Characterization of various bitumen exposed to environmental chemicals

Xuemei Zhang [*], Inge Hoff, Hao Chen

Department of Civil and Environmental Engineering, Norwegian University of Science and Technology, Høgskoleringen 7A, Trondheim, Norway

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ABSTRACT

As a necessary element of asphalt concrete, bitumen plays a decisive role in influencing the durability and lifespan of asphalt pavement. Environmental chemicals, such as de-icing salt and acid rain, have negative effects on asphalt pavement. However, different bitumen might react differently to environmental chemicals. The purpose of this research is to investigate the influence of environmental chemicals on various bitumen. To achieve this goal, three types of bitumen, base bitumen, polymer modified bitumen, and rejuvenated bitumen, were submerged in three environmental chemicals (sodium chloride, calcium chloride, and acid). The micro-surface, physical properties (penetration, softening point, and dynamic viscosity), low-temperature rheological properties (creep flexural stiffness and relaxation rate), moderate-temperature rheological properties (complex modulus and phase angle), and mechanical properties (non-recoverable creep compliance, recovery percent, and fatigue life) of bitumen were characterized by scanning electron microscopy, physical tests, bending beam rheometer, and dynamic shear rheometer. The chemical bond of three kinds of bitumen was characterized by mean of Fourier transform infrared radiation spectrometer to analyse the reaction between various bitumen and chemicals. Three types of bitumen performed differently to environmental chemicals due to different reactions. The oxidation, stabilization, and polymerization of base bitumen occurred during the chemical process, which leads to apparent changes in bitumen performance. The combination of decomposition and oxidation of polymer modified bitumen lowered the ageing degree and induced the different trend in softening point, dynamic viscosity, non-recoverable creep compliance, and recovery percent. With the addition of the rejuvenator, the effect of environmental chemical on rejuvenated bitumen was reduced. Therefore, polymer modified bitumen had the best resistance to environmental chemicals, followed by rejuvenated bitumen, base bitumen had the worst chemical resistance. Moreover, sodium chloride, calcium chloride, and acid caused the most significant change of base bitumen, polymer modified bitumen, and rejuvenated bitumen, respectively. These findings of this research help engineers understand the effect of environmental chemicals on bitumen performance and select proper bitumen type under different chemical conditions.

1. Introduction

As one of the most significant components of asphalt concrete, bitumen properties are crucial to the durability and lifespan of pavements. The morphological, physical, chemical, rheological, and mechanical performance are five critical characteristics to predict the service life of asphalt pavement (Mandula and Olexa, 2017). Morphology of bitumen is the most intuitive feature for observing changes in bitumen influenced by chemicals. Physical performance of bitumen plays a key role in characterizing the ageing degree of asphalt pavement (Wang et al., 2020). Rheological and mechanical performance of bitumen include the viscoelastic behaviours, permanent deformation resistance, and resistance to fatigue cracking, which are highly related to asphalt pavement distresses (Xue et al., 2020). Investigation on the chemical structure of bitumen is beneficial to analyse the reaction between bitumen and chemicals (Hu et al., 2021).

Spreading de-icing salts is a commonly used method for winter maintenance to prevent the accumulation of snow and the formation of ice in winter (Charola et al., 2017). Sodium chloride and calcium chloride are the most commonly used de-icing salts due to their outstanding effectiveness and low cost (Autelitano et al., 2019; Klein-Paste and Dalen, 2018). Acid rain consisting of sulfuric acid and nitric acid are the results of sulphur dioxides (SO_2) and nitrogen oxides (NO_x) reacting with water in the air, especially in the regions near factories (Feng et al., 2017).

In addition to negative environmental and corrosion problems, the above chemicals also have adverse effects on the quality and durability of asphalt pavements (Lu et al., 2021; Wang et al., 2017). Previous research found that increased air voids, loose structure, and reduced mechanical properties of asphalt concrete were obtained after environmental chemical conditioning (Feng et al., 2020; Goh et al., 2011; Ozgan et al., 2013; Xiong et al., 2019a), which finally results in stripping of bitumen from aggregate, cracking, and short service life of asphalt pavement. It was also found that chemicals had a destructive influence on interfacial properties of asphalt mixtures, and a higher concentration of solution tended to cause stripping easily (Baldino et al., 2019; Yang et al., 2020). These deteriorations can be probably explained by the reduction in adhesion between bitumen and aggregate and its physico-chemical reaction with bitumen (Darwin et al., 2009; Xiong et al., 2019b; Yang et al., 2020; Zou et al., 2021). Therefore, the rheological, chemical structure, and composition of base bitumen and aged bitumen exposed to environmental chemicals were widely studied. As a result, oxygen contained functional groups, elastic components, and asphaltenes proportion within bitumen increased after chemical conditioning (Noguera et al., 2014; Zou et al., 2021). These results are attributed to the oxidation, replacement, and dissolution of bitumen that occurred during the immersion period.

However, only base bitumen or aged bitumen was extensively studied under different environmental chemicals. Other common types of bitumen have been paid little attention. In view of the above background, this research aims to evaluate the influence of environmental chemicals on the behaviours of various bitumen. 10% NaCl, 10% $CaCl_2$, and acid of pH 4 solutions were employed to submerge base bitumen, polymer modified bitumen, and rejuvenated bitumen for 30 days. Scanning electron microscopy, penetration, softening point, dynamic viscosity, bending beam rheometer, dynamic shear rheometer, and Fourier transform infrared radiation spectrometer tests were conducted to characterize the surface, physical, rheological, and mechanical properties of bitumen, as well as chemical reaction between chemicals and bitumen. The findings of this study are expected to provide guidance and reference on selecting the proper bitumen type to minimize the damage caused by environmental chemicals.

2. Methodology

2.1. Materials

2.1.1. Bitumen

A wide range of bitumen was selected in this research, including base bitumen with Pen 70/100, polymer modified bitumen, and rejuvenated bitumen. The bitumen type mainly used for pavement construction in Norway is base bitumen (BB). Polymer modified bitumen (PMB) is mostly used for high-volume roads. Rejuvenated bitumen (RB) as an environmentally friendly bitumen is also a good choice for asphalt pavement. Base bitumen of pen 70/100 was collected from the company Veidekke (Trondheim, Norway). Polymer modified bitumen (SBS modified bitumen) with the penetration of 65–105 mm was ordered from the company Nynas (Göteborg, Sweden). The commercial rejuvenator (refined vegetable oil) used for rejuvenated bitumen was obtained from company ARSTEC. The rejuvenated bitumen was prepared by mixing short-term aged bitumen and 3% commercial rejuvenator based on previous references (Chen et al., 2018; Kuang et al., 2019). The mixing process is introduced as follows: firstly, the bitumen was aged using the thin film oven test (at 163 °C for 5 h) in accordance with standards EN 12607–2:2014; the aged bitumen was then preheated at 110 °C for 1 h; the weighed aged bitumen and rejuvenator was mixed and stirred for 30 s at room temperature; the last step is to put the rejuvenated bitumen specimen back to heating cabinet for 10 min. This is one cycle, and the mixing process is finished after five cycles. The properties of three types of bitumen are shown in Table 1.

Table 1
Properties of three types of bitumen.

Experiment	Unit	BB	PMB	RB	Specification
Penetration (25 °C)	0.1 mm	71	79	206	EN 1426: 2015
Softening point	°C	48.2	64.6	39.6	EN 1427:2015
Dynamic viscosity (60 °C)	Pa•s	179.6	397.5	53.7	EN 13702:2018

2.1.2. Environmental chemical

Three environmental chemicals were applied: sodium chloride, calcium chloride, and acid. 10 wt% sodium chloride and 10 wt% calcium chloride as the estimated average for field condition were prepared by diluting salt solid with distilled water, respectively. Acid of pH 4 was made by diluting a blend of sulfuric acid and nitric acid in a ratio of 1:2 using distilled water based on previous research (De Marco et al., 2019).

2.2. Methods

2.2.1. Soaking process

The soaking process of bitumen is set according to previous references (Pang et al., 2018; Meng et al., 2021) and shown in Fig. 1. First of all, 28 g bitumen was prepared in a glass container with a 190 mm diameter. A homogeneous bitumen film (0.85 mm thickness) was obtained after heating at 90 °C for 20 min (base bitumen and rejuvenated bitumen) or 130 °C for 30 min (polymer modified bitumen). The container with bitumen was then cooled for 2 h to proceed with the soaking process. For the soaking process, 150 ml chemical solution was added to completely submerge bitumen film, and the container was covered by a black plastic bag. Finally, the container with bitumen was placed at 25 °C for 30 days. After the soaking process for bitumen, the surface of bitumen was cleaned with distilled water, and bitumen was dried in a fume hood for three days for subsequent tests.

2.2.2. Surface characterization

Morphology is the fundamental factor for further characterization of bitumen influenced by chemicals. In this case, the morphology of bitumen under various conditions was captured to study the effect of environmental chemicals on bitumen using Flex Scanning Electron Microscopy (SEM) 1000. The bitumen samples were taken at a voltage of 5 kV with 200 magnifications. At least three similar pictures were captured for each specimen, and the most typical one was selected in this research.

2.2.3. Physical property test

The physical property of bitumen is considerably related to asphalt pavement ageing. To investigate the effect of chemicals on the physical properties of bitumen, penetration test, softening point test, and dynamic viscosity test were conducted according to EN 1426: 2015, EN 1427:2015, and EN 13702:2018, respectively. Penetration at 25 °C, softening point, and dynamic viscosity in the range of 60 °C–100 °C of three kinds of bitumen under environmental chemical were analysed. Three determinations, two replicates, and two measurements were tested for penetration, softening point, and dynamic viscosity tests, respectively. The average value was calculated as the test results.

2.2.4. Bending beam rheometer test

Bending beam rheometer test was conducted to investigate the low-temperature rheological properties of bitumen under different conditions following EN 14771:2012. Each specimen is made to the beam with the dimension of 127 × 6.4 × 12.7 mm^3 and tested at two temperatures (−12 °C and −18 °C). Flexural creep stiffness (S(t)) and relaxation rate (m-value) at loading time of 60 s were calculated and analysed for characterizing the low-temperature rheological properties of bitumen. Two replicates were tested, and the mean of two values was used as the final measurement.

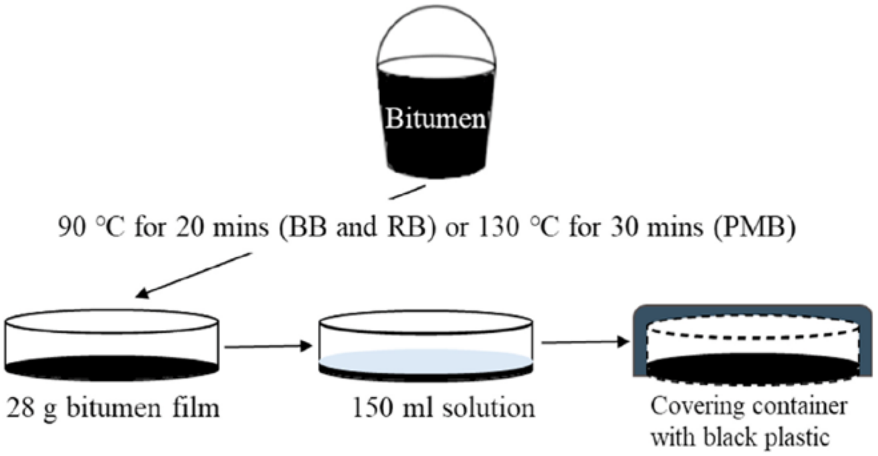


Fig. 1. Soaking process.

2.2.5. *Dynamic shear rheometer test*

2.2.5.1. Temperature sweep test. The rheological behaviours at moderate temperature of bitumen influenced by chemicals were measured using the Dynamic Shear Rheometer. In this case, temperature sweep test was performed at a constant frequency of 10 rad/s in the temperature range of 5–30 °C with an increment of 1 °C. The diameter of the plate was 8 mm, the thickness of bitumen sample was 2 mm. Each specimen was tested twice, and the average value was finally applied.

2.2.5.2. Multiple shear creep recovery (MSCR) test. To determine the effect of three chemicals on the permanent deformation and elastic recovery behaviours of bitumen, the MSCR test was conducted at 60 °C following EN 16659:2015 standard. The specimen is prepared with 25 mm of diameter and 1 mm thickness. In this test, two constant creep stresses (0.1 kPa and 3.2 kPa) were loaded on the specimen for ten cycles. Each cycle consists of 1 s duration of loading and 9 s duration of recovery. J_{nr} and %R were obtained from the MSCR test as two measurement indicators: J_{nr} is defined as non-recoverable strain divided by applied stress; %R is the ratio of recovered strain to total strain. Two replicates were applied for each kind of bitumen. The averaged value is applied in the research.

2.2.5.3. Linear amplitude sweep test. The Linear amplitude sweep (LAS) test was carried out to characterize the fatigue resistance of bitumen based on the principle of Viscoelastic Continuum Damage (VECD). According to AASTHO TP 101–12, LAS test was conducted at 25 °C using dynamic shear rheometer with an 8 mm diameter parallel plate and 2 mm gap. Each specimen was tested with two replicates, and the mean value was calculated and used for analyses. Two steps are included for LAS test. First step is frequency sweep conducted at a strain of 0.1% over a range of frequencies from 0.2 to 30 Hz. Second step is amplitude sweep controlled at a fixed frequency of 10 Hz with an increasing strain from 0.1% to 30%. The fatigue life of bitumen (N_f) is calculated by Eq. (1):

$$N_f = A(\gamma_{max})^{-B} \qquad \text{Eq. 1}$$

Where γ is the expected maximum strain level, A and B are viscoelasticity related coefficients of bitumen.

2.2.6. *Chemical bond analysis*

In this research, Nicolet 8700 Fourier transform infrared (FTIR) radiation spectrometer with an attenuated total reflectance (ATR) accessory was used to explore the chemical bonds of bitumen under different conditions, which can reflect the interplay between bitumen and environmental chemical. Three replicates were tested for each specimen, and the FTIR spectrum with the largest absorbance peaks was selected and analysed. Fig. 2 shows the infrared spectrum of three kinds of bitumen with specific peaks. N–H group at 1540 cm^{-1} of BB is different with PMB and RB, which can be interpreted by different sources of various bitumen. Butadiene double bond (C=C) and C–H bond of polystyrene located at 964 cm^{-1} and 698 cm^{-1} are the specific peaks of PMB, which are highly related to the amount of styrene-butadien-styrene molecule in PMB (Wu et al., 2009; Xu et al., 2021). Regarding RB, the C–O group of esters at 1174 & 1195 cm^{-1} indicates the rejuvenator whose major component is ester. The C=O group at 1745 cm^{-1}, which is also a typical indicator of ester regarded as the characteristic peak for rejuvenator, occurred in the infrared spectrum of RB (Jacobs et al., 2021; Lin et al., 2021).

3. Results and discussions

3.1. *Surface characterization*

As shown in Fig. 3, images of bitumen after chemical conditioning were taken to indicate the micro-surface characteristics of each sample. Figs. 3 A-1, B-1, and C-1 show the original three types of bitumen as a reference, where the surfaces of BB and RB were smooth, and the surface of PMB was rougher and structured with more granules. Exposed to environmental chemicals, the changes in bitumen surface therefore varied from type to type. As indicated in Figs. 3 A-2, A-3, and A-4, the addition of chemicals made BB surface more spots and sharp angles,

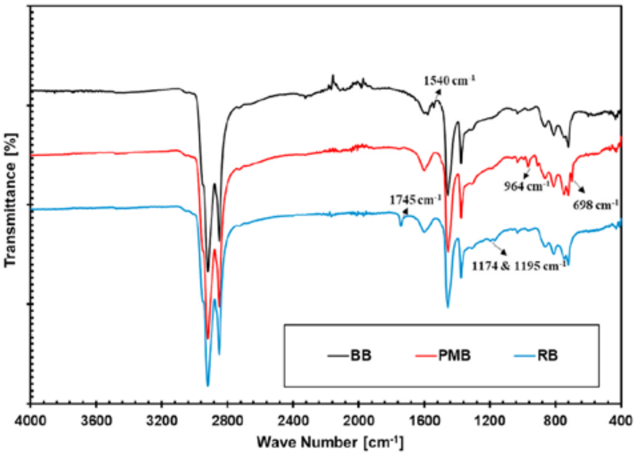
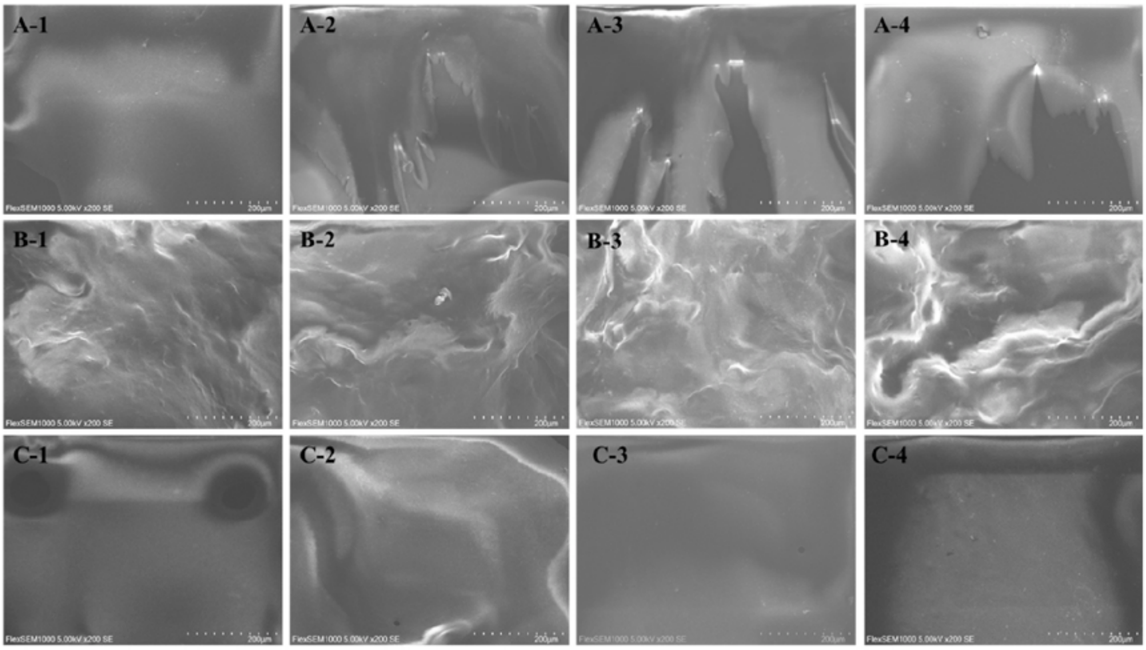


Fig. 2. The infrared spectrum of BB, PMB, and RB bitumen.



A-1: Original BB; A-2: BB-NaCl; A-3: BB-$CaCl_2$; A-4: BB-Acid.
B-1: Original PMB; B-2: PMB-NaCl; B-3: PMB-$CaCl_2$; B-4: PMB-Acid.
C-1: Original RB; C-2: RB-NaCl; C-3: RB-$CaCl_2$; C-4: RB-Acid.

Fig. 3. SEM image of bitumen under chemical conditioning.

which suggests that corrosion and ageing occur during chemical conditioning. As shown in Figs. 3 B-2, B-3, and B-4, the PMB surface was mildly polished by environmental chemicals, and the granules on PMB surface were transferred to smaller granules, which might be the result of the decomposition of polymer. However, RB showed few differences in bitumen surface. This phenomenon can be interpreted that the rejuvenator used in RB mitigates the deterioration of chemicals on the RB surface (Huang et al., 2021).

3.2. The physical property of bitumen influenced by chemicals

The physical parameters for three kinds of bitumen, penetration, softening point, and dynamic viscosity indicating the consistency, stability, and flow resistance (Jailani et al., 2021; Nizamuddin et al., 2020), were analysed. Fig. 4 shows the penetration of bitumen exposed to chemicals. Chemicals significantly decreased the penetration of three kinds of bitumen to different extents, which indicates that chemicals significantly improve the consistency of three kinds of bitumen. For BB, it is observed that three chemicals apparently reduced the penetration of bitumen to different extents. The greatest influence was recorded for NaCl since the penetration of NaCl conditioned bitumen was changed to 4.6 mm from 7.1 mm, followed by acid and $CaCl_2$. These results indicate that the hardening effect takes place on bitumen due to chemicals, arranging the hardening effect of three chemicals in descending order: NaCl, acid, and $CaCl_2$. In terms of PMB bitumen, two salts had the same impacts on penetration and decreased the penetration by 27%, and acid had the most severe impact on penetration of bitumen. Regarding RB, about 28% reduction on the penetration of RB was obtained after chemical conditioning, and acid had the most significant impact on the penetration of RB among the three chemicals.

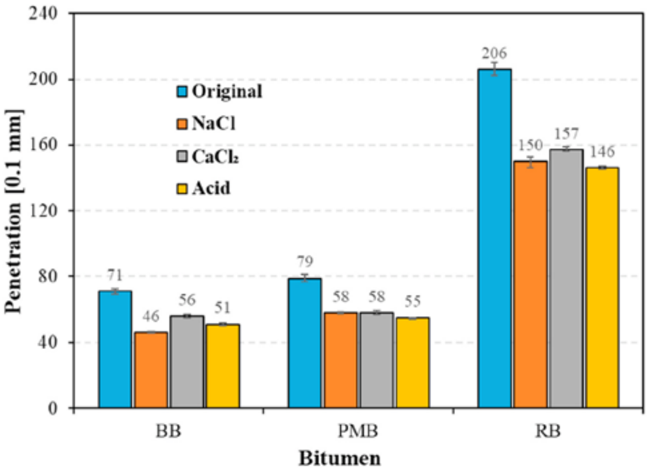


Fig. 4. The penetration of bitumen versus chemicals.

The changes in softening point of three kinds of bitumen influenced by chemicals are shown in Fig. 5. BB showed an increase in softening point after chemical treatment. And NaCl induced the highest softening point of bitumen (53.6 °C), followed by acid (52.0 °C) and $CaCl_2$ (50.8 °C). These findings indicate that the stability of BB enhanced by chemicals, and the influence of chemicals on bitumen stability: NaCl > acid > $CaCl_2$. However, PMB had the reverse response to environmental chemicals compared to BB. The decreased softening point of PMB was obtained after chemical conditioning, which indicates that chemicals induce deteriorated stability of bitumen. Meanwhile, each chemical lowered the softening point of PMB by about 4 °C, which indicates similar impacts of three chemicals on PMB stability. A slight increment in softening point of RB was observed after chemical conditioning, and acid-conditioned bitumen showed the highest softening point among all RB bitumen. These results indicate that three chemicals make RB more stable, and acid had the most significant impact on the high-temperature stability of RB among three environmental chemicals.

The dynamic viscosity of bitumen influenced by chemicals is shown in Fig. 6. For BB, three chemicals increased the dynamic viscosity of bitumen over temperature, and NaCl induced the highest dynamic

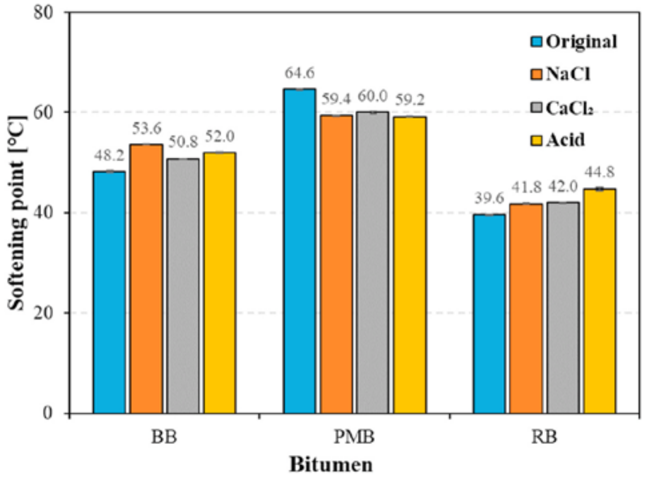


Fig. 5. The softening point of bitumen versus chemicals.

viscosity value of BB among the three chemicals. The chemicals' effect on BB is the improvement on the flow resistance of bitumen, and the improvement of NaCl is the most apparent among the three chemicals. Regarding PMB, the changing trend of dynamic viscosity over temperature was changed by environmental chemicals, i.e., the temperature sensitivity of PMB was influenced by chemicals in terms of dynamic viscosity. Specifically, chemicals increased the dynamic viscosity of bitumen in the range of 60–85 °C and decreased the dynamic viscosity of bitumen in the range of 85–100 °C, which indicates that chemicals make the dynamic viscosity of PMB susceptible to temperature. Besides, three chemicals had similar impacts on the viscosity (flow resistance) of PMB. The dynamic viscosity value of the chemical treated RB was twice that of original bitumen, which indicates that the chemical increased the resistance to flow of RB irrespective of chemical type. Three chemicals had similar impacts on RB viscosity.

3.3. *The low-temperature rheological property of bitumen influenced by chemicals*

The low-temperature rheological performance of bitumen influenced by chemicals was evaluated by the bending beam rheometer test. Table 2 summarizes the creep flexural stiffness (S(t)) and relaxation rate (m-value) at −12 °C and −18 °C. The higher S(t) value indicates the higher rigidity of bitumen, and the bigger m-value represents the better flexibility of bitumen (Liu et al., 2019). As demonstrated from Table 2, it can be noticed that the chemicals induced the increment of S(t) and decrement of m-value of BB, PMB, and RB at two temperatures regardless of chemical type. This result implies that a stiffer bitumen with worse flexibility is acquired after chemical soaking. In terms of BB, NaCl conditioned bitumen showed the highest S(t) and lowest m-value among three chemical conditioned bitumen at both −12 °C and −18 °C, indicating the highest stiffness and worst flexibility at low temperature. At both −12 °C and −18 °C, $CaCl_2$ led to the most considerable increase on S(t) and decrease on m-value of PMB compared to NaCl and acid. In contrast, acid resulted in the bitumen with the highest S(t) value and smallest m-value among the three chemicals. It can be concluded that NaCl, $CaCl_2$, and acid have the most impact on the low-temperature

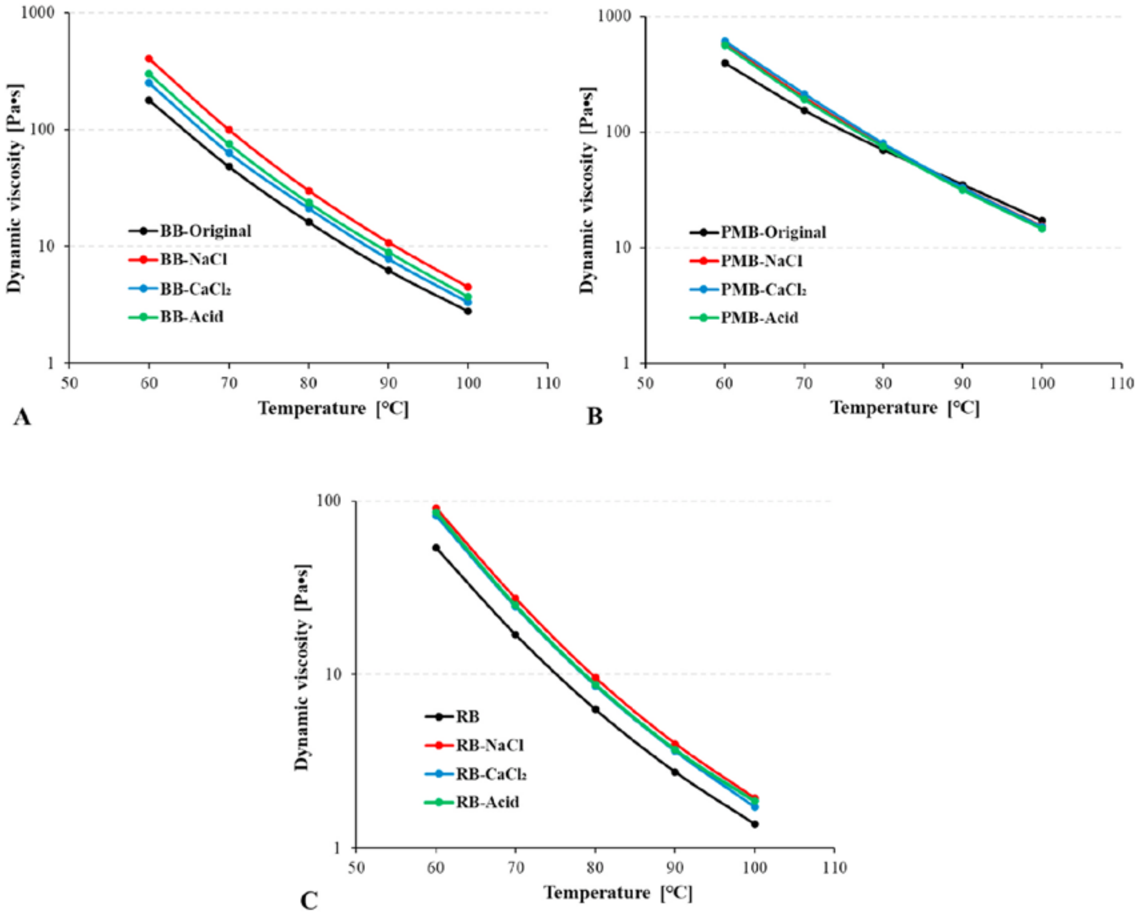


Fig. 6. The dynamic viscosity of bitumen after chemical conditioning (A: BB; B: PMB, C: RB).

Table 2
The low-temperature rheological parameters of bitumen influenced by chemicals.

Bitumen	−12 °C		−18 °C	
	S(t) [MPa]	m-value	S(t) [MPa]	m-value
BB	39.2	0.410	228.0	0.320
BB-NaCl	64.7	0.351	271.0	0.298
BB-$CaCl_2$	51.3	0.399	264.0	0.301
BB-Acid	49.2	0.401	243.0	0.312
PMB	45.2	0.450	133.0	0.333
PMB-NaCl	70.0	0.388	195.0	0.309
PMB-$CaCl_2$	72.4	0.384	208.0	0.294
PMB-Acid	69.0	0.392	188.0	0.318
RB	26.8	0.461	188.0	0.364
RB-NaCl	33.8	0.416	200.0	0.334
RB-$CaCl_2$	30.1	0.444	195.0	0.356
RB-Acid	39.2	0.390	215.0	0.328

rheological properties of BB, PMB, and RB, respectively.

3.4. *The moderate-temperature rheological property of bitumen influenced by chemicals*

All bitumen specimens under different chemical conditions were tested to evaluate their rheological properties at moderate temperature shown in Fig. 7. Complex modulus (G*) is defined as the gross resistance to deformation under load, and bigger G* indicates better deformation resistance (Jiang et al., 2021). δ is defined as the ratio of the loss to the storage components of the complex modulus, and smaller δ means worse viscous and better elastic behaviour of bitumen (Duan et al., 2021).

The complex modulus and phase angle of three bitumen conditioned by different chemicals are shown in Fig. 7. It is obvious that chemicals changed both complex modulus and phase angle of three kinds of bitumen to different degrees, resulting in increased complex modulus and decreased phase angle. The increases in complex modulus and the decreases in phase angle are related to better deformation resistance and elastic behaviour of chemical conditioned bitumen irrespective of bitumen and chemical type. For BB, NaCl and $CaCl_2$ induced the significant increase in deformation resistance (about 3000 kPa increment in complex modulus at 5 °C), and acid resulted in worse viscous behaviour (3° reduction in phase angle at 5 °C). Regarding PMB, $CaCl_2$ led to the biggest changes in complex modulus (1618 kPa) and phase angle (1.2°) at 5 °C, which results in the best deformation resistance and worst viscous behaviour simultaneously. Regarding RB, apparent differences between chemical-conditioned bitumen and original bitumen were found, and acid has a more significant impact on both deformation resistance (1235 kPa increment at 5 °C) and viscoelasticity (2.3° reduction at 5 °C) of RB compared to the other two chemicals.

3.5. *The permanent deformation and elastic recovery behaviour of bitumen influenced by chemicals*

Non-recoverable creep compliance (J_{nr}) is employed to characterize the permanent deformation resistance of bitumen. A higher J_{nr} indicates the bigger permanent deformation caused by the repeated load. Recovery percent (%R) is an index used for characterizing the elastic properties of bitumen. A higher %R means better elastic behaviour. The non-recoverable creep compliance and recovery percent influenced by

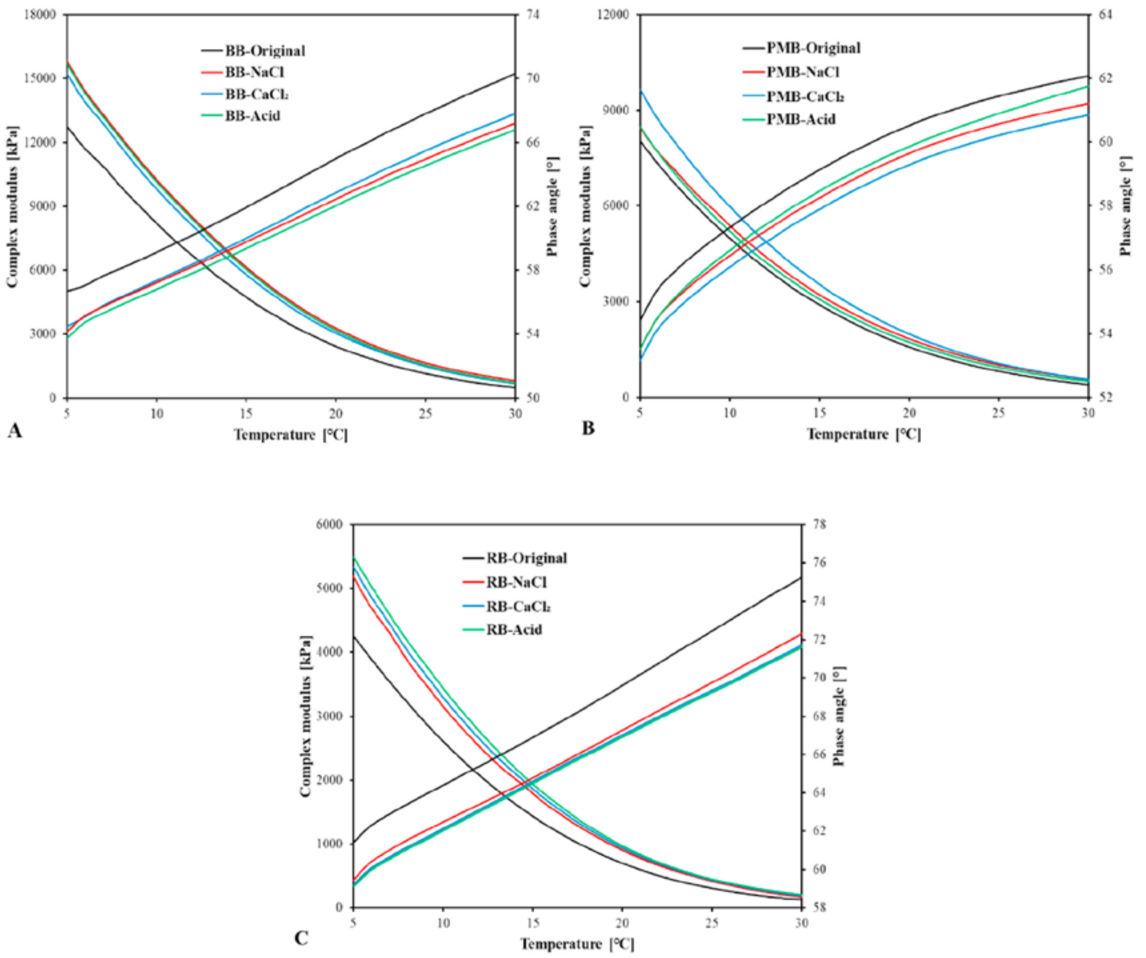


Fig. 7. The complex modulus and phase angle of three kinds of bitumen under chemical condition (A: BB; B: PMB; C: RB).

chemicals are shown in Fig. 8. It is observed that three chemicals decreased the J_{nr} of BB and RB irrespective of stress level. However, there is a tiny change in J_{nr} of PMB at two stress levels after chemical conditioning. The above findings reveal that the permanent deformation resistance of BB and RB was improved after chemical soaking under both slight and heavy loading, whereas the permanent deformation resistance of PMB was hardly influenced by the chemicals. The effect of chemicals on the permanent deformation resistance of PMB is different from that of oxidative ageing on bitumen (Zhang et al., 2018). This behaviour can be interpreted as the combination of the stable structure of PMB and the complex reaction between bitumen and chemicals. Regarding the recovery percent shown in Fig. 8, the %R of BB and RB after chemical soaking is much higher than that of bitumen before conditioning at different stress levels, which indicates that chemicals promote the recovery potential and elasticity of BB and RB. This result is in line with the results of section 3.4. However, PMB differed from BB and RB in terms of %R: %R of PMB decreased by 20–40% under chemical conditions at both 0.1 and 3.2 kPa of stress. This phenomenon is caused by the demolishment of the internal structure of PMB and the degradation of the polymer within PMB (Wang et al., 2021).

NaCl induces the smallest non-recoverable creep compliance value and the biggest recovery percent value of BB among three chemicals; PMB-$CaCl_2$ results in the highest J_{nr} (at 0.1 kPa), the lowest J_{nr} (at 3.2 kPa) and %R among three PMB specimens; BB-Acid has smaller J_{nr} value and the bigger %R value compared to BB-NaCl and BB-$CaCl_2$. These results indicate that BB, PMB, and RB are particularly susceptible to NaCl, $CaCl_2$, and acid, respectively.

3.6. *The fatigue resistance of bitumen influenced by chemicals*

The fatigue life (N_f) is used to evaluate the ability of bitumen to resist fatigue damage (Elkashef and Williams, 2017). Typically, a higher N_f value represents the better resistance to fatigue cracking of bitumen. Fig. 9 shows the fatigue life (N_f) of bitumen under various chemical conditions over the applied strain (1%–10%). It was observed that three environmental chemicals resulted in shorter fatigue life of bitumen irrespective of bitumen type. The impact of environmental chemicals on fatigue life of BB was the most pronounced, followed by RB, the impact of chemicals on PMB is the weakest. Besides, NaCl induced the shortest fatigue life of BB compared to the other two chemicals; $CaCl_2$ led to the smallest N_f value of PMB among three chemicals; acid decreased the fatigue life of RB by 63.7%, which is significantly higher than the reduced value caused by NaCl and $CaCl_2$. These results demonstrate that NaCl, $CaCl_2$, and acid have the most significant impact on the fatigue life of BB, PMB, and RB among three chemicals, respectively.

3.7. *Changing degree of properties of three kinds of bitumen under chemical condition*

Apart from the bitumen surface, it can be found that different environmental chemicals had different influencing levels on different kinds of bitumen. To rank the influencing degree on three kinds of bitumen, the changing degree of physical, rheological, and mechanical parameters are calculated according to Eq. (2). The higher the changing degree (CD), the more severe the change of bitumen properties.

$$\textit{Changing degree (CD)} = \frac{Parameter_{after\ chemical} - Parameter_{original}}{Parameter_{original}} \times 100\% \qquad \text{Eq. 2}$$

Where $Parameter_{original}$ indicates the physical or rheological parameter without chemical condition, $Parameter_{after\ chemical}$ indicates the parameter value after chemical conditioning.

Fig. 10 shows the summed changing degree of physical, rheological, and mechanical parameters of three kinds of bitumen after three chemicals conditioning. The gross CD indicated in Fig. 10 is the summation of CD of penetration, softening point, dynamic viscosity at 60 °C, complex modulus at 5 °C, phase angle at 5 °C, creep flexural stiffness at −12 °C and −18 °C, m-value at −12 °C and −18 °C, non-recoverable creep compliance at stress of 0.1 kPa and 3.2 kPa, recovery percent at stress of 0.1 kPa and 3.2 kPa, and fatigue life (at strain of 1%). In comparison, NaCl induced the biggest summed difference of all parameters of BB; $CaCl_2$ changed the physical, rheological, and mechanical parameters of PMB significantly; Acid influenced the ten parameters of RB mostly. Thus, NaCl, $CaCl_2$, and acid had the most severe impact on BB, PMB, and RB in terms of physical, rheological, and mechanical properties, respectively. Three chemicals had the most significant impact on BB, followed by RB, the most negligible impact on PMB as a whole. The above information provides guidelines on the selection of bitumen type when facing different environmental chemicals. For example, PMB might be a better choice in acid rain and snowy region requirement of spreading sodium chloride or calcium chloride on the road.

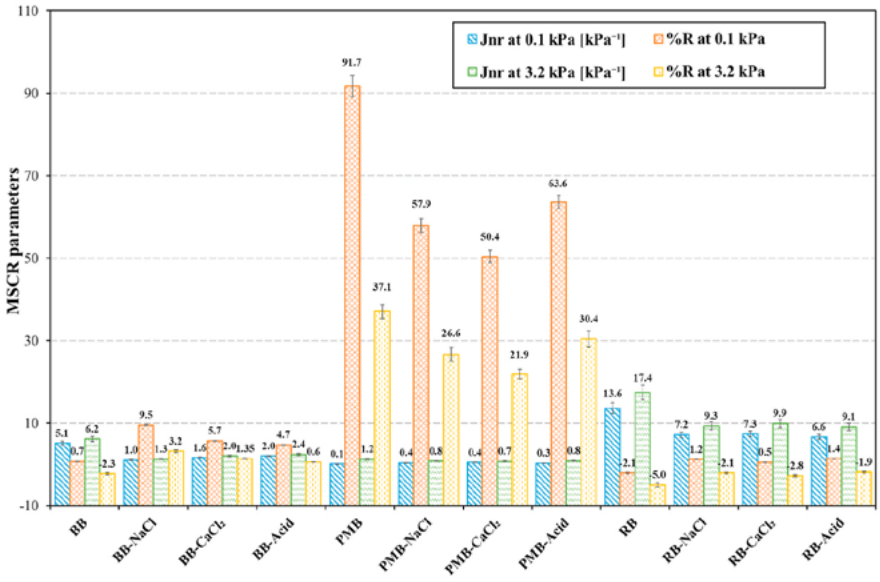


Fig. 8. J_{nr} and %R of bitumen under chemical conditioning.

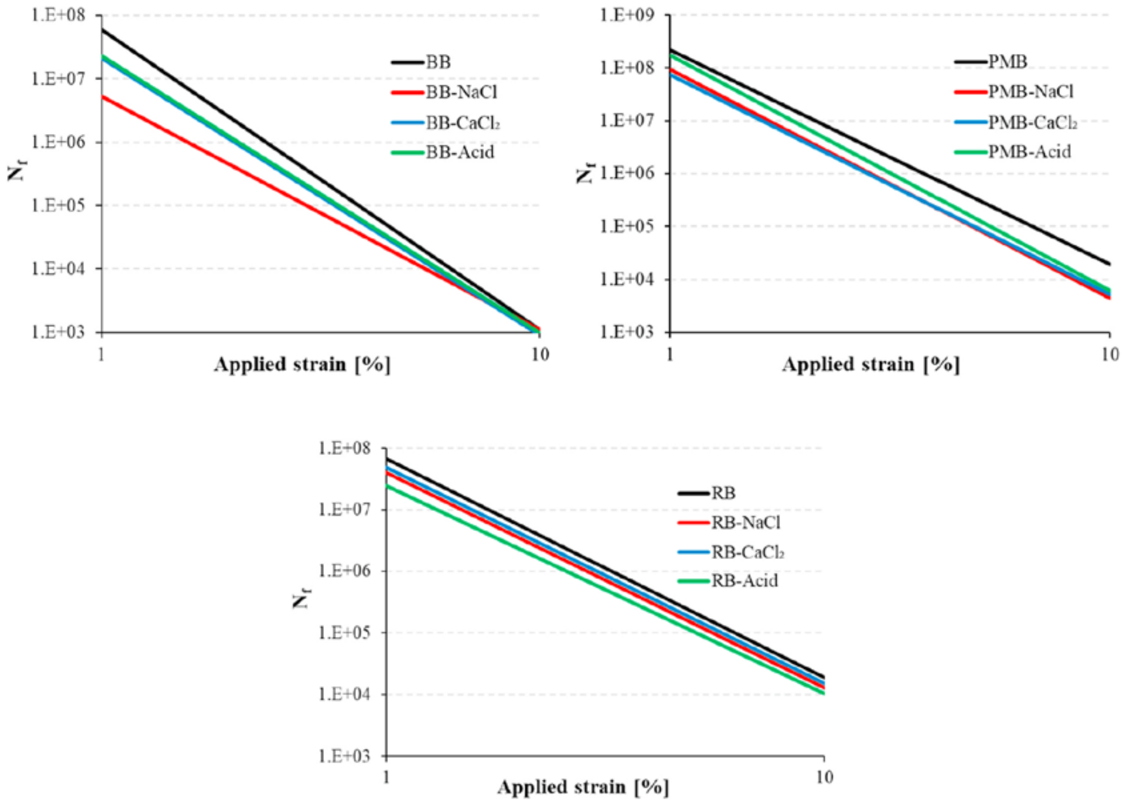


Fig. 9. Fatigue life of bitumen after chemical condition.

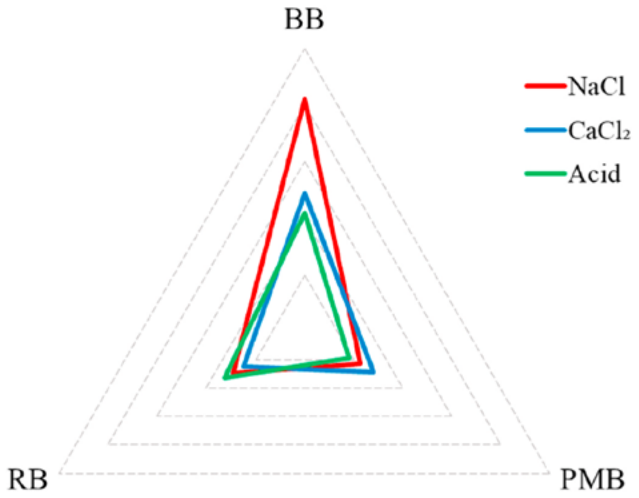


Fig. 10. The summed difference in bitumen performance caused by chemicals.

3.8. Reaction between three kinds of bitumen and chemicals

To clarify the reaction between bitumen and environmental chemicals, the chemical bonds of three kinds of bitumen were studied. Fig. 11 shows the chemical bonds of three types of bitumen influenced by chemicals. By inspecting Fig. 11A, four functional groups (S═O, C–OH, C═C, and N–H) of BB changed apparently as a function of chemicals. It is observed that the S═O group indicating the oxidative degree of bitumen was growing up at a wavenumber around 1030 cm^{-1} after chemical conditioning. C–OH group indicating the stability of bitumen increased at wavenumber around 1133 cm^{-1} after NaCl and $CaCl_2$ conditioning and migrated to 1157 cm^{-1} after acid conditioning. The peaks of C═C and N–H groups located around 1579 cm^{-1} and 1540 cm^{-1}, corresponding to asphaltenes of bitumen (Bukka et al., 1991), increased after NaCl and $CaCl_2$ process and combined to one more prominent peak after acid conditioning. The above phenomena show that oxidation, stabilization, and polymerization of bitumen simultaneously occur during the environmental chemical process, which results in the most susceptible bitumen type to environmental chemicals and the changes in surface, physical, rheological and mechanical properties. Different chemicals also have other interactions with BB, which can explain the various changing degrees of different chemicals on bitumen performance.

As observed in Fig. 11B, the number and position of the spectral bands remained unchanged for PMB. However, the peak of S═O group around 1030 cm^{-1} became sharper, two distinct groups of PMB (butadiene double bond (C═C) at 964 cm^{-1} and C–H bond at 698 cm^{-1} of polystyrene) became weaker (Nian et al., 2018). These results indicate that chemicals induced an increased ageing degree of PMB and less polybutadiene and polystyrene blocks within PMB, that is oxidation and decomposition simultaneously happened in PMB during chemical conditioning. However, the decomposition has a reverse effect on bitumen compared to oxidation (Xu et al., 2020), which might be the reason of decreased softening point, the changed trend of dynamic viscosity, non-recoverable creep compliance, and recovery percent of PMB after chemical conditioning. With the combination of oxidation and decomposition, PMB showed the best chemical resistance among three chemicals concluded from chapter 3.7. There were no obvious variations in S═O and C–H groups between three chemicals conditioned PMB, which is in line with the similar changes in micro-surface, softening point, dynamic viscosity, of PMB caused by three chemicals. However, the changes in C═C group caused by acid were the smallest, which means the PMB is less affected by acid. This result is consistent with the least impact of acid on rheological and mechanical properties of PMB.

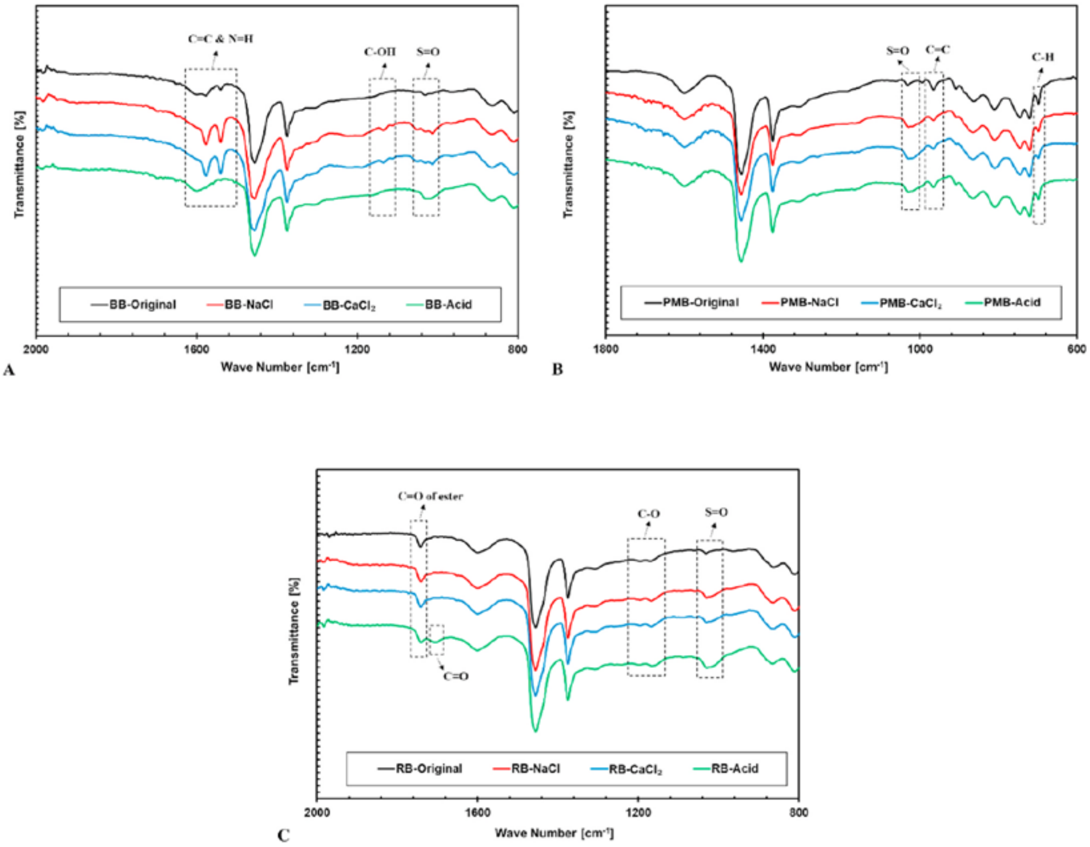


Fig. 11. FTIR spectrum of three kinds of bitumen. (A) BB; (B) PMB; (C) RB.

As indicated in Fig. 11C, two typical functional groups of RB indicating its ageing degree, S=O (1030 cm^{-1}) and C=O of carbonyl acid (1704 cm^{-1}) changed apparently. The peaks of S=O increased obviously after chemical conditioning, which strongly indicates that environmental chemicals lead to severe ageing of bitumen. In the comparison of the three chemicals' effect, acid induced the biggest ageing group peak. The occurrence of C=O of carbonyl acid at 1704 cm^{-1} after acid conditioning indicates that acid promotes the ageing of RB (Hou et al., 2018). The above reactions of RB with acid induce the most significant impact of acid on the physical, rheological, and mechanical properties of RB. Furthermore, C=O of ester (1745 cm^{-1}) group and C–O (1174 and 1195 cm^{-1}) group of esters, the typical functional groups of rejuvenators, remained unchanged. This result indicates that the rejuvenator within bitumen is hardly affected by environmental chemicals, which could explain the less impact of chemicals on RB than that on BB.

Different changes in the chemical bond of three kinds of bitumen are due to various reactions between chemicals and different types of bitumen. The alterations in chemical bonds of three kinds of bitumen help to understand the different responses of bitumen performance to environmental chemicals.

4. Conclusions

Environmental chemicals have pronounced impacts to bitumen performance. However, three kinds of bitumen performed differently to chemicals in terms of micro-surface, physical, rheological, mechanical, and chemical properties. The principal conclusions are summarized as follows.

Under environmental chemical conditions, the penetration, low-temperature rheological properties, moderate-temperature rheological properties, and fatigue resistance of three bitumen showed similar changing trends but different degrees. The completely different changing trends in bitumen surface, softening point, dynamic viscosity, permanent deformation resistance, and elastic recovery behaviour were found in three kinds of bitumen. These various changes in bitumen performance were caused by different reactions between three kinds of bitumen and environmental chemicals. The oxidation, stabilization, and polymerization of base bitumen during chemical conditioning make it the most susceptible type to environmental chemicals. The decomposition and oxidation of polymer modified bitumen can resist the ageing caused by chemicals and lead to different phenomena compared to base bitumen and rejuvenated bitumen. Oxidation is the major reaction of rejuvenated bitumen with chemicals, and the rejuvenator within rejuvenated bitumen helped to mitigate bitumen ageing.

Sodium chloride, calcium chloride, and acid had the most severe impact on base bitumen, polymer modified bitumen, and rejuvenated bitumen in terms of physical, rheological, and mechanical properties, respectively. Besides, polymer modified bitumen presented the greatest chemical resistance based on the summed difference of physical, rheological, and mechanical parameters, followed by rejuvenated bitumen, base bitumen had the worst ability to resist environmental chemicals.

This work principally studied the characterization of three types of bitumen to environmental chemicals and their resultant reaction mechanisms. For further studies, more types of bitumen such as rubber-modified bitumen and short-term aged bitumen are recommended to be included. According to the results in this study, proposals for selecting bitumen type under different environmental chemicals and de-icing salt during winter maintenance are provided from the perspective of minimizing pavement damage. For instance, polymer modified bitumen might be a best choice for pavement design in acid rain and snowy regions; calcium chloride instead of sodium chloride can reduce the negative effect on base bitumen and rejuvenated bitumen during winter maintenance.

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Xuemei Zhang: Conceptualization, Methodology, Software, Writing – original draft. **Inge Hoff:** Conceptualization, Resources, Writing – review & editing. **Hao Chen:** Methodology, Writing – review & editing.

Declaration of competing interest

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

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