Effects of the softening point of hydrophobic polymers on the salt-based filler used in antifreeze asphalt concretes

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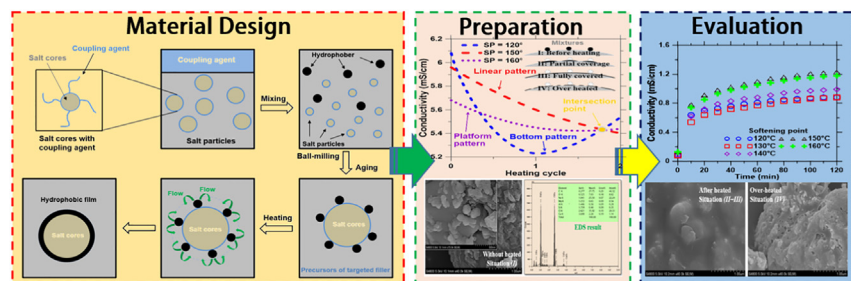[a] School of Highway, Chang'an University, Xi'an, Shaanxi, China
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HIGHLIGHTS

- A novel salt-based filler with surface modification was developed and to be contained in antifreeze asphalt concretes (AFACs).
- Softening point of modifiers, together with the heating treatment and heating cycles, affects the salt-releasing behavior, performing three typical patterns.
- Moisture susceptibility and antifreeze property of AFACs are associated with the softening point of hydrophobic polymer.

GRAPHICAL ABSTRACT

ABSTRACT

In order to investigate the effect of hydrophobic polymer softening points on salt-based fillers used in antifreeze asphalt concretes (AFACs), moisture absorption, salt-release property and thermal stability were studied and the performance of antifreeze and moisture susceptibility of AFACs were also assessed. Without preheating procedure, the softening point did not show a positive effect on the conductivity of modified salts, but changed the salt-releasing property after being mixed with the asphalt concrete. Further testing through simultaneous thermal analysis and scanning electron microscope has shown that the experience of high temperatures (between 100 and 200 °C) softens the small hydrophobic particles into thin layers coated on the surface of the salt, while hydrophobers decompose at temperatures above 200 °C. The result of heating cycles indicates that, based on the SEM observation, there are four situations of hydrophobic polymer particles on the salt surface. The salt-releasing property trends could be divided into three typical patterns. Generally, a higher softening point of hydrophober produces a better moisture susceptibility of the AFACs, while the pre-heating treatment on salts reduced the moisture susceptibility of AFACs.

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1. Introduction

The coefficient of skid resistance between pavement and vehicle tires greatly affects traffic safety [1,2]. The key cause of accidents in winter is the reduction in skid resistance resulted from the covering of snow or ice on the surface of pavements [3]. It is necessary to clear the snow or ice without too much delay to ensure a good skid resistance [4,5]. Winter road maintenance procedures include snow removal, deicing, and anti-icing in field applications [6,7]. The use of salt is expensive and has detrimental effects for the ecosystem, as well as for corrosive vehicles and road infrastructures [8,9]. Anti-icing technology has a safer and more sustainable solution [10–12] compared to deicing with

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chemical salts [13,14] and also has the significant benefit of reducing salt-induced harm to constructures and materials [15].

Antifreeze asphalt concrete (AFACs), produced by the incorporation of salts, have attracted a great deal of interest since it was recorded from Europe in the 1970s [16]. Japan has completed more than 6.5 million m^2 of antifreeze asphalt pavements [17]. The selection of modified salts used in AFACs that can be divided into salt-based fillers, salt-based aggregates, and salt-based coatings is one of the biggest challenges [16]. The salts interlocked in the void of AFACs are released by chemical and mechanical coupling function including osmotic pressure due to differential concentration, abrasion by vehicle tires, and pump-priming by dynamic loading [18]. In order to control the rate of salt release at a balance of engineering efficiency and antifreeze ability, filler-like or aggregate-like additives have to be modified. After a temperature drop, AFAC cannot supply adequate salts to ensure good friction in a heavy long-lasting snowstorm or freezing water. However, even a small amount of salt will avoid the forming of rime on the surface in some situations.

There has been a growing amount of literature on the development of salt-based additives in recent years. Initially, flaxseed oil [19] was used to coat salt particles, after which water repellent and resin [20] were used to modify the salts. Inorganic cement binder [21] and porous carriers [22] have also been used to manufacture salt-based fillers and aggregates thus far. The antifreeze performance of the AFACs was well-confirmed based on these salt-based materials [23–27], not only observed in experimental studies [28,29], but also implemented in the field [30,31]. In the engineering efficiency literature, there has been substantial consideration of the relative importance of adding salt-based filler where there is a critical salt content in the asphalt mixture [16,25].

Although no effort was reported to detail the softening point of the salt particle modifier, hot mix asphalt (HMA) has to experience high temperature as hot as 180 °C in plants. The salt-based additive's thermal behavior during production of HMA must be linked to the modifier's softening point. In order to reveal the connections between the softening point of the modifier and the engineering performance of salts and that of AFACs, a further and more comprehensive study is required.

In the laboratory, salts modified by resinous modifiers with different softening point were synthesized in current study. Effects of softening point on sustained release of the filler and salt releasing behavior of AFACs were evaluated. In consideration of the hot mix asphalt production process, aging effects on salts and AFACs were also observed. The synthesis of the additive can be motivated by a better understanding of the softening point of the salt-based filler. In addition, the evaluation of aging effects during the processing of hot asphalt mixtures can raise further questions about the quality control of AFAC asphalt mixtures in plants.

2. Materials and methods

2.1. Raw materials

Sodium chloride (NaCl, industrial grade) was provided by Qinghai Salt Industry Co., Ltd. Anhydrous calcium chloride (CaCl$_2$, analytical grade) and calcium chloride dehydrate (CaCl$_2$.2H$_2$O, analytical grade) derived from Dacheng Calcium Industry were also used in the study. For both the alteration of salt crystals, the industrial silane coupling agent (KH560) and hydrophobic polymers (softening points = 120, 130, 140, 150, and 160 °C) were used. Manufacturing company (SD QiLong Chemical Industry, China) provided the softening points data. The asphalt mixture was produced using SBS modified asphalt (SBS I—C, penetration at 25 °C = 71, softening point = 89.5 °C, ductility at 5 °C = 37.6 cm), qualified basalt aggregate (density = 2.92 g/cm^3) and machine-glazed limestone filler (density = 2.83 g/cm^3). The adapted asphalt was produced by Xi'an Guolin SK Asphalt Company. Aggregates and limestone filler were taken from Qinling Mountains nearby Xi'an City, China.

2.2. Synthesis of salt-based fillers

The synthesis procedure of the salt-based filler is illustrated in Fig. 1. The first step was to self-assemble surface-silanized salt cores by mixing dried sodium chloride (NaCl) and silane coupling agent (0.5 wt%) in a container for 5 min. Hydrophobers (12.5 wt%) were then added to the surface-silanized salts and mixed for another 5 min until forming a homogeneous mixture. Thirdly, the pre-treated mixtures were crushed into ultrafine particles with a ball grinder. After 15 min of ball milling, mixtures were moved into an aging chamber for 15 min. In the aging chamber, salts, polymers, and silane coupling agent react on their boundaries where coupling agents bind inorganic salts (sodium chloride) and organic polymers (hydrophober). The last step of the synthesis of the salt-based filler preparation was to keep the mixtures at 180 °C for 15 min in the chamber to soft the hydrophobic polymer into a thin film layer coated around the salt cores. During the preparation, all materials have to be kept in dry conditions.

2.3. Preparation of antifreeze asphalt mixtures

Antifreeze asphalt mixtures were prepared as reported previously [23,29]. In the mixture, AC-13, a general type of asphalt mixture world widely used, was designed which contained 5.0 wt% salt-based filler, 1.0 wt% limestone filler, and 94.0 wt% mineral aggregates. The asphalt content of AFAC was set as 4.9 wt%. The preparation of antifreeze asphalt mixture was done according to the procedure as detailed in previous literature [24].

2.4. Laboratory testing methods

2.4.1. Moisture absorption test

It was suggested that the AFAC should limit moisture absorption to keep a good skid resistance [32]. In laboratory condition (temperature = 20 ± 3 °C and relative humidity = 60 ± 5%), 10 ± 0.1 g salts were put in open containers. The mass increment of the sample was weighted and moisture absorption could be described by the increment rate ($\Delta m/m_0$) defined as the ratio of weight variation (Δm) and initial weight (m_0). The weight of sample was recorded after 12 h and 24 h.

2.4.2. Conductivity test

The conductivity approach was adapted to describe the salt releasing behavior [24]. A DDS-11A conductivity meter with a platinum black electrode (DJS—1D, electrode constant = 0.993) produced by Ridao Scientific Instrument Co., LTD (Shanghai, China) was used in the study. The conductivity was measured with two kinds of specimens. The first one is to observe the salt dissolution behavior of the modified salt by putting 1 ± 0.01 g salt-based filler in 500 mL deionized water in a glass container, as shown in Fig. 2a. The second one is to measure the salt releasing behavior from antifreeze asphalt mixtures (AFACs) by immersing 500 g mixture into 2500 mL deionized water, as presented in Fig. 2b. It should be noted that to accelerate the salt dissolution in Fig. 2a, an electromagnetic stirrer was used. Similarly, the solution in Fig. 2b was also stirred by a glass agitator to make the concentration homogeneous. The electrode of conductivity meter must be cleaned each time before measurements.

2.4.3. Moisture susceptibility test

The moisture susceptibility of AFAC was evaluated by Marshall test [33]. Two subsets of approximately equal Marshall specimens were prepared [34]. One subset is maintained dry while another is immersed in 60 °C water for 48 h. As such, the residual Marshall stability (MS_R), defined as the ratio of the immersed specimens in 60 °C water and the general Marshall specimens, was adapted to describe the moisture susceptibility. A higher MS_R indicates a lower degree of susceptibility to moisture damage.
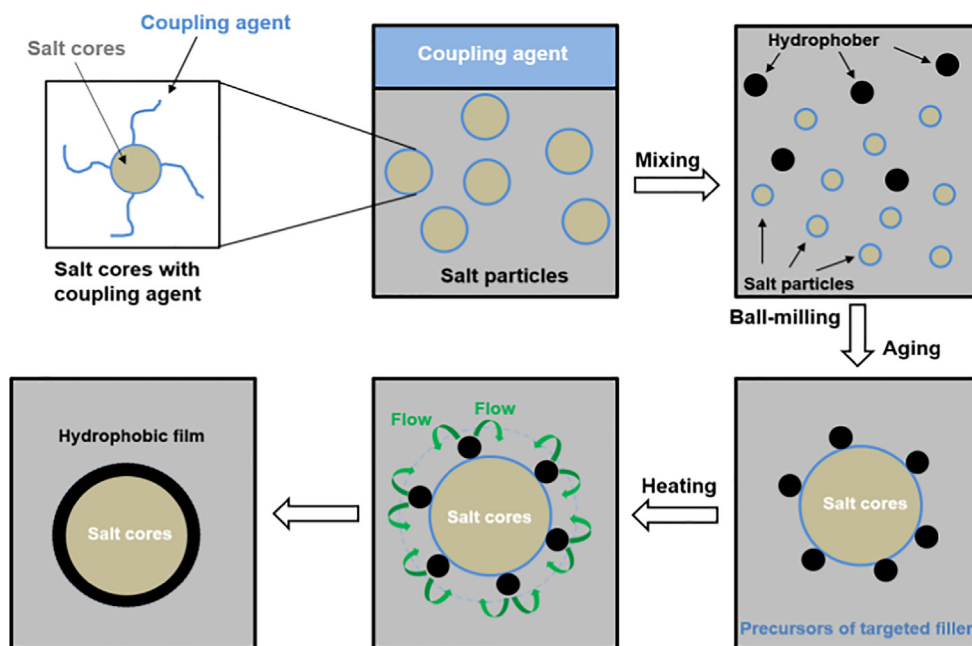
Fig. 1. Schematic illustration to prepare the salt-based filler.

2.4.4. Simultaneous thermal analysis (STA)

In order to evaluate the thermal stability of the prepared material, salt-based filler was observed by thermogravimetric and differential scanning calorimetry (TG-DSC) using a simultaneous thermal analysis device (TGA/DSC^{3+}, Mettler Toledo, Switzerland). Powder samples were analyzed between 10 and 1000 °C under general air condition with a heating rate of 10 °C/min, meanwhile the weight loss of samples and heat flow data were recorded.

2.4.5. Scanning electron microscope (SEM)

For microstructure observation, scanning electron microscope (SEM) was adapted using S-4800 (Hitachi, Japan). In experiment, considering the polymer modifier on salt particles, samples were coated with 10 nm Platinum layer. During the SEM analysis, electron energy disperse spectroscopy (EDS) technology was also employed to collect the distribution of elements on salt surface.

3. Results and discussion

3.1. Moisture absorption

Moisture absorption results are plotted in Fig. 3. There are three subsets of the experimental data including prepared salt-based fillers, $CaCl_2$-NaCl mixtures, and pure chemicals (i.e., sodium chloride (NaCl), anhydrous calcium chloride ($CaCl_2$), and calcium chloride dehydrate ($CaCl_2.2H_2O$)). The result of pure chemicals (the right part of Fig. 3) indicates that $CaCl_2$ and $CaCl_2.2H_2O$ are very positive in open condition absorbing as much as 40% water after 24 h. Actually, those samples of
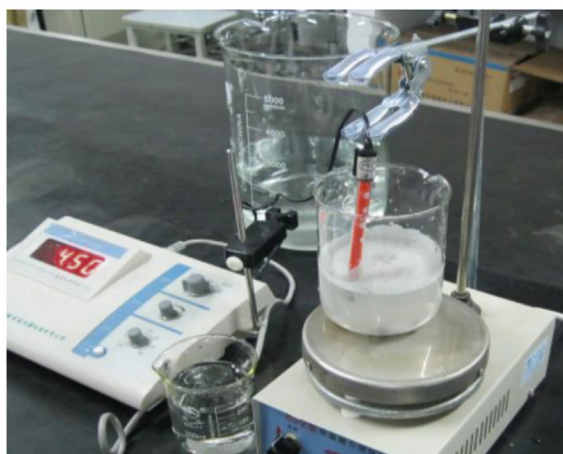
Fig. 2. Conductivity measurement for: **(a)** salt dissolution from salt-based filler and **(b)** salt releasing from AFACs.
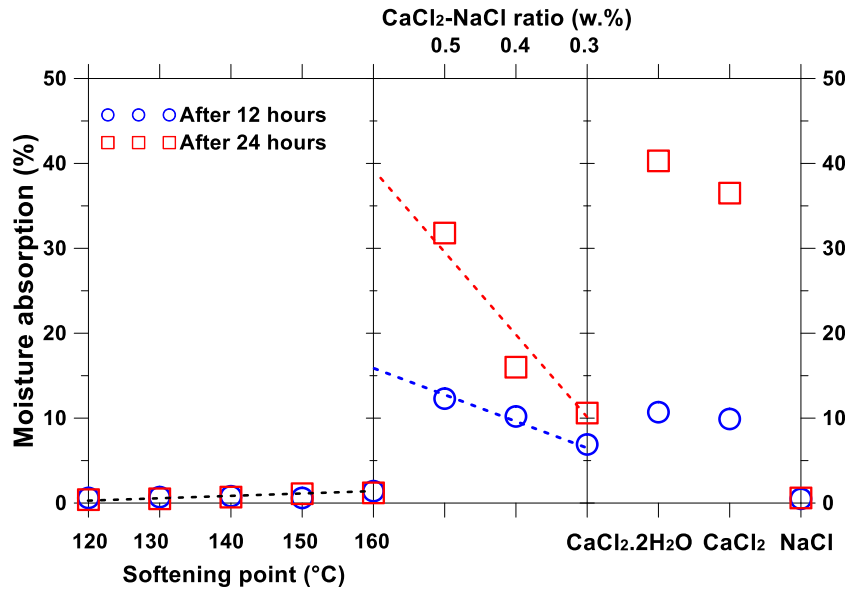
Fig. 3. Water absorption of antifreeze filler.

$CaCl_2$ and $CaCl_2.2H_2O$ were observed changing from solid into liquid after 24 h in experiment. This can explain the slippery surface of asphalt pavement containing $CaCl_2$-based additive as reported [32]. On the contrary, the pure sodium chloride (NaCl) showed a very stable weight in experiment. We also want to control the moisture absorption of $CaCl_2$ by mixing with NaCl, as shown in the middle part of Fig. 3. Although the moisture absorption at 24 h was reduced significantly to the mixtures containing 70 wt% NaCl and 30 wt% $CaCl_2$, it failed that there was still at least 10% moisture absorbed by salts. Hence, in the following experiment only sodium chloride was used to prepare salt-based filler. The result of salt-based filler modified by hydrophobers with different softening point, as plotted in the left part of Fig. 3, indicates that although a higher softening point caused a little bit higher moisture absorption, the highest value was still lower than 1.0%, much lower than pure $CaCl_2$. In applications, it must be paid as much as attention on keeping dry the salt-based additive, not only NaCl-based fillers but also $CaCl_2$-based aggregates.

3.2. Salt releasing property

Fig. 4 illustrates the effects of softening point (120, 130, 140, 150, and 160 °C) of hydrophobic polymer on conductivities of solution. What should be noted is that all salt-based fillers used in this section were not heated. With the same proportion and procedure of salt-based filler preparation, hydrophobers modified salts with different softening points were measured by conductivity tester, as plotted in Fig. 4a. As can be seen, the trend of conductivity from salts dissolution in the solution was nearly the same, which means the softening point of hydrophobers does not affect the salt dissolution performance.

However when looking at the conductivity results of salt-containing asphalt mixtures (AFACs), there was a significant difference in the trend, as shown in Fig. 4b. The AFAC specimen containing salt-based filler with 150 °C and 160 °C softening points gained the highest conductivity, while the lowest conductivity was achieved by the one with 120 °C and 130 °C. In comparison with the data in Fig. 4a, this
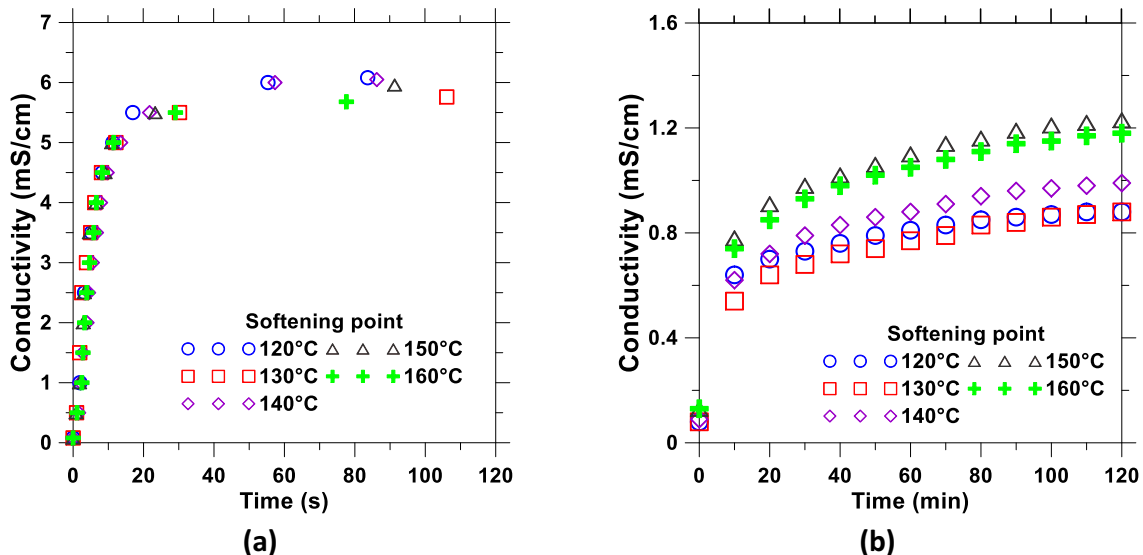

Fig. 4. Softening point effects on the conductivity of: (**a**) salt-based fillers, and (**b**) salt-based asphalt mixtures. Noted that the fillers in this section were not pre-treated by artificial heating.

phenomenon was not expected. The production of hot asphalt mixture must therefore change the salt. Three possible reasons may explain this result:

(i) Modification effect: During the production of asphalt mixture, the hydrophober also acts as a modifier to asphalt bitumen, thus the softening point affects the performance of the modification, making the asphalt mixture structure different;

(ii) Softening effect: the hydrophober will be also softened during the hot asphalt mixture production experienced as high as 160 °C temperature. The hydrophober with higher temperature (i.e., 150 and 160 °C) might be less softened than the one with lower temperature (i.e., 120 and 130 °C). The hot mixing during production acts as the final step in Fig. 1 in which the one with lower temperature gained a better modification;

(iii) Coating effect: The bitumen also acts on the salt particle surface as a modifier surface. The thicker asphalt film surrounding the salt particles is the one with the lower softening point.

3.3. Heating effects

According to the result in section 3.2, the salt dissolution and releasing performances were both influenced by the heating effect. Hence, more effort is worth to understand the behavior of salt-based materials in heating operation, as stated in Fig. 1 as the last step. Fig. 5 illustrates the conductivity of salt-based fillers and antifreeze asphalt mixtures. As expected, the heating treatment (180 °C) significantly changed the salt dissolution behavior (Fig. 5a) compared with the one without heating (Fig. 4a), especially for the one with 120 °C. However, the trend in Fig. 5b differs, strangely. The salt releasing from AFAC (Fig. 5b) showed that the heated filler with a softening point = 120 °C gained the highest conductivity while the one with a softening point = 150 °C gained the lowest conductivity. The salt releasing trend from AFAC was different with that from salt-based fillers. To better analyze the results of conductivities of salt-based fillers and AFACs, the final conductivities were summarized from Fig. 5 and then plotted in Fig. 6.

Fig. 6a presents the conductivity result of salt dissolution. Obviously, the final conductivities of salts were reduced by heating treatment. For instance, the largest difference between the treated and non-treated samples was close to 1.0 mS/cm. To the sample without heating treatment, the conductivity (blue circle) was reduced by increase of softening point. On the other hand, the conductivity of treated sample (red block) showed a similar trend going in opposite directions.
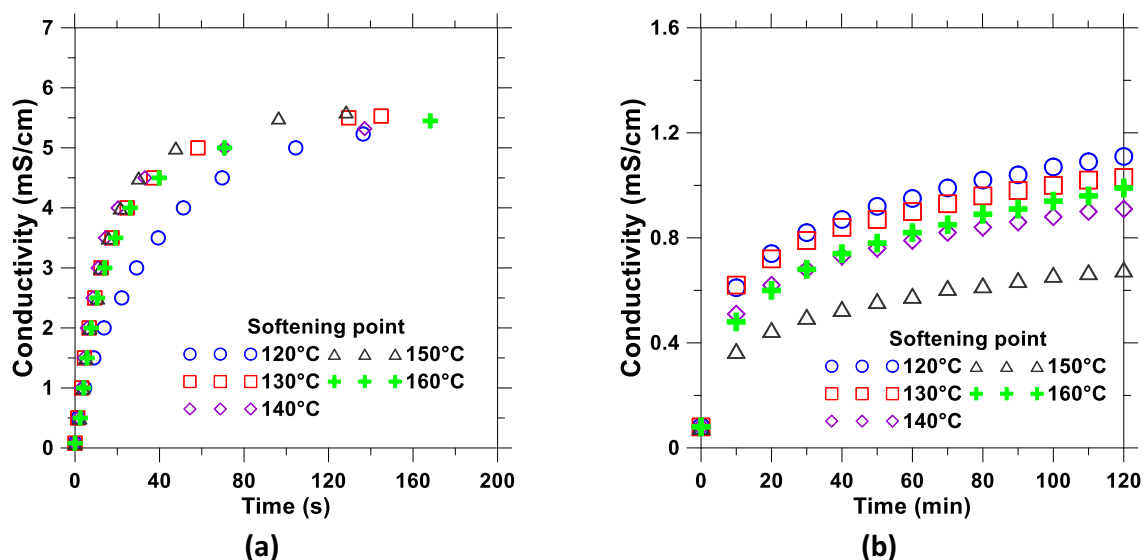
Fig. 6b illustrates the conductivity of samples from AFAC. Unlike the trends in Fig. 6a, a non-linear relation between conductivity and the point of softening is shown. Conductivity was increased by a higher softening point for salts without heating treatment, thus reaching a peak at 150 °C. To the sample with pre-heating, salts dissolved in solution were reduced by softening point increasing and reached a bottom at 150 °C. The heating treatment increased the dissolved salt rate for modified salts with a softening point of 120 °C and 130 °C, whereas the heating reduced its conductivity while the softening points are located at 140 °C and 160 °C. The reason of direction changed non-linear relationship phenomenon would be explained by the heating cycles discussed below in Section 4.2.

3.4. Microstructure of salt-based filler

Fig. 7 illustrates the scanning electron micrographs of modified salt particles based on scanning electron microscope (SEM). Figs. 7(a-c) are the particles without heating treatment, meanwhile Figs. 7(b-d) were preheated under 180 °C. The SEM images are highly in agreement with the schematic illustration in Fig. 1 where polymer modifiers, in smaller granules, surrounded the salt particles after ball-milling. After 180 °C heating treatment, hydrophober granules were softened and coated on the surface of salt particles. Compared with Fig. 7a and c, the microstructure was not affected by the softening point of hydrophobers, however, their modifier layers surrounding salt particles looks different after heating, as showing in Fig. 7b and d. The hydrophober with higher softening point gained a rougher surface. This phenomenon must be reflected on the macro-performance of salts and AFACs what will be discussed below.

4. Heating cycle effects

4.1. Thermal stability

Fig. 7 illustrates the thermal stability of salts in asphalt mixtures evaluated by simultaneous thermal analysis (STA), as AFACs has to be manufactured at a temperature of up to 180 °C [35,36]. The TG-DSC result is presented in Fig. 8 in which samples experienced temperature between 20 and 1000 °C. The thermogravimetric analysis (TGA) of modified salts in the 20–200 °C range shows good stability. The weight loss of the samples, whether heated or non-heated, was less than 0.5% in this range. The differential scanning calorimetry (DSC) data indicates
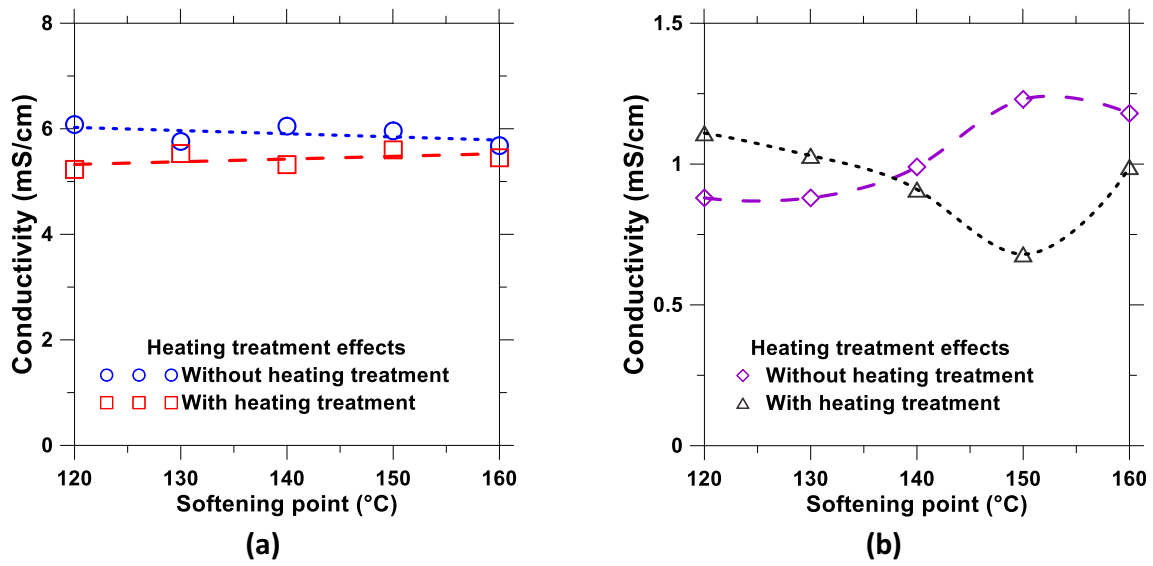

Fig. 5. Heating effect on the conductivity of: **(a)** salt-based fillers, and **(b)** salt-based asphalt mixtures.

Fig. 6. Softening point effect on the heating treatment by the final conductivity: **(a)** dissolved from salt-based filler, **(b)** released from antifreeze asphalt mixtures.
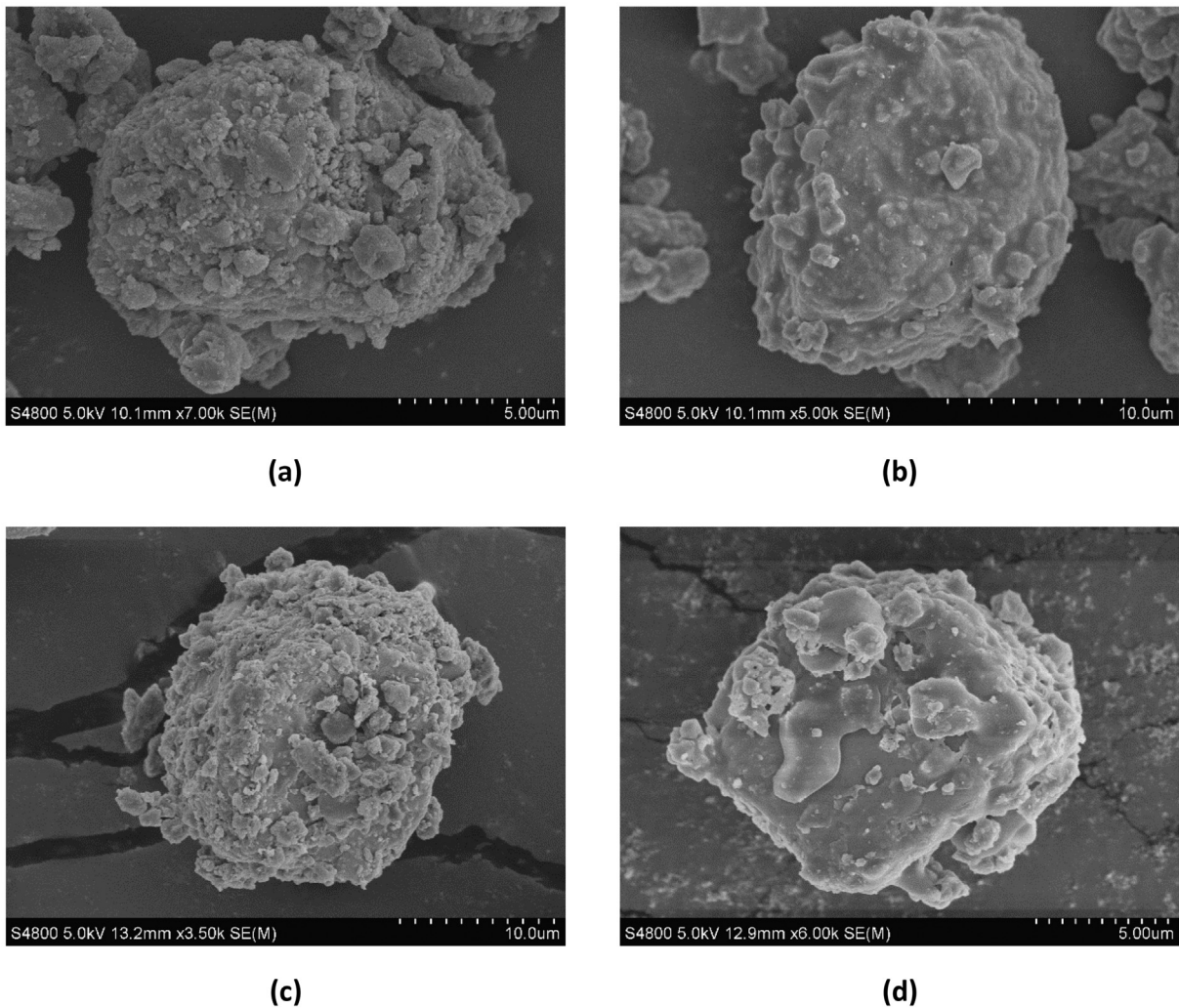

Fig. 7. Microstructures of salt-based filler by hydrophober whose softening point is: **(a-b)** 120 °C and **(c-d)** 160 °C, respectively. What should be noted is that **(a)** & **(c)** were not treated by heating while **(b)** & **(d)** were experienced with 180 °C treatment.
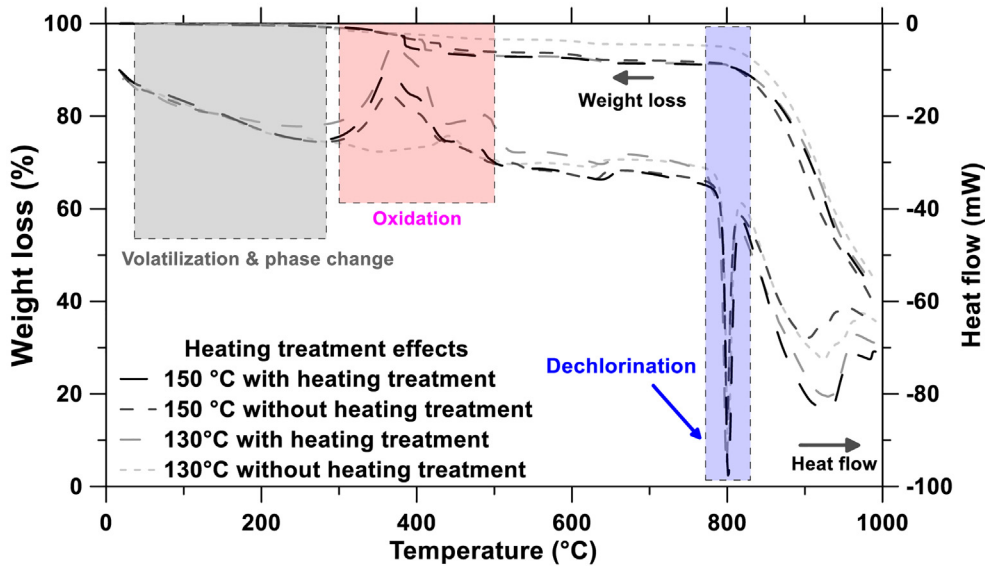
Fig. 8. TG-DSC curves of salt-based fillers among 20 to 1000 °C.

that this small weight loss is caused by volatilization and phase change of hydrophobers. The difference of softening point of hydrophobers didn't significantly influence the thermal stability of salts. There were two main peaks at temperatures above 300 °C, one of which resulted from the oxidation of polymers in salts (e.g. hydrophobers) with an exothermic process at an interval of 300–500 °C, while another peak was caused by de-chlorination as an endothermic process. Fortunately, the oxidation and de-chlorination will not appear during manufacture of the AFAC mixture.

4.2. Feeding process

Generally, fillers are introduced to the AFAC during processing before feeding on asphalt. However, with regard to the fact that the asphalt film coated around salt particles also acts as a modifier that can affect the performance of salt release, the effect of the feeding process was also evaluated. Before and after adding asphalt, the salt-based filler was introduced into the AFAC mixture, and then the solution conductivity, as shown in Fig. 2b, has also been observed here. Fig. 9 illustrates the
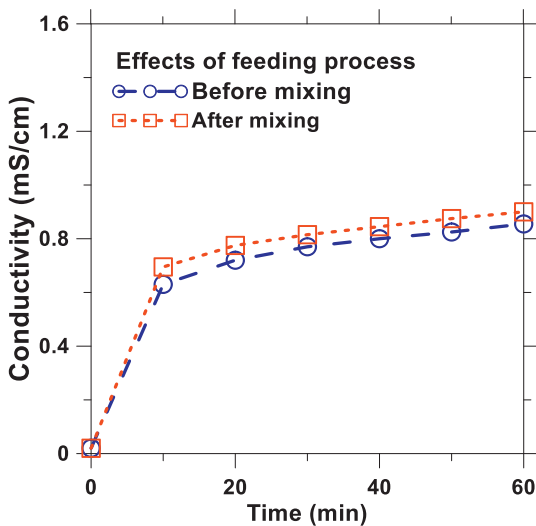
conductivity affected by salt feeding process. It shows that asphalt mixture containing salts feed after mixing caused the conductivity about 0.8 mS/cm higher than the salts feed before mixing. It is confirmed the hypothesis that the asphalt film coated on salt particle also acting as a modifier reducing the salt released from AFACs.

To evaluate the antifreeze performances of AFACs, antifreeze temperature (F_t) and antifreeze time (T_a) were adapted based on the conductivity test [24]. Antifreeze temperature (F_t) was previously defined as the minimum temperature at which ice or snow layer would not be formed on the pavement surface after the winter event occurred, and antifreeze time (T_a) was stated as the time from winter event occurring before the ice or snow covering the pavement surface without melting. These two parameters could be calculated according to Eqs. (1) and (2) based on the phase equilibrium of natural solutions of salts [23].

$$F_t = -3.9067 \frac{12 \cdot (1.7641 C_d - 0.0098)}{M \cdot \rho_{H2O} \cdot SF \cdot t \cdot \left(2\pi Rh + 2\pi R^2\right)} \times 10^3 + 0.5235 \qquad (1)$$

$$T_a = -3.9067 \frac{12 \cdot (1.7641 C_d - 0.0098)}{M \cdot \rho_{H2O} \cdot SF \cdot (F_t - 0.5235) \cdot \left(2\pi Rh + 2\pi R^2\right)} \times 10^3 \qquad (2)$$

where C_d is the conductivity of solution (mS/cm, 2 h); SF is the precipitation/12 h (mm); t is precipitating time of snow event (hour, 2 in this case); R is the diameter of specimen (5.08×10^{-2} m), h is the height of specimen (6.35×10^{-2} m) and $M = 58.5$ g/mol. The C_d above was observed from the compacted specimen, however in the current study all asphalt mixtures containing salts were not compacted, as shown in Fig. 2b. The relationship of conductivity between compacted and uncompacted asphalt mixtures was also evaluated. The conductivity of compacted AFAC (at 2 h) is equal to 58.33% of that of un-compacted AFAC mixture (at 1 h). Therefore, the conductivity in Fig. 9 could be input into the Eqs. (1) and (2).

Fig. 10 illustrates the antifreeze temperature and antifreeze time according to the experimental measurements. Accordingly, the antifreeze temperature of AFACs was evaluated concerning the precipitation among 0-12 mm per half day (12h). Although the feeding process showed an evident influence on the conductivity, as shown in Fig. 9 above, the antifreeze temperature (Fig. 10a) was not that sensitive like the conductivity. There was just about 0.1 difference between two specimens. A similar trend can also be gained if looking
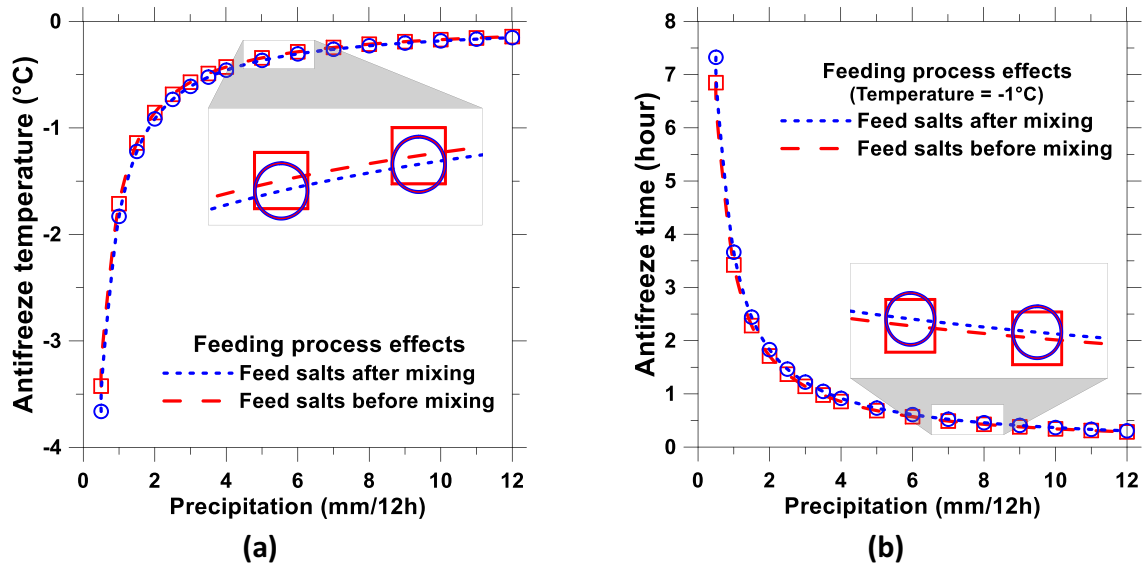

Fig. 9. Salt feeding effects on the salt releasing from antifreeze asphalt mixture.

Fig. 10. Salt feeding effects on antifreeze performance of AFACs: **(a)** antifreeze temperature and **(b)** antifreeze time. Noted that all antifreeze temperature and antifreeze time were calculated based on the given precipitation = 1 mm/12 h and (b) was calculated based on the assumption of temperature = −1 °C. The hydrophober with a softening point of 160 °C was used.
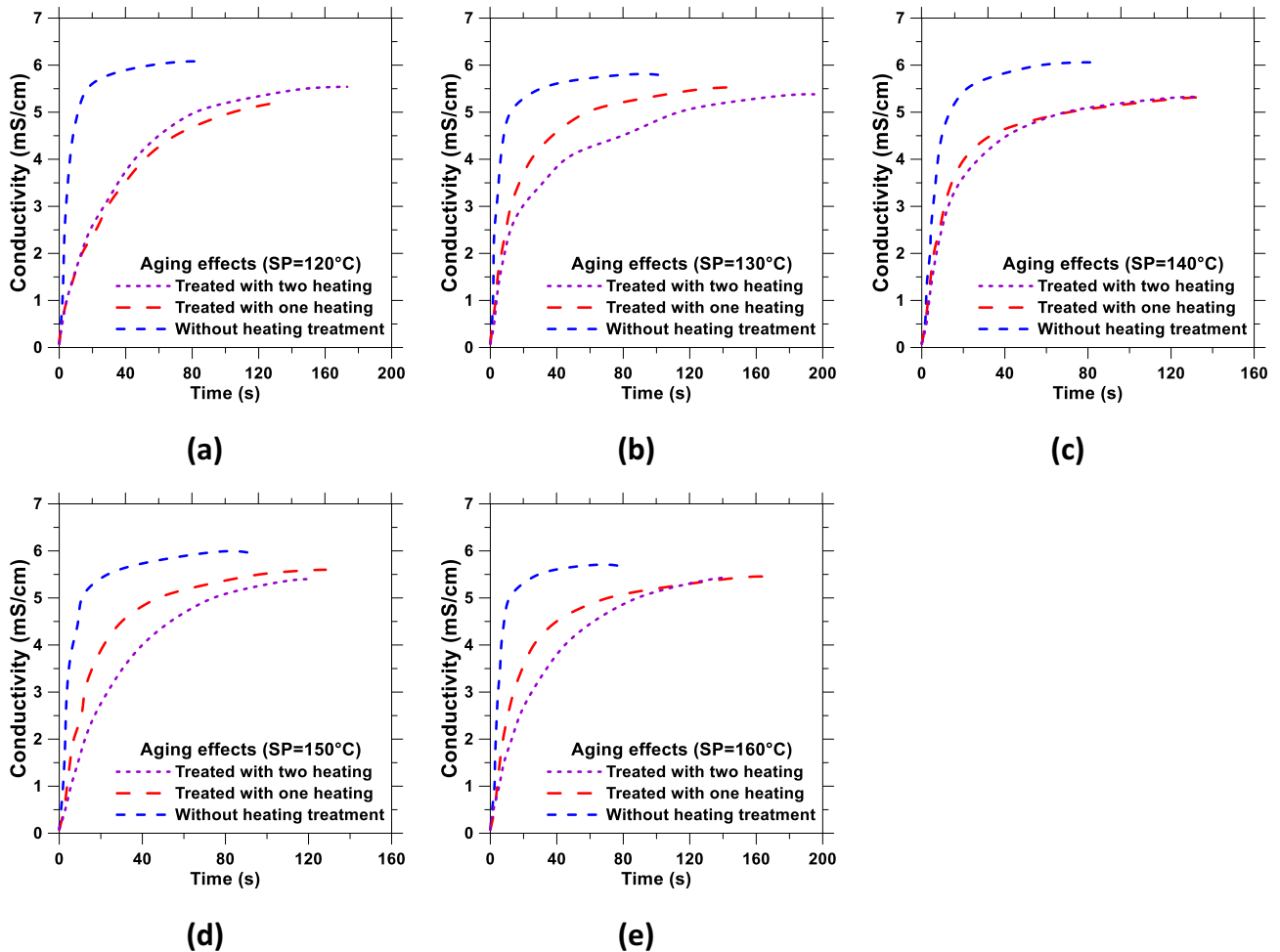

Fig. 11. Heating cycle effect on the conductivity of salt-based filler with softening points of: **(a)** 120 °C, **(b)** 130 °C, **(c)** 140 °C, **(d)** 150 °C, and **(e)** 160 °C.

at the antifreeze time in Fig. 10b which was calculated under a given temperature (−1 °C).

4.3. Heating cycles

As mentioned in detail in Fig. 1, after ball-milling, the salt particles were heated for 15 min at 180 °C to soften the polymer modifier so that to form a thin coating layer around salts. However if the process of production of asphalt mixtures is concerned, asphalt mixtures must also be manufactured under temperature up to 185 °C. This means that the salt particles have to be subjected to two heating cycles, known as the aging effect, in particular the second heating. For instance, the trend of salt releasing was changed from Fig. 6a to Fig. 6b. The aging effects on salt dissolution were therefore evaluated by two cycles of heating the well ball-milled salt particles. The first heating treatment is to soften the thin-coating layer of the polymer, while the second heating cycle is to simulate the aging effect during the production of hot-mix asphalt. The conductivity of the salt-based fillers treated was measured as described in Fig. 2a.

Fig. 11 illustrates the conductivity of synthesized salt particles modified by hydrophobes with different softening points (SP). While the softening points of hydrophobes changed from 120 °C to 160 °C, the trend of conductivity, as presented in Fig. 4a above, showed there was no difference between samples without pre-heating treatment, but a significant difference was achieved to those with pre-heating at 180 °C.

To better understand the effects of the softening point of hydrophober on salt releasing behavior, the final conductivities of modified salts with pre-heating treatment, determined as the conductivity value in Fig. 11 when the curve reached nearly horizontal, was compared. There are three typical patterns showing in Fig. 12a in which curves were sourced from the ones with softening points of 120 °C (blue line), 150 °C (red line), and 160 °C (purple line). If looking at the start point, it shows an inverse correlation between the softening points and conductivity values. However, after first heating, the salt with a softening point of 120 °C had the lowest conductivity. After two heating cycles, although the conductivities are nearly the same, the one with the lowest softening point achieved a little bit higher value than others. If focused on the curves above, there are three typical trends, which are

noted as Bottom pattern (blue line), Linear pattern (red line), and Platform pattern (purple line). As we can see, the blue line (softening point = 120 °C) is reduced quickly after the first heating and reached the bottom; the red line (softening point = 150 °C) decreased incessantly after two heating cycles, and the purple line (softening point = 160 °C) has achieved a platform since first heating.

Based on the schematic illustration (Fig. 1) and the microstructure of salts (Fig. 7), polymer particles absorbed or adhered on the salt's surface after ball-milling in a fine particles manner. However, polymer particles are softened during heating treatment, and forms a little thin coating layer around salt particle, as shown in Fig. 12. The softening effect is supported by the STA data in Fig. 8 while phase changes were observed between 100 and 200 °C.

There are four situations of the polymer coated on salt particles as following, whose microstructures were also presented in Fig. 12b, in which EDS data proves that more than 40% atoms are carbon which comes from hydrophobic polymers.

I. Fine polymer particles surround the salt particle linking with the conditions of salt without heating treatment which could be also observed in Fig. 7a&c. As SEM images showing, particle size is as small as 100 nm.

II. Polymers were partially softened and main parts of the salt surface were coated. In this case, the heating temperature is not as high as spreading the entirely coated modifier on the surface of salts. Non-melted polymer particle remains on the surface.

III. salt particles are evenly covered and sealed by thin polymer layer, which means the salt is the most difficult to be released in all situations. As observed in Fig. 12b, there is no free area exposed.

IV. Part of the salt surface is exposed again. This situation generally appears due to the volatilization of polymer modifiers. The porous structure is very clear in Fig. 12b after over-heating treatment.

Therefore the three patterns referred to in Fig. 12a should be explained. At the first heating, the hydrophober polymer with the lowest softening point of 120 °C reached Situation III (fully covered) on the blue line (Bottom pattern), and then at the second heating, turned
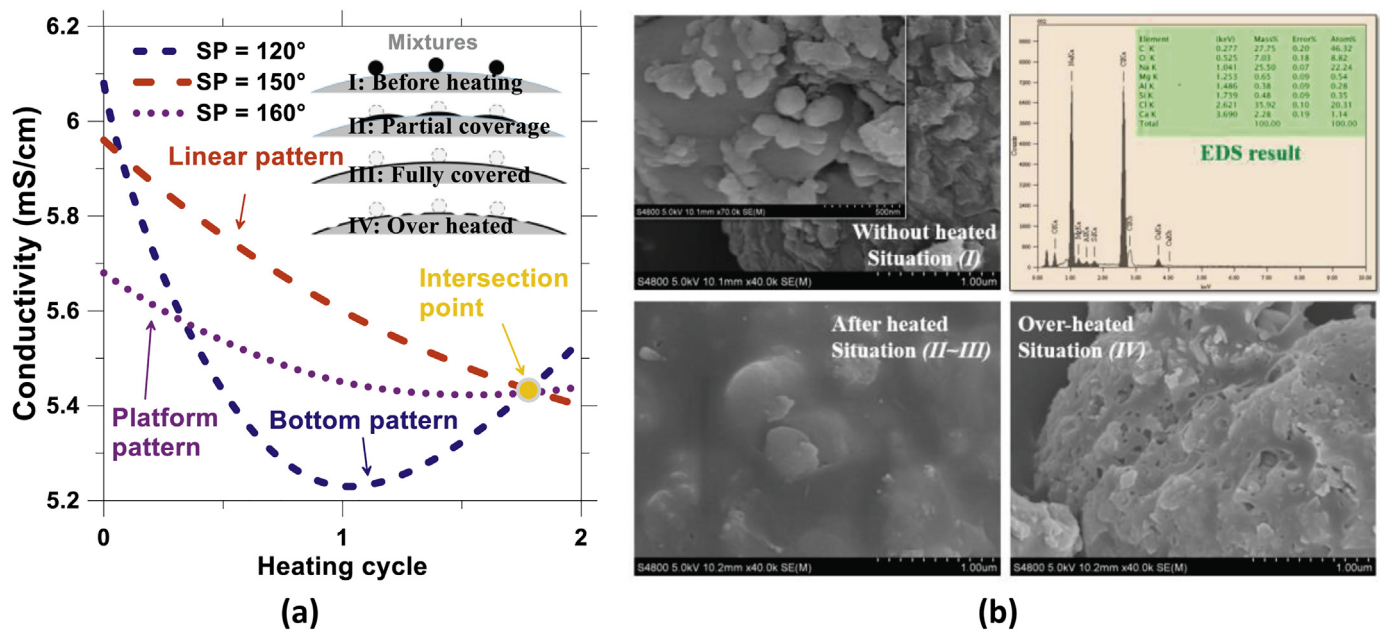

Fig. 12. Three typical patterns of heating effects and four situations on salt-based fillers surface: **(a)** typical trends of conductivity evolution after heated, **(b)** micro-structure and EDS result of salt surface.
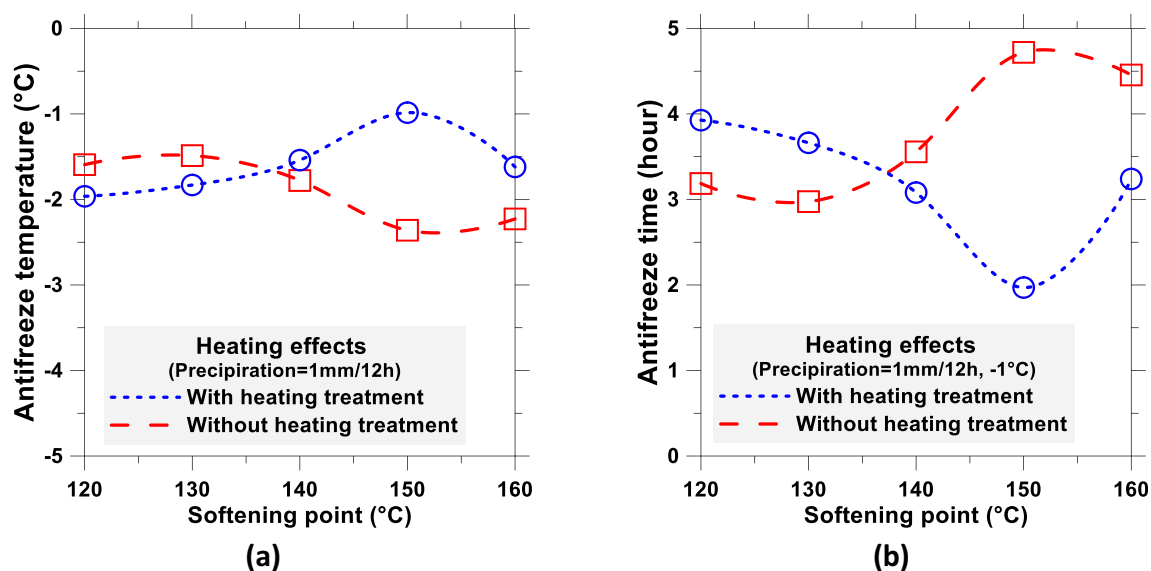
Fig. 13. Heating effects on the antifreeze performance on AFACs: **(a)** antifreeze point and **(b)** antifreeze time. It should be noted that all antifreeze temperature and antifreeze time were calculated based on the given precipitation = 1 mm/12 h and (b) was calculated on the assumption of temperature = −1 °C.

into Situation IV (over heated). After the first heating procedure, the red line (Linear pattern, softening point equal to 120 °C) still did not pass through the situation I (partial covered), as the second heating treatment improved the inhibitive performance of the salt release (Fig. 11d). To the purple line, it stops reducing at the first heating with the highest softening point (160 °C) because the second heating can still not break the hydrophober polymer film on the salt surface.

The antifreeze performance of salt-containing AFACs under heating treatment was shown in Fig. 13 in accordance with Eqs. (1–2). It is very clear that the softening points of hydrophobic polymers influence the performance of antifreeze, i.e. the temperature of the antifreeze and the duration of the antifreeze. At the softening point of 130 °C, the AFAC containing salt without heating treatment (blue lines) achieved the worst antifreeze performance, e.g., the highest antifreeze temperature (Fig. 13a) and the shortest antifreeze time (Fig. 13b). According to the blue lines, the heating process changes the shift in salt release performance. For example, the worst antifreeze performance was

achieved by AFAC containing polymer-modified salt with a softening point of 120 °C. Interestingly, the trends of AFACs here differ greatly with that stated in Fig. 4a. If without heating treatment, the salt releasing behaviors expressed by conductivity in Fig. 4a were similar. However after heating treatment, the hydrophober polymer with a softening point of 120 °C resulted in a lowest released salts in Fig. 5a. Actually, the aforementioned phenomena could be easily understood if the additional heating experience during the production of asphalt mixture is taken into consideration.

4.4. Moisture susceptibility of AFACs

Fig. 14 illustrates the moisture susceptibility of antifreeze asphalt mixtures containing salt-based filler. Previous studies brought out the concern about the moisture susceptibility of AFACs [29,37]. The residual Marshall stability shows the moisture susceptibility is generally improved by the increased softening point of hydrophobes. The heating treatment significantly reduced the moisture susceptibility of AFACs, even lower than the critical value (75%). It was believed that the released salt particles left pore-structures in asphalt concrete [16], as a result, the moisture can invade the asphalt concrete through these pores. Combined the discussion in Section 4.3, pre-heating treatment will bring over-heating to salt particles exposing more surface that causes fast salt releasing.

5. Conclusions

The present study was designed to determine the effect of softening point of hydrophobic polymer on the salt-based filler and antifreeze asphalt concretes (AFACs). To evaluate the softening points effects of hydrophobic polymers on the performance of the salt-based filler used in AFACs, moisture absorption, salt releasing property, thermal stability, and antifreeze performance and moisture susceptibility of AFAC were evaluated in which both quantitative methods (i.e., conductivity and Marshall test) and qualitative methods (i.e., SEM and EDS) were adapted. Based on the current data, the following conclusions could be drawn.

(1) The moisture absorption of sodium chloride (NaCl), anhydrous calcium chloride ($CaCl_2$), calcium chloride dehydrate ($CaCl_2 \cdot 2H_2O$), and $CaCl_2$-$CaCl_2 \cdot 2H_2O$ mixtures was assessed.
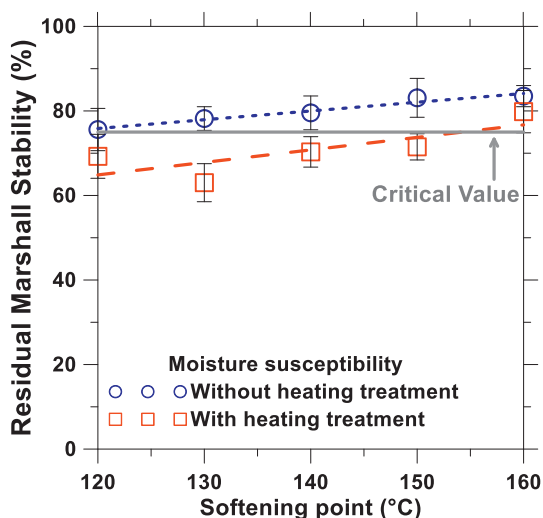

Fig. 14. Effect of softening point of hydrophobers on the moisture susceptibility of antifreeze asphalt mixture (AFAC).

The calcium chloride and their hydrates are not appropriate for producing salt-based filler used in antifreeze asphalt concretes (AFACs) because the moisture absorption of $CaCl_2$ and $CaCl_2 \cdot 2H_2O$ was as much as 40% after 24 h exposure in laboratory condition which will bring challenges in anti-skid-related issues.

(2) There is no significant effect of softening point on the salt releasing property of hydrophobic polymer modified salt (NaCl) without pretreatment by heating, however, after mixed in asphalt mixtures the conductivity was reduced by lower softening points. Three effects should be noticed including binder modification by hydrophobic polymer, difference of softened hydrophobic polymer due to softening points, and the coating layer on salts by asphalt binder. SEM analysis of heated salts observed the softening phenomenon of hydrophobic polymer on salt surface.

(3) Thermal stability and feeding effects were also evaluated during the hot mix asphalt production. Result indicates that the hydrophobic polymer are softened between 100 and 200 °C, but are decomposed among 250–300 °C. As such, the modified salt can remain stable during hot mix asphalt production, in this research. The feeding effect on salt releasing and antifreeze performance was very slight that could be ignored in application.

(4) Because of the high temperature (i.e. 180 °C) during asphalt mixture producing, the influence by multiple heating was also investigated. Based on the current samples, modified salt, using hydrophober with a softening point of 130 °C, achieved the best controlled-release property after the first heating. Meanwhile, after the second heating treatment the best controlled-release property turned to the hydrophober with a softening point of 150 °C. A phenomenon was innovatively summarized that there were four situations of hydrophober polymer particle on salt surface based on the microstructure observation, thereafter, the conductivity trends influenced by heating cycle were divided into three typical patterns.

(5) The softening point of hydrophober used to modify salts also influence the moisture susceptibility of asphalt concrete. Generally, the higher the softening point of hydrophober, the better moisture susceptibility of the AFACs. The pre-heating of salts brought damage to AFACs. To the salts without pre-heating, their AFACs were as good as expected, however, after pre-heated the AFACs containing salt had a residual Marshall stability lower than 75%.

Credit author contribution statement

ZZ Liu initiated the key concepts of the research, collected, and analyzed the experimental data. ZZ Liu and I. Hoff prepared the manuscript. I. Hoff contributed on the writing skill and discussion of the manuscript. ZZ Liu and AM Sha acquired funding for the research.

Declaration of Competing Interest

There is no potential conflict of interest relating to this paper.

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