Laboratory evaluation on water-based and flexible epoxy/SiO₂ nanocomposites to enhance anti-sliding effectiveness of pavement

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Abstract

The anti-slip (AS) layer of the cement concrete pavement (CCP) can probability decrease traffic accidents and extend the service life of the road. Epoxy resin has excellent adhesion and mechanical strength, making it possible in this field. Herein, a flexible waterborne epoxy resin (WER) without a small molecule emulsifier was synthesized by bisphenol A epoxy resin, poly (propylene glycol) diglycidyl ether (PDE), diethylenetriamine (DETA). The mechanism of the group reaction was characterized by fourier transform infrared (FTIR), and dynamic scanning calorimetry (DSC) determined the heat of curing of WER. Then, the physical properties of WER were enhanced by the silane coupling agent modified nano-silica (SCA-NS) and the composite’s water absorption rate and mechanical propriety were evaluated. Finally, the pavement performance of the AS layer was prepared and tested as well as compared with the commercial waterborne epoxy resin (CWER) and emulsified asphalt (EA). The result shows EA has low durability and adhesion strength than epoxy resin. The small molecule emulsifier and low-flexible resistance of CWER decrease water stability and anti-sliding durability of the AS layer. Due to applied nanomaterial reinforced and without small molecule emulsifiers, the WER base AS layer shows extremely high adhesion strength, water stability, and skid-resistance durability at addition 3 wt% of SCA-NS, which have a great potential for CCP.

1. Introduction

Cement concrete pavement (CCP) has high rigidity and good compression resistance, but the surface is prone to friction loss as well as cracks owing to overload or natural aging [1, 2]. This problem not only affects the lifetime of the road itself but also increases the danger of the driving vehicle [3, 4]. In order to solve this problem, the concept of anti-sliding (AS) layer was proposed, in which a polymer layer is introduced to protect the surface of the road without changing original pavement structure [5, 6]. So far, asphalt is the main material used for road maintenance [7]. However, as a thermoplastic material, asphalt has the disadvantages of bad adhesion, easy falling off, and short durability [8, 9]. It is well known that epoxy resin is a thermosetting resin, whose adhesion and thermal stability is better than asphalt [10–12]. In the 1980s, the US Highway Department tried to used epoxy resin coating as an AS layer material for old CCP or bridge decks [13, 14]. The American Concrete Institute (ACI) proposed that the pavement or bridge overlay polymer coating should have an elongation at break 30 ~ 70%, tensile and adhesion strength was 12 ~ 34 MPa, 1.7 MPa, respectively [15]. However, these regulations target oil-based polymer resin containing volatile organic compounds (VOC). Waterborne epoxy resin (WER) refers to disperse oily epoxy resin in water instead of organic solvents, which therefore is considered as environmentally friendly material with low emission of VOC. It’s worth noting that conventional commercial WER is formed by dispersing oily epoxy and curing agent in water separately with the assistance of external
emulsifier or grafting hydrophilic groups to epoxy [16, 17]. Contradictorily, the existence of the emulsifier or hydrophilic group increases water absorption of WER cured films, and this results in the weakening of the bond strength between the substrate interface [18–20]. In order to solve this dilemma, the curing agents with the ability of emulsifying epoxy resin were developed. Yin et al [21] used a modified aliphatic amine to form a curing agent that could directly emulsify epoxy resin.

Zhang et al [22] reported that a curing agent based on modified triethylenetetramine demonstrated a good emulsifying ability and the cured epoxy showed excellent water resistance. These pieces of knowledge pave an important foundation for developing WER-based AS layers. Also, the wear resistance, fatigue and bonding strength of polymer-based AS layer are specifically needed to be considered. Since there is a limited study on this, a new environmentally and friendly WER system urgently needed to meet all these requirements. To achieve this, designed a diethylenetriamine modified curing agents and this new curing agent shows excellent emulsifying and curing effect. A flexible segment poly (propylene glycol) diglycidyl ether (PDE) is specifically introduced into the curing agent in order to maintain the flexibility of AS layers. In addition to the focus on designing appropriate curing agent, also proposed the use of nano-silica (NS) to improve the weakness of organic materials. According to the previous report, the NS particles uniformly distributed in the epoxy resin can improve the mechanical, thermal stability, and abrasion resistance of the polymer matrix which probably enhances the anti-sliding durability of AS layer [23–25]. Thus, our results show that the combination of these design concepts leads to form a new epoxy-based composite material with a strong potential to serve the application of anti-sliding.

2. Experimental programs

2.1. Materials

Cement (Portland cement, OPC, compressive strength = 32.5 Mpa,) was provided by Anhui Conch Cement Co., Ltd. The concrete aggregate was provided Nanjing Shanquan Concrete Co., Ltd. Bisphenol-A type epoxy resin (E44/E51, epoxy value 0.44/0.51 mol/100 g) were supplied by Hangzhou Wuhuigang Adhesive Co., Ltd. Diethylenetriamine (DETA), poly (propylene glycol) diglycidyl ether (PDE, Mn = 500), glycidyl phenyl ether (GPE), acetic acid (HAc), silane coupling agent (SCA) γ-(2,3-epoxypropoxy) propytrimethoxysilane (KH560), Nano-Silica (NS), Ethanol, were purchased from Aladdin Industrial Corporation. Commercial waterborne epoxy resin (CWER) and curing agent were purchased from Guangzhou Kester New Material Co., Ltd. Emulsified asphalt (EA) was purchased from Jinan Xiangfa Chemical Materials Co., Ltd. Deionized water was purchased from Nanjing Wanqing Chemical Glass Instrument Co., Ltd. Skid-resistant aggregate was provided by Beijing AISIMU Technology Co., Ltd. All materials were used as received without further purification.

2.2. Preparation of WERs

The typical procedure for preparing waterborne epoxy resin is shown in figure 1. The steps of one, two, and three are designed for preparing the curing agent and the step of four is to use the prepared curing agent to emulsify epoxy in the water. The details of the experiments are described as follows: in step one of the chain extension reaction, a 250 ml four-necked round bottom flask equipped with a stirrer, thermometer, and reflux condenser were charged with 5.4 g DETA. Then, 10 g E44 was slowly added to the flask and reacted at 55 °C for 4 h was formed the structure of E44–DETA. Then, in step two of the block reaction, the adduct of DETA-E44-GPE was synthesized by reacting to 6.60 g GPE to terminate DETA-E44. After 4 h, in step three of neutralization, 2.64 g acetic acid was added to neutralize the product and the self-emulsifiable WER curing agent was synthesized. Finally, in step four, 26 g liquid epoxy resin E51 and 47.14 g water were added and stirred at 1200 r/min for 10 min and a WER labeled as WER-0 with a solid content of ~50% was prepared. The molar ratio of active hydrogen and epoxy groups in WER is equal. Table 1 presents the recipe of resulting WER via this synthetic route. WER-25 and WER-50 refer to the WER with the introduction of 25 wt% and 50 wt% PDE in the first step of chain extension, respectively.

2.3. Preparation of WER-SCA-NS composites coating

Select a suitable WER for the AS layer and use NS to improve physical performance. In order to improve the dispersibility of NS and interfacial properties, the nanoparticles were modified by SCA (KH560). This principle was reference previous paper [26]. The details of preparing process are as follows: a mixture of 5 g SCA and 10 g ethanol was treated by ultrasonic hydrolysis for 1 h. Afterward, 17 g of an aqueous solution with 30 wt% NS was mixed with the SCA hydrolysate at 60 °C for 12 h. Then, an SCA-NS dispersion was formed. To determine the optimal ratio of WER and nanomaterials, the WER was added with various percentages of SCA-NS particles i.e. 0 wt%, 1 wt%, 3 wt%, 5 wt%, 7 wt%. In order to ensure the homogeneous mixture of WER-SCA-NS composites coating, the SCA-NS aqueous dispersion was mixed with WER at 500 r/min for 10 min in an electric mixer.
2.4. Preparation of AS layer of CCP

The cement concrete specimens were according to the highway engineering cement concrete test procedures (JTJ E30-2005) [27]. The AS layer was composed of a polymer binder a skid-resistant aggregate and the preparation process is shown in figure 2. First, uniform coating of this emulsion on the surface of the concrete was performed by using a brush. The weight was around by ∼0.7 kg m⁻² using a single variable of the different polymer coating. Then, the skid-resistant aggregate was evenly spread on the polymer binder surface according to the standard of 1 kg m⁻². The per square amount of emulsion coating and skid-resistant aggregate of the AS layer are referenced from the previous literature reported [28]. According to the content of SCA-NS in the WER emulsion, it was named AS-0, AS-1, AS-3, AS-5, AS-7, respectively. The comparative samples were also prepared using purchased EA and CWER and named as AS-EA, AS-CWER, respectively. The detail information of EA, CWER, skid-resistant aggregate is shown in tables 2–4. Then, all samples were dried at 30 °C for 48 h and an AS layer having a thickness of 1.2 ± 0.2 mm was formed.

2.5. Characterization

2.5.1. Characterization of WER and WER-SCA-NS composites

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet spectrometer (Nexus-670, Madison, USA) over the range from 400 cm⁻¹ to 4000 cm⁻¹. The laser particle size analyzer (MZ-3000HSA, Marvin, UK) was used to determine the particle size distribution of WER, NS, and SCA-NS. The WER curing thermodynamics behavior measurements were tested using differential scanning calorimetry (DSC, TA-Q20, Delaware, USA) under nitrogen atmosphere, from −10 to 200 °C and the heating rate was 2, 5, 10, 15 k/min, respectively. The emulsion stability test was measured by centrifuge (TG16-WS, Shanghai, China) at 3000 r/min for 15 min. The...
universal testing machine (CMT525, Shenzhen, China) was used to test the mechanical properties of cured films at 10 mm min$^{-1}$, 25 °C. Water absorption of cured films was measured by immersing the dried films in the water at 30 °C. The water absorption rate can be calculated by $(m_1 - m_0) / m_0 \times 100\%$, where $m_0$ = the mass of the dried samples, g; $m_1$ = the mass of the immersed samples, g. The fractured interface between WER and concrete and EDS spectrum of silicon element was imaged by a scanning electron microscopy (SEM, JEM-6510, Tokyo, Japan) according to the ASTM E1508-12a standard[29].

2.5.2. Pavement performance characterization of the AS layer
The cement chemical composition was determined by x-ray fluorescence (XRF-1800, Shimadzu, Kyoto, Japan) in the light of the ASTM E1621–13 standard[30].

The initial and final time of concrete was evaluated according to the ASTM C403/C403M-1 standard[31].

The density of concrete was tested follow by ASTM C138/C138M-17a standard[34].

Wet track abrasion tester (SYD-0752, Hubei, China) was used to evaluate the water resistance of the AS layer. The operating specifications were following the ASTM E303-93.

Table 2. Parameters of emulsified asphalt.

| Properties                      | Test results                        |
|---------------------------------|-------------------------------------|
| Particle charge                 | Cation (+)                          |
| Amount remaining on the 1.18 mm sieve (%) | 0.03                               |
| Viscosity C25.3 (S)             | 13                                  |
| Demulsification rate            | Moderate                            |
| Stability (day)                 | 30                                  |
| Evaporated residue              | 100 g, 25 °C, 5 s Penetration (0.1 mm) | 89 |
| Softening point (°C)            | 50                                  |
| Solid content (%)               | 48                                  |

Figure 2. The process of preparation of the AS layer of CCP.
### Table 3. Parameters of commercial waterborne epoxy resin, curing agent, and cured films.

| Test item          | Solid content (%) | Emulsifier content (%) | Stability (days) | Cured time (25 °C, h) | Water absorption rate (24 h, %) | Tensile strength (MPa) | Elongation at break (%) |
|--------------------|-------------------|------------------------|-----------------|-----------------------|---------------------------------|------------------------|------------------------|
| Waterborne epoxy   | 49.50             | 8.50                   | 30              | —                     | —                               | —                      | —                      |
| Curing agent       | 51.20             | —                      | 90              | —                     | —                               | —                      | —                      |
| Cured films        | —                 | —                      | —               | 24                    | 11.30                           | 23.51                  | 5.12                   |
standard. The BPN value means that the kinetic loss of energy after the rubber sheet at the bottom of the pendulum across the anti-slip layer to overcome the friction [35]. Therefore, the better of the skid-resistance performance, the larger of the BPN value.

In order to simulate the anti-skid durability of the AS layer at true traffic loading, the indoor accelerated loading (MMLS3, 1/3 model mobile load simulator, Guangzhou, China) tested the cured specimens [36]. Figures 10(b), (c) shows the equipment and longitudinal sectional schematic. The specimens (30 × 30 cm) was put down on the platform, and then the tire fixed on the oval track passed through the surface of the sample at 20 km h⁻¹ and put pressure on 0.7 MPa. The test pressure was approximately equal to double the pressure put on the road exerted by the small passenger car. The experimental environment was 30 °C and 60 RH%. Each pass of the tire was recorded as a cycle, the BPN value was recorded after 0, 10 000, 20 000, 30 000, 40 000, 50 000 cycle times, respectively, and mass loss was calculated after the final.

3. Results and discussion

3.1. Effect of E44 and PDE ratio on physical performance of WERs

The preparation process of WER includes the synthesis of the curing agent and the emulsification of epoxy resin. The synthesis mechanism of self-emulsifying curing agent is based on the amine-epoxy chain extension, monooxy group blocking, and acetic acid neutralization methods [22]. This method can improve compatibility with epoxy resin, and enhance the emulsifying ability. On the other hand, it can reduce primary amine reactivity and extend operation time.

In order to preparation flexible WER, in the first step of chain extension, 25 and 50 wt% of E44 was replaced by PDE, which contains a large quantity of soft C–O flexible covalent bonds. Figure 3(a) reveals that the emulsion particle size gradually decreases from 1.25 to 0.17 μm when increasing the content of the PDE in the curing agent. Figure 3(b) demonstrates that the tube with WER-50 emulsion observes less sediment in comparison with others. This indicates that the addition of PDE significantly improves the stability of the WER emulsion. Figure 3(c) shows that the 24 h water absorption of the WER cured films were decreased by 15.5% from 3.12% to 2.60% with the addition of PDE up to 50 wt%. This mainly due to the smaller the diameter of the emulsion can increase the degree of the curing of the coating film, resulting in a decrease in water absorption. Figure 3(d) shows the flexibility of the WER film has been greatly improved, and the elongation at break from 6.46 to 65.35%. However, as the PDE content increases, the tensile strength of WER decreased to 18.3 MPa. It was indicated that the effective way to prepared the flexible WER can by changing the structure of the curing agent.

3.2. FTIR and DSC characterization results of WER

Figure 4(a) presents the FTIR characterization of the compounds in each step of our proposed synthetic routes. The absorption peaks at 1607 cm⁻¹ and 1509 cm⁻¹ are the characteristic peaks of the benzene ring in the epoxy resin [24]. Comparing the spectrum (a) and (b), the peak intensity of the epoxy group at 915 cm⁻¹ is significantly reduced, and this owes to ring-opening of the epoxy group induced by the active hydrogen. This confirms the reaction between E44 and DETA [37, 38]. Furthermore, it was observed that the peaks at 3300 cm⁻¹ and 3350 cm⁻¹ in the spectrum (b) that are associated with primary amine (NH₂) disappear in the spectrum (c), which indicates the formation of DETA-E44-GPE in step two. In spectrum (d), the curing of WER-0 after 30 °C for 24 h results in the disappearance of the N–H groups (3300 cm⁻¹), which inferred that N–H in the curing agent was consumed by E51, and a large number of -OH groups were generated [38–40].

As an engineering application material, the curing process parameters of WER are very important. The WER-50 has excellent performance and can be as an AS layer material. Therefore, it was studied reaction thermodynamics by the non-isothermal DSC method. Figure 4(b) shows the DSC scanning curves of WER from −10 to 200 °C, and at the heating rate of 2, 5, 10, and 15 k/min, respectively. The initial temperature (Tᵢ), the peak reaction temperature (T_p), the final temperature (T_f), and heating rate (β) in the DSC curve was listed in table 5. During the process of the WER curing reaction, the effective activation energy (E_a) was important conditions for WER to be cross linked and cured at room temperature [41]. The E_a can be calculated by the following kissinger equation [42].

| Table 4. Parameters of skid-resistant aggregate. |
|-----------------------------------------------|
| Test item | Ingredient | Diameter (mm) | Moisture content (%) | Mud content (%) | Wear value (%) | Mohs scale |
|-----------|------------|--------------|---------------------|----------------|----------------|------------|
| Results   | Al(OH)₃, 97% | 0.36 ~ 0.51 | 1                   | 0.5            | 15             | 7          |
Where the A and R are the pre-exponential factors and the universal gas constant. From Table 6 and Figure 4, the straight-line equation $y = 6.96 \times 8.56$ can be obtained by plotting $\ln(\beta / T_p^2)$ versus $(1 / T_p) \times 10^3$. Then, substituting the obtained slope of the straight line into formula (1) can conclude the $E_a = 57.8 \text{ kJ mol}^{-1}$ which the value $< 60 \text{ kJ mol}^{-1}$ means that the WER can be cured well at room temperature [43]. In order to obtain curing process temperature, as Figure 4 shows an equation of $y = 2.4 \times 28.6$ is obtained by fitting the $\beta$ versus $T_i$ [44], and the intercept 28.6 °C is the initial reaction temperature. It was indicated that the WER can be crosslink at $\sim 25$ °C without requiring severe curing process conditions.

3.3. SCA modified NS and physical properties of WER-SCA-NS composite films

The above results point out that the addition of PDE substantially enhances the stability of WER emulsion and flexibility of WER films. The combination of rigid nanoparticles and polymers has been proved to a powerful route to enhance the mechanical properties of polymers [45]. It drives us to investigate the use of silica nanoparticles to further improve the hardness and strength of WER. Figure 5(a) shows the FTIR spectra of NS before and after SCA modification. It was observed that the characteristic peak of silica was the stretching vibration peak of $\text{Si}-\text{O}-\text{Si}$ at around 1100 cm$^{-1}$ as well as bending vibration of 471 cm$^{-1}$, and the vibration frequency of Si stretching at 800 cm$^{-1}$ [46]. The difference was that the $-\text{CH}$ asymmetric vibration absorption peak was found at 3000–2800 cm$^{-1}$ [47], which is from SCA. In addition, the $\text{Si}-\text{OH}$ bending vibration peak at 959 cm$^{-1}$ in the spectrum (a) and almost disappears in spectrum (b), which further indicates that the SCA reacts with NS [46].

The particle size distribution of NS and SCA-NS was presented in Figure 5(b). It was observed that the particle size dispersion of NS is uniform and concentrated. Also, it can be seen that the average particle size of NS and SCA-NS was changed 63.4 into 116.2 nm which due to the reaction between the silane coupling agent and the $-\text{OH}$ group on the surface of the nanoparticles.

Figures 5(c), (d) shows the effect of SCA-NS particles on the mechanical properties and water absorption of composite films. It was revealed that the addition of 5 wt% SCA-NS increases the tensile strength by $\sim 77\%$, and the elongation at break is still around 45%. This composite shows a great deal of potential to serve as an AS layer.
with balanced strength and flexibility. However, when the added amount was more than 5 wt%, the mechanical properties decrease, which is due to the agglomeration of the nanoparticles and destroys the 3-dimensional network structure as well as reduces the mechanical properties of the epoxy resin. Figure 5(d) shows the water absorption of SCA-NS-filled WER over 100 h. At 3 wt% SCA-NS content, the rate of water absorption on days 1
and 7 was reduced by ∼17% and ∼23%, respectively. However, excessive addition of SCA-NS particles leads to an increase in water absorption of the composite.

3.4. Morphology analysis

Figure 6 shows the fractured surface SEM images between WER and concrete and image (a)-(e) means that the WER is associated with 0 wt%, 1 wt%, 3 wt%, 5 wt% and 7 wt% SCA-NS particles, respectively. Figure 6(a) shows the interface between pure epoxy and concrete has porous. These indicate that the existence of a weak interface interaction between WER and concrete. Denser interaction will facilitate the transfer of tire pressure to the CCP substrate, otherwise, the AS layer will fall off due to continuous transverse shear force. From images (b)-(e), the interface is denser as a result of the addition of SCA-NS particles into the WER. These because of the siloxane bonds in the SCA-NS particle tends to interact with the hydroxyl group on the concrete surface, and this is possible to enhance the bonding strength between the composite-based and the concrete surface [48–50].

Figures 6(c) and (f) show the dispersion of SCA-NS in WER. It was shows the nanoparticles are uniformly distributed in a dot shape, and the EDS spectrum of the Si element indicates the uniform dispersion of SCA-NS in WER matrix. This was key to maximize the reinforcing effect of nanoparticles for WER.

3.5. Pavement performance of AS layer

The adhesion strength, the water stability and anti-flaking of the AS layer on the surface of concrete were tested by puller tester, wet track abrasion and accelerated loading experiment. Also, the AS layer preparation by the EA and CWER was also used for comparison.

Tables 7, 8 shows the chemical composition of the cement and the basic parameters of the concrete substrate of the AS layer base. Figure 7 shows the XRD pattern of the concrete after 28d of AS layer base, the main composition is quartz sand (SiO2), calcium silicate hydrate, calcium hydroxide (Ca(OH)2), ettringite, Calcium carbonate (CaCO3), Calcium silicate. This is a representative XRD pattern of cement concrete after hydration [51].

Figure 5. (a), (b) FTIR spectra and particle size distribution of NS, SCA-NS, respectively; (c), (d) The mechanical properties and water absorption rate (24–168 h) of WER-SCA-NS composites films, respectively.
The static adhesion strength of the AS layer at 30 °C is presented in figure 8(b). The adhesion strength mainly depends on the physical and chemical properties of the polymer. The result shows the adhesion of AS-EA was smaller than other samples, due to EA was non-polar and thermoplastic materials. The small molecule emulsifier in AS-CWER system will reduce the degree of cross-linking of epoxy resin, which the main reason the adhesion strength low than AS-0. From the AS-0 to AS-7, with the addition of modified nanomaterials, the bonding strength gradually improves and increased by ∼37%, reached 3.24 MPa. This can be explained by the above fractured SEM image, the SCA-NS improves the interface compactness between WER and concrete and enhances the adhesion strength.

Figure 6. SEM image of fractured interface between WER and concrete; (a) WER, (b) WER/1 wt% SCA-NS, (c) WER/3 wt% SCA-NS, (d) WER/5 wt% SCA-NS, (e) WER/7 wt% SCA-NS; (f) EDS spectrum of silicon element in the selected area in (c).

Figure 7. XRD pattern of concrete for AS layer substrate.

| Chemical composition | SiO₂ | Al₂O₃ | CaO | SO₃ | Fe₂O₃ | MgO | Na₂O | K₂O | TiO₂ | LOI |
|----------------------|------|-------|-----|-----|-------|-----|------|-----|------|-----|
| Cement (wt%)         | 19.02| 4.77  | 63.42| 4.23| 3.29  | 1.87| 0.28 | 1.05| 0.31 | 1.76|

LOI: Loss on ignition.

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Figure 9(b) shows the resulting mass loss rate of the wet track abrasion test after 2 days of immersion in water. The mass loss rate of WER-base was smaller when compared AS-EA. This indicated that epoxy resin with a cross-linked structure has higher water resistance and abrasion resistance than emulsified asphalt. Compared with the AS-CWER and AS – 0, the former has a higher quality loss rate, it was mainly due to the emulsifier inside absorbs water from long duration immersion would reduce the adhesion to skid-resistant aggregate. With the addition of nanomaterials, the mass loss rate of the samples was decreased, the rigid nanoparticles can improve the wear and water resistance of WER.

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Figures 10(d), (e) shows the accelerated loading simulates was evaluated the friction and mass loss under continuous tire load. Image (d) shows the relationship between BPN and cycle times, with the number of cycles increases, the coefficient of friction on the sample gradually decreases, which the phenomenon consistent with the previous report [52]. From the structure of the AS layer, it was mainly composed of skid-resistant aggregate and a binder. The former provides a friction coefficient and the latter ensures that the aggregate does not fall off

### Table 8. The indicators of cement concrete specimen.

| Test item | Density (g/cm³) | Fineness | Moisture content (min) | Compressive strength (MPa) | Flexural strength (MPa) |
|-----------|----------------|----------|------------------------|---------------------------|------------------------|
| Results   | 3.12           | 1.4      | Initial: 175            | 35.7                      | 5.4                    |
|           |                |          | Final: 356             | 46.8                      | 7.2                    |
|           |                |          | 7 days: 28 days        |                           |                        |

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under load and has a certain resistance to deformation. Therefore, determining the durability of the AS layer is mainly determined by the physical and mechanical properties of the binder. The results show that the BPN of AS-EA near the original value after 50,000 cycle times, and the mass loss rate finally approaches by $\sim 1000 \text{ g m}^{-2}$, which mainly due to the loose structure of the surface. CWER elongation at break was only 5.12%, insufficient deformation capacity, resulting in more BPN loss after more than 20,000 times, and the mass loss rate finally reached $\sim 400 \text{ g m}^{-2}$. Relatively speaking, the self-made WER has a certain degree of flexibility. At the same time, the mechanical properties of WER were enhanced due to the presence of nano-materials, so the friction loss and mass loss are smaller than the former. After simulate test, the AS-3 has a frictional loss of only $\sim 90 \text{ g m}^{-2}$ and the BPN is still greater than 70, and much larger than the initial value of 43. However, when the nanoparticles exceed 3 wt%, the friction loss of the sample increases, which may due to excessive addition results in reduced flexibility of the AS layer. In summary, it is feasible to fabrication the AS layer based on the flexible self-emulsifying WER with 3 wt% SCA-NS particles.

### 4. Conclusion

In this research, from the perspective of polymer synthesis and application, the potential use of WER-SCA-NS composites as a novel cement concrete pavement AS layer material was evaluated. By adjusting the ratio of E44/PDE in the self-emulsifying curing agent, a flexible WER suitable for AS layer was prepared, which has an elongation at break exceeds 60% and the tensile strength reaches 18 MPa. FTIR spectrum analysis demonstrated the functional group transformation during the preparation of WER. DSC reaction kinetic analysis determined that effective activation energy and initial reaction temperature was 57.8 kJ mol$^{-1}$, 28.6 $^\circ$C, respectively. The addition of 3 wt% SCN-NS to WER, the water absorption was 2.15%, decrease by $\sim 23.13\%$, and meanwhile substantially increases the tensile strength by $\sim 77\%$. By comparison, the adhesion, wet track abrasion, and accelerated loading test result of AS-EA were 0.33 MPa, 387 g m$^{-2}$, 998 g m$^{-2}$, which is significantly low than WER and indicates that the conventional EA not suitable as a AS layer material. The purchased CWER was low water stability and anti-sliding durability owing to its small molecule emulsifier and lack of flexibility. The AS layer preparation by WER-SCA-NS composites coating produced high adhesion strength and water stability, and skid-resistance durability, which have a great potential use for the anti-sliding field of cement concrete pavement.
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Author contributions

This manuscript was written by all the authors listed. All of the authors have agreed with the final version of the manuscript.

Conflict of interest statement

The authors state that they have no conflicts of interest in this work.

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