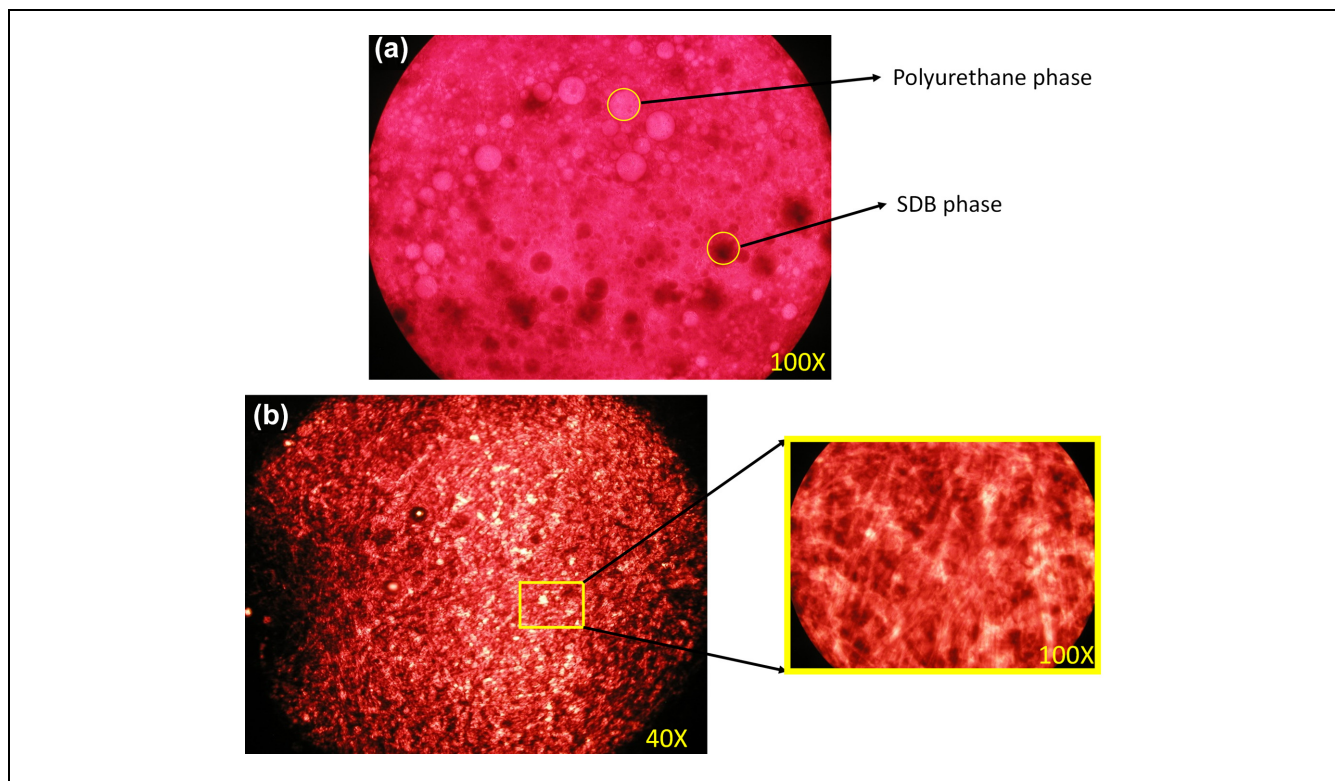


Figure 3. Optical microscopy observation of the polyurethane modified cold binder: (a) start of curing and (b) after 1 h of curing. SDB = Solvent Dissolved Bitumen.

Figure 2, *b* and *c*, the $I_{urethane}$ and I_{urea} increased quickly at the start and the increasing rate gradually decreased with the increase of curing time. The increase of $I_{urethane}$ and I_{urea} followed a significant exponential function, and the fitting curve and function are illustrated in Figure 2. Similarly, the $I_{isocyanate}$ decreased quickly initially and gradually slowed down, which also followed an exponential function. When the curing time was longer than seven days (10,080 min), the reaction rate was relatively slow, and after 20 days (28,800 min), the reaction was almost finished.

Optical and Fluorescent Microscopy. During the polymerization reaction of the PMCB, the urethane/urea linkage leads to the formation of a polymer network between polyurethane polymer and certain bitumen groups, which leads to a significant change in microstructure and morphology (15). To characterize and track the evolution of the morphology and microstructure of the PMCB during curing at 25°C, optical microscope and the fluorescent microscope observations were conducted. The morphology of the PMCB can be seen in Figures 3 and 4.

Figure 3*a* shows that the PMCB is a bi-phase system at the start of the curing, and the polyurethane network has not been established. The light color phase mainly consisted of the mix of polyol and isocyanate, and the

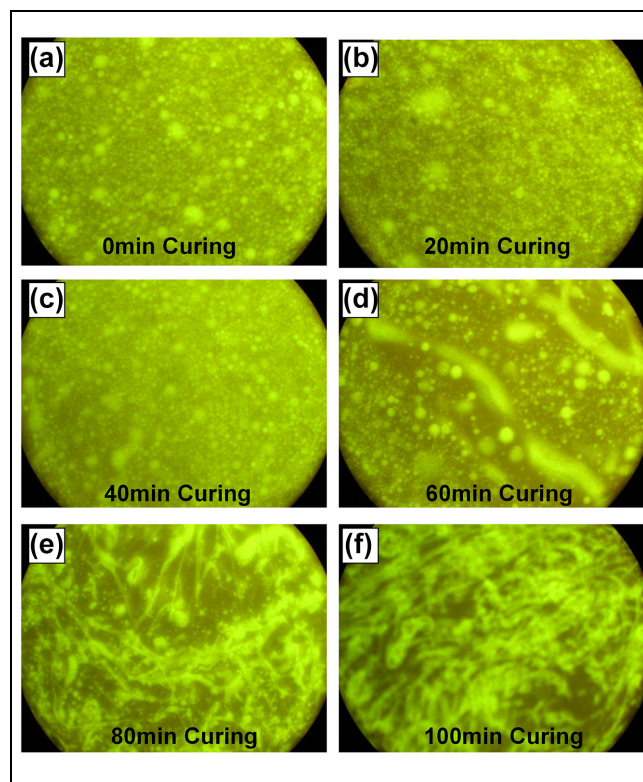


Figure 4. Fluorescent images of the polyurethane modified cold binder at different curing times (magnification = 100×).

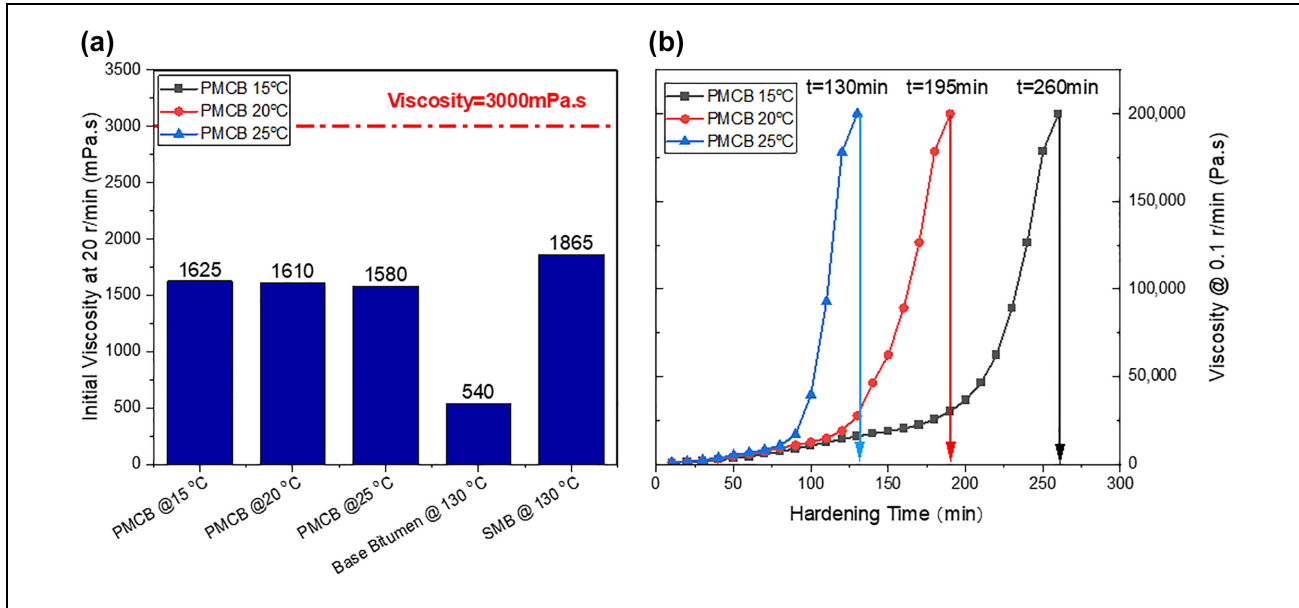


Figure 5. The viscosity of the polyurethane modified cold binder (PMCB) at different curing times: (a) initial viscosity and (b) evolution of viscosity at different curing times.

dark color phase mainly consisted of the bitumen phase. The two phases were homogeneously distributed, indicating no segregation in the PMCB at the beginning of curing. After 60 min of curing time, the microstructure of the PMCB can be seen in Figure 3b. The bi-phase systems in the PMCB are interlocked with each other, indicating the formation of the polyurethane network. Meanwhile, the morphology of the PMCB is uniform in the observation, indicating the binder is in a homogeneous state without segregation after curing.

Figure 4 shows the formation process of the polyurethane network with fluorescent microscopy observation. As shown in Figure 4, *a–c*, the two phases are separated, indicating the polyurethane network was not formed when the curing time was less than 40 min. As shown in Figure 4, *d–f*, the polymeric network structure was gradually formed when the curing time was longer than 60 min, which led to a significant increase in the viscosity and complex modulus.

Rheological Property of the Binder

Viscosity Analysis. The environmental temperature significantly affects the curing speed of polyurethane, while the influence of temperature on the curing of PMCBs is still unclear. In this research, three typical environment temperatures (15°C, 20°C, and 25°C) were chosen to investigate the influence of the temperature on the curing process of the PMCBs. At each temperature, the viscosity tests were firstly conducted at a shear rate of 20 r/min to get the initial viscosity (rotation viscosity of the binder before hardening) to evaluate the workability of the

PMCBs. The viscosity test was then performed at 0.1 r/min at isothermal conditions until the viscosity of the PMCB reached the Brookfield viscometer limit (20,000 Pa.s). The viscosity results of the base bitumen, SMB, and PMCB at different temperatures can be seen in Figure 5.

As illustrated in Figure 5a, the initial viscosities of the PMCB at 15°C, 20°C, and 25°C were nearly the same, which were not temperature sensitive. Meanwhile, the initial viscosity of the PMCB was about 1600 mPa, which was between the viscosity of the base bitumen and SMB at 130°C. This indicates that the workability of the PMCB is suitable at room temperature (15–25°C). The evolution of viscosity with curing time can be seen in Figure 5b. It can be observed that the viscosity increased slowly at the beginning and increased quickly after a specific curing time, and the curing temperature significantly influenced the curing speed. At 25°C, the viscosity increased quickly when the curing time was more than 60 min, which is consistent with the formation of a polymeric structure in the optical microscope and the fluorescent microscope observations. When the viscosity of the PMCB reached 200,000 Pa.s, the PMCB was transferred from the liquid state to the gel state and gradually gained strength. The curing time needed to reach the gel state varies from 130 to 260 min, which was significantly influenced by the curing temperature.

Time Sweep Test Analysis. During the curing process of the PMCB, the viscosity and complex modulus of the PMCBs increase with the increase of curing time, which

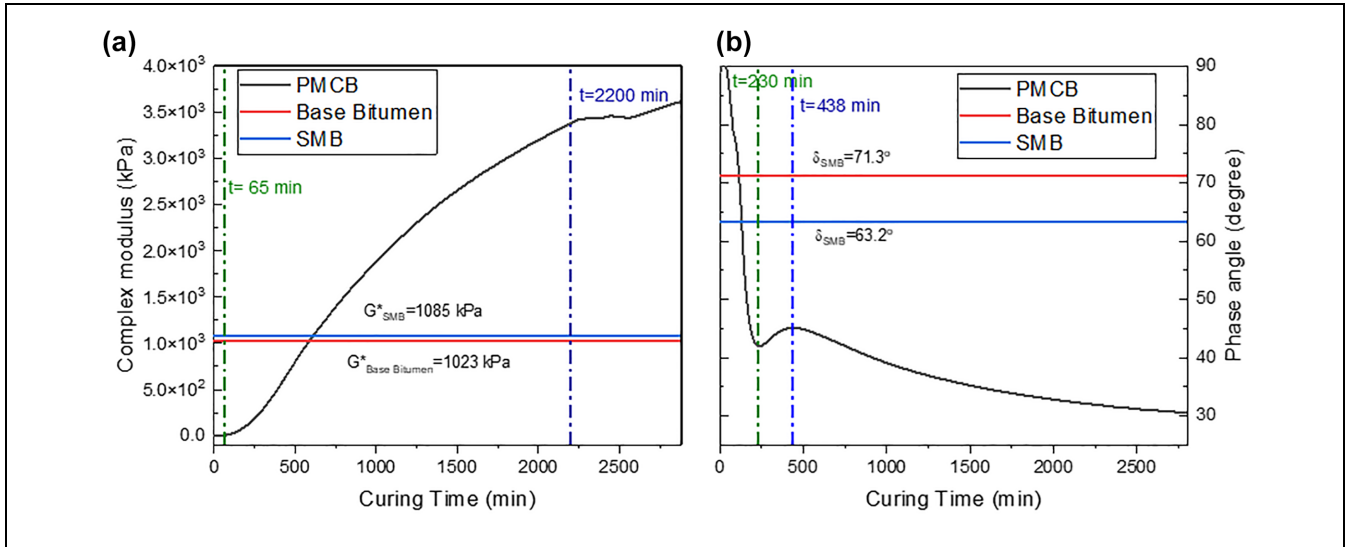


Figure 6. (a and b) Evolution of the complex modulus and phase angle of the polyurethane modified cold binder (PMCB), base bitumen, and styrene butadiene styrene polymer modified bitumen (SMB) with curing time at 25°C.

is caused by the polymerization reaction and the formation of a polymer network structure. To track the curing process of the PMCB at 25°C, an oscillation test was conducted with the DSR at a frequency of 10 rad/s and a strain level of 0.1% for 48 h. The complex modulus and phase angle results can be seen in Figure 6.

As shown in Figure 6, the curing process of the PMCB can be divided into three phases. Firstly, when the curing time was less than 230 min, the phase angle decreased from 90 to 40 degrees and the complex modulus increased slowly, indicating that the PMCB was transformed from the liquid state to the gel state. Secondly, when the curing time was more than 230 min and less than 2200 min, the phase angle of the PMCB decreased slowly, and the complex modulus increased quickly, indicating that the PMCB was transformed from the gel state to the solid state. Finally, when the curing time was more than 2200 min, the complex modulus increased slowly, indicating that the hardening of the PMCB became slow, which may be caused by the decrease of the curing speed.

Temperature Sweep Test Analysis. To evaluate the temperature sensitivity, the PMCB was used to conduct the temperature sweep test with the DSR. The temperature increased from 0°C to 80°C at a speed of 2°C/min, and the oscillation test was conducted at the frequency of 10 rad/s. The complex modulus and phase angle results can be seen in Figure 7.

As demonstrated in Figure 7a, the phase angle of the base bitumen increased continuously from 30° to 90° with the increase of temperature. However, the phase

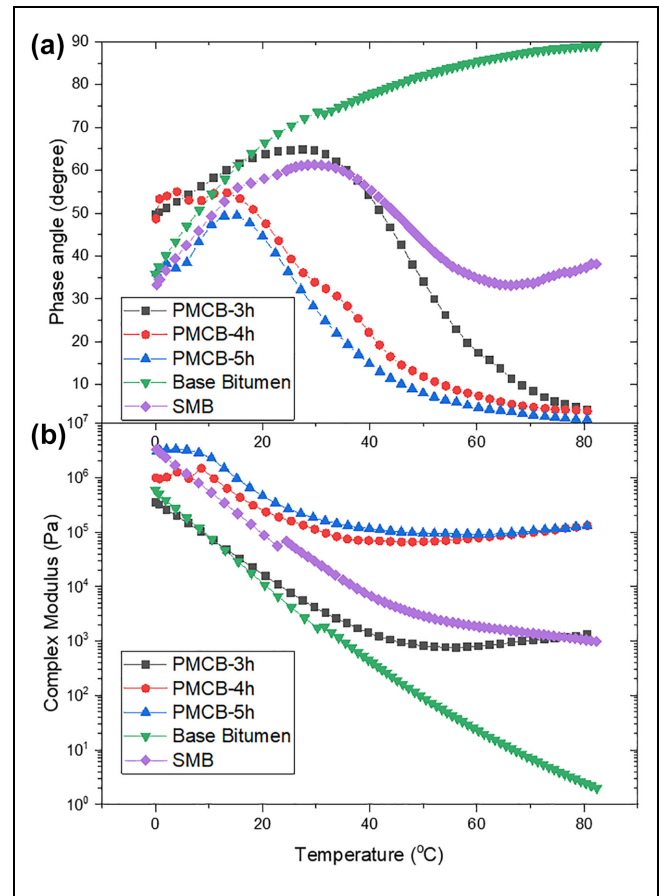


Figure 7. Temperature sweep test results of the base bitumen, styrene butadiene styrene polymer modified bitumen (SMB), and polyurethane modified cold binder (PMCB) at different curing times: (a) phase angle and (b) complex modulus.

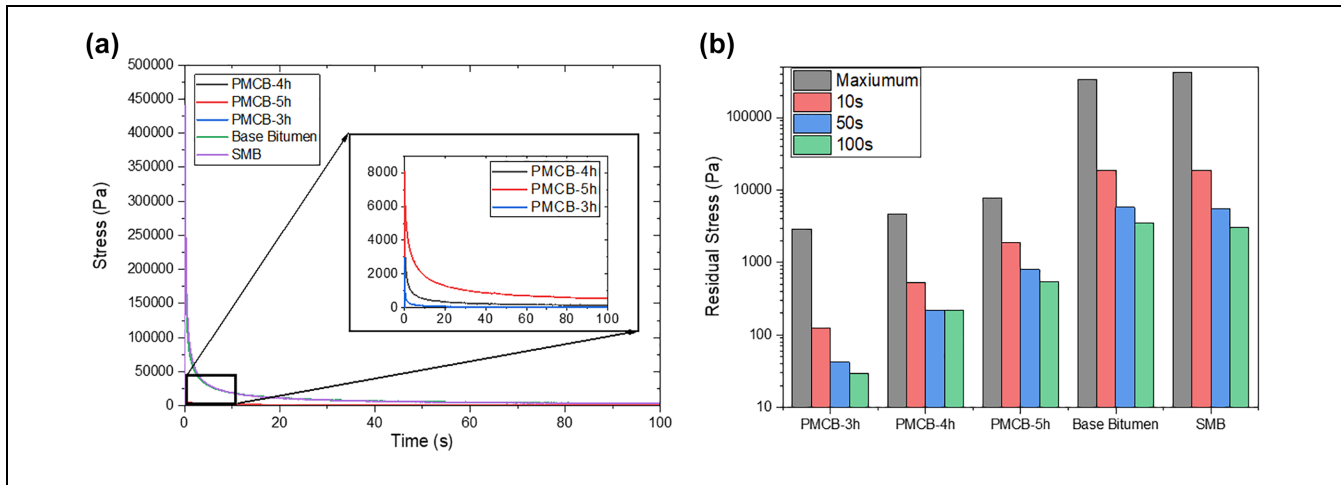


Figure 8. Relaxation test results of the base bitumen, styrene butadiene styrene polymer modified bitumen (SMB), and polyurethane modified cold binder (PMCB) at different curing times.

angle of the SMB and PMCBs increased firstly and then decreased with the increase of temperature. A distinct phase angle plateau is formed in both the SMB and PMCB adhesives, indicating the formation of a polymeric network (1, 3, 4). When the temperature was higher than 40°C, the polymer phase played a prominent role, and the PMCBs were prone to show the elastic property. Meanwhile, with the increase of curing time, the polymeric network was stronger and the phase angle became lower.

Figure 7b shows that the complex modulus of the base bitumen continuously decreased with the increase of temperature. When the temperature reached 80°C, the complex modulus of the base bitumen was nearly zero. As for the 3-h cured PMCB, the complex modulus of the PMCB was much higher than that of the base bitumen and SMB, indicating excellent high-temperature stability of the PMCB. Furthermore, with the increase of curing time, the PMCB became less sensitive to the change of temperature. This indicates that the polyurethane in the binder formed a network structure, which improved the deformation resistance at high temperatures (7, 20).

Relaxation Test Analysis. The low-temperature cracking resistance of the base bitumen, SMB, and PMCBs were evaluated with a relaxation test at 0°C. The relaxation test was conducted first with 1% strain in 0.1 s, followed by a relaxation period of 100 s, and the relaxation results can be seen in Figure 8.

As shown in Figure 8a, the residual stress of the bitumen binders reached maximum stress at 0.1 s and then decreased over time because of their relaxation ability. From Figure 8a, the maximum stress of the PMCBs was much lower than those of the base bitumen and SMB.

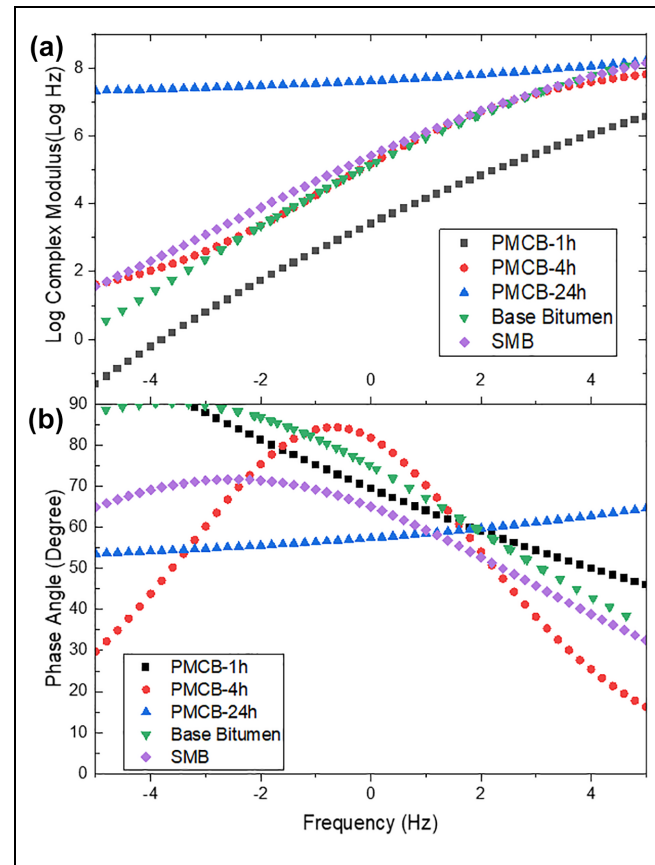


Figure 9. Master curves of the base bitumen, styrene butadiene styrene polymer modified bitumen (SMB), and polyurethane modified cold binder (PMCB) at different curing times: (a) complex modulus master curves and (b) phase angle master curves.

The main reason may be that the PMCB was not as temperature sensitive as the base bitumen and SMB. To quantitatively analyze the low-temperature properties of

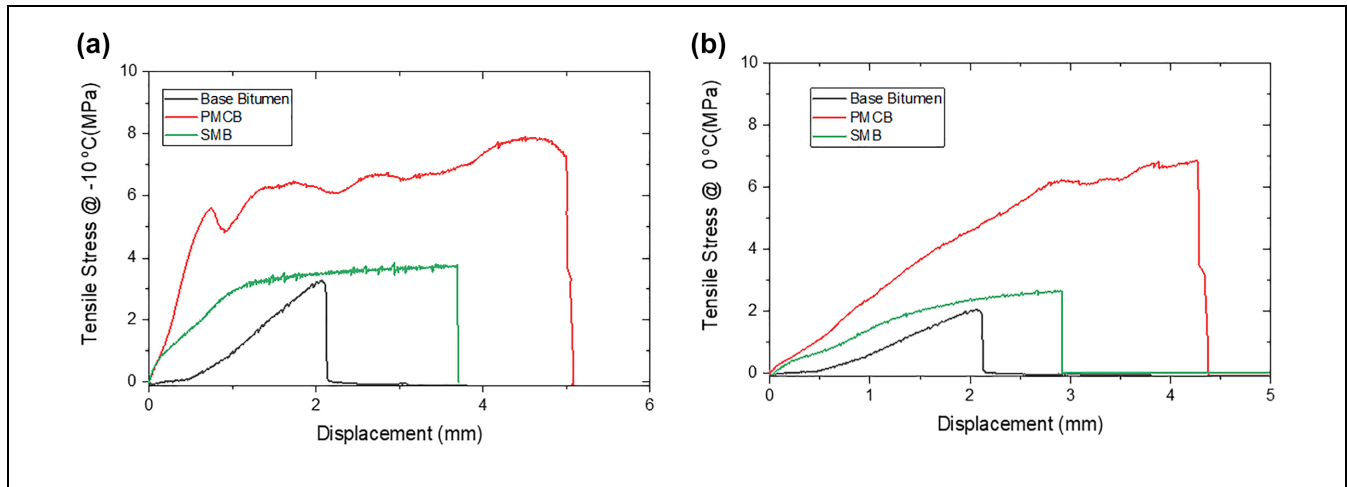


Figure 10. (a and b) The tensile stress of the base bitumen, styrene butadiene styrene polymer modified bitumen (SMB), and polyurethane modified cold binder (PMCB) mortar samples at -10°C and 0°C .

bitumen binders, the residual stress at different relaxation times was summarized, and the results can be seen in Figure 8b. Consistent with Figure 8a, the maximum stress and residual stress of the PMCBs are much lower than those of the base bitumen and SMB, which indicates the asphalt mixture with the PMCB has a lower possibility to have low-temperature cracking. Meanwhile, with the increase of curing time, the maximum stress and residual stress of the PMCB increased, which may be caused by the hardening of the PMCBs.

Frequency Sweep Test Analysis. As a viscoelastic material, the rheological behavior of bitumen in the LVE range is dependent on time and temperature (21). To comprehensively analyze the viscoelastic properties of the base bitumen, SMB, and the PMCBs, the complex modulus and phase angle master curves were constructed and the results can be seen in Figure 9. It should be noted that PMCB-1 h indicates that the curing time of the PMCB is 1 h.

As shown in Figure 9, PMCB-1 h showed a lower complex modulus master curve than those of the base bitumen and SMB and showed a similar phase angle master curve to that of the base bitumen. With 1 h of curing time, the PMCB was frequency sensitive in the complex modulus and phase angles. With increasing curing time, PMCB-4 h demonstrated a similar complex modulus master curve to those of the base bitumen and SMB. Meanwhile, there was an obvious phase angle plateau in the phase angle master curve, indicating the formation of a polymer network (1, 3, 4). When the curing time reached 24 h, the complex modulus and phase angle master curves of PMCB-24 were not frequency sensitive, which may be caused by the extremely strong polymer network formed in the PMCB.

Performance of PMCB Mortar

Tensile Strength. The asphalt mortar is the first decentralized system of an asphalt mixture and represents the matrix of the asphalt mixture between the aggregates. To compare the cohesive property of PMCB mortar, the tensile strength of mortar samples was evaluated under controlled isothermal temperature conditions. The mortar samples were conditioned at -10°C , 0°C , 15°C , and 25°C for 2 h, respectively. Finally, the mortar samples were used to conduct the monotonic tensile test, and the results can be seen in Figure 10.

According to Figure 10, the PMCB mortar samples showed an advantage in tensile strength and ductility compared with the base bitumen and SMB mortar samples at -10°C and 0°C . To quantitatively evaluate the performance of the mortar samples, the tensile strength and dispatched energy were calculated and are summarized in Figure 11. It can be observed that the PMCB mortar samples are not as temperature sensitive as the base bitumen and SMB mortar samples. In particular, when the temperature is at 25°C , the tensile strength of the base bitumen mortar samples decreased to zero, while the tensile strength of the PMCB mortar samples remained at 5.8 MPa. Because of the higher tensile strength and ductility, the dissipated energy of the PMCB mortar samples was approximately twice that of the SMB mortar sample and a fourth that of the base asphalt mortar sample, which revealed the excellent cracking resistance of the PMCB mortar samples.

Tensile Fatigue Performance. Besides the monotonic tensile performance, the tensile fatigue performance of mortar samples was also characterized. As the PMCB becomes very stiff after curing, it is in doubt whether the PMCB has good mechanical properties at low temperatures. To study the fatigue response of mortar samples at low

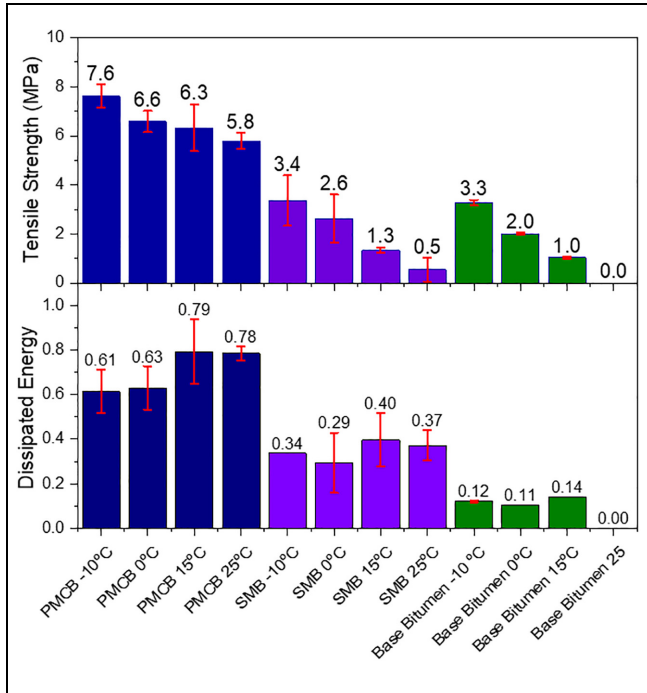


Figure 11. The cohesive strength and dissipated energy of mortar samples at -10°C , 0°C , 15°C , and 25°C . Note: PMCB = polyurethane modified cold binder; SMB = styrene butadiene styrene polymer modified bitumen.

temperature, the cyclic sinusoidal repeat load is utilized, and the loading magnitude is defined as 35% of the peak force in the monotonic tensile test. The loading frequency was 10 Hz, and all the tests were carried out at -10°C .

As demonstrated in Figure 12, it can be observed that the base bitumen and SMB mortar samples show the three stages process of deformation, namely the stretch stage, creep stage, and failure stage. The fatigue lives of the base bitumen and SMB mortar samples were 135,000 and 406,800 cycles, respectively. However, the PMCB mortar samples showed only the stretch and creep stages and did not show a tendency of failure even after 1,000,000 cycles of loading. This revealed the excellent fatigue toughness of the PMCB mortar under cyclic loading at 35% of the peak force in the monotonic tensile test.

Performance of the Polyurethane-modified Cold Asphalt Mixture

Indirect Tensile Strength. After preparation, all the PMCM specimens were stored at 20°C for 2, 4, 6, 8, 24, and 72 h, respectively. Afterward, the mixture samples were used to assess ITS to evaluate the tensile strength at different curing times.

As shown in Figure 13, the ITS increased as time went on, and when the curing time was more than 6 h, the ITS of the PMCM was higher than that of the hot mixed porous asphalt mixture with fresh aggregate and base bitumen.

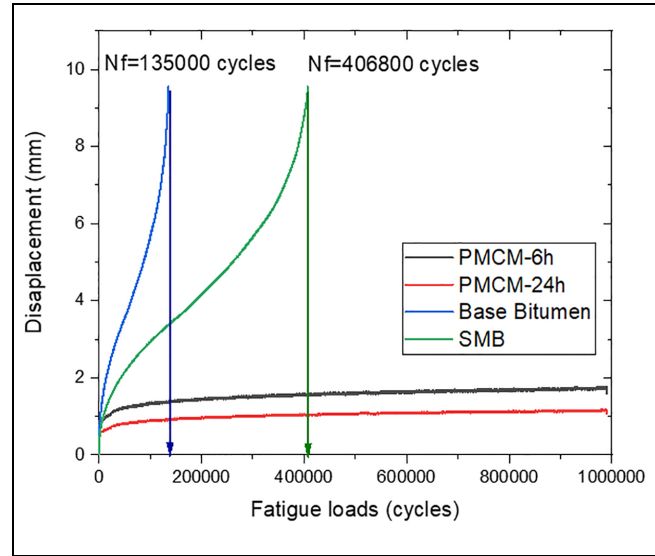


Figure 12. The fatigue life of the base bitumen, styrene butadiene styrene polymer modified bitumen (SMB), and polyurethane modified cold binder (PMCB) mortar samples at -10°C .

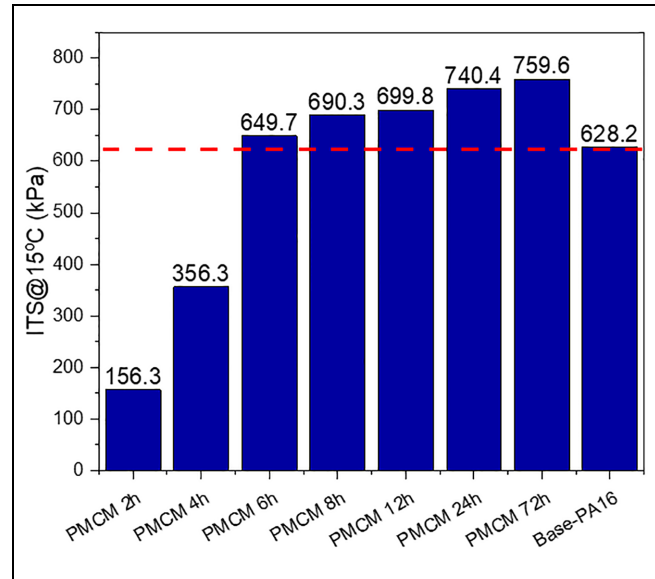


Figure 13. Time-dependent indirect tensile strength of the polyurethane-modified cold asphalt mixture (PMCM) specimens.

The ITS results showed that the pavement constructed with the PMCM had the potential to be opened to traffic after 6 h of curing. However, the final open traffic time will also be determined based on rutting resistance, raveling resistance, fatigue resistance, and so forth.

Conclusions

In this research, a PMCB was designed and investigated for the fast and high-quality cold in-place recycling of reclaimed asphalt. Firstly, FTIR and fluorescent microscopy were used

to reveal the curing process and the modification mechanism of the PMCB. Afterward, the frequency sweep test, temperature sweep test, relaxation test, and time sweep test were used to comprehensively evaluate the rheological properties of the PMCB at different curing stages. Finally, a monotonic tensile test and tensile fatigue test were conducted to evaluate the mechanical performance of the PMCB mortar sample, and an ITT was performed to evaluate the tensile strength of the polyurethane-modified asphalt mixture. The findings and conclusions can be drawn as follows.

- (1) The polymerization reaction of the PMCB during the curing process mainly consists of three reactions. The urethane/urea linkage leads to the formation of the polymeric network, which establishes a homogeneous polymer modified binder system.
- (2) The curing process of the PMCB includes three stages. Firstly, the polymeric network was preliminarily formed, and the binder is transferred from the liquid state to the gel state. Secondly, the polymeric network is enhanced, leading to a significant decrease of the phase angle and an increase of the complex modulus and cohesive strength. Finally, the remaining free isocyanate in the modified system gradually completes its reaction, and the reaction slows down until it is finished.
- (3) The PMCB exhibits suitable workability, excellent rutting resistance, low-temperature cracking resistance, and relatively less temperature sensitivity. Compared to the base asphalt and SMB mortar samples, the PMCB mortar samples showed significant advantages in tensile strength, dissipation energy, and tensile fatigue properties.
- (4) The PMCM showed better ITS than the porous asphalt mixture with fresh aggregate and bitumen when the curing time reaches 6 h.

Future Work

This investigation of the PMCB mainly focuses on the research at the binder and mortar levels. Further evaluation of the workability, rutting resistance, raveling resistance, moisture stability, and aging stability of the PMCM is needed to verify the performance. Meanwhile, the health, safety, and environmental influence of PMCB applications will also be considered. Furthermore, as the properties of the PMCB are different from those of hot-mix bitumen, the corresponding design methodology for the PMCM will also be investigated in the future.

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Author Contributions

The authors confirm contribution to the paper as follows: study conception and design: X. Liu, P. Lin; data collection: P. Lin; analysis and interpretation of results: X. Liu, S. Erkens, B. Welvaarts, K. Brouns; draft manuscript preparation: P. Lin. All authors reviewed the results and approved the final version of the manuscript.

Declaration of Conflicting Interests

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