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LABORATORY INVESTIGATION ON DEVELOPMENT OF BITUMEN EXPOSED TO CHEMICALS

Doctoral thesis

NTNU
Norwegian University of Science and Technology
Thesis for the Degree of
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PREFACE

This PhD thesis is submitted to the Norwegian University of Science and Technology (NTNU) for the fulfilment of the requirements for the degree of Philosophiae Doctor (PhD).

The work was carried out between April 2019 and March 2022 at the Department of Civil and Environmental Engineering at NTNU, Trondheim.

Professor Inge Hoff, NTNU, has been the main supervisor. Chief engineer, PhD Rabbira Garba Saba has been the co-supervisor.

Xuemei Zhang

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Special thanks to my husband Hao Chen, your encouragements and jokes supported me at difficult moments. Last but not least, my deepest gratitude to my dear parents and brother for your endless love and support during these years.

ABSTRACT

As one of the most significant components of asphalt concrete, bitumen is crucial to the durability and lifespan of asphalt pavement. The asphalt pavement is exposed to different external conditions, such as traffic loading, temperature, ultraviolet radiation and chemicals. These external factors can significantly reduce the durability and longevity of asphalt pavement and are accompanied by high maintenance and reparation cost. Therefore, knowledge about how these factors affect bitumen performance is of significance for pavement design and precaution measures. Many of these external factors have been investigated in several research projects in the past. However, researchers have paid less attention to the influence of external chemicals on bitumen.

This research simulates the practical situation of asphalt pavement under chemical conditions in the laboratory to study the chemical effect on bitumen performance and the resultant mechanisms. To do this, three common chemical solutions were prepared in the laboratory based on Norwegian or European situations: Sodium chloride (10 wt%), calcium chloride (10 wt%) and acid rain (pH 4); Five variations of bitumen were selected: neat bitumen, short-term aged bitumen, long-term aged bitumen, polymer modified bitumen and rejuvenated bitumen; Three immersion time were applied: seven, twenty-eight and ninety days. After the immersion process, the pH value test was conducted to investigate the hydrogen ion concentration in the residual solution. Scanning electron microscopy with energy dispersive spectrometer test was applied to analyse the morphology and element content of the bitumen. Penetration, softening point and viscosity tests were carried out to characterise the physical properties of the bitumen. Attenuated total reflectance Fourier transform infrared radiation spectroscopy was used to analyse the chemical structure of the bitumen and the reaction between the bitumen and the chemicals. Besides, the rheological properties of the bitumen were evaluated by temperature and frequency sweep modes of dynamic shear rheometer test and bending beam rheometer test. The mechanical properties of the bitumen were characterised by multiple stress creep recovery test and linear amplitude sweep test.

The experimental results show that the three chemicals have similar effects on the physical, rheological and mechanical properties of neat and short-term aged bitumen as conventional thermal-oxidative ageing, resulting in a stiffer and aged bitumen. The hardening and oxidative degrees were accentuated over immersion time. However, different observations on the morphology, element content and chemical structure of the bitumen were found because of the

distinct deterioration mechanisms caused by various chemicals. Furthermore, the various bitumen responded differently to the chemicals due to various reaction mechanisms, especially in the surface characterisation, softening point, dynamic viscosity, non-recoverable creep compliance and recovery percent. It is concluded that polymer modified bitumen has the best resistance to the chemicals; Neat bitumen has the worst resistance to the chemicals; Rejuvenated bitumen and short-term aged bitumen have the moderate ability to resist the chemicals. Besides, NaCl, $CaCl_2$ and acid rain exert the most significant impacts on neat bitumen and aged bitumen, polymer modified bitumen and rejuvenated bitumen, respectively.

The experimental results suggest that chemical immersion should be paid the same attention to thermal-oxidative ageing. Calcium chloride is a better option for de-icing strategy compared to sodium chloride during winter maintenance from the perspective of damage (but much more expensive). Moreover, polymer modified bitumen could be the best choice for pavement design in acid rain and snowy regions where a “bare road strategy” is applied for winter maintenance. It is hoped that this study can contribute to understanding the effect of environmental chemicals on asphalt pavement and establish a standard for the solution ageing of bitumen.

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LIST OF ABBREVIATIONS

TFOT	Thin film oven test
PAV	Pressure ageing vessel
SEM-EDS	Scanning electron microscopy with energy dispersive spectrometer
ATR-FTIR	Attenuated total reflectance Fourier transform infrared radiation spectroscopy
DSR	Dynamic shear rheometer
BBR	Bending beam rheometer
LAS	Linear amplitude sweep
MSCR	Multiple stress creep recovery
N/ NB/UT	Neat bitumen
T/TB/AT	TFOT aged bitumen
PMB	Polymer modified bitumen
RB	Rejuvenated bitumen
Δ_A	Difference in absorbance [%]
$A_{N/T}$	The absorbance of neat/aged bitumen
$A_{N/A,D}$	The absorbance of neat/aged bitumen after D days immersion
S	Flexural creep stiffness
m-value	Stress relaxation ability
N_f	Fatigue life
J_{nr}	Non-recoverable creep compliance
%R	Recovery percent
G^*	Complex modulus
δ	Phase angle
G^*/δ	Rutting factor
$G^* \cdot \delta$	Fatigue factor
AF	Ageing factor

1. INTRODUCTION

The introduction includes the research background (1.1), research objective (1.2), thesis structure (1.3) and publications and contributions (1.4). This chapter emphasises the significance of the study, the main purposes and related variables and publications of this research work, the brief contents and structure of the thesis, and the contributions of this research to road administration and engineers.

1.1 Background

Asphalt pavement, for its excellent driving performance and low noise advantages, is widely applied in the world. Therefore, the long-life asphalt pavement with outstanding performance is desired from environmental, sustainable and economical aspects. However, external circumstances would influence the performance of bitumen, such as temperature, oxygen, ultraviolet radiation, moisture, chemicals and traffic loading (Chatti et al., 2004; Micaelo et al., 2020; Miller and Bellinger, 2003; Wu et al., 2008; Zou et al., 2021). The effects of temperature, oxygen, traffic loading, moisture and ultraviolet radiation on asphalt pavement and their resultant deterioration mechanisms have been investigated by a large number of researchers (Ameri et al., 2011; Bell, 1989; Bell et al., 1994; Caro et al., 2008; Hicks, 1991; McLean and Monismith, 1974; NEW, 2004; Wang, D.W. et al., 2021). In brief, repeated traffic loadings at a moderate temperature typically lead to fatigue cracking due to insufficient tensile strength, resulting in bottom-up (thin asphalt layer) and top-down fatigue cracking (thick asphalt layer) (Huang, 1993; Islam, 2015). Repeated traffic with heavy loading at high temperatures causes permanent deformation of the asphalt pavement due to its weak stiffness (Colombier, 2004; Zhang et al., 2009). High temperature accoupling with oxygen named thermal-oxidative ageing results typically in a stiffer and fragile asphalt pavement (Dehouche et al., 2012). Thermal-oxidative ageing is a physicochemical reaction comprising the evaporation of light components and the oxidation of bitumen (Pipintakos et al., 2021; Tauste et al., 2018). Ultraviolet radiation can also make bitumen harder and more brittle with different mechanisms compared to thermal-oxidative ageing (Wu et al., 2010). The deterioration mechanism of ultraviolet on bitumen can be briefly stated as bitumen absorbs the energy of ultraviolet radiation, leading to the chemical bond break of various chromophores contained in the molecule and the formation of oxygen-contained groups (Zeng et al., 2018). Chemicals or moisture can shorten the service life of the asphalt pavement by degrading the performance of asphalt mixtures, the interface of bitumen and aggregates and bitumen properties (Aigner et al., 2009; Cong et al., 2021). However, the mechanism and characterisation of bitumen under chemical conditions are still unclear.

The most common chemicals of asphalt pavement are de-icing salts and acid rain. To ensure a safe driving condition during cold seasons especially in Nordic countries, de-icing salts are spread on asphalt pavement to prevent the accumulation of snow and the formation of ice, which is one of the most effective measures for winter maintenance (Charola et al., 2017). Even if de-icing salt has a lot of negative environmental and economic consequences and is unpopular among parts of the population, it is very challenging to imagine winter maintenance in Norway to provide safe and efficient roads for traffic users without using salt. Calcium chloride is one of the commonly used de-icing salts due to its remarkable effectiveness, and sodium chloride is the most popular de-icing salt due to its reasonable effectiveness and low cost (Autelitano et al., 2019; Klein-Paste and Dalen, 2018). While the salt application is limited to the weather situation, Norem gave the proposals on salt application under different weather situations as shown in Figure 1 (Norem, 2009). It suggested that de-icing salt could be a reasonable choice when the road surface temperature is over -8 ℃. The average temperature of Norway in winter is around -6 ℃, but with large local variations, which basically fulfils the requirement for de-icing salt applications. Figure 2 illustrates the phase diagram for sodium chloride and calcium chloride in water, which describes the relationship between the freezing point and salt concentration. Combining the former proposals with the phase diagram of NaCl, 10% NaCl is sufficient to decrease the freezing point to -8 ℃ for keeping asphalt pavement free from snow and ice. In order to compare the effect of different salts on the bitumen, the same concentration of salts should be selected. In this research, 10% NaCl and 10% $CaCl_2$ were selected to simulate the influence of the de-icing salt on bitumen performance.

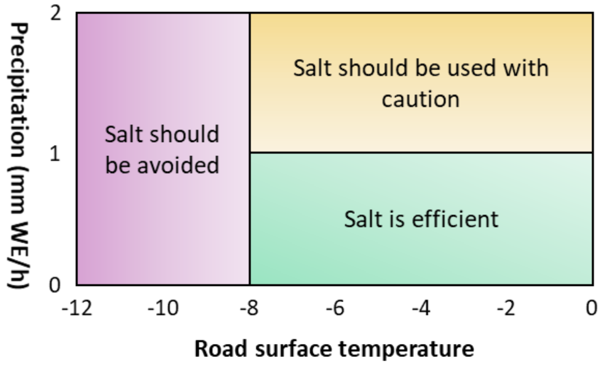

Figure 1. Suggestions on application of salt under different weather condition (Norem, 2009)

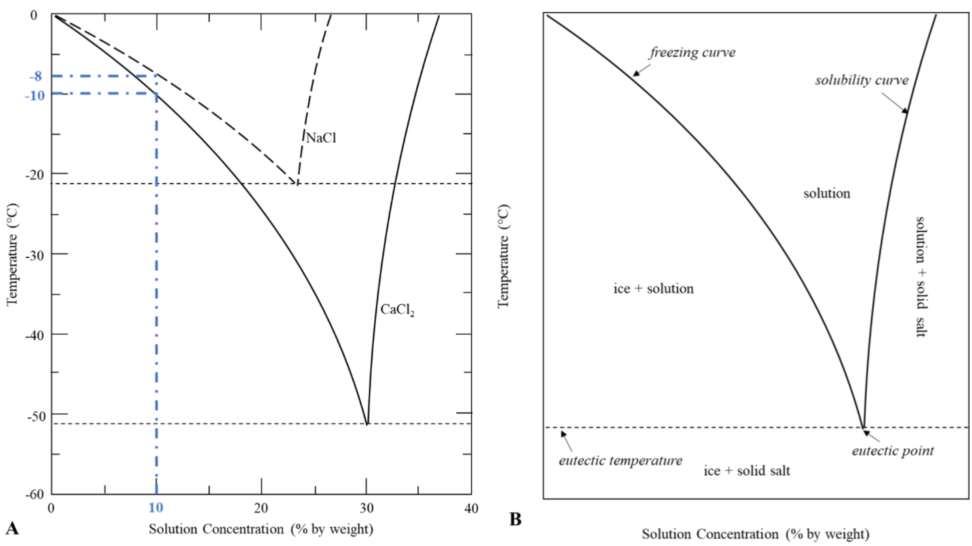

Figure 2. Phase diagram of NaCl and $CaCl_2$ in water (A) and component of salt solution under different conditions (B) (Ketcham et al., 1996; Klein-Paste and Wahlin, 2013)

Industrial and production cause negative impacts to the environment. In many years, there has been a problem related to acid rainfall. Acid rain composed of sulfuric acid and nitric acid is defined as precipitation with a pH value lower than 5.6 (Li et al., 2021). The content of sulfuric acid and nitric acid in acid rain is determined by the emission of SO_2 and NOx into the atmosphere. In Europe, the NOx emission is almost twice the SO_2 emission in 2017 according to the emissions of air pollutants shown in Figure 3 (De Marco et al., 2019), even though the level of emissions of the five pollutants has been apparently decreased since 2010. Moreover, the pH value of the precipitation is generally between 4 and 6 (Keresztesi et al., 2019). Therefore, the acid rain in this study was simulated by diluting the blend of sulfuric acid and nitric acid with a proportion of 1:2 to pH 4.

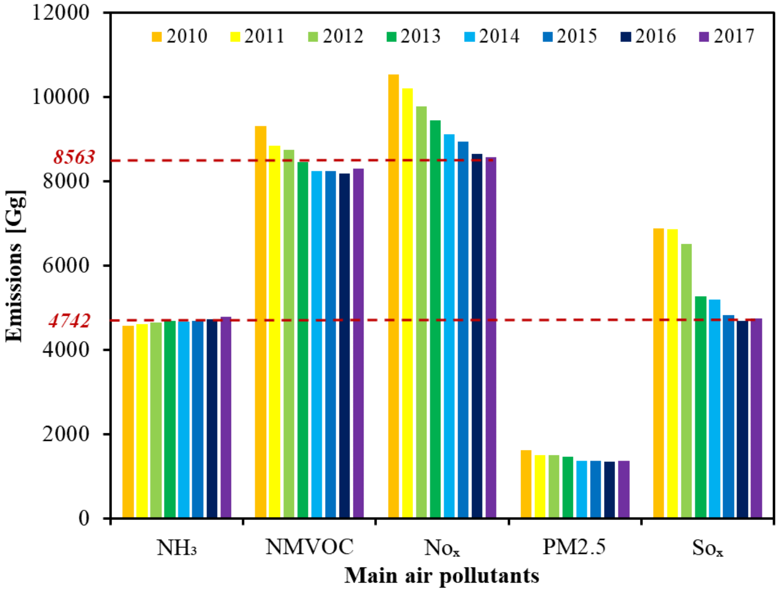

Figure 3. Pollutant emissions (EEA, 2018)

In addition to adverse environmental and corrosion problems, the three environmental chemicals (sodium chloride, calcium chloride and acid rain) seem to deteriorate the performance of bitumen and asphalt concrete to various extents (Wang et al., 2017). Aside from the chemicals, water can reduce the performance of asphalt mixtures, namely moisture damage (Hicks, 1991; Omar et al., 2020). With the addition of chemical components, the damage degree on asphalt mixtures was intensified, which has been proven to be a typical issue (Santagata et al., 2013; Yang et al., 2020). Moreover, the water has been approved to influence the bitumen performance with a slighter degree compared to chemical solutions, resulting in a light-yellow oil patch on the residual solution, stiff and aged bitumen (Pang et al., 2018; Yang et al., 2020; Zou et al., 2021). These outcomes on bitumen are the result of oxidation and dissolution. Due to the complexity and more elements of chemicals, the deterioration of chemicals on bitumen and the resultant mechanism are more complicated.

Regarding sodium chloride, it is a neutral solution or slightly alkaline solution (with a higher concentration) (Shu et al., 2016). Bitumen presenting weakly acidic is prone to react with sodium chloride solution, resulting in a chemical neutralization reaction. Emulsification, defined as the process of dispersing two or more insoluble liquids to a semi-stable compound also happens on asphalt mixtures under sodium chloride exposure. In this case, the oil generated from the bitumen is mixed with sodium chloride solution (Pang et al., 2018). Thus, the asphalt mixture properties are deteriorated by the sodium chloride solution based on the above two mechanisms. Studies also showed that sodium chloride could shorten the durability of the asphalt mixture by degrading its mechanical properties, such as adhesion failure, decreased tensile strength, resilient modulus and rutting resistance, and shortened fatigue life (Anastasio et al., 2015; Guo et al., 2019; Zhang et al., 2019). Juli-Gándara et. (Juli-Gandara et al., 2019) compared the effect of sodium chloride on two different mixtures, it was found that the porous asphalt mixture is more prone to sodium chloride than the hot mix asphalt mixtures. This conclusion is attributed to the loose structure of the porous asphalt mixture, which allows sodium chloride to react with mixtures in a larger contact area.

Distinct from sodium chloride, calcium chloride solution is weakly acidic, which might affect the chemical structure of alkaline aggregates (Shu et al., 2016). Emulsification also exists during the process between the asphalt mixture and calcium chloride. Calcium chloride has a similar influencing trend on asphalt mixtures as sodium chloride: decreased tensile strength, resilient modulus, rutting resistance, increased air voids, more cracks, shortened fatigue life and adhesive failure (Gilani et al., 2021; Guo et al., 2019; Ozgan et al., 2013). However, calcium chloride was found to cause less impact on asphalt mixtures compared to sodium chloride (Fakhri et al., 2019; Ozgan et al., 2013). This conclusion provides a suggestion for road administration and civil engineers to choose calcium chloride from the review of road sustainability when winter operations entailing de-icing salts.

In addition, salt immersion is usually accompanied by freeze-thaw cycles as the road surface temperature varies at different periods (Feng et al., 2010). With the addition of the freeze-thaw process, the mechanical properties of asphalt mixtures, including high-temperature stability, tensile strength, crack resistance and water stability, are severely weakened, and the adhesion between bitumen and aggregates is significantly reduced (Goh et al., 2011; Wang et al., 2021). The deterioration mechanism can be concluded that de-icing salts penetrate the inner structure of asphalt concrete and crystalize in the interface of bitumen and aggregates, resulting in bad adhesion and moisture damage of asphalt concrete (Xiong et al., 2019b; Yang et al., 2020). Above all, the reaction between sodium chloride/calcium chloride and asphalt mixtures under freeze-thaw conditions is a combination of chemical reactions, emulsifications and the generation of stress in the asphalt mixture (Shi et al., 2009).

Different from the de-icing salts, acid rain has adverse effects on aquatic organisms, plants, soils and constructions from a chemical review point (Singh and Agrawal, 2008; Zeng et al., 2018). The asphalt pavement is also damaged by acid rain from three aspects: asphalt concrete structure, interface between bitumen and aggregates and bitumen (Feng et al., 2020). The bitumen is eroded by acid rain resulting in degraded properties, such as mass loss, asperity surface and increased stiffness (Feng et al., 2020). The interface between bitumen and aggregates is damaged by the chemical reaction between the acid rain and the suboxides of the aggregates and the emulsification, resulting in the peeling of the bitumen film from aggregate particles (Zhang et al., 2004). These two actions accelerate the degrading process of asphalt mixtures, resulting in the damaged structure of asphalt concrete, reduced stiffness, strength, stability and self-healing capacity (Azarhoosh et al., 2017; Feng et al., 2020; Gerengi et al., 2013; Lu et al., 2020; Shu et al., 2020).

In addition, a few studies also investigated the influence of alkali on asphalt pavement and bitumen. In these studies, severe damage on bitumen and asphalt mixtures was found as the strong alkaline solution neutralizes the acidic part of bitumen and erodes aggregates surface and asphalt structure, leading to a bad adhesion and loose structure of the asphalt mixture (Shu et al., 2020; Yang et al., 2020; Zhang et al., 2018). However, alkali is not one of the common chemicals for asphalt pavement, so alkali is not considered in this thesis.

The deterioration and mechanisms of asphalt concrete under chemical conditions have been extensively studied, and comprehensive conclusions, failure mechanisms and proposals have been made. Bitumen, as a significant component, plays a significant role in resisting chemicals and is crucial to pavement durability and service life. However, the detailed introduction of chemical effects on bitumen was still unclear. Therefore, this research simulates the practical situation of asphalt pavement under chemical conditions to study the impact of chemicals on bitumen performance and the resultant mechanisms, which is of significance to prevent chemical damage on asphalt pavement and provide proper measures and suggestions to road administration and engineer.

1.2 Research objective

The objective of this research is to investigate the development of various bitumen exposed to different chemicals over immersion time, as well as the reaction mechanism between bitumen and chemicals. Besides, the bitumen type that has the best chemical resistance was provided by comparing the responses of different types of bitumen to chemicals. The chemical immersion was found to have similar effects on bitumen with thermal-oxidative ageing during the immersion process. Thus, the comparative study of the chemical effect and conventional thermal-oxidative effect on bitumen performance was investigated. Above all, this project is divided into four sub-objectives as follows:

1) Determination of chemical solutions based on practical situations (Norwegian or European environment) for asphalt pavement. Introduction of thesis and all four papers
2) Evaluation of the mutual effect of bitumen exposed to the three chemicals and the reaction mechanism over immersion time. Paper I and II
3) Characterisation of different types of bitumen under chemical conditions. Paper III
4) Comparison of bitumen performance after chemical immersion and thermal-oxidative ageing. Paper IV

The first sub-objective refers to the Introduction of the thesis and all four papers. The second, third and fourth sub-objectives corresponds to chapter 3, 4 and 5 in the thesis, respectively. The discussed experimental variables and related publications in this study are summarised in Figure 4.

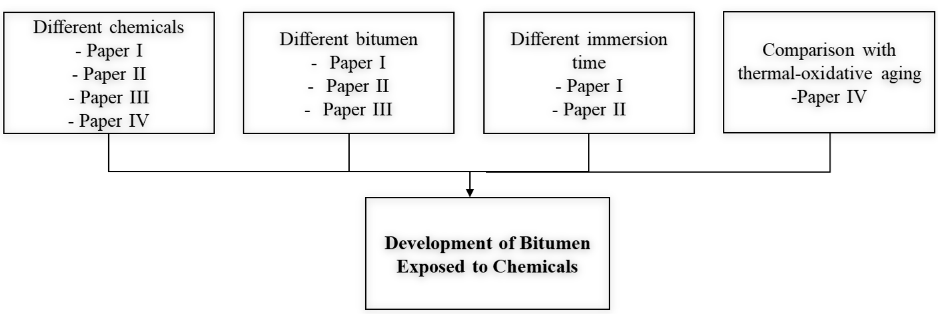

Figure 4. Related variables and related publications

1.3 Thesis structure

The thesis is divided into seven sections from project setting, experiment tests, result analyses and conclusions. Four related published papers are attached as Appendices A to D. Four additional studies were also performed and published during the PhD period. They are related to the experimental method and other aspects of bitumen and asphalt mixture, which are also introduced in the thesis. Chapter 1 introduces the background and scope of the study and determines the chemical solutions. Chapter 2 illustrates the materials, immersion process, and test methods used in this research. Chapter 3 discusses the effect of the three chemicals on bitumen performance and the resultant mechanisms, as well as the effect of bitumen on chemical solutions. Chapter 4 analyses the responses of different kinds of bitumen to chemicals. The comparison between thermal-oxidative and chemical ageing on bitumen performance is investigated in Chapter 5. The conclusions are drawn in chapter 6. Besides, recommendations for future work will be provided based on the conclusions of this study in chapter 7.

1.4 Publications and Contributions

This section provides an outline of the papers written during the PhD period. The conclusions obtained from these studies can give a systematic understanding of the chemical effects on bitumen, provide the theoretical bases for mitigating the chemical damage on asphalt pavement, establish solution immersion standards for bitumen and propose the best bitumen type for preventing chemicals damage.

The thesis related publication

Paper I

Xuemei Zhang*, Hao Chen and Inge Hoff (2021)

The mutual effect and reaction mechanism of bitumen and de-icing salt solution.

Published October 4, 2021 in Journal of Construction and Building Materials.

(https://doi.org/10.1016/j.conbuildmat.2021.124213)

This paper studies the reaction between the two typical de-icing salts (sodium chloride and calcium chloride) and the two types of bitumen (neat bitumen and short-term aged bitumen) over immersion time. The changes in the residual de-icing salt solution and bitumen performance were characterised, and their reaction mechanisms were revealed.

Contributions:

Xuemei Zhang: Conceptualization, Methodology, Investigation, Data curation, Writing - original draft. **Hao Chen**: Methodology, Writing - original draft, Writing - review & editing. **Inge Hoff**: Conceptualization, Resources, Writing - review & editing.

Paper II

Xuemei Zhang*, Inge Hoff and Rabbira Garba Sara (2021)

Response and deterioration mechanism of bitumen under acid rain erosion.

Published August 29, 2021 in Journal of Materials.

(https://doi.org/10.3390/ma14174911)

This paper investigates how the simulated acid rain affects bitumen performance, as well as the correlation between the bitumen performance, the pH value of acid rain and erosion time. Based on the experimental results, the different deterioration mechanisms were obtained for neat bitumen and short-term aged bitumen.

Contributions:

Xuemei Zhang: Conceptualization, Methodology, Investigation, Formal analysis, Data curation, Writing - original draft. **Inge Hoff**: Conceptualization, Investigation, Resources, Writing - review & editing, Supervision. **Rabbira Sara:** Investigation, Writing - review & editing.

Paper III

Xuemei Zhang*, Inge Hoff and Hao Chen (2022)

Characterization of various bitumen exposed to environmental chemicals.

Published February 20, 2022 in Journal of Cleaner Production.

(https://doi.org/10.1016/j.jclepro.2022.130610)

This paper characterises the behaviour of the three types of bitumen (neat bitumen, polymer modified bitumen and rejuvenated bitumen) exposed to the three environmental chemicals (sodium chloride, calcium chloride and acid rain). The underlying mechanisms between various bitumen and chemicals were also investigated. Consequently, the polymer modified bitumen had the best resistance to environmental chemicals, followed by the rejuvenated bitumen, and the base bitumen had the worst chemical resistance.

Contributions:

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

Paper IV

Xuemei Zhang* and Inge Hoff (2021)

Comparative Study of Thermal-Oxidative Aging and Salt Solution Aging on Bitumen Performance.

Published March 3, 2021 in Journal of Materials.

(https://doi.org/10.3390/ma14051174)

This paper compares the effect of thermal-oxidative ageing and salt solution ageing on bitumen performance. The thermal-oxidative ageing in this study comprises short-term ageing (thin film oven test) and long-term ageing (pressure ageing vessel ageing), and the salt solution ageing includes 10% NaCl ageing and 10% $CaCl_2$ ageing. The result shows that both the thermal-oxidative ageing and the salt solution ageing had similar influencing trends in the oxygen content, physical, low-temperature and high-temperature properties of bitumen but had different changes in the morphology.

Contributions:

Xuemei Zhang: Conceptualization, Methodology, Investigation, Formal analysis, Data curation, Writing - original draft. **Inge Hoff**: Conceptualization, Resources, Writing - review & editing, Supervision.

Other significant publication

Paper V: Optimization of experimental method

Xuemei Zhang* and Inge Hoff (2021)

Experimental investigation on rheological property of bitumen with different preparation times.

Published November 2021 in 11th international Conference on the bearing capacity of roads, railways and airfields.

This study investigates the rheological properties of bitumen influenced by preheating process. The experimental results imply that the preheating process has experienced three stages: the rapid change stage, stable stage and aged stage. It is recommended to avoid preheating bitumen specimens more than six times, as more preheating time could age bitumen to some extent and affect the subsequent test results.

Contributions:

Xuemei Zhang: Conceptualization, Methodology, Investigation, Formal analysis, Data curation, Writing - original draft. **Inge Hoff**: Conceptualization, Resources, Writing - review & editing, Supervision.

Paper VI: Extended investigation of chemical effect on asphalt mixture

Xuemei Zhang*, Hao Chen, Diego Maria Barbieri and Inge Hoff (2022)

Experimental Laboratory Evaluation of Mechanical Properties of Asphalt Mixtures Exposed to Sodium Chloride.

Published March 2022 in Journal of Transportation Research Record.

This paper is relevant to the topic of the thesis, which is an extended investigation of the chemical effect (sodium chloride) on asphalt mixture. The experimental results showed that the behaviour of the asphalt mixture was degraded by the exposure to sodium chloride, which is in line with previous study results (Luo et al., 2017; Xiong et al., 2019a; Zhang et al., 2020). Moreover, the mixture with polymer modified asphalt binder showed the best overall performance. This outcome can be connected to the better chemical resistance of polymer modified bitumen concluded from Paper III. In contrast with stone mastic asphalt mixtures with neat bitumen, traditional asphalt mixtures with neat bitumen were proposed for asphalt pavement entailing frequent winter maintenances due to the better resistance against sodium chloride solution.

Xuemei Zhang: Study conceptualization and design, Data collection, analysis and interpretation of results, draft manuscript preparation. **Hao Chen**: Analysis and interpretation of results, draft manuscript preparation. **Diego Maria Barbieri**: Analysis and interpretation of results, draft manuscript preparation. **Inge Hoff**: Analysis and interpretation of results, draft manuscript preparation.

Paper VII: Investigation on the effectiveness of special method used for calculating rejuvenator dosage

Xuemei Zhang*, Tawab Fidai, Inge Hoff, Bjørn Ove Lerfald and Hao Chen (2022)

Determination of rejuvenator proportion within the recycled bitumen: Empirical double-logarithmic formula and calibration.

Accepted by Journal of Materials in Civil and Engineering.

This paper proposes a method, the empirical double-logarithmic formula and calibration, to determine the appropriate rejuvenator dosage within aged bitumen for the desired properties. The study results verifies that this method can determine the rejuvenator dosage of recycled/aged bitumen with limited physical parameters.

Xuemei Zhang: Conceptualization, Methodology, Investigation, Formal analysis, Data curation, Writing - original draft. **Tawab Fidai**: Conceptualization, Methodology, Investigation, Formal analysis, Data curation, **Inge Hoff**: Conceptualization, Resources, Formal analysis, Writing - review & editing, Supervision. **Bjørn Ove Lerfald**: Conceptualization, Resources, Formal analysis, Supervision. **Hao Chen**: Formal analysis, Writing - review & editing.

Additional publication

Baowen Lou, Aimin Sha*, Diego Maria Barbieri, **Xuemei Zhang**, Hao Chen and Inge Hoff. *(2022). Evaluation of microwave aging impact on asphalt mixtures. Road Materials and Pavement Design, 1-14.*

2. RESEARCH METHODOLOGY

2.1 Materials

2.1.1 Bitumen

There are five types of bitumen applied in the thesis. The bitumen type mostly used for pavement construction in Norway is neat bitumen with a penetration of 70/100, which was collected from the company Veidekke. To simulate the ageing of bitumen during paving, transportation and serving, the thin-film oven test (TFOT) and pressure ageing vessel (PAV) test were conducted on neat bitumen in the laboratory. Besides, polymer modified bitumen and rejuvenated bitumen as good performance and environmentally friendly bitumen were also used. The polymer modified bitumen was supplied by the company Nynas, and the rejuvenated bitumen was obtained by mixing aged bitumen and 3% rejuvenator. The properties of the five kinds of bitumen are shown in Table 1. As seen from Table 1, the neat bitumen meets the penetration requirements of 7-10 mm, softening point of 43-51℃ and minimum dynamic viscosity of 90 Pa·s (NPRA, 2018). The penetration and dynamic viscosity of neat bitumen decrease, and softening point increases with the increasing ageing degree. In comparison with the neat bitumen, the polymer modified bitumen is stiffer and more stable. The rejuvenator can apparently soften aged bitumen with a small dosage.

Table 1. Basic properties of the bitumen

Property	Penetration (25 °C) [0.1 mm]	Softening point [°C]	Viscosity (60 °C) [Pa·s]
Neat bitumen	70	48.2	188
TFOT aged bitumen	56	53.8	306
PAV aged bitumen	34	58.4	731
Polymer modified bitumen	79	64.6	398
Rejuvenated bitumen	206	39.6	54
Test standard	EN 1426:2015	EN 1427:2015	EN 13702:2018

2.1.2 Chemical

To simulate the practical situation of asphalt pavement suffering chemical exposure, the chemical concentration is determined in the Introduction as: 10 wt% de-icing salt solution and acid rain of pH 4. The preparation of chemical solutions was shown as follows:

De-icing salt: 10% NaCl and 10% $CaCl_2$ solutions by weight were prepared by mixing distilled water with NaCl and $CaCl_2$ solids. The NaCl and $CaCl_2$ solids are obtained from companies VWR Internal BVBA and Honeywell Fluka™, respectively.

Simulated acid rain: Firstly, 1 g sulfuric acid (98%) was added to 2.84 g nitric acid (69%) to a blend of concentrated acids. Then, the concentrated acid was dropped into 5 L distilled water to an acid rain solution with a pH of 4. Finally, the pH value of the simulated acid rain was verified by the pH meter.

2.2 Immersion process

The preparation of bitumen immersing in chemical solution referencing previous studies is shown in Figure 5 (Meng et al., 2021; Pang et al., 2018; Yang et al., 2020). Two processes are included: the preparation of bitumen film and the immersion process. The preparation of bitumen film is stated as follows: the container of bitumen was heated at 90 ℃ for 20 mins (neat bitumen and rejuvenated bitumen) and 30 mins (polymer modified bitumen) to fluid status. 28±0.2 g bitumen sample was weighted and distributed on a glass dish with a diameter of 190 mm. The bitumen film was heated at 100 ℃ to an even and smooth bitumen film with 0.85 mm. The immersion process is described as follows: a uniform bitumen film was prepared to be immersed in 150 ml salt/acid solution, then isolating bitumen and solution from light and external oxygen using a black plastic bag. The prepared bitumen samples immersing in salt solution were placed at 25 ℃ for 7, 28 and 90 days. After the immersion process, the solution was collected in a plastic cup for subsequent testing, and the bitumen was cleaned and dried to constant weight for the next steps.

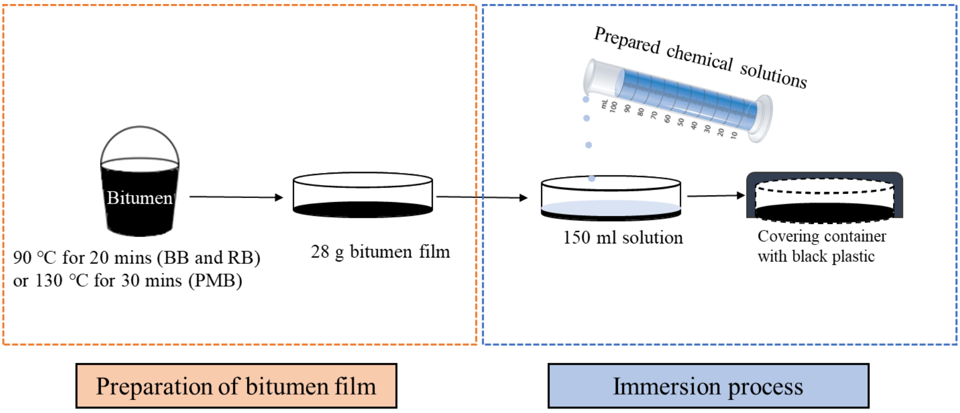

Figure 5. The preparation of bitumen immersing in solution

2.3 Test method

2.3.1 Conventional thermal-oxidative ageing test

Thermal-oxidative ageing is one of the most concerning issues of asphalt pavement, which negatively affects its service life and durability. According to the service situations, two forms of ageing occur on bitumen during the whole lifespan of asphalt pavement: short-term ageing and long-term ageing. Short-term ageing refers to bitumen ageing in the storage, transportation, mixing and paving processes; Long-term ageing presents the bitumen ageing throughout, including the short-term ageing period and servicing stage (Chen and Huang, 2000; Zhang et al., 2018). However, the short-term and long-term ageing of asphalt pavement in the field could be several days and a dozen years, which would be a long period for studying its reaction procedure and mechanism in the laboratory. Thus, thin-film oven test (TFOT ageing) and pressure ageing vessel ageing (PAV ageing) methods in the laboratory are used to simulate the short-term ageing and long-term ageing of bitumen by increasing the ageing temperature and air pressure (Airey, 2003; Tian et al.). The parameters of the two thermal-oxidative ageing methods are shown in Table 2.

Table 2. Parameters of thermal-oxidative ageing.

Parameter	TFOT Ageing	PAV Ageing
Temperature	163 °C	100 °C
Pressure	-	2.1 MPa
Ageing time	5 h	20 h
Bitumen mass	50 g	50 g
Standard	EN 12607-2:2014	EN 14769:2012

2.3.2 Mixing process of rejuvenated bitumen

A general mixing procedure was used for adding rejuvenators in bitumen based on a mixing recipe from the company Kraton (Kraton, 2021). The used rejuvenator (refined vegetable oil)) in this research is obtained from the company ARSTEC, and its chemical structure is characterised by Fourier transform infrared radiation spectrum shown in Figure 6. The main steps for the mixing process are as follows:

(1) Aged bitumen is melted in a heating cabinet at 130 ℃ for 1 hour.
(2) Aged bitumen is stirred with a glass rod, and the contents are weighed in a tared sample box.
(3) The estimated amount of rejuvenator is added dropwise with a plastic pipette to the sample box.
(4) The mixture is stirred with a glass rod for 30 seconds and put back in the heating cabinet for 10 minutes.
(5) Finally, the mixture is stirred for 30 seconds at 5-minute intervals. This mixing process is finished after five cycles.

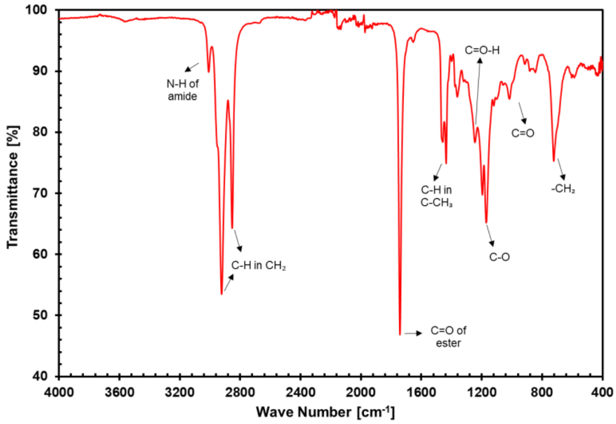

Figure 6. The FTIR spectrum of the rejuvenator

2.3.3 pH Value test

The sodium chloride, calcium chloride and acid rain solutions with and without immersion process were collected in a plastic cup. The pH values of the solutions were tested by a pH 1000 H meter, and the pH value was allowed to reach an equilibrium (a stable value). Its measuring range is -2 – 20 with a resolution of 0.01. The pH value inversely represents the concentration of hydrogen ions in the solution. A higher pH value demonstrates a lower concentration of hydrogen ions in the solution, an vice versa. The relationship between hydrogen ions and the pH value is formulated as follows:

$$pH=-log_{10}(a_{H^+})=log_{10}(\frac{1}{a_{H^+}}) \qquad \text{Eq. 1}$$

Where a_{H^+} indicates the hydrogen ion activity in a solution.

2.3.4 Scanning electron microscopy (SEM) with energy dispersive spectrometer (EDS) test

The bitumen surface before and after salt/acid solution immersion was captured using scanning electron microscope (FlexSEM 1000) at a magnification of 50/100/200 times, which gives the most intuitive results of chemical effects on the bitumen. The smooth bitumen surface is generally indicated by a fresh bitumen sample without ageing or damaging, while a rough bitumen surface is normally a result of deteriorated structure.

The element analysis was performed using energy dispersive spectrometer (EDS) based on the captured pictures from the SEM test. The changes in element content and the addition of elements can reflect the chemical and physical reactions between bitumen and chemicals. To avoid the experimental error, the elemental analysis of each specimen is tested with three replicates, the mean value is applied for studies.

2.3.5 Physical test

The physical properties of bitumen are the principles for pavement design and bitumen grade from the engineering perspective. Penetration, softening point and viscosity are three typical parameters characterising the physical properties of bitumen, and they demonstrate the stiffness, high-temperature stability and the ability to resist flowing of bitumen (Mirsepahi et al., 2020; Xu et al., 2019; Yan et al., 2013), respectively. In this research, the three physical parameters were evaluated before and after the immersion process to assess the chemical effects on bitumen. In this case, penetration at 25 ℃, softening point and dynamic viscosity at 60-100 ℃ were obtained following EN 1426:2015, EN 1427:2015 and EN 13702:2018, respectively. For the penetration test, three validated determinations (within the error range) are required for one sample, and the mean value was used as the test result. Two replicates were required for softening point and viscosity tests, and the average of two measurements was taken as the test results.

2.3.6 Attenuated total reflectance (ATR) Fourier transform infrared radiation (FTIR) spectroscopy test

The chemical structure of the bitumen might be influenced by environmental chemicals. The chemical functional groups were characterised by Nicolet 8700 Fourier transform infrared (FTIR) radiation spectrometer with an attenuated total reflectance (ATR) accessory to study the chemical structure changes of the bitumen under different conditions. The bitumen samples were tested in an atmosphere without moisture and carbon dioxide by Parker Balston 74-5041 FTIR Purge Gas Generator. The formation, addition and decomposition of chemical bonds can be found by FTIR analysis so that the physiochemical reactions or concentration variations can be studied. In this research, qualitative analysis was performed by observing the FTIR spectra, and quantitative analysis was performed by comparing the difference in absorbance values between unconditioned bitumen and conditioned bitumen.

Regarding the qualitative analysis, the FTIR spectra are provided with corresponding chemical bonds. The chemical structure changes during the immersion process would be characterised by identifying the specific functional group. Table 3 lists the major functional groups and the corresponding position and related vibration modes of bitumen, polymer and rejuvenator. As indicated in Table 3, the C-Cl group at 745 cm^{-1} indicates the substitution reaction of Cl provided by de-icing salts (De Lorenzi et al., 1999); C-H bond of polystyrene at 698 cm^{-1} and butadiene double bond (C=C) at 965 cm^{-1} are two typical functional groups of styrene-butadien-styrene within polymer modified bitumen (Xu et al., 2021); Sulfoxide groups (S=O) around 1030 cm^{-1} and Carbonyl group (C=O) around 1700 cm^{-1} are normally employed as two ageing indicators of bitumen (Ren et al., 2021); C-OH of tertiary alcohol at 1133 cm^{-1} represents the stability of bitumen, since tertiary is the most stable state among all alcohols of bitumen (Asemani and Rabbani, 2020); C-O group of esters at 1174 cm^{-1}/1195 cm^{-1} and C=O group at 1745 cm^{-1} are the indicator of rejuvenators within bitumen (Jacobs et al., 2021); C-O of carbonyl acid around 1301 cm^{-1} can reflect the dissolution of acid to chemical solutions.

The qualitative measurement was performed by comparing the absorbance of the bitumen before and after chemical conditioning. The difference in absorbance (Δ_A) of functional groups was calculated according to Eq. 2 (Bora and Das, 2020; Jelle and Nilsen, 2011). The positive value of Δ_A means the increased concentration of the functional group, and the negative value of Δ_A results in decreased concentration.

$$\Delta_A = \frac{A_{N/T,D} - A_{N/T}}{A_{N/T}} \times 100\% \qquad \text{Eq. 2}$$

Where Δ_A is the difference in absorbance (%), $A_{N/T}$ is the absorbance of neat/aged bitumen, $A_{N/A,D}$ is the absorbance of neat/aged bitumen after D days immersion.

Table 3. Chemical functional groups of bitumen (Asemani and Rabbani, 2020; Bukka et al., 1991; De Lorenzi et al., 1999; Feng et al., 2021; Hou et al., 2018; Jelle and Nilsen, 2011; Xu et al., 2021; Yao et al., 2015; Zhang et al., 2011).

Wavenumber (cm^{-1})	Chemical bond and vibration mode	Represent
725	-CH_2 rocking	-
745	C-Cl stretching in bitumen after NaCl and $CaCl_2$ immersion	NaCl/$CaCl_2$ influence
812	Two adjacent C-H on the aromatic ring	-
866	C-H of benzene derivative, out of plane bending	-
1012	C-O of easter, stretching	-
698	C-H bond of polystyrene, Bending	Existing of SBS
965	Butadiene double bond (C=C), Bending	
1030	Sulfoxide groups (S=O), Stretching	Ageing
1700-1725	Carbonyl group (C=O), Stretching	
1133	C-OH of tertiary alcohol, stretching	Stability
1174 1195	C-O group of esters, stretching	Existing of Rejuvenator
1745	C=O group, stretching	
1210-1320	C-O of Carbonyl acid, Stretching	Acid dissolution
1460/1370	Branched (C-H) of aliphatic, Symmetric deformation	-
1540	N-H of amide, Bending	Asphaltenes
1579	C=C stretching	
2850	C-H of aliphatic hydrogen, CH_2, Symmetric stretching	-
2918	C-H of aliphatic hydrogen, CH_3, asymmetric stretching	-

2.3.7 Dynamic shear rheometer (DSR) test

Bitumen is a viscoelastic material, which shows not only viscosity but also elasticity. The viscosity can combine different sizes of aggregates together to a stable Marshall or asphalt slab sample, and the elasticity can make the asphalt pavement resist permanent deformation and be more comfortable to drivers. The changes in the viscoelasticity of bitumen can highly influence the performance of asphalt pavement. Therefore, the viscoelastic performance of bitumen should be investigated.

The dynamic shear rheometer (DSR) is capable of quantifying both viscous and elastic properties of all kinds of bitumen. Five test modes were applied in this research: low-temperature creep, high-temperature creep and frequency creep tests were carried out following EN 14770:2012; Linear amplitude sweep test (LAS) and multiple stress creep and recovery test (MSCRT) were conducted according to AASTHO TP 101–12 and EN 16659:2015 standards. The test parameters for the different modes are described in Table 4.

Table 4. Test parameters of the test modes

Mode	Low-temperature creep	High-temperature creep	Frequency creep	Linear amplitude sweep (LAS)		Multiple stress creep and recovery test (MSCR)
				Step 1	Step 2	
Sweep frequency	10 rad/s	10 rad/s	0.1-400 rad/s	0.1-30 Hz	10 Hz	-
Temperature range	5-30 ℃	30-80 ℃	30-80 ℃	25 ℃	25 ℃	60 ℃
Temperature interval	1 ℃	10 ℃	10 ℃	-	-	-
Strain	1%	1%	1%	0.1 %	0.1%-30%	0.1 kPa and 3.2 kPa (stress)
Diameter of the plate	8 mm	25 mm	25 mm	8 mm		25 mm
Sample thickness	2 mm	1 mm	1 mm	2 mm		1 mm

(1) Temperature sweep test

A temperature sweep test is conducted to analyse the rheological properties of bitumen over temperatures. There are two test modes for temperature sweep test: low-temperature sweep test (5 - 30 ℃) and high-temperature sweep test (30 - 80 ℃) presented in Table 4. After conducting the two tests, the phase angle δ and complex modulus G^* at low temperature and high temperature, fatigue factor (G^*•δ) and rutting factor (G^*/δ) as a function of temperature and failure temperature were obtained. The phase angle, in the range of 0-90 °, is the lag between the applied shear stress and the final shear strain (Liu et al., 2021). A higher value of phase angle indicates the better viscous behaviour of bitumen, and a lower value means better elastic behaviour. The complex modulus represents the total resistance of bitumen to deformation (Jiang et al., 2021). A higher complex modulus value demonstrates higher deformation resistance and vice versa. The rutting factor and fatigue factor are derived by the complex modulus and phase angle, which are respectively applied to characterise the resistance to rutting and fatigue cracks (Pang et al., 2018). A higher rutting factor and lower fatigue factor indicate a better ability to resist rutting and fatigue cracks. Moreover, failure temperature is the temperature at which the rutting factor is equal to 1 kPa (Das and Panda, 2017). The higher the failure temperature, the better the stability of the bitumen is, and vice versa (Duan et al., 2021).

(2) Frequency sweep test

The frequency sweep test was conducted to construct the master curves of complex modulus and phase angle, which investigates the rheological properties of bitumen over a range of temperature and frequency. Firstly, the complex modulus and phase angle as a function of frequency at different temperatures (normally 30 ℃, 40 ℃, 50 ℃, 60 ℃, 70 ℃, 80 ℃) were obtained after the frequency creep test. Then, the master curve of complex modulus and phase angle were constructed by shifting individual complex modulus/ phase angle curves along the time axis to a smooth master curve at a reference temperature (in this case, 30 ℃) using the time-temperature superposition principle (Al-Haddad, 2015). The shift factor is defined as Eq. 3:

$$log[\alpha(T)] = logf_r - logf \qquad \text{Eq. 3}$$

Where $\alpha(T)$ is the shift factor at T temperature relative to the reference temperature; f_r is the reduced frequency; f is the tested frequency.

The master curve of complex modulus and phase angle are developed using modified Huet-Sayegh (MHS) model expressed as follows (Liu et al., 2013; Woldekidan et al., 2012):

$$(G^*(\omega))^{-1} = (G_0^* + \frac{G_\infty^* - G_0^*}{1+\delta(i\omega\tau)^{-m_1}+(i\omega\tau)^{-m_2}})^{-1} - \frac{i}{\eta_3\omega} \qquad \text{Eq. 4}$$

Where $G^*(\omega)$ is complex modulus at frequency of ω; G_∞^* and G_0^* are the complex modulus at the frequency of infinity and infinitesimal; δ, τ, m_1, m_2 and η_3 are model coefficients; i is the imaginary number of the complex number notation.

(3) Linear amplitude sweep (LAS) test

Fatigue crack is one of the typical distresses of asphalt pavement, which should be considered when characterising bitumen properties influenced by chemicals. Compared to the fatigue factor obtained from the DSR test, the fatigue life of bitumen calculated from the Linear amplitude sweep (LAS) test can better simulate the actual traffic condition and evaluate the fatigue lifespan of polymer modified bitumen based on the accumulated damage by repeated loading (Huang et al., 2021). The LAS test includes two steps: frequency creep and amplitude sweep according to AASTHO TP 101–12. The first step (frequency creep) is intended to obtain rheological information of bitumen samples for determining the α parameter at 25 °C over a range of loading frequencies shown in Table 3. By the relationship of complex modulus G^* and phase angle δ versus frequency, α parameter is determined shown in Eq. 5.

$$logG'(\omega) = 1/\alpha(log\ \omega) + b \qquad \text{Eq. 5}$$

The second step (amplitude sweep) is designed to calculate the damage on bitumen based on the results of Step 1 and run at 25 °C and a fixed frequency of 10 Hz with an increasing strain from 0.1% to 30%. The accumulated damage on the bitumen sample is calculated as Eq. 6. Thus, the relationship between $C(t)$ and $D(t)$ can be derived as Eq. 7, the C_0, C_1, C_2, D_f, A and B can be calculated following Eq. 8. Finally, the A and B parameters are used to calculate the fatigue life of bitumen according to Eq. 9.

$$D(t) \cong \sum_{i=1}^{N}[\pi\gamma_0^2(c_{i-1} - c_i)]^{\frac{\alpha}{1+\alpha}}(t_i - t_{i-1})^{\frac{1}{1+\alpha}} \qquad \text{Eq. 6}$$

Where $C(t) = \frac{|G^*|(t)}{|G^*|_{initial}}$ which is the ratio of $|G^*|$ at time t to the initial $|G^*|$ (undamaged condition); t represents the test time, seconds; γ_0 is the applied strain at time t, percent; $|G^*|$ is the complex modulus, MPa; α corresponds to the parameter obtained from first step.

$$log(C_0 - C_t) = log(C_1) + C_2 \cdot log(D(t)) \qquad \text{Eq. 7}$$

$$D_f = (\frac{C_{at\ Peak}}{C_1})^{1/C_2} \quad A = \frac{10(D_f)^{(1+(1-C_2)\alpha)}}{(1+(1-C_2)\alpha)(\pi I_D C_1 C_2)^{\alpha}} \quad B = 2\alpha \qquad \text{Eq. 8}$$

$$N_f = A(\gamma_{max})^{-B} \qquad \text{Eq. 9}$$

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

(4) Multiple stress creep recovery test (MSCRT)

The permanent deformation resistance and elastic response of specimens were evaluated by multiple stress creep recovery test in accordance with EN 16629:2015, characterised as non-recoverable creep compliance (J_{nr}) and percent recovery (%R). To acquire the two parameters, a test was carried out: the MSCRT is composed of 20 cycles at 60 °C. The first ten cycles were performed at the load of 0.1 kPa, followed by another ten cycles at the stress of 3.2 kPa. Each cycle consists of 1 s creep and 9 s recovery. Two replicates were tested for each specimen, and the average was used for analysis.

Non-recoverable creep compliance (J_{nr}) is indicated as the residual strain after the one cycle divided by the applied stress. Percent recovery (%R) is defined as the recovered stain in the recovery period. A higher J_{nr} indicates better permanent deformation resistance of bitumen; a higher %R refers to a better elastic response of bitumen. Non-recoverable creep compliance (J_{nr}) and percent recovery (%R) are determined as follows:

$$J_{nr_{0.1\ kPa}} = \frac{1}{10}\sum_{N=1}^{10}(J_{nr_{0.1\ kPa}}^{N}) \qquad \text{Eq. 10}$$

$$J_{nr_{3.2\ kPa}} = \frac{1}{10}\sum_{N=1}^{10}(J_{nr_{3.2\ kPa}}^{N}) \qquad \text{Eq. 11}$$

Where $J_{nr_{0.1\ kPa}}^{N} = \varepsilon_{10}^{N}/0.1$ and $J_{nr_{3.2\ kPa}}^{N} = \varepsilon_{10}^{N}/3.2$.

$$\%R_{0.1\ kPa} = \frac{1}{10}\sum_{N=1}^{10}(\%R_{0.1kPa}^{N}) \qquad \text{Eq. 12}$$

$$\%R_{3.2\ kPa} = \frac{1}{10}\sum_{N=1}^{10}(\%R_{3.2kPa}^{N}) \qquad \text{Eq. 13}$$

Where $\%R_{0.1kPa}^{N} = 100 \times (\varepsilon_{1}^{N} - \varepsilon_{10}^{N})/\varepsilon_{1}^{N}$ and $\%R_{3.2kPa}^{N} = 100 \times (\varepsilon_{1}^{N} - \varepsilon_{10}^{N})/\varepsilon_{1}^{N}$.

Where ε_{0}^{N} represents the strain at the start of cycle N (thus, ε_{0}^{1} should be 0); ε_{c}^{N} is the strain after 1 s loading of cycle N; ε_{r}^{N} indicates the strain at the end of one cycle for N cycle; ε_{1}^{N} is the loaded strain at the end of creep process (at N cycle), denoted as $\varepsilon_{1}^{N} = \varepsilon_{c}^{N} - \varepsilon_{0}^{N}$; ε_{10}^{N} is the unrecoverable strain at N cycle, calculated as $\varepsilon_{10}^{N} = \varepsilon_{r}^{N} - \varepsilon_{0}^{N}$.

2.3.8 Bending beam rheometer (BBR) test

The low-temperature properties of bitumen were characterised using a bending beam rheometer according to Norwegian standard EN 14771:2012. Bitumen samples were made to 6.4 ± 0.1

mm high, 12. 7 ± 0.25 mm wide, 127 ± 5 mm long and tested at -12 ℃ and -18 ℃. For each type of bitumen, two samples were made for the BBR test.

The test force and deflection are detected by the BBR apparatus. According to the above-given parameters, the measured stiffness as a function of time is calculated in Eq. 14. The stiffness at loading time of 8, 15, 30, 60, 120, 240 s is calculated following Eq. 15 to obtain the required parameters (B and C) for m-value. Then, the m-value as a function of time is determined according to Eq. 16.

$$S_m(t) = \frac{PL^3}{4bh^3\delta(t)} \quad \text{Eq. 14}$$

$$logS_c(t) = A + B \times log(t) + C \times [log(t)]^2 \quad \text{Eq. 15}$$

$$m(t) = \left|\frac{dlog[S(t)]}{dlog(t)}\right| = |B + 2 \times C \times log(t)| \quad \text{Eq. 16}$$

Where $S_m(t)$ is the flexural creep stiffness at tome t, MPa; P is the test load at time t, N; L is the distance (102 mm) between two supports; b is the width (12.7 mm) of bitumen sample; h is the thickness (6.4 mm) of bitumen sample; $\delta(t)$ is the deflection at time t, mm.

Finally, average values of flexural creep stiffness (S) and stress relaxation ability (m-value) at the loading time of 60 s and corresponding limited temperature were calculated and used for evaluating the stiffness and the ability to relax the stress of bitumen at low-temperature. A higher S value and m-value indicate that the bitumen has higher stiffness and bad ability to relax stress. A lower limited temperature indicates a better low-temperature rheological properties of bitumen.

3. DEVELOPMENT OF BITUMEN EXPOSED TO CHEMICALS

Due to the intrinsic properties of chemicals and their long-term existence, the asphalt pavement is inevitably affected by chemicals with different reaction mechanisms. Many recent studies investigated the influence of a single chemical on asphalt mixture performance (Hu et al., 2022; Vega-Zamanillo et al., 2020; Zhang et al., 2021), while a systematic framework of bitumen under three typical chemicals is still missing, and the underlying reaction mechanisms remain unclear. Given these premises, this chapter aims to investigate the development of bitumen exposed to typical chemicals. The chemicals used in this research are de-icing salt and acid rain: de-icing salts of which sodium chloride and calcium chloride are two main chemicals due to their great effectiveness and low costs are the important agents for winter maintenance; Acid rain, a chemical resulting of sulphur dioxides and nitrogen oxides pollutants, is a strong acid solvent. Neat bitumen and TFOT aged bitumen were respectively exposed to 10 wt% sodium chloride, 10 wt% calcium chloride and acid rain with pH 4. The pH value of the residual solution and the physical, chemical, rheological, and mechanical properties of the bitumen over immersion time (0, 7, 28 and 90 days) were characterised to investigate the chemical effects. Based on the experimental results, the reaction mechanism between the bitumen and the three chemicals were revealed. This chapter is detailly studied in Paper I, II and III.

3.1 Characterisation of bitumen exposed to chemicals

3.1.1 Hydrogen ions concentration of the residual chemical solution

The hydrogen ion concentration of the residual chemical solution with and without immersion was tested by a pH meter. Bitumen as an acid substance is suspected of releasing hydrogen ions into the solution during the immersion process. The decreased pH value of the de-icing salt and the acid rain solutions after immersing bitumen shown in Figure 7 verified this assumption. The sodium chloride, calcium chloride and acid rain promoted the releasing of hydrogen ions of the bitumen, resulting in a lower pH value of the residual solutions. The dissolution of acid substances in the de-icing salt solution was promoted by the extension of immersion time. Specifically, the pH value of the NaCl solution was more influenced by bitumen compared to $CaCl_2$, which indicates that the NaCl solution reacts more vigorously with the bitumen than the $CaCl_2$ solution. The pH value of the acid rain was slightly affected by bitumen and immersion time, which is attributed to the strong acidity of the acid rain and the mild reaction between acid rain and bitumen.

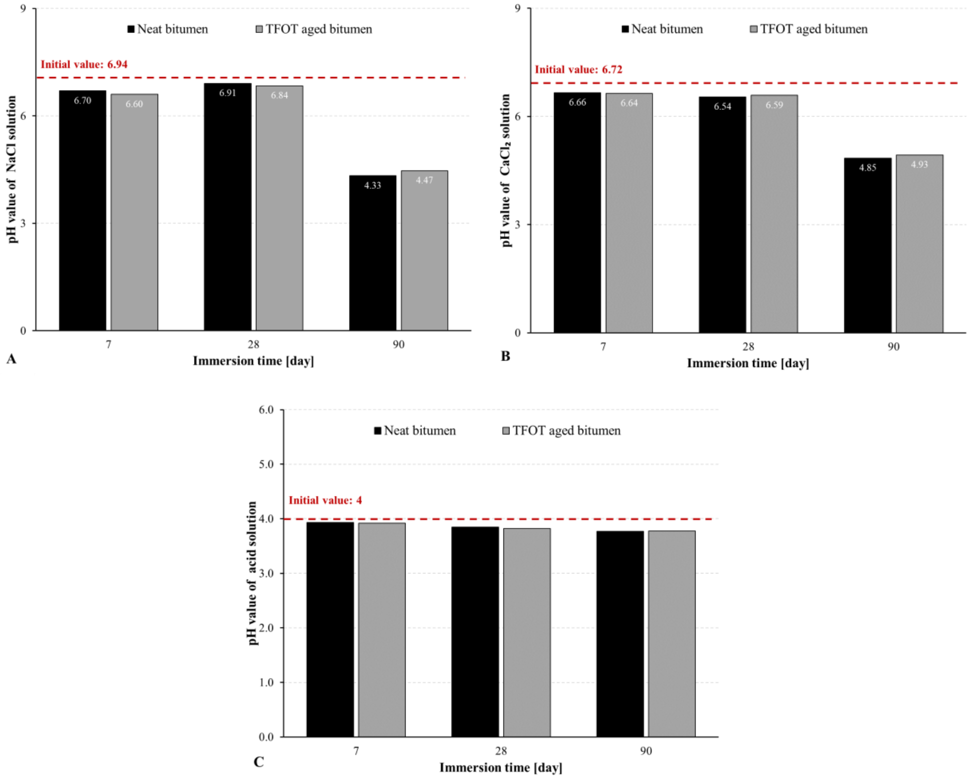

Figure 7. The pH values of the residual NaCl (A), $CaCl_2$ (B) and acid rain (C) solution versus immersion time

3.1.2 Element analysis of bitumen

In turn, fewer hydrogen ions within the bitumen and the physicochemical reaction are reflected in some changes in the bitumen morphology. The bitumen surface became uneven with certain particles after chemical conditions. The roughness and the number of particles increased with the prolonged immersion time in Paper I and II. To reveal the causes of the roughness of the bitumen surface, an element analysis test was implemented by EDS. The element analyses revealed more O content and appearance of Cl, Na and Ca exiting within the bitumen after de-icing salt condition and presented in Table 5. The O element is the typical factor characterising oxidative ageing (Stangl et al., 2007; Thurston and Knowles, 1941). Thus, these results are originated from the oxidative reaction of the bitumen and physicochemical replacement between the bitumen and the de-icing salts, which are in accord with Zhou’s results (Zou et al., 2021). Moreover, a higher percentage of O, S and N elements occurred after acid rain immersion. These phenomena indicate that acid accelerates bitumen ageing and increases asphaltenes content since S and N elements mainly exist in the asphaltenes fraction of bitumen (Glozman and Akhmetova, 1970; Sun et al., 2020). In addition, the NaCl solution resulted in more increment in O and S content than the $CaCl_2$ solution and the acid rain, which shows that the NaCl causes the most severe ageing of the bitumen.

Table 5. Element analysis of the bitumen under different conditions

Bitumen	Salt solution-immersion time	Element content [%]						
		C	O	S	N	Cl	Na	Ca
Neat bitumen	Original	98.6	1.0	0.4	-	-	-	-
	NaCl-90D	93.2	3.2	2.0	-	0.7	0.9	-
	$CaCl_2$-90D	93.8	3.0	2.2	-	0.6	-	0.4
	Acid-90D	95.9	2.8	1.1	0.2	-	-	-
TFOT aged bitumen	Original	96.1	2.4	0.6	0.9	-	-	-
	NaCl-90D	86.7	4.3	6.4	1.3	1.0	0.4	-
	$CaCl_2$-90D	87.2	4.0	6.2	1.3	0.8	-	0.5
	Acid-90D	94.3	3.3	0.9	1.5	-	-	-

3.1.3 Chemical structure of bitumen

The chemical structure of bitumen is a determinative factor influencing its physical and rheological properties, and it is also changed due to the immersion process. Four typical functional groups were used to characterise the chemical structure of the bitumen affected by the de-icing salt and immersion time. As Table 3 presented, the C-Cl functional group located at 745 cm^{-1} indicating the replacement of Cl increased, the S=O and C=O functional groups (located at 1030 and 1720 cm^{-1}) representing the oxidation of bitumen increased, the C-OH functional group located at 1133 cm^{-1} indicating bitumen stability increased after de-icing salt immersion. After the de-icing immersion, the quantitative results showed that the C-Cl functional group of bitumen decreased, the S=O, C=O and C-OH functional groups increased over immersion time, as shown in Figures 8A and 8B. The results indicate that the de-icing salt solutions enhance the replacement, oxidation and stabilisation of the bitumen, which is in line with the acquired results from the element analysis. The immersion time was positively related to the reactions between the bitumen and the de-icing salt solution. This finding shows that the reactions between bitumen and chemicals are continuous so that the changes in the chemical structure of bitumen are superimposed over time.

Regarding the chemical structure of bitumen influenced by acid rain, two functional groups (C=O and S=O) representing the oxidative degree of bitumen increased over erosion time presented in Figure 8C. In comparison, a typical group (C-O) indicating the dissolution of acid to a solution (introduced in Table 3) decreased over erosion time, which implies that the bitumen dissolves certain acid groups to the solution. Based on the absolute difference in absorbance after 90 days of erosion, the biggest changes were found for the C=O group of neat bitumen and the C-O group of aged bitumen. These results indicate that oxidation and dissolution are the dominant reaction of neat bitumen and aged bitumen, respectively.

In contrast, the NaCl resulted in the higher values of difference in absorbance (0-70 %) as a whole, followed by the $CaCl_2$ (0-40%), the acid rain led to the smallest difference in absorbance (0-16%). The comparison demonstrates that the NaCl has a more apparent effect on the chemical structure of the bitumen, followed by the $CaCl_2$ and the acid rain.

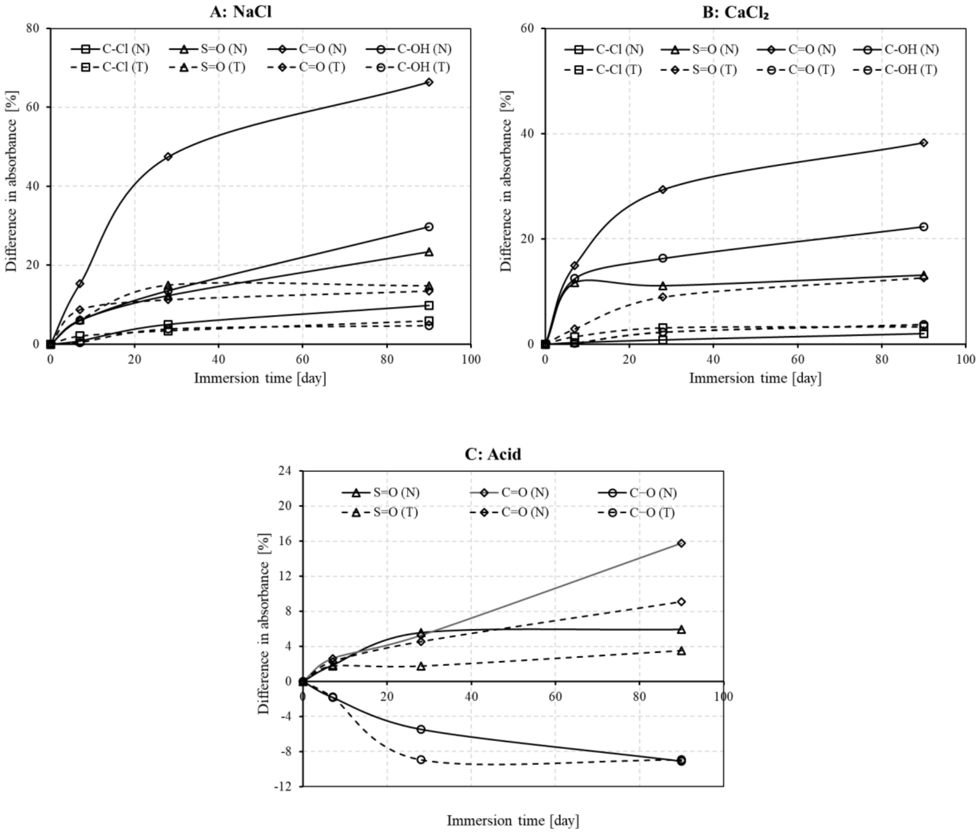

Figure 8. The absorbance difference of the functional groups under NaCl (A), $CaCl_2$ (B) and acid rain (C) immersion

3.1.4 Physical properties of bitumen

Physical properties of the bitumen also changed after the chemical solution immersion shown in Figures 9, 10 and 11. Three physical parameters, penetration, softening point and dynamic viscosity, characterise the stiffness, high-temperature stability and flow resistance of bitumen. The higher value of the three physical parameters demonstrates the better stiffness, high-temperature stability and better flow resistance of bitumen.

As indicated in Figure 9, the penetration of the bitumen decreased after the chemical immersion, which suggests that chemical immersed bitumen showed better stiffness than the one without chemical immersion. The improved stiffness might be originated from the oxidation and stabilisation of bitumen under chemical conditions. Ranking the influencing degree of the three chemicals on bitumen stiffness in descending order: NaCl, $CaCl_2$ and acid rain.

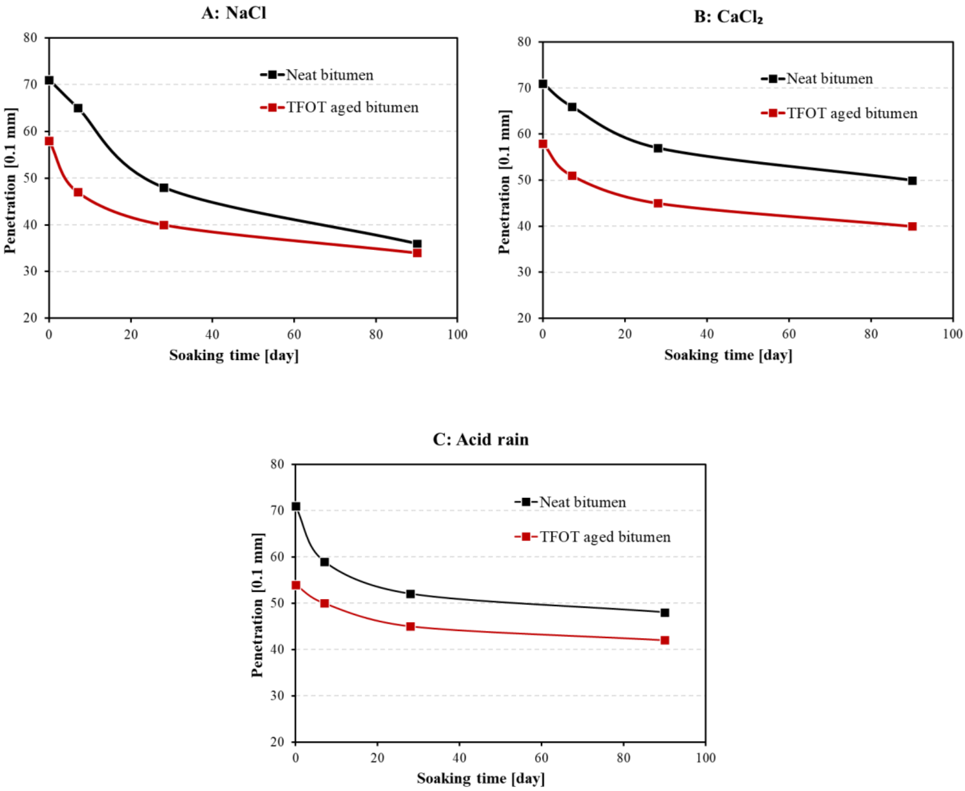

Figure 9. Penetration of bitumen under NaCl, $CaCl_2$ and acid rain conditions

The softening point of the bitumen with and without chemical immersing is shown in Figure 10. It was observed that the three chemicals have similar influences on the softening point of the bitumen, resulting in a higher softening point. The results imply that the high-temperature stability of the bitumen is improved by the chemical immersion. The stabilisation and oxidative ageing during the immersion process are the primary causes to improve the high-temperature stability of the bitumen. However, different chemicals have varying influencing degrees on the bitumen, ranking the influencing degree in descending order: NaCl, $CaCl_2$ and acid rain.

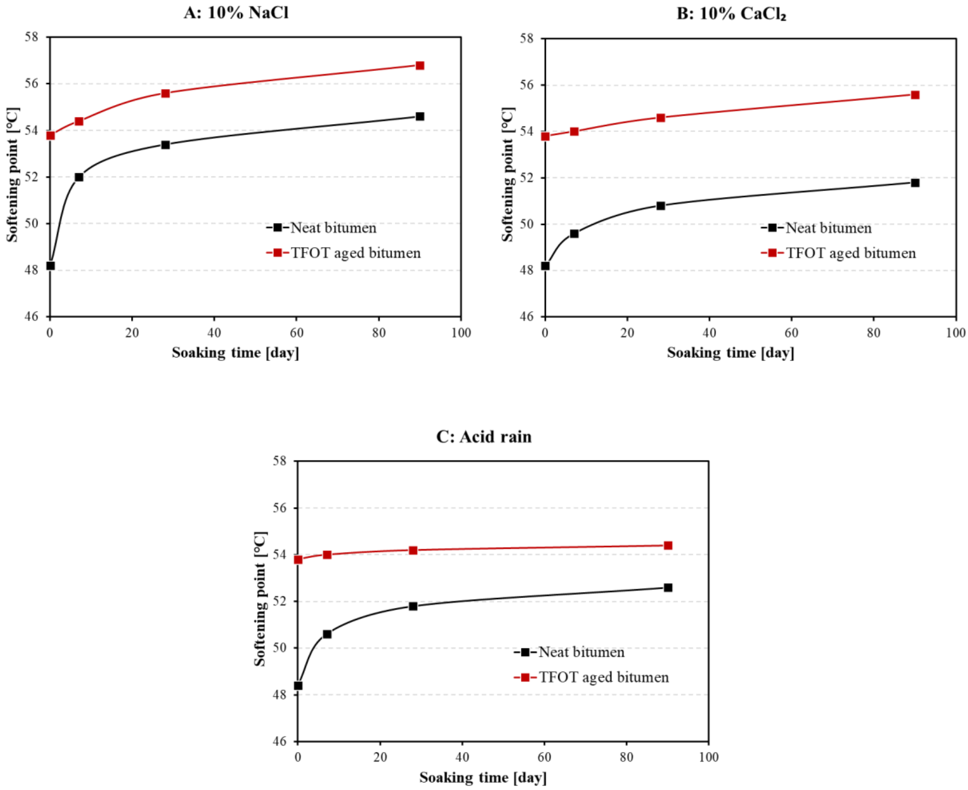

Figure 10. Softening point of bitumen under NaCl, $CaCl_2$ and acid conditions

Figure 11 shows the dynamic viscosity of the bitumen under chemical conditions. The increase in dynamic viscosity was observed after chemical immersion for each bitumen specimen, which indicates chemicals induce better flow resistance of the bitumen. This outcome was connected with the hardening of bitumen caused by oxidative ageing and physiochemical reaction. To compare different chemicals effect on the bitumen, the changes in dynamic viscosity caused by the three chemicals were ranked as follows (except for AT-90D): NaCl > acid rain > $CaCl_2$. For AT-90D, the acid rain had a more significant impact on the dynamic viscosity than the other two chemicals.

The physical properties of the bitumen were significantly influenced, resulting in a stiffer and more stable bitumen. Besides, the increment or decrement in physical parameters of the bitumen was positively correlated with the erosion time, which verifies that immersion time has a continuous effect on bitumen performance. In comparison with the three chemicals, the NaCl solution induced more extensive variations on physical parameters, which indicates that the NaCl solution has the most impact on the physical properties of the bitumen than the other two chemicals.

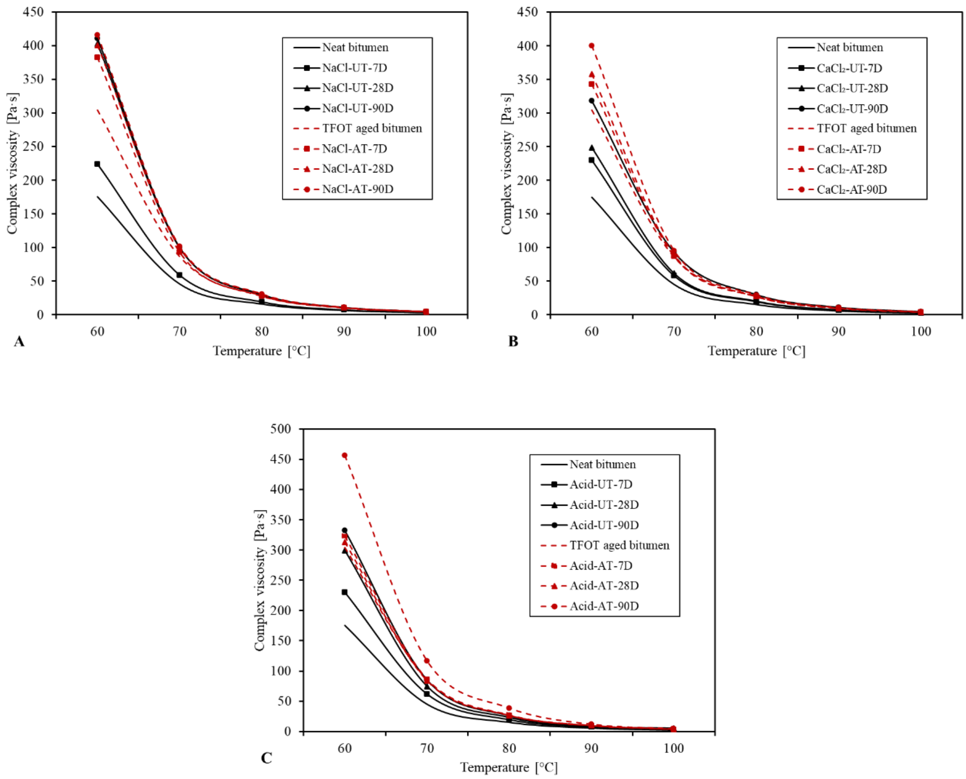

Figure 11. Dynamic viscosity of bitumen under NaCl (A), $CaCl_2$ (B) and acid (C) conditions

3.1.5 Rheological and mechanical properties of bitumen

In terms of rheological properties of bitumen, dynamic shear rheometer (DSR) and bending beam rheometer (BBR) tests were carried out. Complex modulus, phase angle, rutting factor, and fatigue factor were evaluated from the DSR test to study the rheological response of bitumen to chemicals. The flexural creep stiffness (S) and stress relaxation ability (m-value) were calculated from the BBR test to investigate the low-temperature rheological properties of bitumen.

(1) Dynamic shear rheometer test

Figure 12 presents the complex modulus and phase angle at 10 ℃ and 20 ℃ of the bitumen under chemical conditions. Complex modulus (G*) is defined as the total resistance to deformation of bitumen, a higher value of complex shear modulus relates to the better resistance to deformation (Jiang et al., 2021); Phase angle (δ) is calculated as the ratio of the loss to the storage components of the complex modulus, a smaller δ indicates better elastic behaviour and worse viscous behaviour of bitumen (Remišová et al., 2016). As shown in Figure 11, it is found that the bitumen showed increased complex modulus and decreased phase angle with the extension of immersion time, indicating better deformation resistance and worse viscous behaviour of the bitumen. The improvement in deformation resistance and the reduction in viscous behaviour are attributed to the oxidative, physical and chemical reactions between bitumen and chemicals.

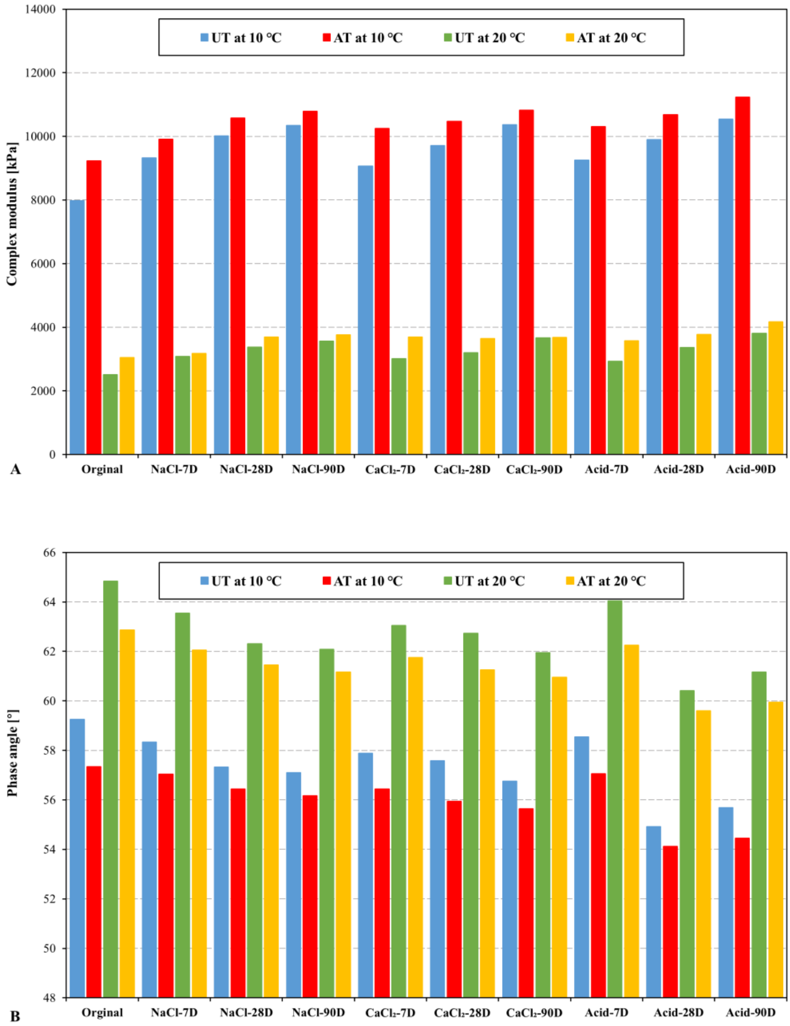

Figure 12. Rheological parameters of bitumen over immersion time (A: complex modulus at 10 ℃ and 20 ℃; B: phase angle at 10 ℃ and 20 ℃)

Moreover, the rutting factor (G*/sinδ) and fatigue factor (G*•sinδ) at 20 ℃ were obtained by the dynamic shear rheometer test shown in Figure 13. The higher value of rutting factor and fatigue factor refers to better ability against rutting and worse ability to resist fatigue cracking, respectively. As expected, the resistance to rutting exhibited an improvement, and the resistance to fatigue cracking showed a decrement after chemical immersion as that after oxidative ageing. These are shown in Figure 13 by the increase in rutting factor and fatigue factor over immersion time. The conclusions from section 3.1.4 corroborate the above results, which state that the stiffer bitumen (concluded from section 3.1.4) tends to behave better resistance to rutting but worse performance to resist fatigue cracking (Cong et al., 2020).

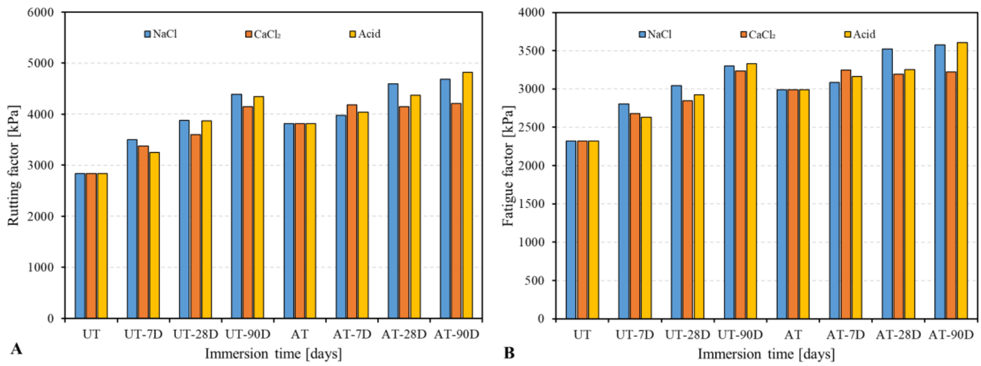

Figure 13. Fatigue factor (A) and rutting factor (B) of bitumen at 20 ℃ after three chemical conditioning

According to the DSR test results, it is concluded that the acid rain has a more slightly important effect on the rheological properties of bitumen and the two de-icing salts have similar impacts on bitumen rheological properties. The severe effects on the rheological properties of the bitumen caused by acid rain might be by reason of the changes in the specific chemical group (C-O), which is the typical result of erosion. Thus, the rheological response of the bitumen is more susceptible to erosion.

(2) Bending beam rheometer test

The flexural creep stiffness (S) and stress relaxation ability (m-value) at -12 ℃ and -18 ℃ of different specimens are calculated in Table 6. The flexural creep stiffness describes the stiffness of bitumen specimens at low temperature, bitumen with higher S is more resistant to low-temperature cracking (Rys et al., 2020). The m-value illustrates the increasing speed of stiffness modulus with the decrease in temperature, a higher m-value indicates more rapid relaxing speed and better stress relaxation ability (Rys et al., 2020).

Based on Table 6, it is stated that chemicals increased the stiffness of bitumen denoted by the increased S value. In contrast, the ability to relax stress was deteriorated by chemicals, as the m-value of chemical treated bitumen was far lower than that of original bitumen. The increment on the flexural creep stiffness is in agreement with the observations of the DSR test. Comparing the three chemical treated bitumen, NaCl-UT-90 showed the most significant changes in both

S and m-value, indicating the most impact of NaCl on low-temperature rheological properties of bitumen among the three chemicals.

Table 6. The flexural creep stiffness (S) and stress relaxation ability (m-value) of bitumen under de-icing salt immersion

BBR test	S [MPa]		m-value	
	-18 ℃	-12 ℃	-18 ℃	-12 ℃
UT	236.0	40.0	0.332	0.42
NaCl-UT-90	303.0	98.3	0.292	0.320
$CaCl_2$-UT-90	292.0	94.4	0.278	0.382
Acid rain-UT-90	300.0	97.8	0.287	0.331

After chemical immersion, bitumen showed increased stiffness and elasticity, decreased stress relaxation ability over immersion time. These variations in rheological properties are attributed to the changed chemical structure of the bitumen caused by oxidation, replacement, stabilisation and dissolution. The changes and changing trends in bitumen performance are in line with Zou and Yang's observations (Yang et al., 2020; Zou et al., 2021).

3.2 Reaction mechanism between bitumen and chemicals

The reaction mechanisms between bitumen and three chemicals are summarised based on the observed results. It is found that the de-icing salts have different reaction mechanisms with bitumen to acid rain due to their distinct acidity or alkalinity and contained ions. The separate discussions about the reaction mechanisms between the de-icing salt or bthe acid rain and the bitumen are presented as follows and in Paper I and II.

3.2.1 Reaction mechanism between bitumen and de-icing salts

Based on Chapter 3.1 and Paper I, the reaction mechanism between the bitumen and the de-icing salts can be divided into three sub-mechanisms: (1) the ionization of hydrogen ions from the bitumen; (2) the formation of C-Cl through replacing H by Cl; (3) the oxidation of the bitumen. The changes in the pH values of the residual chemical solution, chemical composition and component, physical properties, rheological properties and mechanical properties of the bitumen were contributed to the three reaction mechanisms.

(1) The ionization of hydrogen ions from the bitumen

Bitumen is a polymer mixture composed of hydrocarbons of different molecular weights and non-metallic derivatives. Its components include organic acid, which might influence the reaction between bitumen and solution. The organic acid within the bitumen ionizes hydrogen ions to the solution during the immersion procedure. Na or Ca element then combines with the rest of organic acid to the new compound "R-COOCa or R-COONa". These chemical reactions finally lead to a lower pH value of the solution and new elements within the bitumen, as well as a rough bitumen surface.

(2) The formation of C-Cl through replacing H by Cl

In terms of the chemical bond of bitumen, C-H bond energy is weak (about 414 kJ/mol) among all chemical bonds (De Lorenzi et al., 1999). Thus, the C-H bond is easily broken and replaced by Cl provided by the de-icing salts. This mechanism accounts for the reduction in H element content and the increase in Cl element content, as well as a decreased number of the C-Cl group of the bitumen.

(3) The oxidation of the bitumen

The bitumen was also continuously reacting with the air within the solution or in the air. Thus, the oxidation of the bitumen is also one of the reaction mechanisms between de-icing salt and bitumen. Due to the oxidation of the bitumen, some oxygen-contained functional groups such as carbonyl and sulfoxide groups increased, the O element content and stiffness of the bitumen also increased.

Even though the two de-icing salts selected in this research have the same reaction mechanisms with the bitumen, the influencing degree on bitumen properties caused by NaCl is different from $CaCl_2$. The above results demonstrate that NaCl has a more severe impact on bitumen properties compared to $CaCl_2$, which can be interpreted that NaCl with a high concentration showed slightly alkaline, which is more prone to react with the bitumen (slightly acid material).

3.2.2 Reaction mechanism between bitumen and acid rain

The erosion mechanism of acid rain on bitumen is concluded based on the effect of acid rain on bitumen performance. Two sub-mechanisms simultaneously occur during the erosion process: oxidation and dissolution of the bitumen. Two sub-mechanisms induced changes in bitumen performance. Oxidation of the bitumen during the acid rain erosion period is in line with the oxidation of bitumen during de-icing salt immersion, which is mainly reflected in the increased amount of C=O and S=O groups and influenced physical properties. Dissolution also accompanies oxidation, resulting in fewer C-O groups and a higher concentration of hydrogen ions.

Due to distinct reactions during the immersion process, NaCl, $CaCl_2$ and acid rain affect the bitumen to different extents. To diminish the damage of chemicals on bitumen, various methods can be used based on the deterioration mechanisms. For instance, anti-ageing agents are effective to lower the chemical sensitivity of bitumen; some modifiers that hardly react with chemical can mitigate the influence of chemicals on bitumen.

4. INVESTIGATION OF CHEMICAL EFFECT ON VARIOUS BITUMEN

As mentioned in chapter 3, the effect of chemicals on neat bitumen and aged bitumen was discussed detailly, and current studies have also paid more attention to the response of neat bitumen and aged bitumen influenced by chemicals (Li et al., 2020; Meng et al., 2021; Yang et al., 2020; Zou et al., 2021). The results showed that the chemicals influence neat and aged bitumen properties in four mechanisms: oxidation, stabilisation, dissolution of acid and replacement of Cl. However, the effect of chemicals on different types of bitumen has not been intensely investigated. Therefore, this chapter aims to clarify the responses of four kinds of bitumen to three typical chemicals and the reasons for different responses. For this purpose, four kinds of bitumen (neat bitumen, TFOT aged bitumen, polymer modified bitumen and rejuvenated bitumen) were selected and submerged into three chemical solutions (10 wt% NaCl, 10 wt% $CaCl_2$ and acid rain with pH 4). The mico-surface, physical, chemical, rheological and mechanical properties were characterised by means of SEM test, traditional binder tests, FTIR tests, DSR test and BBR test. The detailed description of this chapter is described in Paper III, I, II and IV.

4.1 Characterisation of four types of bitumen

The properties and development of bitumen are determined by the chemical composition, the source and refining methods. The selected types of bitumen in this chapter are neat bitumen (NB), TFOT aged bitumen (TB), polymer modified bitumen (PMB) and rejuvenated bitumen (RB). Neat bitumen was used as it is the most common bitumen type in Norway. TFOT aged bitumen was applied to simulate short-term ageing during the storage, transportation and paving processes. Polymer modified bitumen is generally used for heavy traffic roads. Rejuvenated bitumen as an environmentally friendly bitumen is also widely applied.

Figure 14 presents the Fourier transform infrared radiation spectroscopy spectrum of the four kinds of bitumen. It is observed that there is a specific peak around 1540 cm^{-1} for neat bitumen and TFOT aged bitumen, indicating the N-H group. This phenomenon is explained as the same source of neat bitumen and the aged bitumen, while the other two types of bitumen are from other factories. Different transmittances of the peak around 1540 cm^{-1} are found for the two types of bitumen, representing different proportions of the N-H group. Moreover, the S=O group located at 1030 cm^{-1} of TFOT aged bitumen and rejuvenated bitumen indicates that ageing exists in the two types of bitumen. Two small peaks at 964 cm^{-1} and 698 cm^{-1} of PMB indicate the styrene-butadiene-styrene molecule, which is consistent with the provided information from the factory. Furthermore, one distinct peak at 1745 cm^{-1} and two connected peaks of rejuvenated bitumen around 1174&1195 cm^{-1} are the characteristic indicators of ester, which are the specific groups of rejuvenated bitumen.

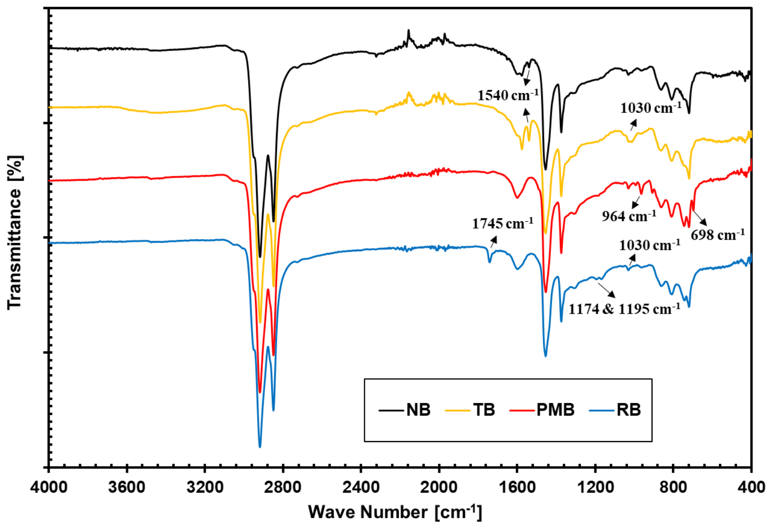

Figure 14. FTIR spectra of the four kinds of bitumen: neat bitumen (NB), TFOT aged bitumen (TB), polymer modified bitumen (PMB) and rejuvenated bitumen (RB)

4.2 Influence of chemicals on four types of bitumen

The summaries of the property change of the four kinds of bitumen after submerging in chemical solutions are shown in Table 7. Similar changing trends were observed on the different kinds of bitumen under chemical conditions, including rough surface, decreased penetration, phase angle, m-value, J_{nr} at 3.2 kPa and fatigue life, increased complex modulus, flexural creep stiffness (S), S=O and C=O groups. These outcomes are connected to the hardening and the oxidation of the bitumen. However, the hardening and oxidative speed vary from bitumen to bitumen due to their different chemical structures. Taking all quantitative parameters into account, the holistic chemical resistance of the four types of bitumen was ranked as: neat bitumen > TFOT aged bitumen ~ rejuvenated bitumen > polymer modified bitumen.

Table 7. Summary of the changes in three kinds of bitumen to environmental chemicals

Performance	Parameters	NB	TB	PMB	RB
Surface characterisation		Significant effect	Slight effect	Least effect	Slight effect
Physical property	Penetration	↓	↓	↓	↓
	Softening point	↑	↑	↓	↑
	Dynamic viscosity	↑	↑	↑ (60-85 ℃) ↓(85-100 ℃)	↑
Rheological property	S(t)	↑	↑	↑	↑
	m-value	↓	↓	↓	↓
	Complex modulus	↑	↑	↑	↑
	Phase angle	↓	↓	↓	↓
Mechanical properties	J_{nr} at 0.1 kPa	↓	↓	↑	↓
	J_{nr} at 3.2 kPa	↓	↓	↓	↓
	%R	↑	↑	↓	↑
	Fatigue life	↓	↓	↓	↓
The most severe chemical		NaCl	NaCl	$CaCl_2$	Acid rain
Changing degree caused by chemicals		NB > TB ~ RB > PMB			
Chemical bond	Affected chemical groups	S=O, C-OH, C=C, N-H, C=O (1704 & 1745 cm^{-1}), C-Cl, C-O,	S=O, C-OH, C=C, N-H, C=O (1704 and 1745 cm^{-1}), C-Cl, C-O	C=C, C-H, S=O	C-O, C=O, S=O

As Table 7 shown, however, the four kinds of bitumen performed differently in surface characterisation (Figure 13), softening point (Figure 14), dynamic viscosity (Figure 15) and MSCR parameters (Figure 16). Regarding the micro-surface of bitumen, various surface features were captured for various bitumen. Neat bitumen and rejuvenated presented smooth surfaces with a few particles, representing their slight ageing or damage degree. TFOT aged bitumen showed more roughness than neat bitumen, indicating severe ageing or damage degree. PMB was structured with more granules, which is interpreted by the network structure and the existence of styrene-butadiene-styrene molecules (Li et al., 2019; Liu et al., 2019). Therefore, the micro-surface of various bitumen responded to chemicals in different ways. Regarding neat bitumen and TFOT aged bitumen, sharp angles and small particles occurred on the bitumen surface after chemical conditioning. The granules of polymer modified bitumen were decomposed and polished to smaller granules. The smooth surface of rejuvenated bitumen also seemed to grow rougher with more minor swellings.

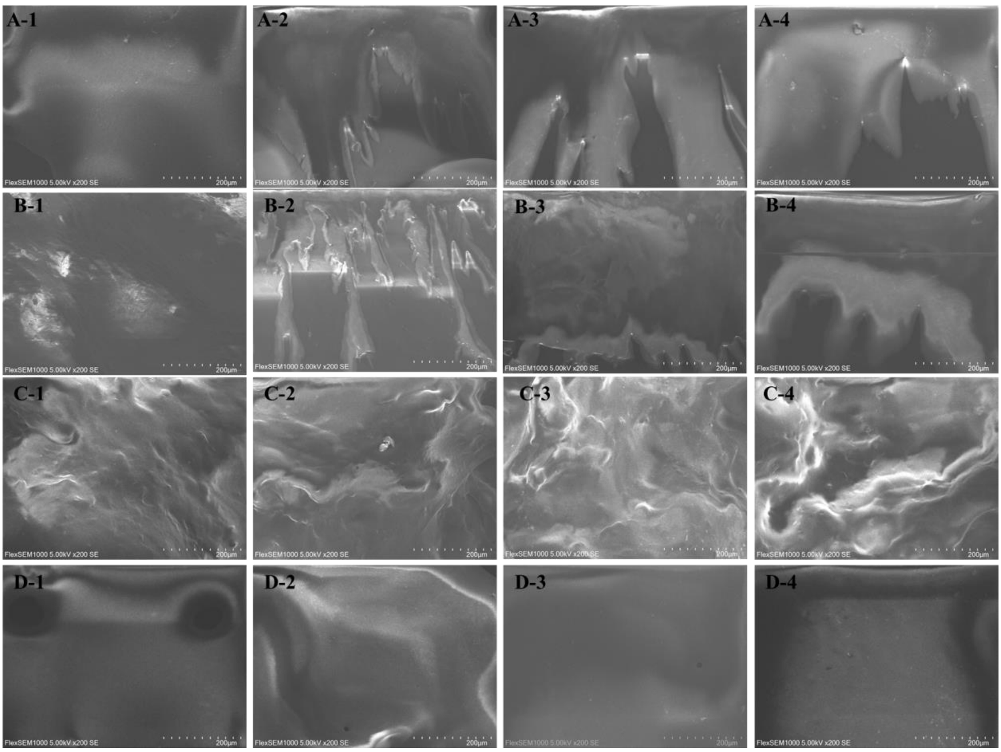

Figure 15. SEM images of bitumen under chemical conditioning (A-1: Original NB; A-2: NB-NaCl; A-3: NB-$CaCl_2$; A-4: NB-Acid. B-1: Original TB; B-2: TB-NaCl; B-3: TB-$CaCl_2$; B-4: TB-Acid. C-1: Original PMB; C-2: PMB-NaCl; C-3: PMB-$CaCl_2$; C-4: PMB-Acid. D-1: Original RB; D-2: RB-NaCl; D-3: RB-$CaCl_2$; D-4: RB-Acid.)

As shown in Figure 16, neat bitumen, aged bitumen and rejuvenated bitumen showed similar trends in softening point, resulting in increased high-temperature stability under chemical conditioning. Different from the three types of bitumen, the softening point of polymer modified bitumen was decreased by 8% after chemical conditioning, which indicates that the stability of PMB was reduced by chemicals. The opposite changes in softening point are attributed to the complex chemical structure and the decomposition of polymer groups of PMB. Besides, three chemicals had similar effects on the softening point of TB and PMB, which might be due to their stable structure. Comparing the influencing degree of the three chemicals on the high-temperature stability of all bitumen, NaCl had the most pronounced impact on BB and TB; $CaCl_2$ induced the most extensive changes on PMB; acid rain resulted in the highest softening point of RB.

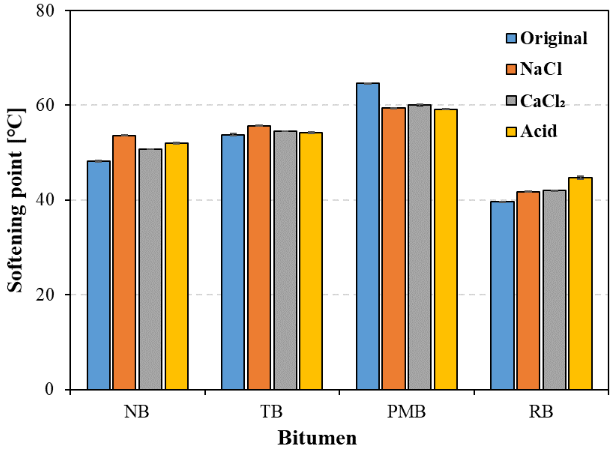

Figure 16. The softening point of bitumen versus chemicals

Figure 17 displays the dynamic viscosity of various bitumen after chemical conditioning. With the application of chemicals, the viscosity curves of neat bitumen, aged bitumen and rejuvenated bitumen shifted upward to various extents. These phenomena demonstrate that the sensitivity of bitumen (NB, TB and RB) viscosity remains unchanged, and the flow resistance of bitumen is improved after chemical conditioning. An evident different changing trend was observed for PMB: the slope of the PMB curve increased after chemical immersion. In specific, the flow resistance of PMB was increased at lower temperatures and decreased at higher temperatures after chemical conditioning, indicating the altered temperature sensitivity of PMB. This phenomenon is attributed to the complicated structure of PMB and the intricate reaction between bitumen and chemicals. In addition, similar effects of the three chemicals on the dynamic viscosity of TB and PMB are observed, whereas NaCl has the most significant impact on the dynamic viscosity of BB and RB.

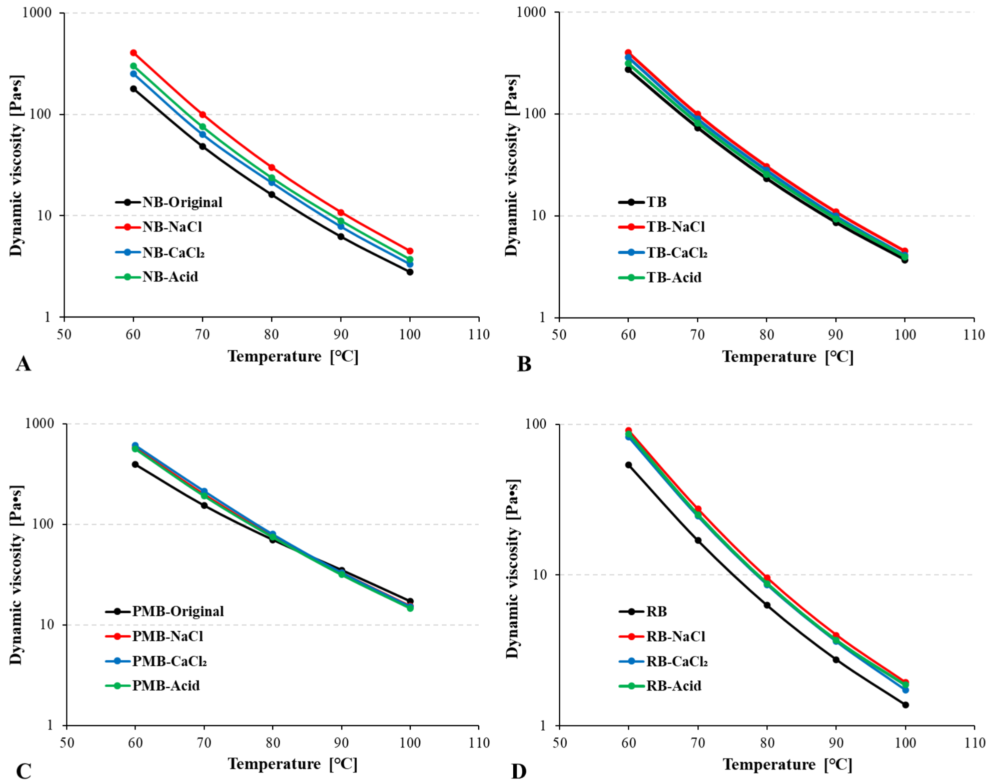

Figure 17. The dynamic viscosity of bitumen after chemical conditioning (A: NB; B: TB; B: PMB; C: RB)

The permanent deformation resistance and recovery behaviour of the bitumen influenced by chemicals shown in Figure 18 were evaluated by non-recoverable creep compliance (J_{nr}) and Recovery percent (%R), respectively. The higher J_{nr} and %R indicate more severe permanent deformation and better elastic behaviour of the bitumen. Figure 18 A, B and D show that the resistance to permanent deformation and recovery behaviour of BB, TB and RB were improved by the chemicals at two stress levels, which is in agreement with the ageing effect on bitumen (Wang et al., 2021; Zhang et al., 2018). Differently, the permanent deformation resistance (J_{nr}) at 0.1 kPa of PMB was slightly deteriorated by chemicals. J_{nr} at 3.2 kPa of PMB was enhanced, which is the same phenomenon as the other three types of bitumen. The recovery response at two stress levels of PMB also differed from that of the other three types of bitumen under chemical conditioning, that is, the recovery properties of PMB was worse than the original one without chemical immersion. In contrast with BB, TB and RB, the inverse changes in the permanent deformation behaviour of PMB are contributed to the demolishment of the internal structure and the degradation of existed polymer of PMB.

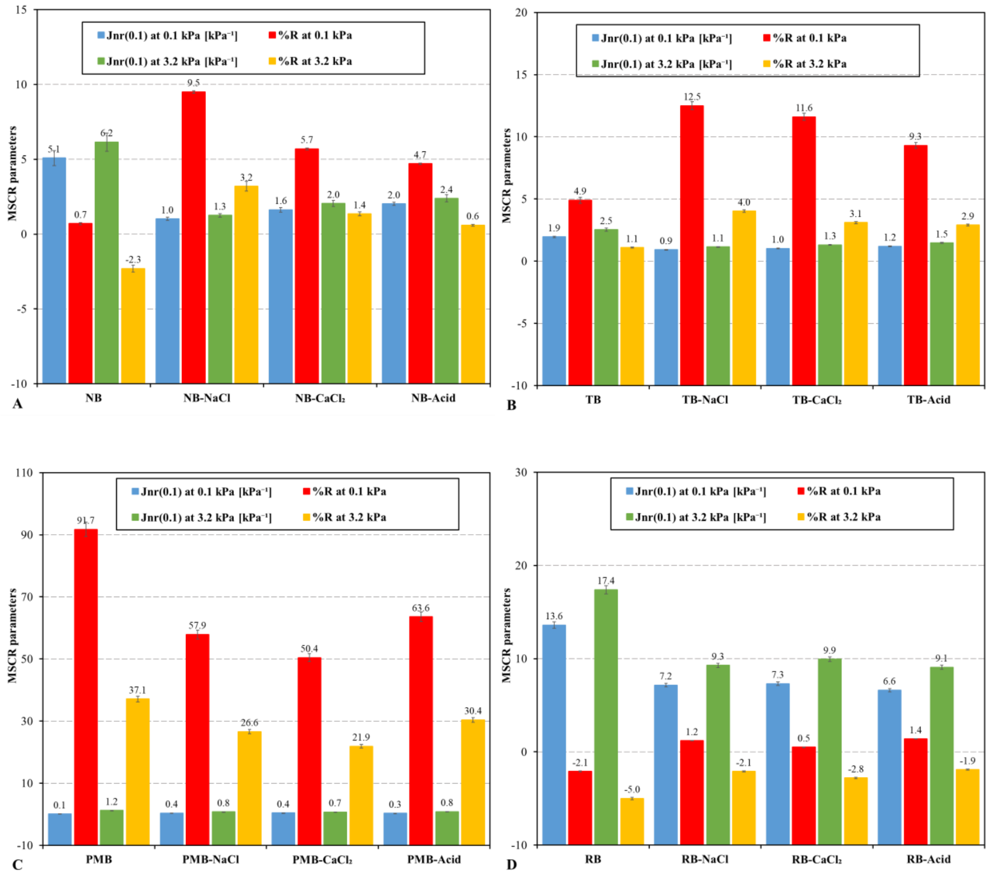

Figure 18. The J_{nr} and %R of bitumen under chemical conditioning (A: NB; B: TB; B: PMB; C: RB)

Integrating all property parameters together, PMB has the best resistance to chemicals, neat bitumen is the most susceptible type to chemicals, rejuvenated bitumen and short-term aged bitumen show moderate ability to resist chemicals. Additionally, NaCl, $CaCl_2$ and acid rain have the most severe impacts on neat bitumen and aged bitumen, polymer modified bitumen and rejuvenated bitumen, respectively.

4.3 Reaction mechanisms of four types of bitumen under chemical conditions

In order to reveal the influencing mechanism of chemicals on the different types of bitumen, the FTIR spectra of the bitumen are presented in Figure 19. Based on the changes in chemical functional groups, the main reaction mechanisms between the four types of bitumen and the three chemicals are summarised as follows. More details about the reaction mechanisms between various bitumen and different chemicals are introduced in Paper I, II and III.

Figure 19A illustrates the FTIR spectra of neat bitumen under different chemical conditions. Four functional groups of neat bitumen, C=C, N=H, C-OH and S=O, were greatly influenced by chemicals. As shown in Figure 19A, the peak of the S=O group located around 1030 cm^{-1} increased after chemical conditioning, which follows that oxidation occurred during the immersion process. The C-OH group located around 1133 cm^{-1} used for characterising the stability of bitumen was increased after NaCl and $CaCl_2$ conditioning and migrated to 1157 cm^{-1} after acid rain conditioning, which demonstrates that bitumen is stabilised during the immersion process and the acid rain induced different chemical reactions in neat bitumen compared to the two de-icing salts. Furthermore, the peaks of the C=C and N-H groups (located at 1579 cm^{-1} and 1540 cm^{-1}), the typical functional groups of asphaltenes, were increased under NaCl and $CaCl_2$ conditioning and integrated to one prominent peak under acid rain conditioning, indicating the polymerisation of the bitumen. The different changes in the C-OH, C=C and N-H groups caused by the de-icing salts and acid rain can explain the different changing degrees of bitumen performance after various chemical conditions. The three main mechanisms concluded above, oxidation, stabilisation and polymerisation, have the same tendency in affecting bitumen performance, resulting in neat bitumen being the most chemical sensitive type.

In terms of aged bitumen presented in Figure 19B, the peak of the S=O group at 1030 cm^{-1} became shaper under the condition of chemicals, resulting in a severe ageing degree of bitumen. The peak of the C-OH group (1133 cm^{-1}) was sharpened by NaCl and $CaCl_2$ and weakened by acid rain, which indicates the stability of aged bitumen was enhanced by the de-icing salts and deteriorated by the acid rain. The apparent changes in C=C and N-H groups (1579 cm^{-1} and 1540 cm^{-1}) of NaCl and acid rain immersed bitumen were observed compared to original aged bitumen, which contributes to the noticeable changes in physical and rheological properties. Diverse changes in the four functional groups account for the different changing degrees of bitumen performance exposed to various chemicals. The above phenomena show that oxidation, stabilisation and polymerisation mainly take place during the chemical process, which is the same as that of neat bitumen. Therefore, chemicals led to the same changing trend on properties of aged bitumen to neat bitumen. However, the reaction degree between aged bitumen and chemicals was less severe than neat bitumen and chemicals due to its more stable structure. Thus, aged bitumen was less susceptible to chemicals than neat bitumen.

Regarding the polymer modified bitumen shown in Figure 19C, the peaks of two specific groups (C=C at 966 cm^{-1} and C-H bond at 699 cm^{-1}) of PMB were weakened by the chemicals. This phenomenon is assigned to the decomposition of polymer within PMB. The decomposition has a reverse effect on bitumen properties compared to oxidation (Xu et al., 2020), which could be the reason for decreased softening point, the changed trend of dynamic viscosity, non-recoverable creep compliance and recovery percent of PMB after chemical conditioning. Another peak at 1030 cm^{-1} corresponding to the S=O group became obvious after chemical conditioning, indicating the more severe ageing degree of PMB. Due to the opposite effects of decomposition and oxidation on bitumen performance, PMB manifests the results of either decomposition or oxidation. This conclusion can reasonably explain the similar changing trend of PMB in penetration, phase angle, m-value, J_{nr} at 3.2 kPa, fatigue life, complex modulus, flexural creep stiffness (S), and oxidative groups and opposite changing tendency in surface characterisation, softening point, dynamic viscosity, J_{nr} at 0.1 KPa and %R. To some extent, the combination of decomposition effect and oxidation effect cancels each other out, leading to a PMB that is hardly affected by chemicals.

As observed in Figure 19D, two ageing indicators (S=O group at 1030 cm^{-1} and C=O group at 1704 cm^{-1}) of rejuvenated bitumen was increased considerably after chemical conditioning, indicating the severe ageing of bitumen. In contrast, acid conditioned bitumen had the most prominent peak of the S=O group among the three chemical conditioned bitumen, which results in the most significant impact of acid rain on rejuvenated bitumen. The appeared peak at 1704 cm^{-1} of acid conditioned bitumen also verifies its severe ageing level. Besides, two representative groups (C-O group located at 1174 and 1195 cm^{-1} and C=O group located at 1745 cm^{-1}) of esters are characteristic of the rejuvenator. It is observed that the two functional groups of the rejuvenator were barely affected by chemicals. This result can be assigned to its excellent resistance to chemicals. Under the function of oxidation and rejuvenator, the effect of the chemicals on the bitumen was reduced.

In brief, these different variations and changing trends in bitumen behaviour are originated from different reactions of various bitumen and chemicals. For neat bitumen, the oxidation, stabilisation, substitution reaction (from chapter 3) and polymerisation of bitumen simultaneously occurred under the chemical condition, which causes the severe ageing of the bitumen. Due to the more stable status of aged bitumen, the chemical effects on aged bitumen were faded. Besides, both decomposition and oxidation took place in PMB, resulting in a lowered ageing degree and the opposite trend in some properties. With the addition of the rejuvenator, the chemical effects on RB were reduced.

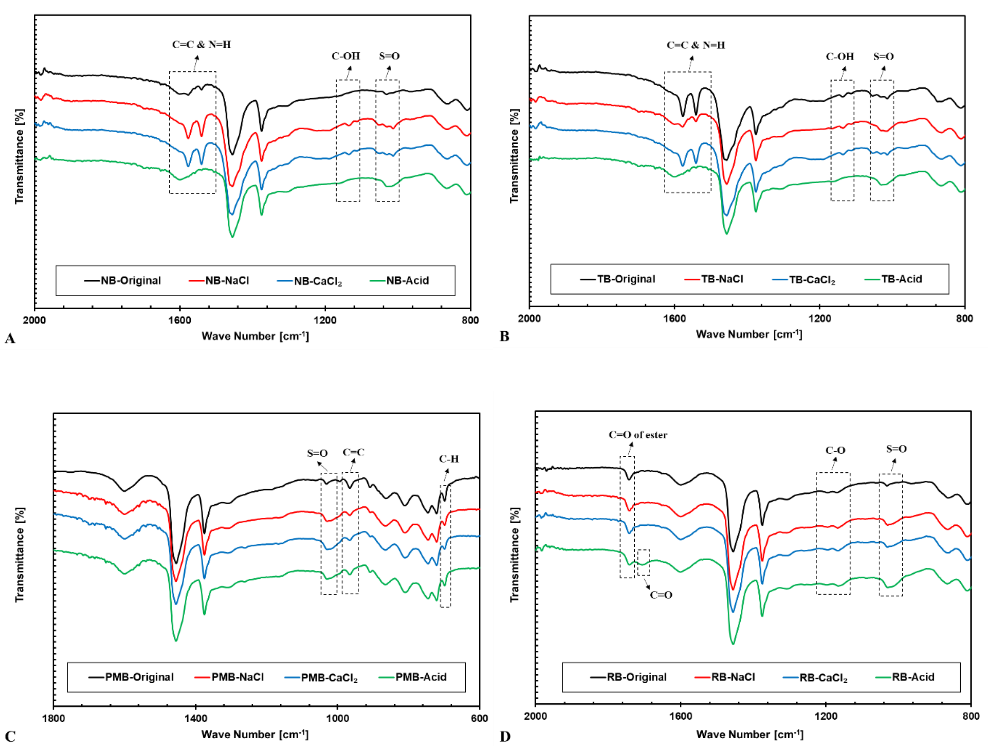

Figure 19. FTIR spectra of the four kinds of bitumen after chemical conditioning (A: neat bitumen; B: TFOT aged bitumen; C: Polymer modified bitumen; D: rejuvenated bitumen)

5. COMPARISON OF THERMAL-OXIDATIVE AGEING AND CHEMICAL AGEING ON BITUMEN

Based on chapter 3 and chapter 4, the chemical immersion has a similar impact on bitumen performance as traditional thermal-oxidative ageing, leading to a stiffer bitumen with more oxidizing functional groups. Based on this premise, the purpose of this chapter is to provide foundational knowledge for establishing chemical ageing standards by comparing thermal-oxidative ageing and chemical ageing on bitumen. To achieve this goal, the chemical ageing was selected to immerse neat bitumen samples in 10% NaCl, 10% $CaCl_2$ and simulated acid rain for 90 days. Thermal-oxidative ageing was chosen as TFOT ageing and PAV ageing. The morphology, oxygen content, physical properties and rheological properties of bitumen were mainly studied. The detailed description of this chapter is shown in Paper IV and II.

5.1 Morphology and oxygen content analysis

The morphology of bitumen at a magnitude of 50 times was captured by SEM. Figure 20 shows the SEM images of the bitumen before and after different ageing methods. It is observed that the bitumen surface after TFOT ageing was rougher with some smaller white particles and floccules compared to the neat bitumen surface. These particles and floccules result from the accumulation of large molecules within the bitumen. The bitumen surface was heavily cracked and deteriorated to numerous separated pieces by PAV ageing. These phenomena could be interpreted that the thermal oxidation ageing enhances the formation of large molecules resulting in a rough surface with a few cracks (Lu and Isacsson, 2000). In contrast, the bitumen samples after chemical ageing showed fewer differences than thermal-oxidative ageing. Sharp angles were distributed in the salt solution aged bitumen, and eroded bitumen surface with a few particles was obtained after acid rain immersion. These results imply that salt solution might deteriorate the outmost layer of the bitumen resulting in component segregation and certain residual salt crystals left on the bitumen surface; acid rain as a strong acid solvent significantly erodes the bitumen surface, decompose and recombine the components.

The oxygen content in the bitumen can quantitatively characterise the ageing degree of specimens. It is observed in Figure 20 that the bitumen after five types of ageing methods presented higher oxygen content than the neat bitumen, indicating severe ageing caused by five ageing methods. It is worth noting that the highest and lowest oxygen content were observed for PAV aged bitumen and acid rain aged bitumen, and two de-icing salt aged bitumen showed similar value in oxygen content. These results demonstrate the bitumen was oxidised to different extents by the five ageing methods. The ageing effect was in the order of PAV>NaCl>$CaCl_2$>TFOT>Acid rain.

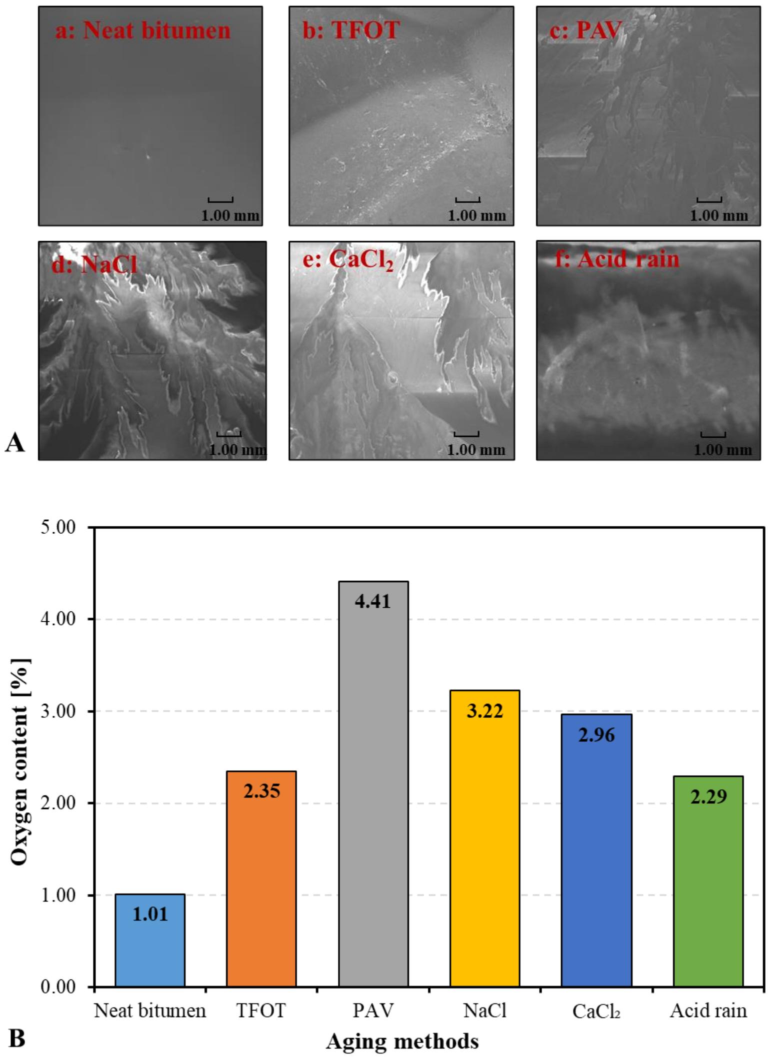

Figure 20. SEM images (A) and Oxygen content (B) of bitumen before and after ageing.

5.2 Physical properties

Figure 21 shows three physical variables of bitumen (penetration, softening point and viscosity) after different ageing methods. It is demonstrated that both thermal-oxidative ageing and chemical ageing showed the same influencing tendency in the physical parameters, demonstrating the decreased penetration, increased softening point and viscosity of the bitumen. However, the increment and decrement in the three variables are determined by ageing time, reaction mechanisms and reaction speed. Arranging the influencing rate in bitumen penetration caused by five kinds of ageing methods in descending order: PAV, NaCl, acid rain, $CaCl_2$ and TFOT; arranging the influencing rate in softening point in descending order: PAV, NaCl, TFOT, acid rain and $CaCl_2$; arranging the influencing rate in viscosity in descending order: PAV, NaCl, acid rain, $CaCl_2$ and TFOT. Combining the three orders, PAV has distinct ageing effect in bitumen physical properties, which is interpreted by the harsh ageing condition and long ageing period of PAV ageing. In contrast with PAV ageing, NaCl affects bitumen stiffness to the same extent but affects high-temperature stability and resistance against flowing to a smaller degree. Besides, TFOT, acid rain and $CaCl_2$ have almost identical impacts on three physical properties of bitumen, indicating their close ageing effects.

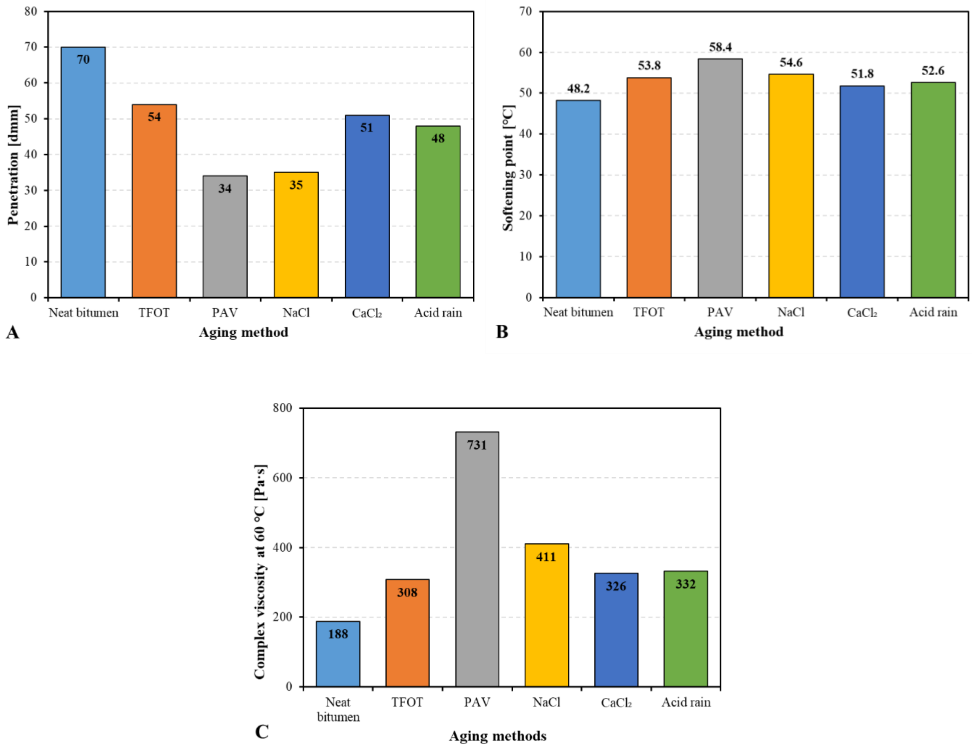

Figure 21. Three typical physical properties of bitumen (A: penetration; B: softening point; C: complex viscosity)

5.3 Rheological properties

The rheological properties of bitumen play a significant role in asphalt pavement performance (Huang, 1993). In this section, DSR and BBR tests were conducted to investigate the high-temperature and low-temperature rheological properties of bitumen, respectively. The master curves of complex modulus and phase angle, standard inputs for pavement design for the asphalt layer, are evaluated to contrast the effect of five methods on bitumen. The low-temperature rheological properties of bitumen under different ageing methods are studied by flexural creep stiffness (S) and stress relaxation ability (m-value) at 60 s.

The master curve of complex modulus and phase angle of the bitumen after different types of ageing was constructed in Figure 22. It is observed that the complex modulus curves of TFOT, NaCl, $CaCl_2$ and acid rain aged bitumen were slightly above the neat bitumen curve, while the curve of PAV aged bitumen shifted upwards than that of the other four aged bitumen. These phenomena demonstrate that TFOT, NaCl, $CaCl_2$ and acid rain had a slight and similar effect on the complex modulus of bitumen and the relationship between complex modulus and frequency (temperature). However, PAV has a notable impact on the master curve of bitumen, presenting a higher value of complex modulus and more severe frequency/temperature sensitivity. The above results indicate that both thermal-oxidative ageing and chemical ageing increase the deformation resistance of the bitumen. The descending order of deformation resistance of bitumen samples: PAV aged bitumen, NaCl aged bitumen, TFOT aged bitumen, acid rain aged bitumen, $CaCl_2$ aged bitumen, neat bitumen.

Regarding the master curve of phase angle, PAV ageing shifted the master curve of the phase angle of neat bitumen to the left, resulting in a lower phase angle under the same frequency. However, bitumen after TFOT, NaCl, $CaCl_2$ and acid rain ageing showed few changes at a lower frequency, but similar and apparent changes at a higher frequency with PAV aged bitumen. The above results indicate that PAV aged bitumen has a worse viscous behaviour than the other bitumen regardless of the frequency. However, TFOT, NaCl, $CaCl_2$ and acid rain aged bitumen samples have the worse viscous behaviour at a higher frequency and similar viscoelastic behaviour at a low frequency than neat bitumen.

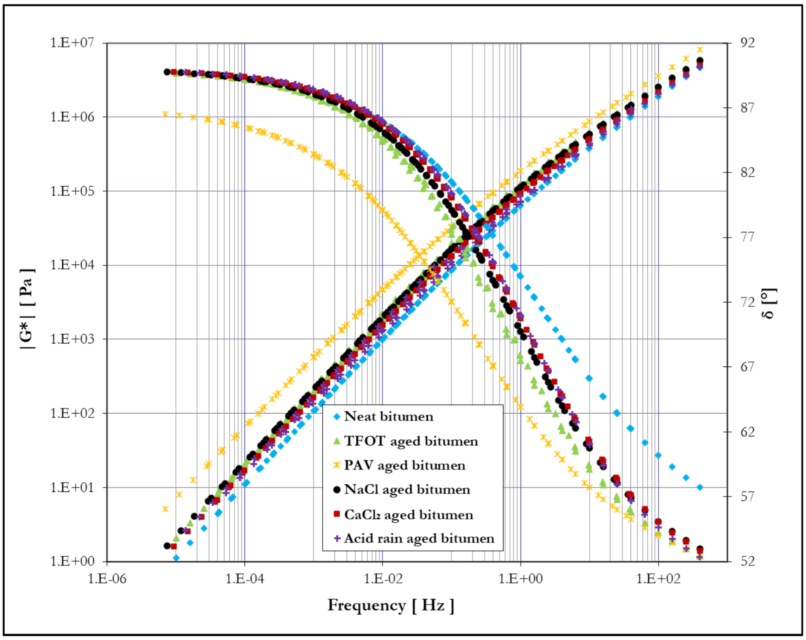

Figure 22. The master curve of complex modulus and phase angle

The low-temperature rheological parameters are presented in Figure 23. As the figure shows, both chemical and thermal-oxidative ageing increased the stiffness of bitumen and decreased the ability to relax stress to different extents. The increased stiffness and decreased resistance against relaxing stress at low temperature are susceptible to the presence of cracks, which is an undesired distress of asphalt pavement. PAV ageing has the most negative impact on S and m-value among all ageing methods, followed by NaCl, acid rain has a similar effect on the low-temperature rheological properties of bitumen as $CaCl_2$ and TFOT ageing.

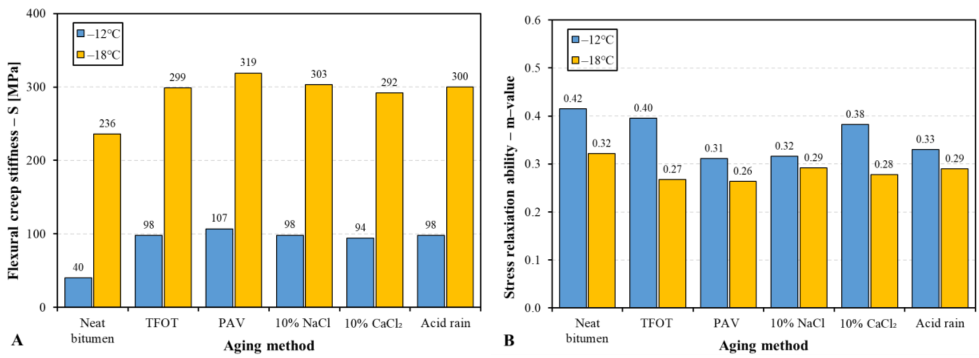

Figure 23. S (A) and m-value (B) of bitumen

5.4 Quantitative comparison of five ageing methods

The decrease in penetration, phase angle and m-value and the increase in softening point, viscosity, complex modulus and S are the results of bitumen ageing. This section aims to quantitatively evaluate the ageing degree of the five methods by an ageing factor (AF) (Wang et al., 2020) using available performance parameters shown in Table 8. AF is defined as the ratio of the changed value of each parameter to the value of neat bitumen, which is detailly introduced in Paper III. In all, PAV resulted in the highest ageing degree of bitumen (16.21), NaCl induced the severe ageing with the AF of 8.02, TFOT, $CaCl_2$ and acid rain had similar ageing effects on bitumen reflected by the closed AF values.

Table 8. Ageing degree of bitumen caused by the five ageing methods

Property parameter	TFOT	PAV	NaCl	$CaCl_2$	Acid rain
AF-Oxygen content	1.33	3.37	2.19	1.93	1.27
AF-Penetration	-0.23	-0.51	-0.50	-0.27	-0.32
AF-Softening point	0.12	0.21	0.13	0.07	0.09
AF-Viscosity	2.00	9.05	3.71	2.29	2.40
$\overline{AF}$-Complex modulus	0.75	1.75	0.49	0.35	0.28
$\overline{AF}$-Phase angle	-0.05	-0.10	-0.03	-0.02	-0.02
$\overline{AF}$-S	0.86	1.01	0.87	0.80	0.86
$\overline{AF}$-m-value	-0.11	-0.21	-0.17	-0.11	-0.15
Sum of absolute value of all AF	5.45	16.21	8.02	5.84	5.39

Overall, both thermal-oxidative ageing and chemical ageing make bitumen stiffer and aged. This result is verified by the morphology, oxygen content, physical and rheological properties of bitumen. However, the reaction mechanisms between thermal-oxidative ageing/chemical ageing and bitumen are different, leading to different changing degrees. The ageing mechanism of thermal-oxidative ageing (TFOT and PAV) is a combination of oxidation, volatilisation, exudation and physical hardening (Branthaver et al., 1993; Curtis et al., 1993; Petersen, 2000;

Traxler, 1961). Furthermore, PAV simulates the overall ageing of bitumen during the whole lifespan of asphalt pavement, which is expected to have the most severe ageing of bitumen. TFOT is designated to simulate the bitumen ageing when restoring, transporting and paving the asphalt pavement, presenting a slighter ageing degree. In light of chemical ageing, molecular and chemical reactions are occurred, presenting a modest ageing impact on bitumen. Therefore, PAV ageing has the dominant effect on bitumen performance, and chemical ageing has a similar effect on bitumen performance with TFOT ageing. The experimental design used in this research and the comparison results can provide theoretical bases for establishing bitumen solution ageing standards. For example, 90 days can be considered as the basic period when establishing the chemical/solution standard that entails the 10% chemical solution.

6. CONCLUSIONS

The objective of this doctoral thesis was to reveal the response of various bitumen exposed to three common chemicals. The research was conducted as part of efforts to improve the durability and service life of asphalt pavement. Several conclusions are summarised from this study.

The de-icing salt solutions were found to negatively affect the bitumen performance, including a rough bitumen surface, increased stiffness, worse fatigue crack resistance and deteriorated viscous behaviour. These alternations in bitumen properties were increased over immersion time. The impacts on bitumen properties were attributed to three reactions: the release of hydrogen from the bitumen to the de-icing salt solution, the displacement of Cl provided by the de-icing salt and the oxidation of the bitumen with oxygen. In comparison with calcium chloride, sodium chloride reacted more vigorously with the bitumen, resulting in a severe impact. These results suggest that de-icing salt is an environmental variable that can be considered when designing the asphalt pavement.

The simulated acid rain degraded bitumen in terms of morphological, physical, chemical and rheological properties. The changes in the bitumen properties were originated from two reaction mechanisms that occurred during the immersion process: oxidation and dissolution of carbonyl acid. The outcomes of oxidation were mainly the increased oxygen-containing groups. The dissolution of carbonyl acid typically resulted in fewer carbonyl acid groups within the bitumen and more hydrogen ions within the acid rain. Both oxidation and dissolution induced the rough bitumen surface, improved high-temperature stability, stiffness, deformation and rutting resistance and worse viscous characteristic of bitumen. Furthermore, the changes in bitumen properties were highly related to the erosion time. In addition, oxidation is the dominant action for neat bitumen during the erosion process; dissolution is the typical action for aged bitumen. Distinct dominating actions lead to different changing degrees of neat bitumen and aged bitumen to acid rain. The conclusions would provide a reference for understanding the distresses of asphalt pavement caused by acid rain.

Under environmental chemical conditions, different kinds of bitumen performed the same changing trends in penetration and rheological properties but to different degrees. The completely different changing tendencies in the bitumen surface, softening point, dynamic viscosity, non-recoverable creep compliance and recovery percent were found in the four kinds of bitumen. These various changes in bitumen performance are attributed to different reactions between the four kinds of bitumen and the three environmental chemicals. The oxidation, stabilisation, substitution and polymerisation of neat bitumen and aged bitumen during chemical conditioning make it the most chemical susceptible type to environmental chemicals. Compared to neat bitumen, aged bitumen is less prone to chemicals because of its more stable status. The decomposition and oxidation of polymer modified bitumen can resist the ageing caused by chemicals and lead to different phenomena compared to neat bitumen and rejuvenated bitumen. The oxidation is the major reaction of rejuvenated bitumen with chemicals, and the rejuvenator within rejuvenated bitumen can mitigate the ageing degree. Furthermore, sodium chloride, calcium chloride and acid have the most severe impact on neat bitumen and aged bitumen, polymer modified bitumen and rejuvenated bitumen. Besides, polymer modified bitumen presents the most outstanding chemical resistance, followed by rejuvenated bitumen and aged bitumen, and neat bitumen has the worst ability to resist the environmental chemicals. Selecting the proper bitumen type is critical for the durability and lifespan of asphalt pavement under different chemical conditions.

Through the comparison between thermal-oxidative ageing and chemical ageing effects on neat bitumen, it was found that the bitumen showed the same varying trends after chemical ageing and thermal-oxidative ageing in terms of oxygen content, physical properties and rheological properties. However, different effects on the morphology of the bitumen caused by chemical ageing compared to thermal-oxidative ageing were observed. Integrating all property parameters of bitumen, arranging the ageing degree in descending order: PAV > NaCl > acid rain ~ TFOT > $CaCl_2$. These different varying trends or varying degrees are due to various mechanisms between the five ageing methods and the bitumen. The ageing effect of chemical ageing (NaCl, acid rain or acid rain) on bitumen performance is almost equivalent to that of TFOT ageing.

According to the conclusions mentioned above, several proposals are provided to minimise pavement damage. Utilising calcium chloride instead of sodium chloride can mitigate the damage on bitumen during winter maintenance. Polymer modified bitumen is a better choice for pavement design in acid rain and snowy regions, but the higher cost might be a problem. Besides, a standard for chemical ageing on bitumen is required as its impact on bitumen performance is comparable with short-term ageing, and there are no specific standards for chemical ageing of bitumen.

7. RECOMMENDATIONS FOR FUTURE WORK

This research has investigated the effect of chemicals on bitumen and its mechanisms. The conclusions imply that chemical has an unignored effect on bitumen performance with complex reaction mechanisms, which can contribute to knowledge on how chemicals degrade bitumen. Such knowledge is the foundation for mitigating or diminishing the chemical damage on asphalt pavement and providing proposals to engineers or road administration.

- This thesis proposed polymer modified bitumen as the best option to resist chemical conditions. For further studies, it is recommended to find additives to enhance the chemical resistance of bitumen and asphalt concrete.
- In the field, not only chemicals but also other external environmental factors can age bitumen and asphalt concrete. Thus, future work should take all potential factors into account to study the importance of chemicals to all factors. If chemicals only accounted for a tiny proportion of the total damage, the chemical effect can be ignored or transferred to a coefficient of all factors. Otherwise, the chemical effect should be individually considered for developing a mechanistic-empirical pavement design system.
- Numerous studies designed the specific chemical immersion method with different immersion cycles, film thickness and chemical concentrations (Fakhri et al., 2019; Yang et al., 2020); (Shu et al., 2020; Zeng et al., 2018). Thus, a standard chemical process should be provided for all scholars based on practical situations. Moreover, the long-term immersion of chemicals on bitumen is challenging to perform for most researchers. Thus, an accelerated long-term chemical immersion is required to save excessive waiting time.

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APPENDIX A – PAPER I

Xuemei Zhang, Hao Chen and Inge Hoff (2021)

The mutual effect and reaction mechanism of bitumen and de-icing salt solution.

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The mutual effect and reaction mechanism of bitumen and de-icing salt solution

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ABSTRACT

The two most used de-icing salts, sodium chloride and calcium chloride are detrimental to asphalt pavements during winter maintenance. However, limited research focused on the effect and mechanism of de-icing salt on bitumen. To fill the gap, this research aims to investigate the mutual effect and reaction mechanism between bitumen and de-icing salt solutions. 10% NaCl and 10% $CaCl_2$ solutions were prepared to immerse neat bitumen and aged bitumen for 7, 28, and 90 days, respectively. The pH value of the salt solution, the morphology and element analysis, chemical structure, and rheological properties of the bitumen were evaluated by pH meter, scanning electron microscope with energy dispersive spectrometer (SEM-EDS), Fourier transform infrared (FTIR) radiation spectrometer with an attenuated total reflectance (ATR), and dynamic shear rheometer (DSR), respectively. After the immersion process, the pH value of the salt solution can decrease to 4.33; the bitumen surface became rougher, and O content of bitumen increased by 2%, around 1% Cl and Na/Ca element appeared; S = O, C = O, C-OH, C-Cl functional groups increased by up to 60%; and the bitumen showed sufficient deformation resistance and worse viscous behaviour. According to the test results, the reaction mechanism between bitumen and de-icing salt solutions was summarized into three sub-mechanisms: the release of hydrogen ions from the bitumen into the solution; the substitution reaction of Cl provided by de-icing salt; and the oxidative reaction between bitumen and oxygen.

1. Introduction

The asphalt pavement is the most used paving structure. Its service life and durability are thus critical based on safety and economic considerations. In winter conditions, however, the appearance of snow or ice on the asphalt pavement is not desirable for driving. Therefore, the application of de-icing salts is used to prevent snow or ice for providing drivable and safe road conditions [1]. Usually, sodium chloride and calcium chloride are the best choices of de-icing salts due to their outstanding effectiveness and low cost [2,3]. However, a long-term immersion in a de-icing salt solution will inevitably influence the performance of asphalt pavement.

Many studies have found that de-icing salts had adverse impacts on asphalt concrete [4–6]. The effect of de-icing salts (NaCl and $CaCl_2$) or the coupling effect of salt and freeze–thaw cycles on asphalt concrete has been investigated. It was found that the volumetric properties of asphalt concrete were significantly affected by de-icing salt, resulting in the increased mass loss and porosity, as well as a decreased density [7]. The de-icing salts also have negative impact on the morphology of asphalt concrete, resulting in scaling and worn edges of the asphalt concrete [8]. These changes in morphology of asphalt concrete are consistent with the changes in volumetric properties. Furthermore, the variations in morphology and volumetric properties of the bitumen would cause different outcomes in mechanical performance of asphalt concrete. For example, the decreased dynamic modulus of elasticity, compressive strength, Marshall stability, and pull-off tensile strength of asphalt concrete were obtained after de-icing salt solution immersion. The deterioration on asphalt concrete performance finally led to the stripping, cracking, and permanent deformation of asphalt pavement [9–12]. Thus, the deterioration mechanism of de-icing salts on asphalt concrete is mainly thereduced adhesion between bitumen and aggregates [13–15].

Furthermore, a few studies also investigated the effect of sodium chloride on bitumen performance, which focused on the rheological properties, adhesion, and cohesion of bitumen [16–19]. They found that sodium chloride solution immersion improved the high-temperature properties of bitumen. However, the low-temperature properties and cohesion of bitumen were reduced, the adhesion between bitumen and

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aggregates was deteriorated. Overall, less attention has been paid to the effect of calcium chloride on bitumen, although calcium chloride is one of the most commonly used de-icing salts. In addition, very few studies have drawn attention to the distress mechanism of de-icing salt on bitumen.

Therefore, this research aims to study the mutual effect between de-icing salt solution and bitumen and its reaction mechanism. Two types of de-icing salts were prepared: 10% NaCl and 10% $CaCl_2$ solutions. Two states of bitumen were used to be immersed in the salt solution for a specific time (7, 28, and 90 days): neat bitumen and TFOT aged bitumen. The pH value of de-icing salt solution, morphology, element content, chemical composition, and rheological properties of bitumen were analysed to investigate the mutual effect and reaction mechanism between bitumen and de-icing salt solution.

2. Materials and methods

2.1. Bitumen

Two kinds of bitumen were used in this research: neat bitumen (N) and TFOT aged bitumen (T) according to NS-EN 12607–2:2014. The basic properties of bitumen are shown in Table 1.

2.2. Salt solution

10% NaCl and 10% $CaCl_2$ solutions by weight were prepared by mixing distilled water with NaCl and $CaCl_2$ solids. NaCl and $CaCl_2$ solids are obtained from companies VWR Internal BVBA and Honeywell Fluka™, respectively.

2.3. Immersion process

Each bitumen sample is 28±0.2 g paved in a petri dish with a diameter of 190 mm. The preparation of bitumen samples for solution immersion is stated as follows: a uniform bitumen film was prepared to be immersed in 150 ml salt solution, then isolating bitumen and salt solution from light and external oxygen using a black plastic bag. The prepared bitumen immersing in salt solution was placed at 25 ℃ for 7, 28, and 90 days. After the immersion process, the salt solution was collected in a plastic cup for subsequent testing, bitumen was cleaned and dried to a constant weight for the next steps.

2.4. Evaluation methods

2.4.1. pH value analysis

The pH values of the salt solution before and after the immersion process were tested by the pH 1000H meter. The measuring range is −2 to 20, and the resolution of this pH meter is 0.01. The pH value inversely indicates the concentration of hydrogen ions in the solution. A lower pH indicates a higher concentration of hydrogen ions, which is defined by Formula 1:

$$\mathrm{pH} = -\log_{10}(a_{H^+}) = \log_{10}\left(\frac{1}{a_{H^+}}\right) \tag{1}$$

where a_{H^+} indicates the hydrogen ion activity in a solution.

2.4.2. Morphology and element analysis

The morphology of bitumen with and without salt solution immersion was captured using Scanning Electron Microscope (FlexSEM 1000) at a magnification of 100 times. The element analysis was performed using Energy Dispersive Spectrometer (EDS). It is noted that the elemental analysis of each bitumen sample is tested with three replicates, and the averaged value is used in this research.

2.4.3. Chemical structure analysis

The chemical bond test of bitumen was carried out by Nicolet 8700 Fourier transform infrared (FTIR) radiation spectrometer with an attenuated total reflectance (ATR) accessory. Bitumen samples were tested in an atmosphere without moisture and carbon dioxide conducted by Parker Balston 74–5041 FTIR Purge Gas Generator. The wavelength range between 400 cm^{-1} and 4000 cm^{-1} was then obtained with a 4 cm^{-1} resolution. The chemical structure changes during the immersion procedure would be characterized by identifying the specific functional group. In this research, qualitative analysis was performed by observing the transmittance of peaks, and quantitative analysis was performed through the difference in absorbance (Δ_A) of functional groups shown in Formula 2 [20,21]:

$$\Delta_A = \frac{A_{N/T,D} - A_{N/T}}{A_{N/T}} \times 100\% \tag{2}$$

where Δ_A is the difference in absorbance (%), $A_{N/T}$ is the absorbance of neat/aged bitumen, $A_{N/A,D}$ is the absorbance of neat/aged bitumen after D days immersion.

2.4.4. Rheological property analysis

The rheological properties of the bitumen samples were measured by Dynamic Shear Rheometer. The bitumen thickness, the diameter of parallel plates, and the loading rate were 2 mm, 8 mm, and 10 rad/s, respectively. In this case, testing of phase angle and complex modulus at 5 ℃ and 20 ℃ was carried out to characterize the rheological properties of bitumen.

Table 1
Basic properties of bitumen.

Properties	Unit/location	Neat bitumen	TFOT aged bitumen	Test standard
Penetration (25 °C)	0.1 mm	72	58	NS-EN 1426:2015
Softening point	℃	47.8	54.0	NS-EN 1427:2015
The absorbance (A) of functional groups	S=O (1030 cm^{-1})	0.061	0.065	FTIR analysis
	C=O (1720 cm^{-1})	0.018	0.023	
	C-Cl (745 cm^{-1})	0.020	0.019	
	C-OH (1133 cm^{-1})	0.055	0.060	

3. Results and discussions

3.1. pH value of solution

The concentration of NaCl and $CaCl_2$ solutions might change over immersion time during the immersion process. The concentration of the salt solution was found to influence its pH value [22,23]. Thus, in order to meticulously study the effect of the immersion process on the solutions' pH value, a test was carried out to characterize the pH values of salt solutions with different concentrations shown in Fig. 1. Three main results were obtained in Fig. 1: the pH values of 10% NaCl and 10% $CaCl_2$ solutions were not completely equal to 7 in reality; the pH value of NaCl solution increased with the increasing concentration; while the pH value of $CaCl_2$ solution decreased with the increasing concentration. These findings provide basics for subsequent research.

The deveolpment of the pH value of NaCl solution over immersion time is recorded and shown in Fig. 2. The initial pH value of 10% NaCl solution was neutral with a pH of 6.94. While the pH values of the NaCl solution after immersing neat and aged bitumen 7 days decreased to 6.70 and 6.60, then slightly increased to 6.91/6.84 after 28 days, they finally dropped to the lowest values after 90 days (4.33/4.47).

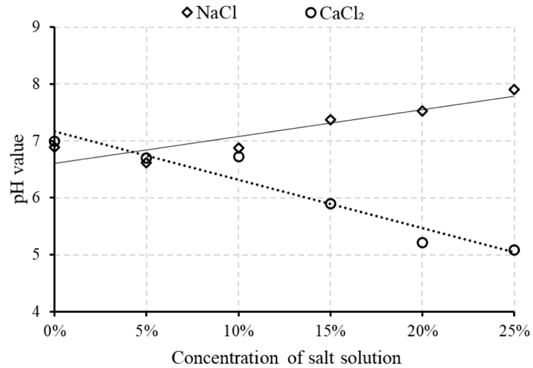

Fig. 1. The pH values of salty solutions with different concentrations.

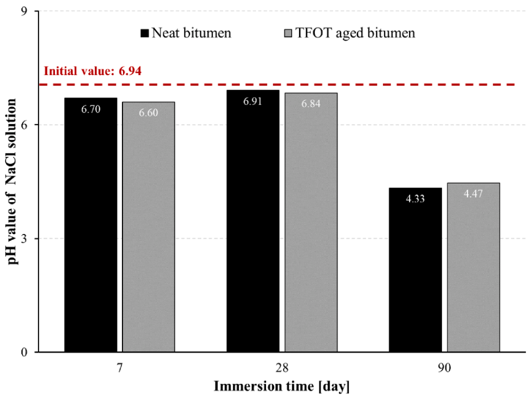

Fig. 2. The pH values of NaCl solution versus immersion time.

Therefore, the pH value of NaCl solution generally decreased with the increasing immersion time, which indicates that a higher concentration of hydrogen ions can be generated through the immersion process. In other words, some hydrogen ions were emitted from bitumen to NaCl solution. This conclusion is also confirmed by the results from Fig. 1. Even though the NaCl concentration increased because of water evaporation, the pH value of NaCl solution should have increased based on the results from Fig. 1. However, the pH value of the NaCl solution in Fig. 2 finally decreased. It is also worth mentioning that the increased pH value after 28 days is attributed to the increased concentration of NaCl due to water evaporation. Comparing the pH values of the NaCl solution after immersing neat bitumen and aged bitumen for 90 days (4.33 and 4.47), neat bitumen has a more significant influence on the pH value of the NaCl solution than aged bitumen. This conclusion can be interpreted that neat bitumen as a less stable bitumen would release more hydrogen ions than aged bitumen.

Fig. 3 shows the pH values of the $CaCl_2$ solution over immersion time. The pH evolution of the $CaCl_2$ solution is slightly different from that of NaCl solution. The initial pH value of 10% $CaCl_2$ solution was 6.72. The pH value of $CaCl_2$ solution gradually decreased with increasing immersion time irrespective of bitumen type. This result indicates that the immersion process continously induces more hydrogen ions within the $CaCl_2$ solution continuously, i.e., bitumen emits certain hydrogen ions to the $CaCl_2$ solution. In order to confirm whether the decreased pH value was mainly caused by bitumen instead of increased concentration of the $CaCl_2$ solution, the concentration of the $CaCl_2$ solution after 90 days should be provided. The mass loss of the $CaCl_2$

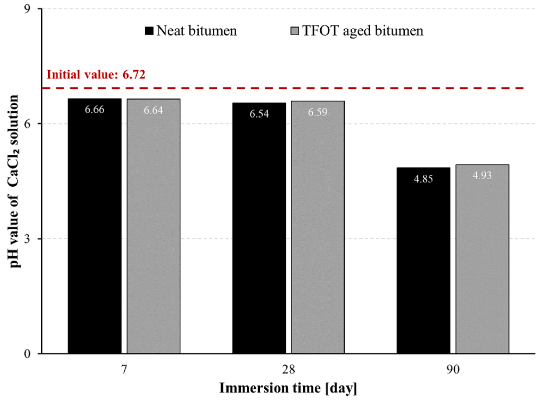

Fig. 3. The pH value of $CaCl_2$ solution versus immersion time.

solution after 90 days was 10 g, which means the concentration of the $CaCl_2$ solution is approximately 11%. However, the pH value of 11% $CaCl_2$ solution should be 6.2 shown in Fig. 1, while the practical pH value of $CaCl_2$ after 90 days were 4.85 (neat bitumen) and 4.93 (aged bitumen), which is far less than 6.2. This result implies the decreased pH value of the salt solution is mainly a result of the emission of hydrogen ions from bitumen. Besides, comparing the effect of neat and aged bitumen on the pH value of the $CaCl_2$ solution, neat bitumen affected the pH value of the $CaCl_2$ solution significantly, which is conformant to NaCl solution. This result implies that neat bitumen tends to ionize more hydrogen ions during the immersion process.

Comparing Fig. 2 and Fig. 3, the pH value of NaCl solution changed more over immersion time than that of $CaCl_2$ solution, which indicates the NaCl solution was more affected by bitumen. Moreover, the reaction of neat bitumen and NaCl solution is more severe than that of aged bitumen and NaCl solution.

3.2. Morphology and element content of bitumen

The morphology of the bitumen influenced by NaCl and $CaCl_2$ solutions is shown in Fig. 4. From Fig. 4A and 4D, neat bitumen (N) showed a relatively smooth surface. In contrast, aged bitumen (T) showed a rougher surface with individual particles. This phenomenon is due to the higher stiffness caused by TFOT aging [24]. In addition, the salt solutions also induced the rough surface of bitumen with certain particles for both neat bitumen and aged bitumen after 90 days immersion. The roughness of bitumen after immersion in NaCl solution is greater than that of the bitumen after immersion in $CaCl_2$ solution, as seen by comparing Fig. 4 B/E and C/F. These phenomena indicate that both NaCl and $CaCl_2$ solutions will deteriorate the micro-structure of bitumen leading to rough bitumen surface, while NaCl solution has a more adverse effect on bitumen morphology.

In order to characterize the distribution and content of typical elements in bitumen, element analyses of bitumen before and after long-term immersion in salt solutions are presented in Table 2. C, H, O, N, and S elements as the typical elements in bitumen should be tested by element analysis. While the molecular mass of H is too small to be detected by EDS apparatus and the N element only accounts for a relatively small part of the bitumen composition [25,26]. Therefore, it showed that C, O, and S are the typical elements within bitumen from Table 2. Aged bitumen showed a higher percentage of O and S and less C content compared to neat bitumen. This result could be interpreted that the oxidation of bitumen induces more O and S, the percentage of C thereby decreases [27]. Under the immersion of 10% NaCl solution, the percentage of O, S, and N in bitumen increased, Na and Cl elements were detected. After $CaCl_2$ solution immersion, the O, S, and N content

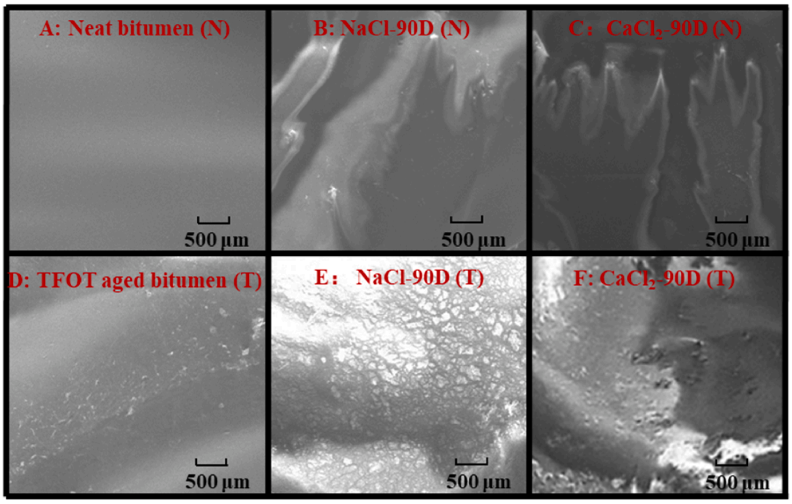

Fig. 4. The micro-surface of bitumen at o and 90 days.

Table 2
Element analysis of bitumen under different conditions.

Bitumen	Salt solution-immersion time	Element content [%]						
		C	O	S	N	Cl	Na	Ca
Neat bitumen	Original	98.6	1.0	0.4	–	–	–	–
	10%NaCl-90D	93.2	3.2	2.0	–	0.7	0.9	–
	10%CaCl₂-90D	93.8	3.0	2.2	–	0.6	–	0.4
TFOT aged bitumen	Original	96.1	2.4	0.6	0.9	–	–	–
	10%NaCl-90D	86.7	4.3	6.4	1.3	1.0	0.4	–
	10%CaCl₂-90D	87.2	4.0	6.2	1.3	0.8	–	0.5

increased, Cl and Ca appeared. The increased content of O element means that the bitumen was oxidised during the immersion process. The increased S and N elements caused by salt solution immersion could be interpreted that the S and N elements normally exist in asphaltene and resins of bitumen which indicates that bigger molecules appear in bitumen after long-term salt immersion [28]. Besides, the addition of Cl, Na/Ca elements within the bitumen indicates that salt immersion would leave certain substances of solution in the bitumen. Therefore, the above results indicate that both the NaCl solution and $CaCl_2$ solution will promote the oxidation of bitumen and add new elements in bitumen. Compared with the bitumen immersed in the $CaCl_2$ solution, the bitumen after NaCl solution immersion consisted of a higher percentage of O and Cl elements. This phenomenon means 10% NaCl solution has a more significant effect on bitumen elements.

3.3. *Chemical structure of bitumen*

To analyse the chemical composition of bitumen under NaCl and $CaCl_2$ solution immersion, the FTIR spectra (transmittance versus wave number) was depicted in Fig. 5. Four peaks were used to characterize the changes in chemical structure of bitumen during NaCl solution or $CaCl_2$ solution immersion process, which are located at 745 cm^{-1}, 1030 cm^{-1}, 1720 cm^{-1}, and 1133 cm^{-1}. The details of four peaks are presented in Table 3. C–H bond in bitumen is easily broken and replaced by Cl atoms provided by NaCl and $CaCl_2$, resulting in the C-Cl group located at 745 cm^{-1} based on previous Refs. [29,30]. S=O and C=O are two typical functional groups indicating the oxidation degree of bitumen [31], as the oxidation might also appear during the immersion process. The C-OH group at 1133 cm^{-1} indicates the plan deformation of tertiary alcohol, tertiary alcohol is the most stable alcohol and is difficult to be oxidized [32]. Thus, the C-OH group at 1133 cm^{-1} indicates the stability of bitumen.

As seen from Fig. 5C, aged bitumen showed more pronounced peaks of S=O, C=O, and C-OH groups than flat peaks of neat bitumen. However, the immersion in NaCl solution or $CaCl_2$ solution sharpened four peaks over immersion time irrespective of bitumen state. These results indicate that the salt solution immersion in NaCl and $CaCl_2$ solutions leads to the replacement of Cl, increased aging degree, and more stable bitumen. The influencing degree increases with increasing immersion time.

In order to quantitatively study the evolution of functional groups during the immersion process, the differences in absorbance of four functional groups versus immersion time in the NaCl and $CaCl_2$ solutions are shown in Fig. 6. From Fig. 6A and 6B, it was found that the absorbance difference of four functional groups increased over immersion time in NaCl solution, which indicated that the content of four functional groups increased as immersion time increases. These results demonstrate that the NaCl solution immersion enhances the replacement of Cl, the aging degree, and the stability of bitumen, which are in line with the results obtained from element analysis. Among four functional groups, C=O group was significantly affected, and C-Cl group was slightly affected by salt solution. Besides, the difference in absorbance of neat bitumen after long-term (90 days) immersion is almost three times as large as that of aged bitumen. This result could be interpreted as a more stable chemical structure in aged bitumen so that the aged bitumen samples are hardly affected by NaCl solution.

In terms of the effect of the $CaCl_2$ solution on functional groups, the results are shown in Fig. 6C and Fig. 6D and demonstrate similar changes as that of the 10% NaCl solution. Due to the addition of the $CaCl_2$ solution, the difference in absorbance of four functional groups increased, and they increased with the immersion time for both neat and aged bitumen. These results indicate that the $CaCl_2$ solution promotes the replacement of Cl, the aging degree, and the stability of bitumen. Meanwhile, C=O group is the most sensitive group to $CaCl_2$ solution among the four groups, since the absorbance difference of this group is the biggest among the four typical groups. Besides, neat bitumen is more sensitive to the $CaCl_2$ solution than aged bitumen, as the difference in absorbance of unaged samples is almost twice that of aged samples. This outcome is also conformant with the results from the pH value analysis of salt solutions.

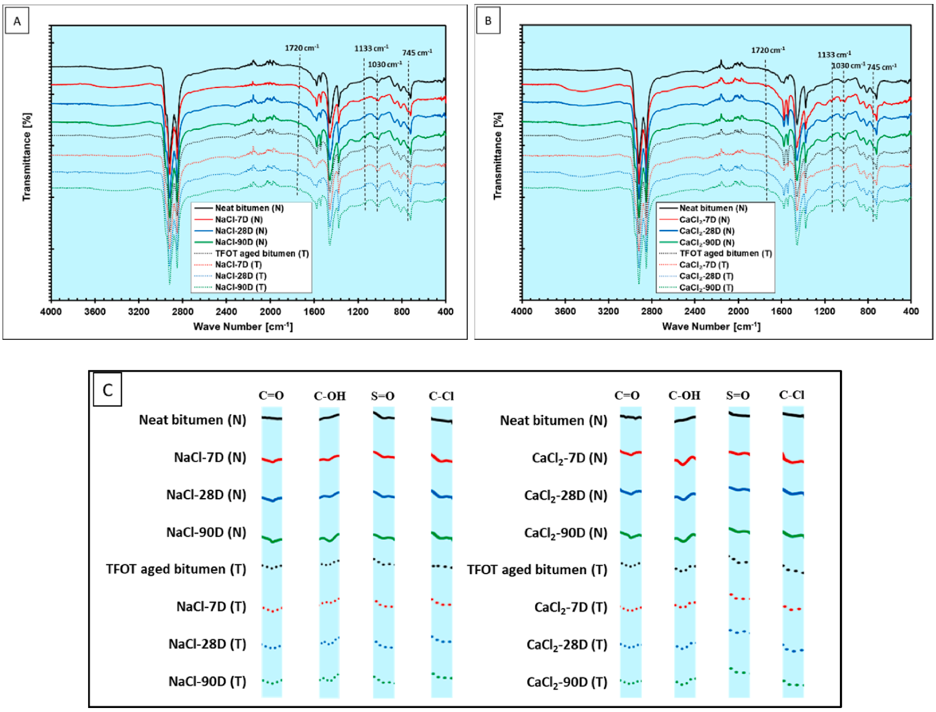

Fig. 5. The FTIR spectra of bitumen before and after NaCl solution immersion (A)/$CaCl_2$ solution immersion (B)/the magnification of four peaks (C).

Table 3
Basic information of four functional groups.

Peak position	Functional group	Details	Indication
745 cm^{-1}	C-Cl	Stretching	Replacement of Cl
1030 cm^{-1}	S=O	Sulfoxide group, stretching	Oxidation
1720 cm^{-1}	C=O	Carbonyl group, stretching	
1133 cm^{-1}	C-OH	Tertiary alcohol, plan deformation	Stability

The four functional groups showed similar variations on absorbance difference after NaCl and $CaCl_2$ solutions immersion, while the differences in absorbance of neat bitumen over immersion time in NaCl solution were almost 20% higher than that in $CaCl_2$ solution. These results indicate that both NaCl and $CaCl_2$ solutions have the same influencing trends on bitumen's chemical composition, leading to more replacement of Cl, adverse aging degree, and more stable structure of bitumen which are in line with the results obtained from element analysis. However, the NaCl solution has a more significant effect on the chemical composition of bitumen compared to the $CaCl_2$ solution.

3.4. Rheological properties of bitumen

The complex modulus at 5 ℃ and 20 ℃ versus immersion time in the NaCl and $CaCl_2$ solutions is shown in Fig. 7. As seen from this figure, the complex modulus of bitumen at 5 ℃ was generally 12000 kPa higher than that at 20 ℃, and aged bitumen behaved higher complex modulus than neat bitumen. These results indicate that bitumen at low temperature and aged bitumen perform better resistance to deformation [33,34]. Observing the relationship between rheological parameters with immersion time in salt solution, it is evident that the immersion in salt solution increases the complex modulus regardless of bitumen state. Also, the complex modulus increased with immersion time. These results indicate that salt solution and immersion time affect the rheological behaviour of bitumen significantly, resulting in better ability to resist deformation. The NaCl solution increased the complex modulus of bitumen by 21% after 90 days immersion. In contrast, the $CaCl_2$ solution increased the complex modulus of bitumen by 18% after 90 days immersion. These results indicate that the NaCl solution has a more significant effect on the complex modulus of bitumen than the $CaCl_2$ solution. In addition, neat bitumen after salt immersion changed obviously than aged bitumen in terms of the complex modulus, which means that the deformation resistance of neat bitumen is more sensitive to salt immersion than that of aged bitumen.

Additionally, the phase angle influenced by salt solution is depicted in Fig. 8. It shows that bitumen had a bigger phase angle at higher temperature (20 ℃), and TFOT aged bitumen had a smaller phase angle than unaged bitumen. These results demonstrate that a better viscous behaviour of bitumen is obtained at higher temperature, and aged bitumen has a better elastic behaviour compared to neat bitumen [35]. The addition of NaCl/$CaCl_2$ solution resulted in reduced phase angle, and the phase angle increased over immersion time. These results indicate that salt solution induces worse viscous behaviour of bitumen, and the viscous behaviour decreases with increasing immersion time. Comparing the effect of NaCl and $CaCl_2$ solutions on phase angle of bitumen, it was found that the similar phase angles were obtained after NaCl and $CaCl_2$ solutions immersion. This phenomenon indicates $CaCl_2$ and NaCl solutions have similar effects on the viscoelastic behaviour of bitumen. In addition, the phase angle of neat bitumen after long-term immersion (90 days) approximately decreased by 2.8, while the phase angle of aged bitumen after 90 days immersion approximately decreased by 1.4. These results indicate that the phase angle and the viscoelastic ratio of neat bitumen are more heavily affected by de-icing salt solution

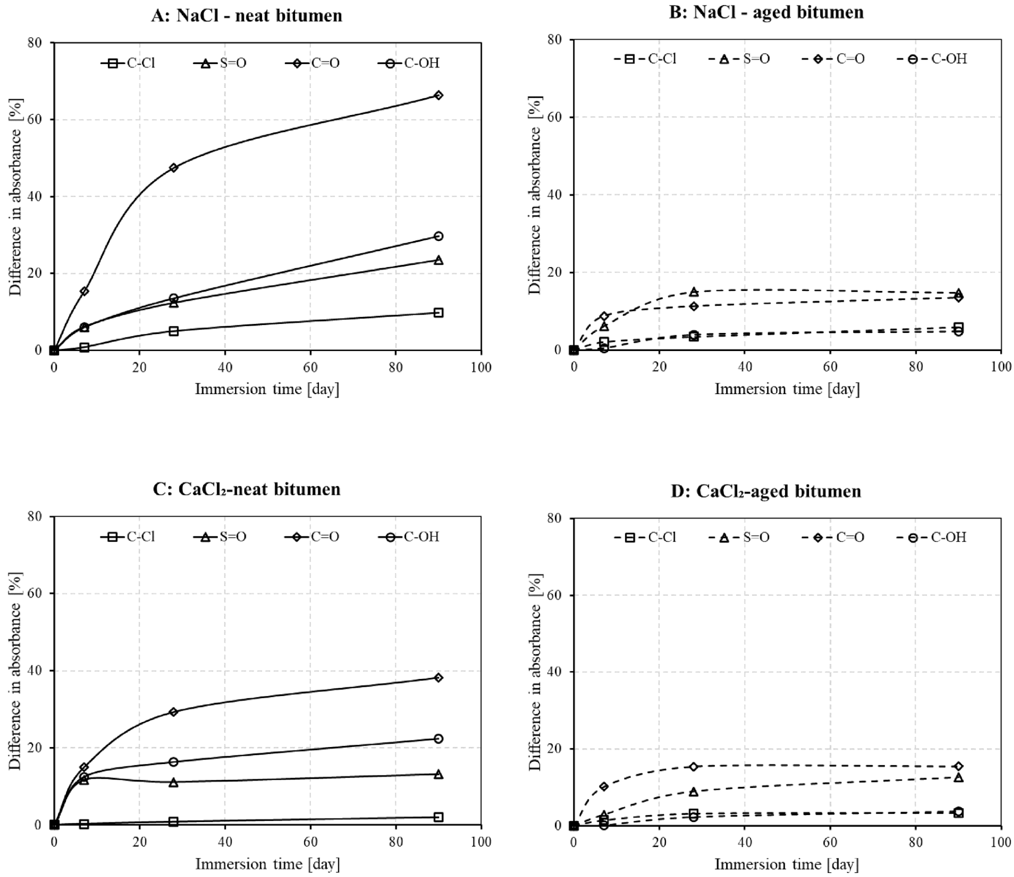

Fig. 6. The absorbance difference of four typical groups versus immersion time in NaCl/$CaCl_2$ solution.

than aged bitumen.

In all, the NaCl solution caused a more significant difference in the deformation resistance of bitumen compared to the $CaCl_2$ solution, while the NaCl solution had a similar effect on the viscoelastic behaviour of the bitumen as the $CaCl_2$ solution. Additionally, neat bitumen is more affected by salt solution than aged bitumen, which is in line with the results from pH value of solution, element analysis, and chemical composition analysis.

4. Reaction mechanism between bitumen and de-icing salt solution

Based on the above results, the reaction mechanisms of NaCl/$CaCl_2$ and bitumen were organized as follows. Firstly, organic acid releases hydrogen ions from the bitumen to the solution during the immersion process. At the same time, Na or Ca of salt solution replaces the H^+ of organic acid. Two procedures denoted by Formula 3 finally lead to a decrease in pH value of salt solution and an addition of Na/Ca element in organics. This process was verified by the reduction in pH value of salt solution, the rougher surface, and the new element of Na/Ca in the bitumen.

$$R\text{ - }COOH + NaCl \text{ or } CaCl_2 \rightarrow R - COOCa \text{ or } R - COONa + HCl \quad (3)$$

Secondly, due to the weak bond energy of C–H, H is prone to replace by Cl provided from the salt solution, this process is presented in Fig. 9 [36]. Thus, the reaction of Cl substituting H of hydrocarbon compounds will increase the C-Cl group within the bitumen. This reaction was confirmed by the addition of the Cl element and the increase in the C-Cl functional group in bitumen.

Finally, the oxidation of bitumen is also one of the reaction mechanisms between salt solution and bitumen. Oxygen in the air or salt solution will oxidize with bitumen to produce carbonyl and sulfoxide groups shown in Fig. 10. In this research, the oxidation between oxygen and bitumen is mainly related to the changes in morphology, O element content, carbonyl and sulfoxide bonds, and rheological properties of bitumen.

In addition, the fact that the NaCl solution has a more significant effect on bitumen than the $CaCl_2$ solution could be explained by the fact that a high concentration of NaCl solution is slightly alkaline, while a high concentration of $CaCl_2$ solutionshows acidity according to Fig. 1. Bitumen as an acidic substance is prone to alkaline solution erosion [18], resulting in worse properties of the bitumen after NaCl solution immersion.

5. Conclusions

The mutual effect of bitumen and de-icing salt solution was studied by observing the changes in pH value of salt solutions, and by analyzing the variations in morphology, element content, chemical structure, and rheological properties of bitumen. The reaction mechanism between de-

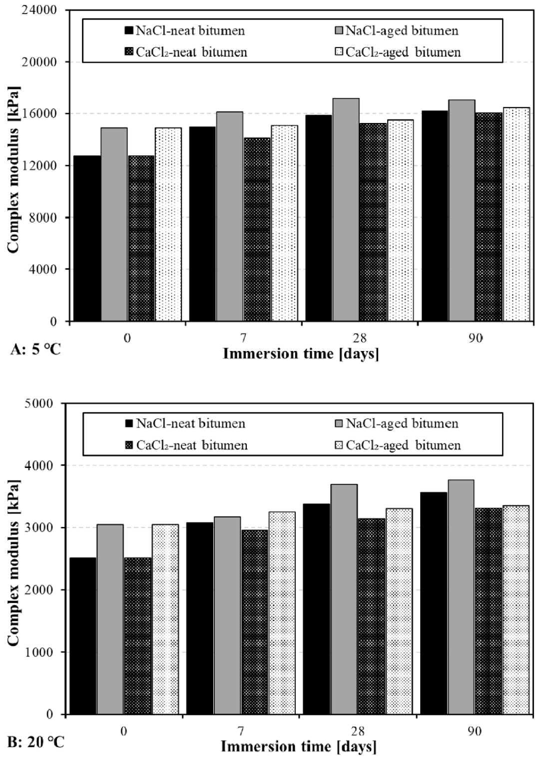

Fig. 7. Complex modulus versus immersion time (A: 5 ℃; B: 20 ℃).

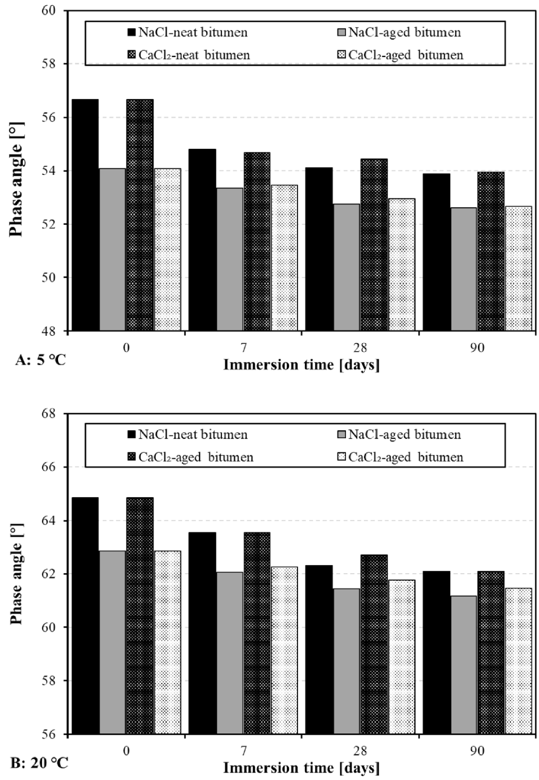

Fig. 8. Phase angle versus immersion time (A: 5 ℃; B: 20 ℃).

icing salt solution and bitumen was summarized based on the above results.

During the immersion process, the organic acid within bitumen released certain hydrogen ions from the bitumen to the solution, resulting in a reduced pH value of de-icing salt solution. On the other hand, the de-icing salt solution also significantly affected the morphology, element content, chemical structure, and rheological properties of bitumen, resulting in a more stable and aged bitumen.

Among NaCl & neat bitumen, NaCl & aged bitumen, $CaCl_2$ & neat bitumen, and $CaCl_2$ & aged bitumen combinations, the mutual effect between 10% NaCl solution and neat bitumen was the most severe. This phenomenon could be explained that neat bitumen being a less stable and an acidic substance is more susceptible to 10% NaCl solution (a weak alkaline solution) than aged bitumen.

Based on the mutual effects between the bitumen and de-icing salt solution, the reaction mechanism was composed of three sub-mechanisms: the release of hydrogen ions from the bitumen into the solution; the substitution reaction of Cl provided by de-icing salt; and the oxidative reaction between bitumen and oxygen.

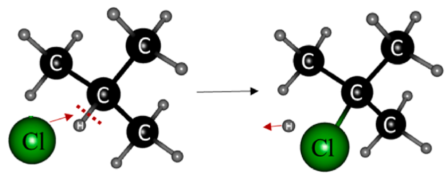

Fig. 9. The substitution reaction of Cl atom.

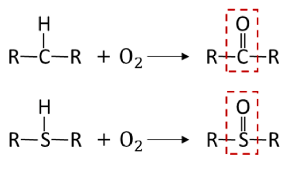

Fig. 10. The oxidation reaction of bitumen.

CRediT authorship contribution statement

Xuemei Zhang: Conceptualization, Methodology, Investigation, Data curation, Writing - original draft. **Hao Chen:** Methodology, Writing - original draft, Writing - review & editing. **Inge Hoff:** Conceptualization, Resources, 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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APPENDIX B – PAPER II

Xuemei Zhang, Inge Hoff and Rabbira Garba Sara (2021)

Response and deterioration mechanism of bitumen under acid rain erosion.

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materials

Article

Response and Deterioration Mechanism of Bitumen under Acid Rain Erosion

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Abstract: Acid rain as an important environmental issue has a negative impact on bitumen performance, thereby shortening the service life of asphalt pavements. Thus, this research aims to investigate the response of bitumen to acid rain and its deterioration mechanism. For this purpose, the simulated acid rain was prepared to erode neat bitumen and short-term aged bitumen. The hydrogen ion concentration of the acid rain, and the morphological, physical, chemical, and rheological properties of the bitumen were evaluated by means of a pH meter, scanning electron microscopy, physical tests, Fourier transform infrared radiation with attenuated total reflectance, and dynamic shear rheometer. The results showed that bitumen properties were severely affected by acid rain, and the changes in bitumen properties were highly related to the erosion time, leading to a reduction in pH value by 0.2 of residual acid rain, rougher bitumen surface, and stiffer bitumen with more oxygen-containing functional groups and fewer carbonyl acid groups (around 10% decrement) after 90 days erosion. These changes contributed to two deterioration mechanisms: oxidation and dissolution of carbonyl acid. Oxidation and dissolution are, respectively, the dominant actions for neat bitumen and aged bitumen during the erosion process, which eventually leads to various responses to acid rain.

Keywords: bitumen; acid rain; erosion; hydrogen ion; morphology; physical property; chemical property; rheological property; deterioration mechanism

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1. Introduction

Rapid industrial and economic development causes negative changes in the environment, including acid rainfall. Acid rain consisting of sulfuric acid (H_2SO_4) and nitric acid (HNO_3) has adverse effects on asphalt pavements, and H_2SO_4 and HNO_3 are the results of sulphur dioxides (SO_2) and nitrogen oxides (NO_x) reacting with water in the air [1]. SO_2 and NO_x are normally released from industrial processes in most regions, such as the north-eastern section of the United States, south-eastern section of Canada, Central Europe, China, and India [2]. Thus, the content of sulfuric acid and nitric acid in acid rain is determined by the emission of SO_2 and NO_x into the atmosphere. According to the latest statistical data collected from Europe [3], NO_x emission is almost twice the SO_2 emission. Therefore, the simulated acid rain in this research comprised sulfuric acid (H_2SO_4) and nitric acid (HNO_3) with the proportion of 1:2. Acid rain is defined as precipitation with a pH value lower than 5.6 [4]. In Northern Europe, the pH value of the precipitation is normally between 4 and 6 [5]. The lowest pH value of 4 was selected for simulating acid rain in this research work. Moreover, the rainfall varies from region to region due to climatic and topographic factors. In this study, 7, 28, and 90 days were chosen as erosion periods to simulate the short-term, mid-term, and long-term acid rain erosion. The different erosion days relate to the service life of pavement in different areas. For example, 7 days can simulate the total erosion time of the roads in arid areas under acid rain conditions, while 90 days for the roads in rainy areas.

As the most common pavement type, asphalt pavements are widely applied worldwide. However, acid rain as an acid solvent will lead to deterioration of asphalt pavements, thereby shortening the service life of the asphalt pavement [6]. Some studies have investigated the effect of acid rain on asphalt mixtures. Due to the erosion caused by acid rain, the physical properties of asphalt mixtures were influenced. For example, increased mass loss and air voids were found after acid rain erosion [7]. Meanwhile, the mechanical properties of asphalt mixtures were also affected by acid rain. For example, the indirect tensile strength, elastic modulus, compressive strength, failure strain, and deformation resistance of asphalt mixture decrease after acid rain erosion [8,9]. Shu found that the acid rain could inhibit the healing ability of asphalt mixtures, inducing bad mechanical performance [10]. It is found that the greater the acidity of an acid rain solution, the more apparent the effect on the mechanical properties of the asphalt mixtures [11]. The changes in physical and mechanical properties of asphalt mixtures finally lead to the stripping of the asphalt layer, which is one of the most significant distresses for asphalt pavements [12]. The detrimental mechanism of acid rain on asphalt mixtures is connected to the adhesion between bitumen and aggregates, which could be significantly reduced after acid rain erosion. Acid rain erosion causes some pieces of the bituminous binder to be exfoliated, which in turn leads to deterioration in mechanical properties of asphalt mixtures [13,14]. Few studies that investigated the influence of acid rain on bitumen have mainly focused on the chemical and adhesion properties of bitumen as influenced by acid rain. For instance, the light components within bitumen decreased, asphaltenes content increased [15,16]; acid makes bitumen more hydrophilic so that the bitumen is vulnerable to acid rain erosion [17].

Therefore, most researchers concentrated more on the influence of acid rain on asphalt mixture performance or the coupling effect of several factors on bitumen performance [18–20]. However, a few studies explored the effect and deterioration mechanism of bitumen and acid rain. This study aims to evaluate the response of bitumen to acid rain and study the deterioration mechanism between bitumen and acid rain. For this purpose, simulated acid rain consisting of sulfuric acid and nitric acid with pH 4 was prepared to erode neat bitumen and short-term aged bitumen for 7, 28, and 90 days, respectively. After the erosion process, the hydrogen ion concentration of the acid rain, and the morphology, physical properties, chemical structure, and rheological properties of the bitumen were analysed by conducting pH meter, scanning electron microscopy, physical tests, Fourier transform infrared radiation spectroscopy with attenuated total reflectance, and dynamic shear rheometer tests, as well as the development of bitumen over erosion time. The findings obtained from this research provide a reference for understanding the causes of asphalt pavement distresses caused by acid rain and drawing up subsequent plans for mitigating damages.

2. Materials and Methods

2.1. Materials and Materials Preparation

2.1.1. Bitumen

The pen 70/100 bitumen is the most widely used bitumen grade in Norway. This bitumen is obtained from the Veidekke company. Two states of the bitumen were studied in this research: neat bitumen and aged bitumen after thin film oven test (TFOT) according to EN 12607-2:2014 [21]. The physical and chemical properties of the neat bitumen and TFOT aged bitumen are displayed in Table 1.

Table 1. The physical and chemical properties of the bitumen.

Properties		Unit	Neat Bitumen	Aged Bitumen	Test Standard
penetration (25 °C)		0.1 mm	71	54	EN 1426:2015 [22]
softening point		°C	48.4	53.8	EN 1427:2015 [23]
viscosity (60 °C)		Pa·s	191	303	EN 13702:2018 [24]
absorbance (FTIR)	S=O	1030 cm^{-1}	0.054	0.057	FTIR analysis [25]
	C=O	1700 cm^{-1}	0.019	0.022	
	C-O	1301 cm^{-1}	0.055	0.055	

2.1.2. Simulated Acid Rain

The process of simulating acid rain is described as follows. A blend of concentrated acids was obtained by mixing 1 g sulfuric acid (98%) and 2.84 g nitric acid (69%) in a ratio of 1 (H_2SO_4):2 (HNO_3). Then, the concentrated acid (0.035 g) was diluted with distilled water (5 L) to an acid rain solution with a pH of 4 verified by the pH meter.

2.1.3. Erosion Process

The erosion process was performed based on a previous study [26]. Twenty-eight grams of bitumen was evenly distributed on a glass container to a 0.85 mm thick film. The bitumen film was immersed in a 150 mL simulated acid rain at 25 °C for 7, 28, and 90 days. To avoid the light and temperature effects, bitumen samples were covered and sealed by a black plastic bag. After the erosion process, the solution was collected in a cup for subsequent testing, and the surface of the bitumen was washed with distilled water. To avoid the effect of moisture on the bitumen properties, the bitumen samples were dried in a fume hood for three days before the next steps.

2.1.4. Abbreviations Used to Represent the Bitumen Samples

To simplify the description of bitumen samples under different conditions, the abbreviations of UT and AT were used to represent neat and TFOT aged bitumen, respectively. Acid-UT-7D, Acid-UT-28D, and Acid-UT-90D represent neat bitumen eroded in acid rain for 7, 28, and 90 days, respectively. Acid-AT-7D, Acid-AT-28D, and Acid-AT-90D indicate that aged bitumen has been eroded in acid rain for 7, 28, and 90 days, respectively.

2.2. Test Methods

2.2.1. The Hydrogen Ions Analysis

The hydrogen ions of simulated acid rain with erosion time were measured by a pH 1000H meter. The pH value of the solution was tested at 20 °C with a resolution of 0.01. Each solution was tested twice, the average value of them was taken as the test result.

2.2.2. Scanning Electron Microscopy (SEM) Analysis

The morphology testing of the bitumen with and without acid rain erosion was performed by scanning electron microscopy (SEM). The SEM images of the bitumen surface were captured at a magnitude of 200 times.

2.2.3. Physical Properties

In this research, three physical parameters were evaluated; penetration at 25 °C, softening point, and complex viscosity at 60 °C, following EN 1426:2015 [22], EN 1427:2015 [23], and EN 13702:2018 [24], respectively. For the penetration test, one sample was tested for three measurements, and the average value of the three measurements was taken as the final penetration. Two samples were prepared for softening point and complex viscosity tests, and the average of the two measurements was taken as the test result.

2.2.4. Attenuated Total Reflectance (ATR) Fourier Transform Infrared Radiation (FTIR) Spectroscopy Analysis

The functional groups of the bitumen were determined through an FTIR spectrometer equipped with a reflection diamond ATR accessory. The quantitative analyses of the functional groups were studied by the absorbance difference based on previous references [27,28]. Two replicates were for each sample, and the average absorbances of S=O, C=O, and C-O were regarded as the test result.

2.2.5. Rheological Behaviour Analysis

The rheological behaviour of the bitumen was evaluated by a dynamic shear rheometer (DSR) according to EN 14770:2012 [29]. The low-temperature and high-temperature rheological properties of the bitumen were studied by conducting low-temperature creep and high-temperature creep, respectively. The test parameters for the different modes are described in Table 2.

Table 2. Test parameters of the two test modes.

Mode	Low-Temperature Creep	High-Temperature Creep
sweep frequency (rad/s)	10	10
temperature range (°C)	5–30	30–80
temperature interval (°C)	5	10
diameter of the plate (mm)	8	25
sample thickness (mm)	2	1

3. Results and Discussion

3.1. The Hydrogen Ions of Simulated Acid Rain

The concentration of hydrogen ions of the acid solution would be influenced by the water content, while the water content would change during the erosion procedure due to the evaporation of moisture. The smaller the pH value, the higher the concentration of hydrogen ions of acid solution. Table 3 shows the volume loss of acid rain after a different number of days and the resultant pH value based on the volume loss. With increasing erosion time, the volume loss increased. Compared to aged bitumen, the acid rain after eroding neat bitumen had a more considerable volume loss under the same condition. This phenomenon can be interpreted by the stronger reaction between neat bitumen and acid rain. As the chemical reactions between bitumen and acid rain are mostly exothermic, and neat bitumen as a less stable substance can strongly react with acid rain than aged bitumen, this finally leads to more evaporation of the solution. According to the volume loss of acid solution, the pH value of acid rain will slightly decrease with erosion time. For instance, the pH value of acid rain after 7 days is 4; the acid rain after 28 days drops by 0.01 in pH value; and the acid rain after 90 days decreases by 0.07 (neat bitumen) and 0.03 (aged bitumen), respectively.

Table 3. Volume loss and calculated theoretical pH value of acid rain under different conditions.

Condition	Acid-UT-7D	Acid-AT-7D	Acid-UT-28D	Acid-AT-28D	Acid-UT-90D	Acid-AT-90D
volume loss (mL)	0.02	0.02	3.67	2.35	22.36	11.50
theoretical pH	4.00	4.00	3.99	3.99	3.93	3.97

Figure 1 shows the actual pH value of acid rain as a function of erosion time. It was found that the acid rain was influenced by the erosion process, reflected in the decrease in the pH value of the acid rain. The pH value of the acid rain decreased with increasing erosion time regardless of the bitumen, resulting in 3.76 (neat bitumen) and 3.77 (aged bitumen) after 90 days. Two slightly different developing trends were observed for neat bitumen and aged bitumen: the pH value of acid rain for neat bitumen decreased evenly, whereas the pH value of acid rain for aged bitumen decreased steeply before 28 days and gently after 28 days. However, the actual tested pH values of acid rain after the erosion process were far smaller than the theoretical pH value of the acid solution based on volume loss, and this difference increased with increasing erosion time. The above results indicate that the decreased pH value of the acid rain is mainly caused by the erosion process, and the influences of neat bitumen and aged bitumen on the pH value of the acid rain were similar. The reduction in pH value of residual acid rain might be originated from more dissolvable organic acid from bitumen to solution than that from solution to bitumen, which is an obvious difference compared to oxidative ageing.

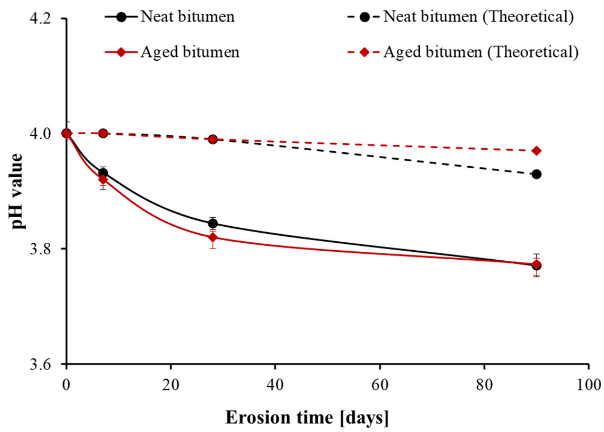

Figure 1. The pH value of simulated acid rain after eroding neat bitumen and aged bitumen.

3.2. Morphology of the Bitumen

The SEM images of the bitumen with and without acid rain erosion are presented in Figure 2. There were fewer visible particles and lower apparent roughness on the surface of neat bitumen compared to aged bitumen for the same erosion time. This result indicates that TFOT ageing will lead to apparent roughness of the bitumen surface with few particles, and the erosion of acid rain would not change this trend. However, both neat bitumen and TFOT aged bitumen showed increased surface roughness with increasing erosion time in acid rain. This finding shows that acid rain might decompose the chemical bond of the bitumen, resulting in a rougher surface with particles.

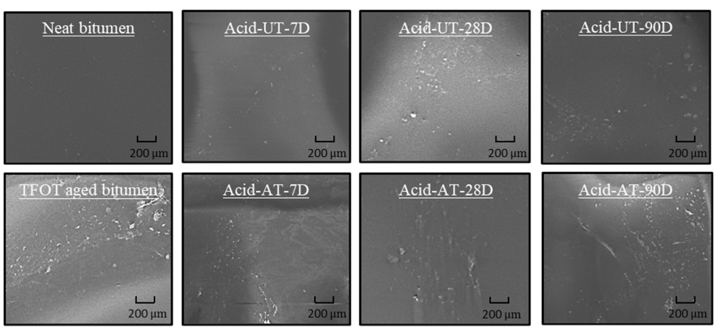

Figure 2. SEM images of the bitumen with and without acid rain erosion.

3.3. The Physical Properties of the Bitumen

Penetration, softening point, and complex viscosity are three typical physical parameters characterising the physical properties of bitumen [30]. The effect of acid rain on the physical properties of the bitumen is shown in Figure 3. It was found that there was a decrease in penetration with acid rain erosion and erosion time, a slight increase in softening point, and a sharp increase in complex viscosity. These results indicate that acid rain erosion makes bitumen stiffer, more stable, and better flow resistant. The degree of changes in the physical properties increased with increasing erosion time. It is worth to note that the physical properties of neat bitumen were more easily affected by erosion than aged bitumen since the increasing/decreasing slopes of the physical parameters with immersion time of neat bitumen were bigger than that of aged bitumen.

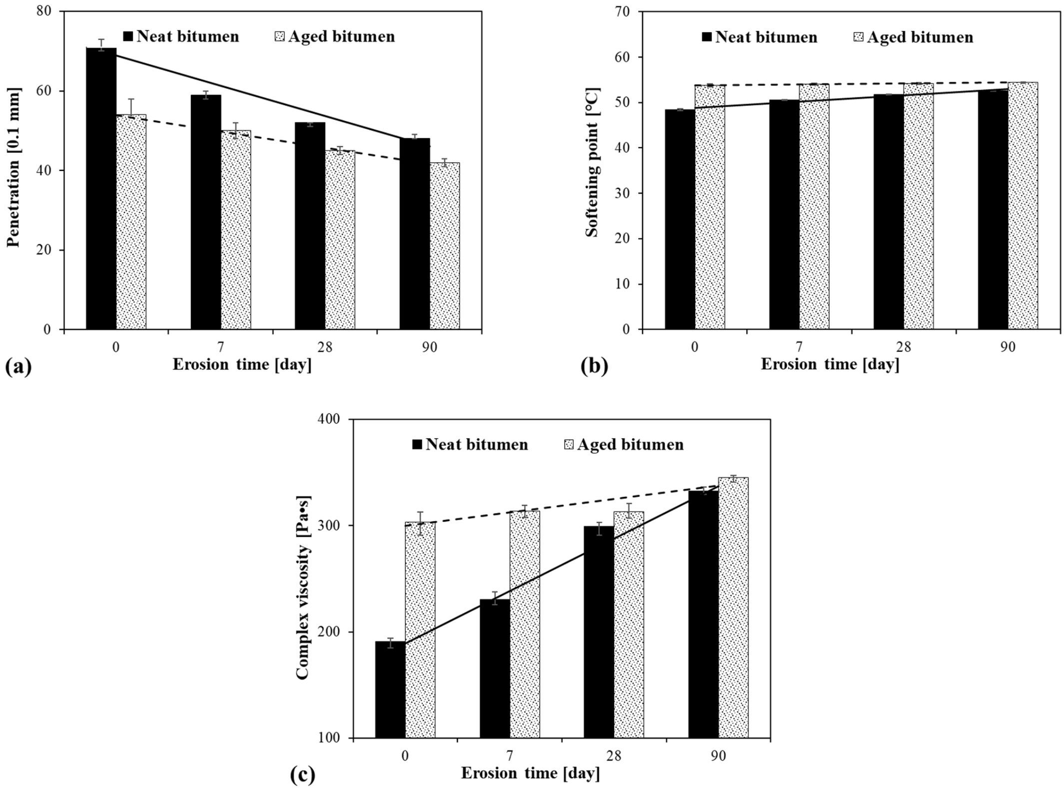

Figure 3. (**a**): Penetration; (**b**): softening point; (**c**): complex viscosity at 60 °C of the bitumen under different conditions versus erosion time.

3.4. Chemical Structure of the Bitumen

There are three peaks worth noticing after acid rain erosion, namely, the carbonyl group, sulfoxide group, and carbonyl acid group located at 1700, 1030, and 1301 cm^{-1}, respectively. Both carbonyl and sulfoxide groups are two oxygen-containing groups employed as two ageing level indicators of bitumen [31,32]. The carbonyl acid group in bitumen might be dissolved in acid rain; this action named the dissolution of carbonyl acid [33]. The information mentioned above for the three functional groups is shown in Table 4.

Table 4. Three typical chemical groups of the bitumen under acid rain erosion.

Peak Position	Functional Group	Description	Indication
1030 cm^{-1}	S=O	Sulfoxide group	Oxidation
1700 cm^{-1}	C=O	Carbonyl group	
1301 cm^{-1}	C-O	Acetate ester/Carbonyl acid	Dissolution

To quantitively analyse the development of chemical bonds of the bitumen during the erosion time, an absorbance difference is calculated at specific wavenumbers and plotted in Figure 4. As can be seen, both the carbonyl and sulfoxide group (C=O and S=O) increased after acid rain erosion, which implies that acid rain leads to ageing of the bitumen. The carbonyl acid group (C-O) decreased after acid rain erosion, which is completely different from oxidative ageing. This result indicates less of the carbonyl acid group within the bitumen. These outcomes will contribute to the hardening of the bitumen and more acid in the solution, resulting in higher stiffness and lower pH value of the solution, which is in line with the results from Chapter 3.3 and 3.1. The absolute values of the three functional groups increased with various speed after acid rain erosion. The C=O group of both neat bitumen and aged bitumen linearly increased with erosion time. The S=O group of both neat bitumen and aged bitumen slowly increased with erosion time and almost remained constant after 28 days of erosion, which changed minimally among the three groups. The absolute value of the C-O group of neat bitumen increased evenly with erosion time, whereas that of aged bitumen increased apparently before 28 days and kept changing slowly afterwards. The changing trend in the C-O group of neat bitumen and aged bitumen is similar to that in the pH value of acid rain. Neat bitumen resulted in a bigger absorbance difference in the C=O group compared to the S=O and C-O groups after acid rain erosion. Aged bitumen showed the most increase in the C-O group among the three groups. The above results indicate that neat bitumen is more easily aged than aged bitumen, while both neat bitumen and aged bitumen are dissolved similarly by acid rain. In other words, oxidation is the dominant action of neat bitumen during the erosion process, while dissolution is the typical action of aged bitumen.

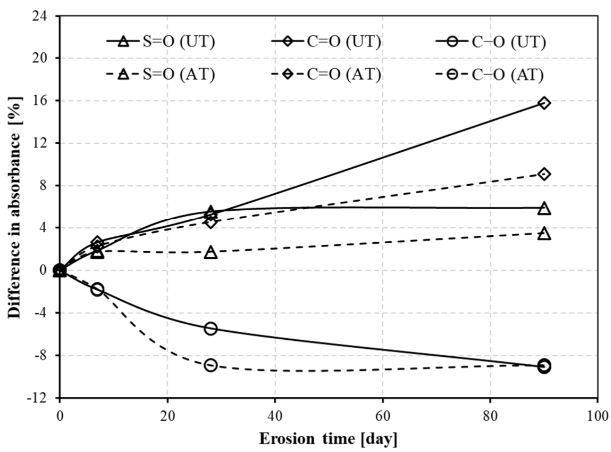

Figure 4. Difference in absorbance of neat bitumen and aged bitumen under acid rain erosion.

3.5. The Rheological Properties of the Bitumen

The low-temperature rheological properties of the bitumen were analysed in the range 5–30 °C. The complex modulus (G*) of the bitumen under acid rain during the erosion process is plotted on the primary axis in Figure 5. Regarding neat bitumen, acid rain increased the complex modulus of the bitumen, and the complex modulus increased with increasing erosion time. Aged bitumen showed a similar trend as neat bitumen for acid rain erosion. These results indicate that acid rain increases the resistance to deformation of both neat and aged bitumen, and the deformation resistance continues to increase with increasing erosion time, which is in line with the results obtained from physical tests. However, better resistance to deformation at low temperature, an adverse effect on bitumen, is suspected of causing temperature cracks on asphalt pavements. Comparing neat bitumen and aged bitumen, the slope of complex modulus of neat bitumen (28.7%) with erosion time was slightly bigger than that of aged bitumen (15.6%). This result indicates that the deformation resistance of neat bitumen at low temperatures is more susceptible to acid rain than aged bitumen. The complex modulus of the TFOT aged bitumen is similar to that of Acid-UT-28D, which indicates that erosion in acid rain for 28 days has a similar impact on neat bitumen as TFOT ageing. The phase angle (δ) of the bitumen under acid rain during erosion time is plotted on the secondary axis in Figure 6. Both neat bitumen and aged bitumen were greatly influenced by acid rain. The phase angle decreased with the increasing erosion time. The results indicate that acid rain improves the elastic characteristic and deteriorates the viscous characteristic of bitumen, and the deterioration in viscous behaviour increases with increasing erosion time. However, the tendency of descending degree in the phase angle for neat bitumen was greater than that of aged bitumen, which indicates that neat bitumen is more vulnerable to acid rain erosion than aged bitumen. The phase angle of TFOT aged bitumen is bigger than for Acid-UT-28D and smaller than for Acid-UT-7D, which reveals that erosion in acid rain for 28 days has a similar impact on neat bitumen as TFOT ageing.

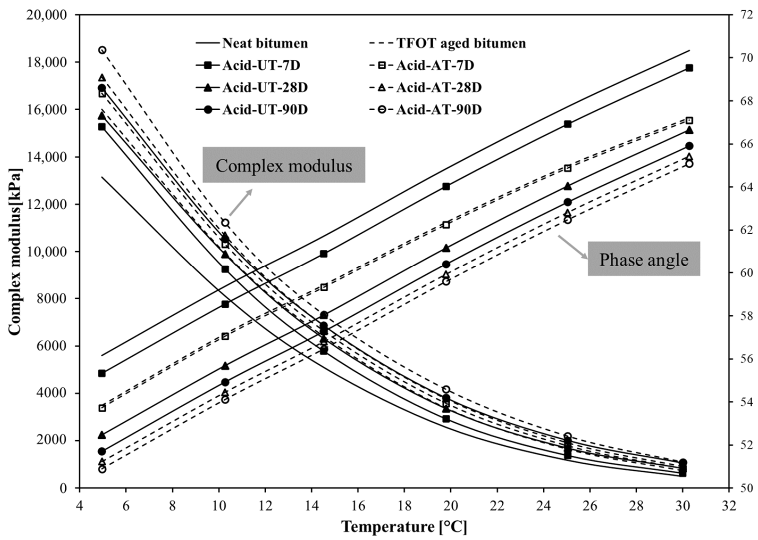

Figure 5. The complex modulus and phase angle of the bitumen under acid rain erosion at low temperature (5–30 °C).

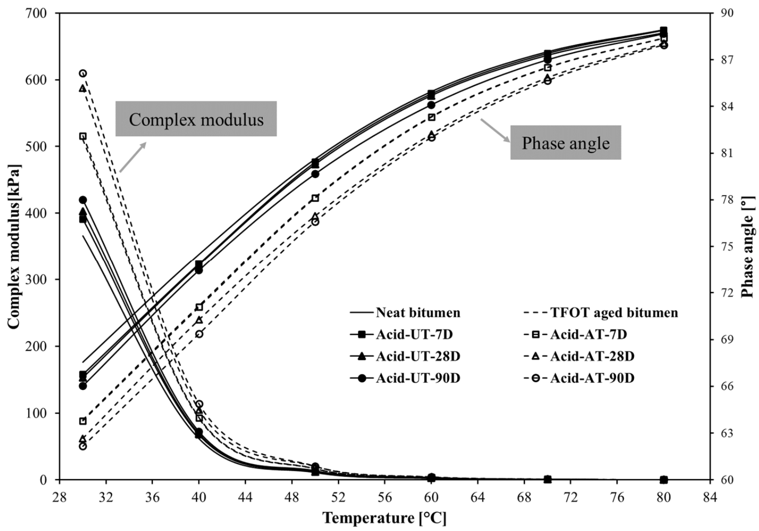

Figure 6. The complex modulus and phase angle of the bitumen at high temperature after acid rain exposure (30–80 °C).

The high-temperature rheological properties of the bitumen were tested using high-temperature creep in the range 30–80 °C. The complex modulus (primary axis) and phase angle (secondary axis) of bitumen under acid rain over erosion time at high temperature is presented in Figure 6. It is observed that acid rain influenced the rheological properties of both neat bitumen and aged bitumen with different extents, resulting in increased complex modulus and decreased phase angle. The complex modulus and phase angle of neat bitumen continuously changed with the erosion time, while that of aged bitumen remained unchanged before 7 days and changed afterwards. Additionally, the changes in complex modulus and phase angle increased with the extension of the erosion time. These results indicate that acid rain leads to better deformation resistance and worse viscous characteristic of the bitumen, and the degree of change slightly increased with erosion time, which is consistent with the results at low temperature. Furthermore, the rate of increase (slope) in the complex modulus of neat bitumen (14.7%) caused by acid rain was smaller than that of aged bitumen (19.8%), and the rate of decrease in the phase angle of neat bitumen (2.3%) was also lower than that of aged bitumen (2.7%). These results indicate that acid rain has a more obvious effect on the deformation resistance and viscoelasticity for the aged bitumen at high temperature than neat bitumen. This phenomenon could be interpreted that the dissolution, the typical action of aged bitumen during the erosion process, makes the high-temperature rheological properties of bitumen more susceptible to acid rain.

The rutting factor $G^*/\sin\delta$ in the range 64–74 °C under the acid rain condition is shown in Figure 7. The acid rain led to an increased rutting factor of both neat bitumen and aged bitumen with erosion time, which indicates that acid rain erosion and longer erosion time resulted in better rutting resistance of bitumen. Based on the rutting factor at 1 kPa, the failure temperature was obtained for each sample recorded on the *X*-axis in Figure 7. The failure temperature indicating the critical temperature to rutting was also affected by acid rain and erosion time. It is found that both acid rain erosion and longer erosion time had a positive effect on the failure temperature of neat bitumen and aged bitumen. The degree of change in the failure temperature of neat bitumen (2.6%) was smaller than that of aged bitumen (2.9%), which reveals that rutting resistance of aged bitumen is more sensitive to acid rain compared to neat bitumen.

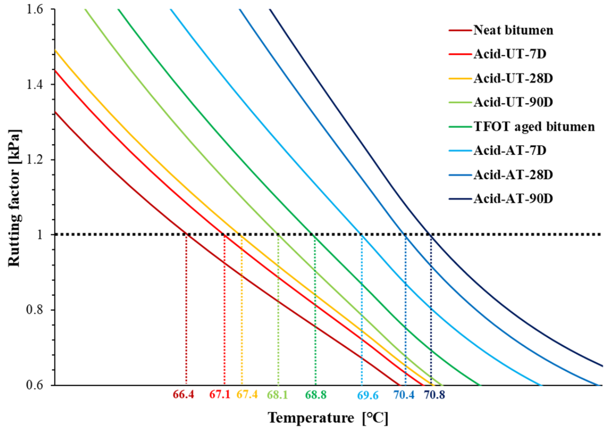

Figure 7. The rutting factor and failure temperature of bitumen.

4. Conclusions

The interaction between bitumen and acid rain was investigated by analysing the morphology, physical properties, chemical structure, low-temperature and high-temperature rheological properties of bitumen, as well as the hydrogen ion concentration of the acid rain. The conclusions are summarised as follows:

After acid rain erosion, neat bitumen and aged bitumen have similar responses: more visible particles and apparent roughness of the bitumen surface regarding the morphology; decreased penetration, increased softening point, and complex viscosity in terms of physical properties; more C=O and S=O groups and fewer C-O groups regarding chemical structure; increased complex modulus, rutting factor, and failure temperature, and decreased phase angle concerning rheological properties. The erosion process led to more hydrogen ions in the acid rain. In addition, the changes in the above properties were positively related to erosion time. The above conclusions demonstrate that the acid rain has a similar effect on the physical and rheological properties of bitumen compared with the oxidative ageing, while different chemical responses of bitumen were found for acid rain compared to the oxidative ageing.

Some differences were found in the response of neat bitumen and aged bitumen to acid rain. The oxidative functional groups (C=O and S=O), physical and low-temperature properties of neat bitumen were more vulnerable to acid rain than for aged bitumen, while the high-temperature rheological properties of aged bitumen were more susceptible to acid rain than neat bitumen. The effect of the erosion process on hydrogen ions of acid rain and the carbonyl acid group of neat bitumen was similar to that of aged bitumen.

The deterioration mechanism could be that both oxidation and dissolution occurred during the erosion process, resulting in ageing of the bitumen and eroding damage on the bitumen. The outcomes of oxidation were mainly increased C=O and S=O groups, and the dissolution typically resulted in fewer C-O groups of the bitumen and higher concentration of hydrogen ions within the acid rain. Both the oxidation and the dissolution caused changes in the morphological, physical, and rheological properties of the bitumen.

The oxidation is the dominant action of neat bitumen during the erosion process, while the dissolution reaction is the typical action of the aged bitumen. The different typical reactions of neat bitumen and aged bitumen eventually lead to different responses to acid rain of neat bitumen and aged bitumen.

The presented results are only valid for neat bitumen and aged bitumen in existing road surfaces. It is meaningful to conduct further tests on different kinds of bitumen for finding the best type of bitumen that resists acid rain erosion.

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APPENDIX C – PAPER III

Xuemei Zhang, Inge Hoff and Hao Chen (2022)

Characterization of various bitumen exposed to environmental chemicals.

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Characterization of various bitumen exposed to environmental chemicals

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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

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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.

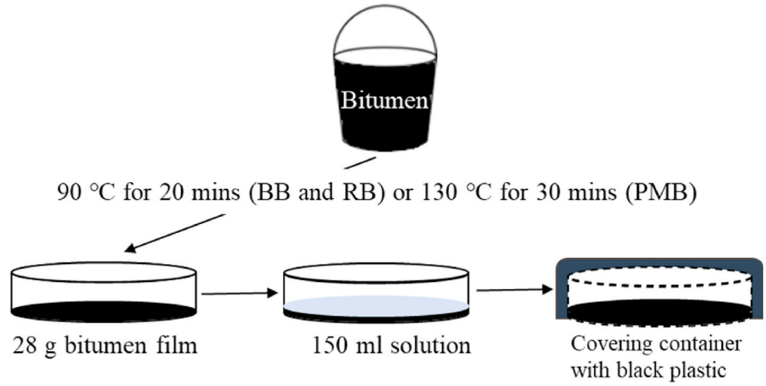


Fig. 1. Soaking process.

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,

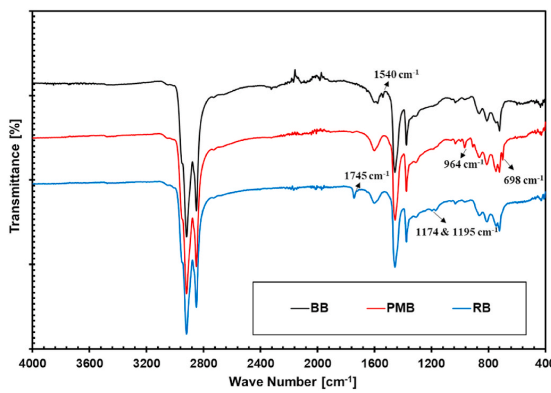
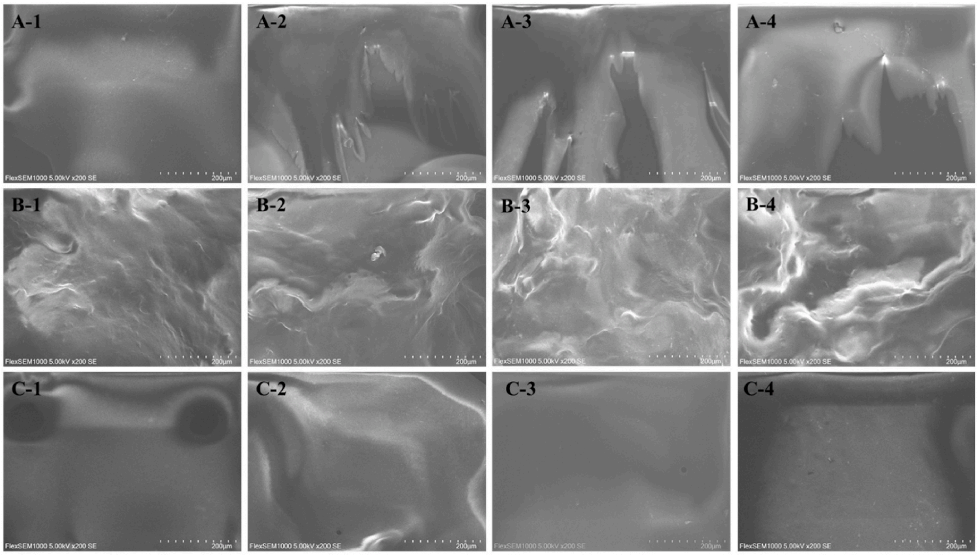


Fig. 2. The infrared spectrum of BB, PMB, and RB bitumen.



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.

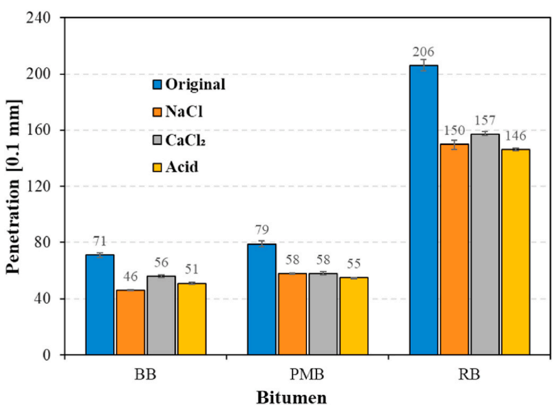


Fig. 4. The penetration of bitumen versus chemicals.

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

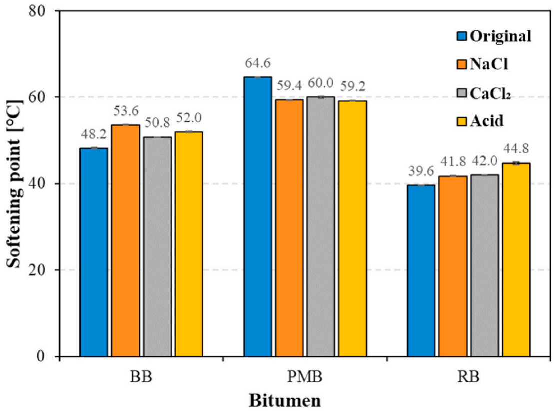


Fig. 5. The softening point of bitumen versus chemicals.

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

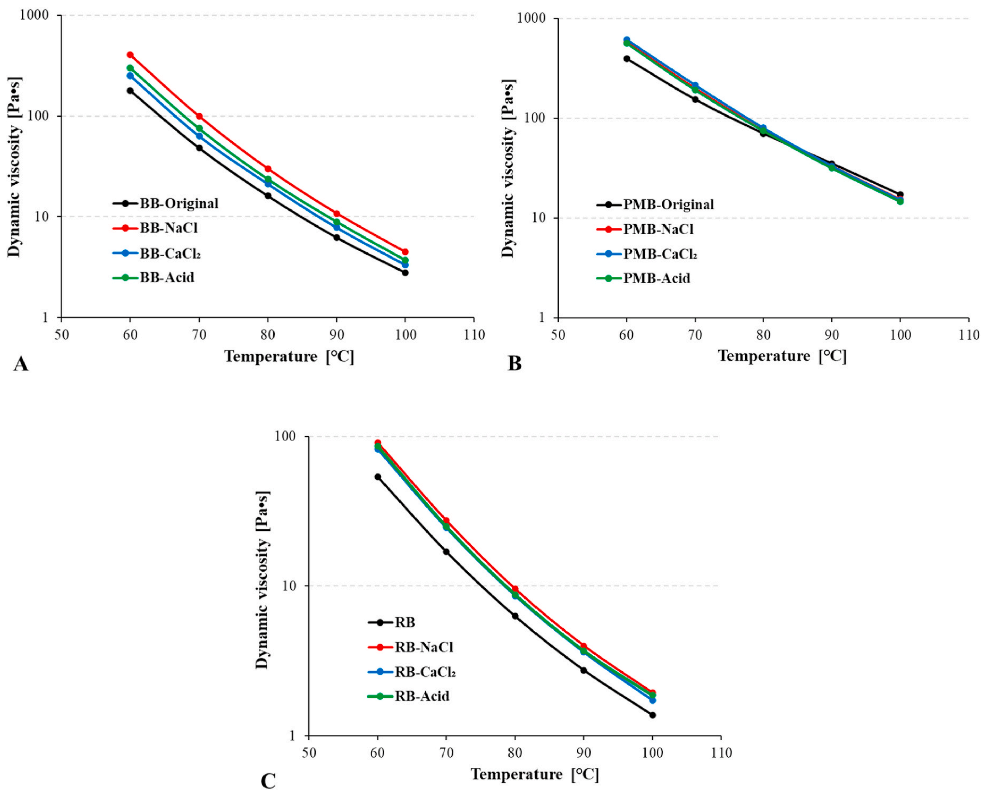


Fig. 6. The dynamic viscosity of bitumen after chemical conditioning (A: BB; B: PMB, C: RB).

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

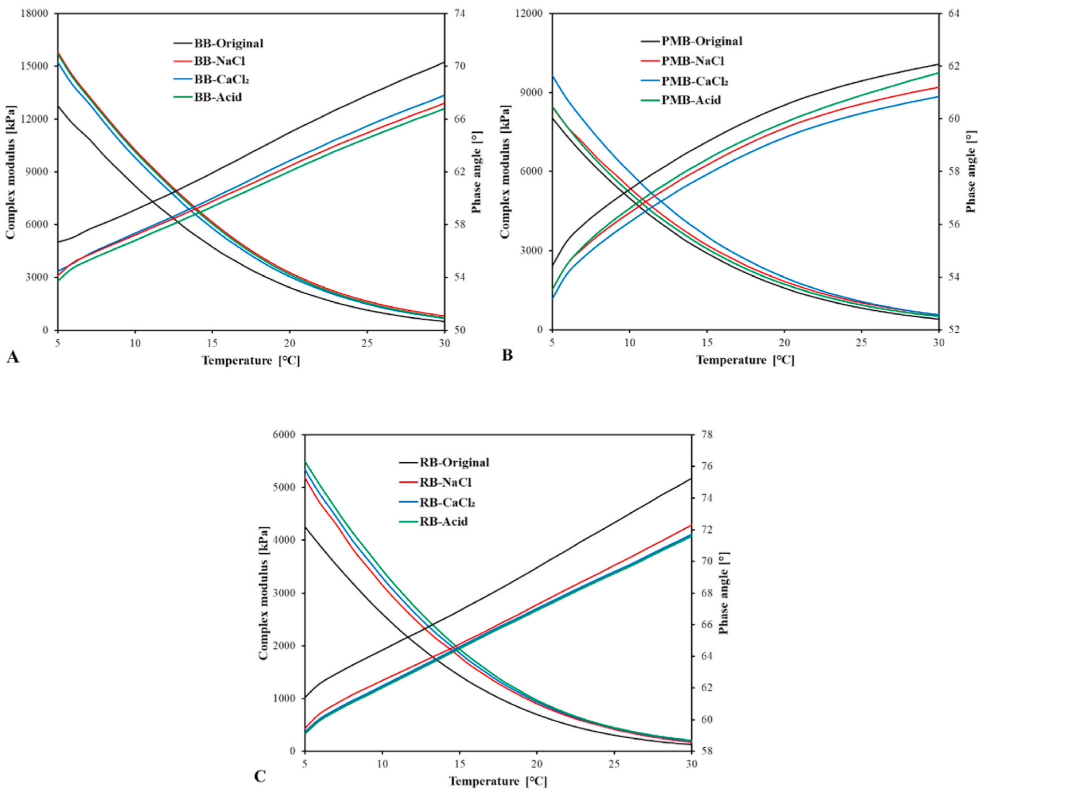


Fig. 7. The complex modulus and phase angle of three kinds of bitumen under chemical condition (A: BB; B: PMB; C: RB).

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.

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

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.

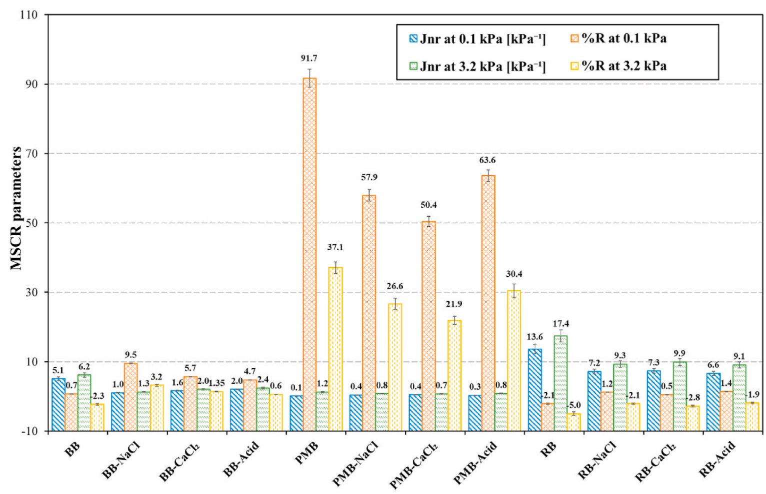


Fig. 8. J_{nr} and %R of bitumen under chemical conditioning.

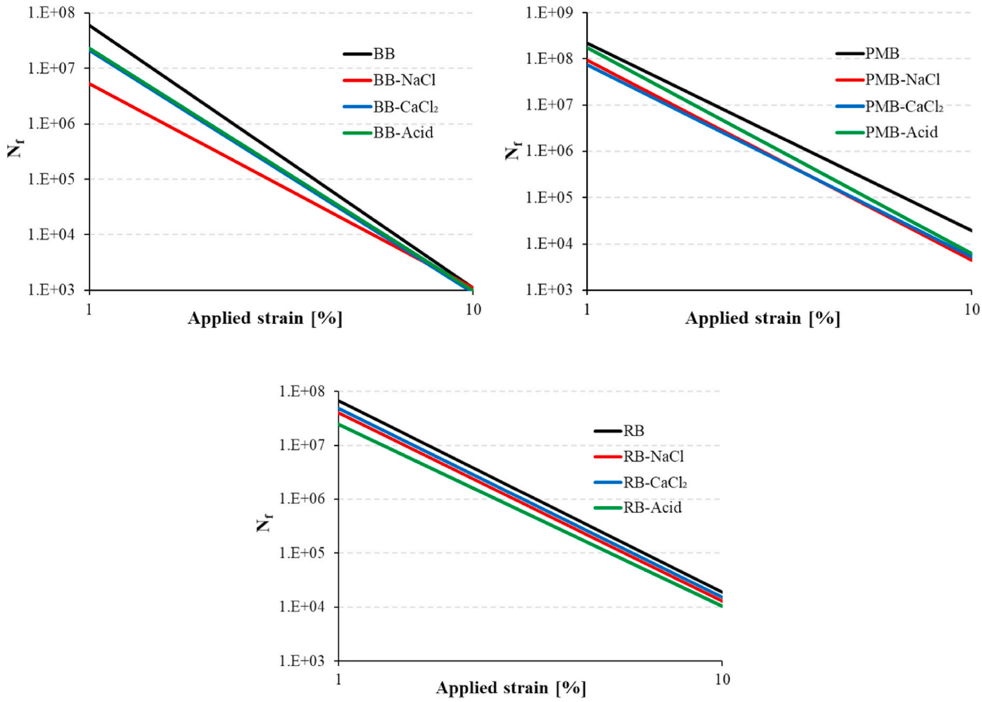


Fig. 9. Fatigue life of bitumen after chemical condition.

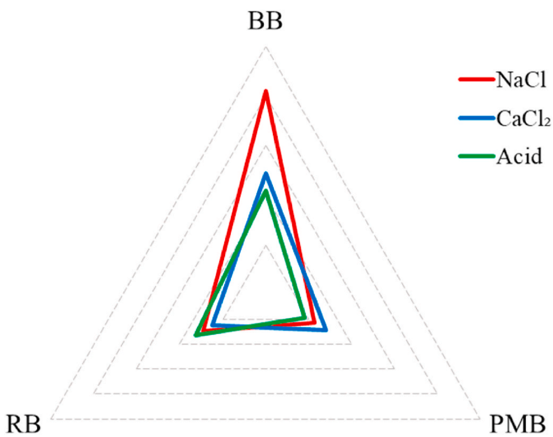


Fig. 10. The summed difference in bitumen performance caused by chemicals.

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.

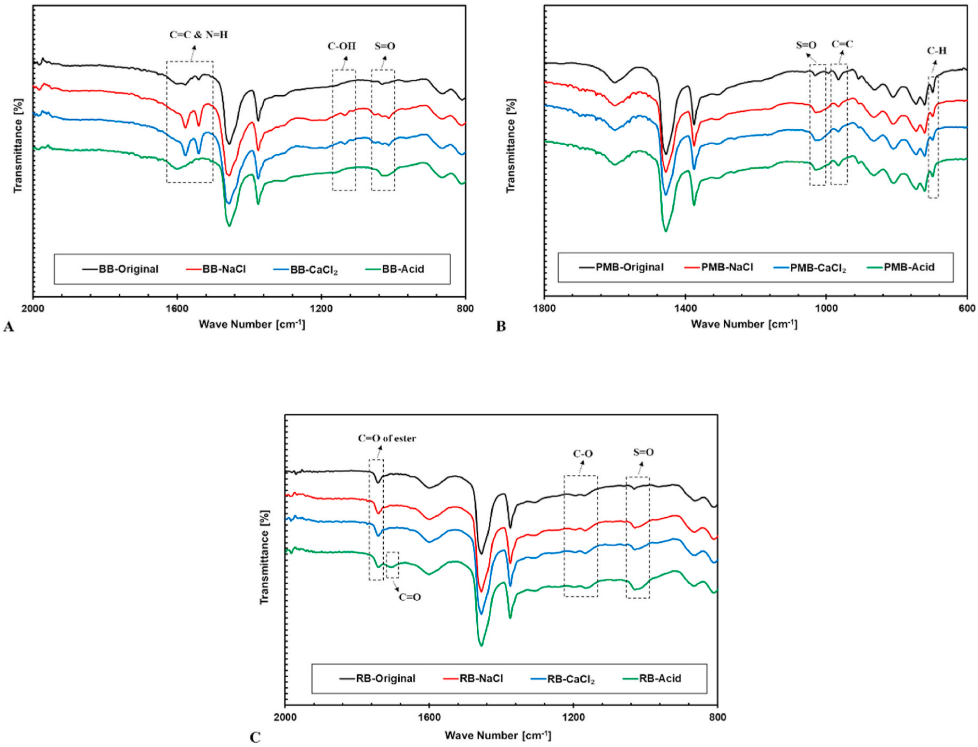


Fig. 11. FTIR spectrum of three kinds of bitumen. (A) BB; (B) PMB; (C) RB.

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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CRediT authorship contribution statement

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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APPENDIX D – PAPER IV

Xuemei Zhang and Inge Hoff (2021)

Comparative Study of Thermal-Oxidative Aging and Salt Solution Aging on Bitumen Performance.

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Article

Comparative Study of Thermal-Oxidative Aging and Salt Solution Aging on Bitumen Performance

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Abstract: The aging of bitumen is detrimental to the durability and service life of asphalt pavement. Previous studies found that bitumen was suspected to be aged by not only thermal oxidation but also solution immersion. This research aims to compare the effect of thermal-oxidative aging and salt solution aging on bitumen performance. For this purpose, a thin film oven test (TFOT) and pressure aging vessel aging (PAV) were selected as thermal-oxidative aging, and 10% NaCl aging and 10% $CaCl_2$ aging were selected as salt solution aging. The morphology, oxygen content, physical properties, low-temperature properties, and high-temperature properties of bitumen were analysed by employing scanning electron microscopy with an energy dispersive spectrometer (SEM-EDS), physical tests, a bending beam rheometer (BBR), and a dynamic shear rheometer (DSR). Test results show that both thermal-oxidative aging and salt solution aging had similar influencing trends in the oxygen content, physical, low-temperature, and high-temperature properties of bitumen but had different changes in morphology. The aging degrees caused by four kinds of aging methods were obtained based on the summed values of the absolute aging factor of all parameters: PAV > 10% NaCl > TFOT > 10% $CaCl_2$. The conclusions could provide a theoretical basis to establish a standard for the solution aging of bitumen.

Keywords: bitumen; thermal-oxidative aging; salt solution aging; morphology; physical property; low-temperature property; high-temperature property

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1. Introduction

The aging of asphalt pavement is among the most concerning issues inducing pavement distresses, such as fatigue cracking, thermal cracking, and low-temperature cracking. These distresses would reduce the service life of the pavement and driver's comfort [1]. The deterioration of asphalt pavement is mainly the result of the aging of bitumen, even though bitumen only accounts for 4–6% of the total mass of the asphalt mixture [2,3]. Based on previous research, the aging of bitumen is attributed to four factors: solar radiation, moisture, time, and temperature [4]. According to the factors influencing the aging of bitumen, different aging modes on bitumen are classified, including thermal-oxidative aging, UV aging, and solution aging [5,6]. Among three aging modes on bitumen, thermal-oxidative aging is the most mature and studied by a large number of researchers, and solution aging is a new formation during recent years [7,8]. Thus, a comparison with thermal-oxidative aging would promote the customization of the specifications of solution aging of bitumen.

The thermal-oxidative aging of bitumen occurs from the construction stage to the end of pavement life. There are two phases for the thermal-oxidative aging of bitumen: short-term aging and long-term aging [9]. Short-term aging presents the thermal aging of bitumen during storage, transportation, and paving, which is normally simulated by the thin film oven test (TFOT) in the laboratory [10]. Long-term aging presents the thermal aging of bitumen during its whole service life, which is simulated by a pressure aging vessel (PAV) in the laboratory [11]. Thermal-oxidative aging of bitumen is principally associated with the oxidative reaction between bitumen and oxygen and the volatilization of light components [12]. Due to the oxidation and the volatilization, the morphological, physical, and rheological properties of bitumen varied [13–17]. These changes in bitumen performance would result in distresses or deteriorations on asphalt pavement.

Although there are no protocols or standards for the solution aging of bitumen, many researchers have found that solution immersion would age the bitumen to some degree. For example, the stiffness of bitumen increased, and oxygen-containing functional groups were produced after solution immersion [18]. Pang [19] also found that solution immersion increased the asphaltene content and complex modulus and reduced the phase angle, which are typical characteristics of the oxidation of bitumen. Additionally, Yang and Wu [20,21] also found that the adhesion and cohesion of bitumen were deteriorated after solution immersion. These changes indicate that the solution immersion would also age bitumen like thermal-oxidative aging but with different mechanisms. Among all solutions based on previous studies, salt solution is among the most used solutions, since salt appears in coastal areas and during winter maintenance, and 10% is used as an estimated average for field condition [22–24].

Therefore, this research aims to compare the similarities and differences of the effect of salt solution aging and thermal-oxidative aging on bitumen performance. The salt solution aging, in this case, was chosen as 10% NaCl aging and 10% $CaCl_2$ aging. The chosen thermal-oxidative aging methods were TFOT aging and PAV aging. Then, scanning electron microscopy with an energy dispersive spectrometer (SEM-EDS) was used to characterize the morphology and oxygen content of bitumen influenced by aging; penetration, softening point, bending beam rheometer (BBR), and dynamic shear rheometer (DSR) were used to evaluate the physical properties, low-temperature, and high-temperature properties of bitumen before and after different aging methods. The conclusions obtained from this research could provide a theoretical basis to establish a standard for the solution aging of bitumen.

2. Materials and Methods

2.1. Bitumen

This research adopted a neat bitumen with a penetration grade of 70/100, which is commonly used for constructing asphalt pavement in Norway obtained from Veidekke company. Table 1 lists the basic properties of bitumen.

Table 1. Basic properties of neat bitumen.

Property	Penetration (25 °C)	Softening Point	Viscosity (60 °C)	Limited Temperature in BBR Test
Neat bitumen	70 dmm	48.2 °C	188 Pa·s	−18 °C
Test standard	NS-EN 1426:2015	NS-EN 1427:2015	NS-EN 13702:2018	Performance grade [25]

2.2. Aging Methods

There are two kinds of aging modes used in this research: thermal-oxidative aging and salt solution aging. Detailed information about two kinds of aging modes is stated as follows.

2.2.1. Thermal-Oxidative Aging

Thermal-oxidative aging includes thin film oven test (TFOT aging) and pressure aging vessel aging (PAV aging) methods, which simulate the short-term aging and long-term aging of bitumen, respectively [26]. The parameters of thermal-oxidative aging are shown in Table 2.

2.2.2. Salt Solution Aging

There are two kinds of salt solution aging methods of bitumen: 10% NaCl aging and 10% $CaCl_2$ aging. The specific parameters of salt solution aging are shown in Table 3. The concentration of salt solution, aging temperature, and aging time were, respectively, selected as 10%, 25 °C, and 90 days based on previous research and the practical situation [27,28]. Therefore, salt solution aging was achieved by immersing bitumen film (28 g) in salt solution (150 mL) for 90 days at 25 °C. To avoid salt solution evaporation, the bitumen immersed in the salt solution was covered by a black plastic bag. After salt solution aging, bitumen samples were cleaned and dried in a fume hood for three days for the following tests.

Table 2. Parameters of thermal-oxidative aging.

Parameter	TFOT Aging	PAV Aging
Temperature	163 °C	100 °C
Aging time	5 h	20 h
Bitumen mass	50 g	50 g
Standard	NS-EN 12607-2:2014	NS-EN 14769:2012

Table 3. Parameters for salt solution aging.

Parameter	10% NaCl/$CaCl_2$ Aging
Temperature	25 °C
Aging time	90 days
Bitumen mass	28 g
Diameter of container	190 mm

2.3. Test Methods

2.3.1. Scanning Electron Microscopy (SEM) with Energy Dispersive Spectrometer (EDS)

SEM-EDS was used to characterize the morphology and the oxygen content of bitumen. The bitumen sample (0.01 g) was prepared, then the conductive tape attached to bitumen sample was put on the specimen tube for the following tests. In terms of the bitumen morphology, the bitumen surface was captured using a scanning electron microscope (FlexSEM 1000) at a magnitude of 50 times. The oxygen content indicating the oxidation degree was obtained using an energy dispersive spectrometer (ESD) [29]. It is noted that three samples for each bitumen were tested, and the averaged value of oxygen content was finally used in this research.

2.3.2. Physical Test

To characterize the aging degree of bitumen caused by different aging methods, the physical properties of bitumen should be provided. In this case, penetration (at 25 °C), softening point, and complex viscosity (at 60 °C) of bitumen before and after aging were evaluated according to NS-EN 1426:2015, NS-EN 1427:2015, and NS-EN 13702:2018, respectively. Three, two, and two valid determinations were, respectively, carried out on penetration, softening point, and complex viscosity tests; the average value of each test was used as the test result.

2.3.3. Bending Beam Rheometer (BBR)

The low-temperature properties of bitumen were characterized using a bending beam rheometer according to Norwegian standard NS-EN 14771:2012. Bitumen samples were made to 6.4 ± 0.1 mm high, 12. 7 ± 0.25 mm wide, and 127 ± 5 mm long and tested at −12 and −18 °C. For each type of bitumen, two samples were made for the BBR test. Then, average values of flexural creep stiffness (S) and stress relaxation ability (m-value) at the loading time of 60 s, and the corresponding limited temperature, were calculated and used for evaluating the low-temperature properties of bitumen.

2.3.4. Dynamic Shear Rheometer (DSR)

The high-temperature properties of bitumen were analysed using the dynamic shear rheometer according to NS-EN 14770:2012. The parameters for frequency sweep are listed in Table 4. The master curve of complex shear modulus and phase angle, rutting factor, and failure temperature was carried out to evaluate the high-temperature properties of bitumen. Each bitumen was tested with two replicates, and the average value was finally used.

Table 4. Parameter settings.

Setting	Sweep Frequency	Strain Value	Test Temperature (°C)
Value	0.1–400 rad/s	1%	30, 40, 50, 60, 70, 80

3. Results and Discussions

3.1. Morphology and Oxygen Content

Figure 1 presents SEM images of five bitumen samples under original, TFOT, PAV, 10% NaCl, and 10% $CaCl_2$ conditions. Some differences can be observed from Figure 1a–c: after TFOT aging, the surface bitumen was rougher with some smaller particles than that of neat bitumen, and these particles were accumulated by large molecules within bitumen; however, the surface of bitumen was cracked and with separated pieces of bitumen after PAV aging. Thus, the thermal oxidation aging increases the proportion of large molecules, resulting in a rough surface with a few cracks [30]. However, from Figure 1a,d,e, salt solution aging induced different changes in the bitumen surface compared to thermal-oxidative aging. Sharp angles of bitumen pieces were observed for salt solution aged bitumen. This result could be attributed to the fact that that salt solution aging would deteriorate the outmost layer of bitumen or lead to residual salt on the bitumen surface, which leads to the loss of bitumen pieces and sharp angles [31]. Thus, bitumen aged by thermal-oxidative aging (TFOT and PAV) showed different phenomena on the morphology of bitumen compared to salt solution aging.

Figure 2 shows the oxygen content of neat bitumen and aged bitumen. The oxygen content in bitumen is one of the most important factors indicating the aging degree of bitumen. The higher oxygen content indicates the more severe aging of bitumen [32]. From Figure 2, it can be seen that the oxygen content of bitumen increased to different extents after four kinds of aging methods were applied. PAV aging led to the most severe aging on bitumen, since the oxygen content of PAV aged bitumen was the highest among four kinds of aged bitumen. The 10% NaCl and 10% $CaCl_2$ had similar effects on bitumen aging. TFOT aging has the least effect on bitumen aging, as the oxygen content of TFOT aged bitumen was slightly higher than that of neat bitumen. Therefore, both thermal-oxidative aging and salt solution aging would increase the oxygen content within bitumen, resulting in the more severe aging of bitumen. However, the aging severity of bitumen is dependent on the aging time and aging mechanisms.

3.2. Physical Properties

Three parameters were used for indicating the aging degree of bitumen: penetration, softening point, and complex viscosity. Penetration is used to characterize the stiffness or softness of bitumen; a lower value of penetration indicates the higher stiffness of bitumen [33]. The softening point indicates the high-temperature stability of bitumen; a higher softening point value presents greater stability of bitumen at a high temperature [34]. Complex viscosity is applied to measure the resistance to flow of bitumen; a higher value of complex viscosity means a better performance of bitumen to resist flowing [35].

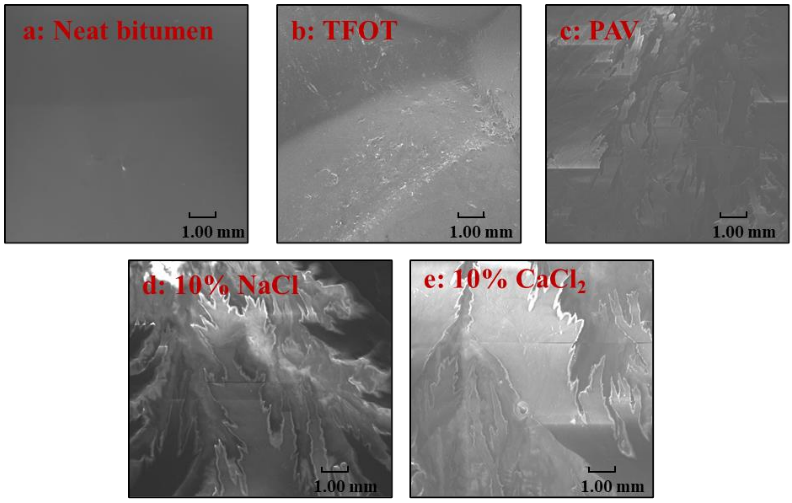

Figure 1. SEM images of bitumen before and aging: (**a**) Neat bitumen; (**b**) TFOT; (**c**) PAV; (**d**) 10% NaCl and (**e**) 10% $CaCl_2$.

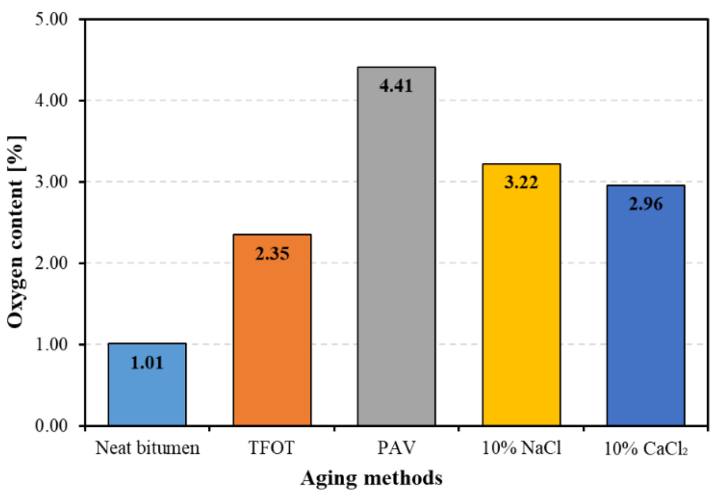

Figure 2. The oxygen content of bitumen before and after aging.

Figure 3 shows the penetration of bitumen with and without aging. It is noted that all aging methods decreased the penetration of bitumen to different extents. For example, PAV aging induced the smallest penetration to 34 dmm, and 10% NaCl also caused a similar reduction in penetration with PAV aging, while TFOT aging and 10% $CaCl_2$ decreased the bitumen penetration to 54 and 51 dmm, respectively. These results indicate that both thermal-oxidative aging and salt solution aging could enhance the stiffness of bitumen. Among four aged methods, PAV aging had a similar hardening effect on bitumen with 10% NaCl, and TFOT aging had a similar hardening effect with 10% $CaCl_2$. These results indicate that the effect of 10% NaCl aging on bitumen stiffness is equivalent to that of long-term aging, and the effect of 10% $CaCl_2$ aging on bitumen stiffness is equivalent to that of TFOT aging.

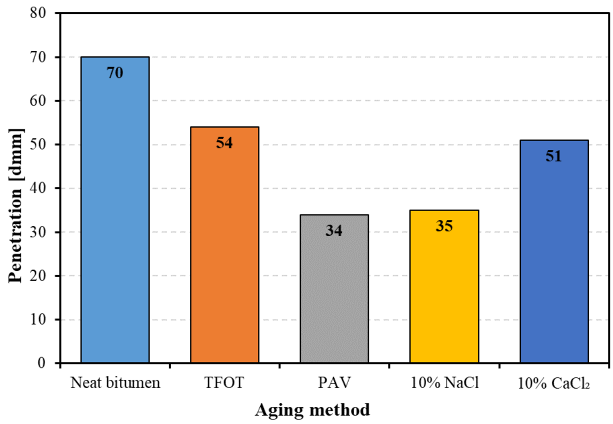

Figure 3. The penetration of bitumen before and after aging.

Figure 4 shows the softening point of bitumen with and without aging. Both thermal-oxidative aging and salt solution aging influence the softening point of bitumen, resulting in a higher value of softening point. However, different aging methods led to different aging degrees of bitumen, arranging the softening point of four kinds of aged bitumen in descending order: PAV aged bitumen, 10% NaCl aged bitumen, TFOT aged bitumen, and 10% $CaCl_2$ aged bitumen. These results demonstrate that both thermal-oxidative aging and salt solution aging positively affect the high-temperature stability of bitumen. The effect of salt solution aging on the high-temperature stability of bitumen is similar with that of TFOT aging.

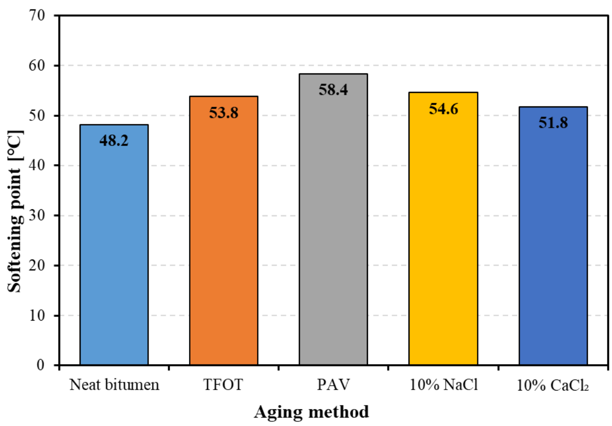

Figure 4. The softening point of bitumen before and after aging.

Figure 5 shows the complex viscosity of bitumen at 60 °C with and without aging. It is obvious that all aging methods increased the complex viscosity of bitumen. Among the five kinds of bitumen, PAV aged bitumen has the largest complex viscosity, which is almost four times that of neat bitumen and twice that of the other three aged bitumen. Salt solution aged bitumen showed a slightly higher value than TFOT aged bitumen. The above results demonstrate that thermal-oxidative aging and salt solution would improve bitumen performance to resist flowing, causing an increase in the stiffening effect. Salt solution aging has a similar effect on the performance to resist flowing with TFOT aging.

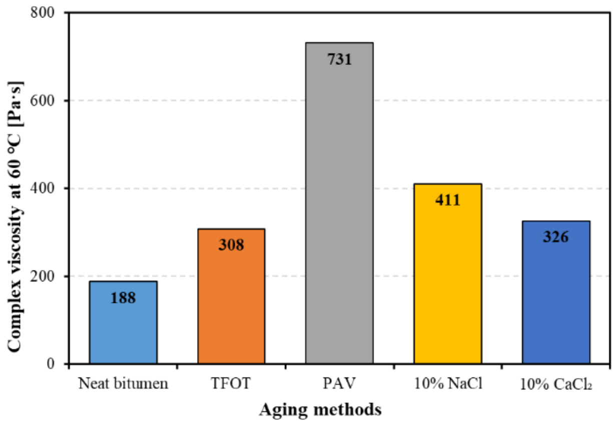

Figure 5. The complex viscosity of bitumen before and after aging.

3.3. Low-Temperature Properties

The low-temperature properties of bitumen were evaluated using flexural creep stiffness (S), stress relaxation ability (m-value), and limited temperature and shown in Figures 6 and 7, and Table 5, respectively. Figure 6 shows the flexural creep stiffness (S) of bitumen (at −12 and −18 °C) before and after aging. The higher the value of flexural creep stiffness, the greater the bitumen stiffness. As seen from Figure 6, it was found that bitumen after four kinds of aging methods presented different increments on S values at a low temperature, arranging the S values of four kinds of aged bitumen in descending order: PAV aged bitumen, 10% NaCl aged bitumen, TFOT aged bitumen, and 10% $CaCl_2$ aged bitumen. These results indicate that both thermal-oxidative aging and salt solution aging would lead to stiffer bitumen at a low temperature, while salt solution aging has a similar effect on the flexural creep stiffness of bitumen with TFOT aging (short-term aging).

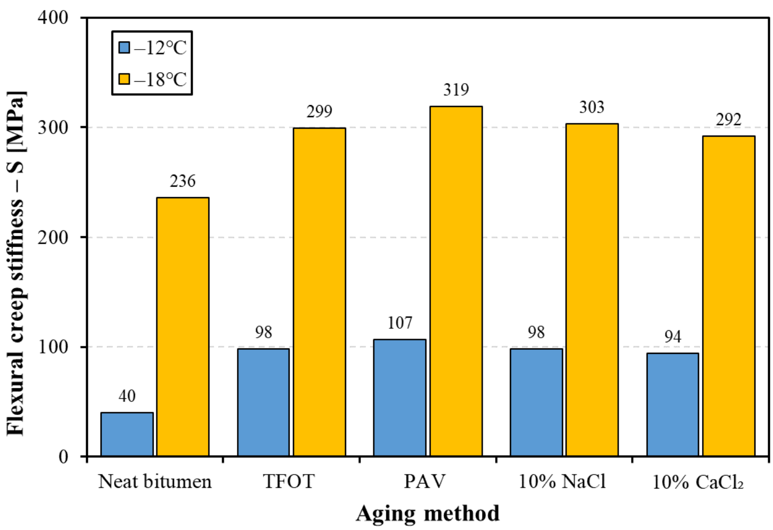

Figure 6. The flexural creep stiffness of bitumen before and after aging.

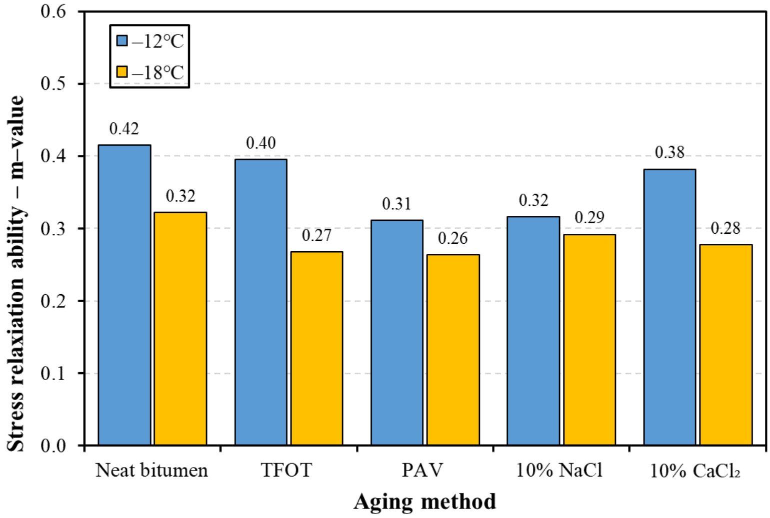

Figure 7. The stress relaxation ability of bitumen before and after aging.

Table 5. The limited temperature of five kinds of bitumen.

Bitumen Type	Neat Bitumen	TFOT Aged Bitumen	PAV Aged Bitumen	10% NaCl Aged Bitumen	10% $CaCl_2$ Aged Bitumen
Limited temperature [°C]	−18	−12	−12	−12	−12

Figure 7 presents the stress relaxation ability of bitumen versus the aging method at −12 and −18 °C. The higher the m-value, the stronger the stress relaxation ability [36]. It could be found that the m-value of bitumen at −12 °C was higher than that at −18 °C, which indicates that bitumen tends to relax more stress at higher temperatures. It is noted that four kinds of aging methods decreased the m-value of bitumen to different extents, arranging the m-value of five kinds of bitumen in descending order: at −12 °C: neat bitumen, TFOT aged bitumen, 10% $CaCl_2$ aged bitumen, 10% NaCl aged bitumen, and PAV aged bitumen; at −18 °C: neat bitumen, 10% NaCl aged bitumen, 10% $CaCl_2$ aged bitumen, TFOT aged bitumen, and PAV aged bitumen. These results indicate that both thermal-oxidative and salt solution aging would decrease the ability of bitumen to relax stress. PAV aged bitumen had the worst ability to relax stress at two temperatures. TFOT aged bitumen had worse stress relaxation ability at −18 °C and better relaxation ability at −12 °C compared to salt solution aged bitumen. The different orders in the relaxation ability of salt aged bitumen and TFOT aged bitumen at −12 and −18 °C could be attributed different mechanisms of salt solution aging and TFOT aging.

The limited temperature in the BBR test of bitumen with and without aging is shown in Table 5. The limited temperature is determined by the lowest temperature that bitumen fulfils the requirement of $S \leq 300$ MPa and $m \geq 0.3$ [37]. As seen from Table 5, neat bitumen showed −18 °C limited temperature, while the limited temperature of the other four aged bitumen was −12 °C. These phenomena indicate that neat bitumen could behave well at a lower temperature compared to the other four types of bitumen, while four kinds of aged bitumen have adverse resistance to cracking at a low temperature. Above all, S, m-value, and limited temperature results indicate that both thermal-oxidative aging and salt solution aging would lead to a bad performance of bitumen at a low temperature to different degrees.

3.4. High-Temperature Properties

Figures 8 and 9 show the master curve of complex shear modulus ($|G^*|$) and phase angle (δ) of bitumen before and after different aging methods, respectively. According to the time–temperature superposition principle, high frequency corresponds to low temperature, and low frequency is in line with high temperature for bitumen [38]. Based on the definition of complex shear modulus and phase angle, a higher value of complex shear modulus relates to an increase in bitumen stiffness, and a smaller value of phase angle indicates a better elastic response of bitumen [39]. As seen from Figures 8 and 9, it is obvious that phase angle decreased, and the complex shear modulus increased with the increase in frequency. This fact indicates that the elastic response and stiffness of bitumen would increase with the increase in frequency (the decrease in temperature).

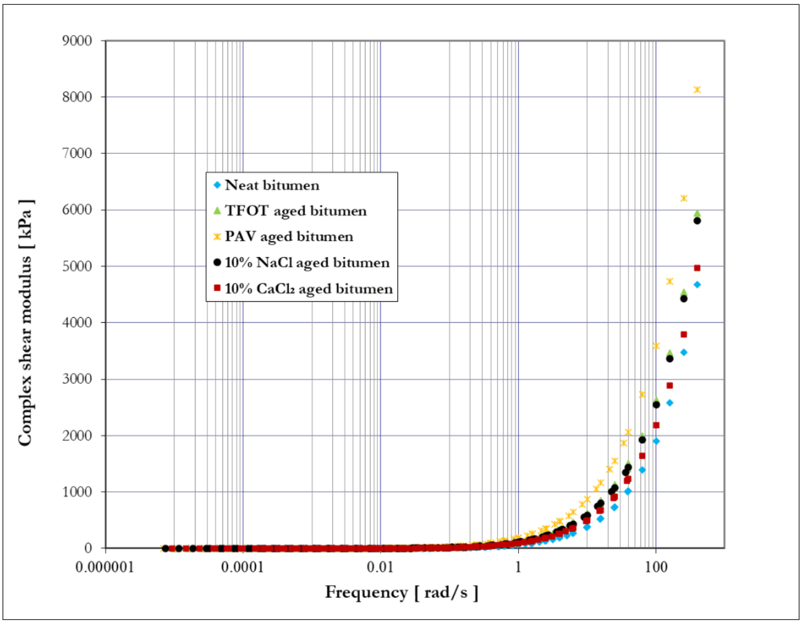

Figure 8. Master curve—complex shear modulus versus loading frequency.

The complex shear modulus of bitumen before and after aging is shown in Figure 8. Both thermal-oxidative aging and salt solution aging increased the complex shear modulus of bitumen, especially at a higher frequency (lower temperature). These results indicate that both thermal-oxidative aging (TFOT and PAV) and salt solution aging (10% NaCl and 10% $CaCl_2$) would improve the stiffness of bitumen, and the improving degree of four aging methods is arranged in descending order: PAV aging, TFOT aging, 10% NaCl aging, and 10% $CaCl_2$ aging. It is worth noting that the difference between aged bitumen and neat bitumen in complex shear modulus increased over frequency, which indicates that the aging process has a more significant effect on the stiffness of bitumen at a high frequency (low temperature) than at a low frequency (high temperature).

Considering the effect of aging on phase angle seen from Figure 9, bitumen showed different reactions on phase angle compared to complex shear modulus. TFOT, 10% NaCl, and 10% $CaCl_2$ aged bitumen presented little changes in phase angle at a low frequency (high temperature) compared to neat bitumen, while they presented large differences in phase angle at a high frequency (low temperature). The above results demonstrate that salt solution aging has a similar effect on bitumen viscoelasticity to TFOT aging. These three aging methods primarily influence the low-temperature properties of bitumen, resulting in a better elastic response of bitumen at a high loading frequency (low temperature). Meanwhile, TFOT aging improved the elastic response of bitumen more than salt solution aging at a high frequency (low temperature). However, a better elastic response of bitumen at a low temperature would cause more risks of cracks, which is regarded as a deterioration of the low-temperature properties of bitumen. Therefore, both TFOT and salt solution aging thus deteriorated the low-temperature properties of bitumen, while TFOT aged bitumen presented slightly worse low-temperature properties of bitumen compared to salt solution aging. These results are consistent with the results from the BBR test. In addition, PAV aging had a dramatic effect on the phase angle of bitumen, resulting in a totally smaller phase angle of bitumen over frequency compared to neat bitumen. This phenomenon demonstrates that PAV aging leads to a better elastic response of bitumen, regardless of frequency or temperature. Additionally, PAV aged bitumen showed a similar phase angle with TFOT, 10% NaCl, and 10% $CaCl_2$ aged bitumen at a high frequency. This fact means that PAV aging has a similar effect on the elastic response of bitumen to the other three aging methods at a high frequency.

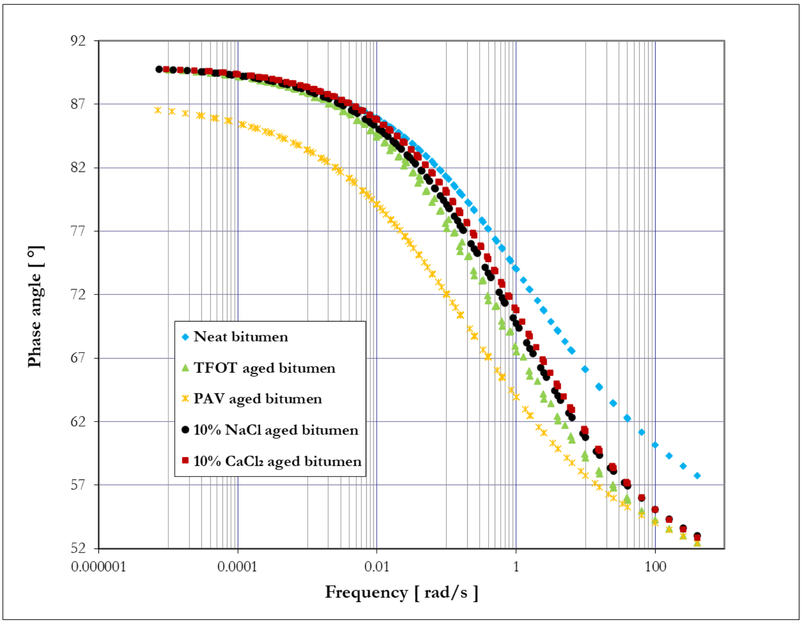

Figure 9. Master curve—phase angle versus loading frequency.

Figure 10 shows the rutting factor of bitumen with and without aging. The rutting factor |G*|/sinδ is a parameter indicating the ability of bitumen to resist rutting at a high temperature. The higher the rutting factor, the greater the ability of bitumen to resist rutting [40]. As seen from Figure 10, the aging increased the rutting factor of bitumen, PAV aged bitumen had the largest rutting factor, and TFOT and salt solution aging had similar effects on the rutting factor of bitumen, whereas neat bitumen had the smallest value of rutting factor. These results indicate that both thermal-oxidative and salt solution aged bitumen have a better ability to resist rutting compared to neat bitumen, arranging the rutting resistance of four kinds of aged bitumen in descending order: PAV aged bitumen, TFOT aged bitumen, 10% NaCl aged bitumen, and 10% $CaCl_2$ aged bitumen.

Additionally, the failure temperature was calculated as the critical temperature at which the rutting factor (at 10 rad/s) was equal to 1 kPa and is shown in Table 6. The failure temperature of bitumen determines the temperature at which the bitumen fails, so it is regarded as a factor indicating high-temperature stability [41]. Aged bitumen showed a higher failure temperature than neat bitumen, which means that aged bitumen is less prone to failure and the aging has a positive effect on the stability of bitumen at a high temperature. Comparing four kinds of aging methods, PAV aging caused the most significant effect on the failure temperature of bitumen, followed by TFOT aging, and NaCl aging; 10% $CaCl_2$ had the smallest effect on failure temperature.

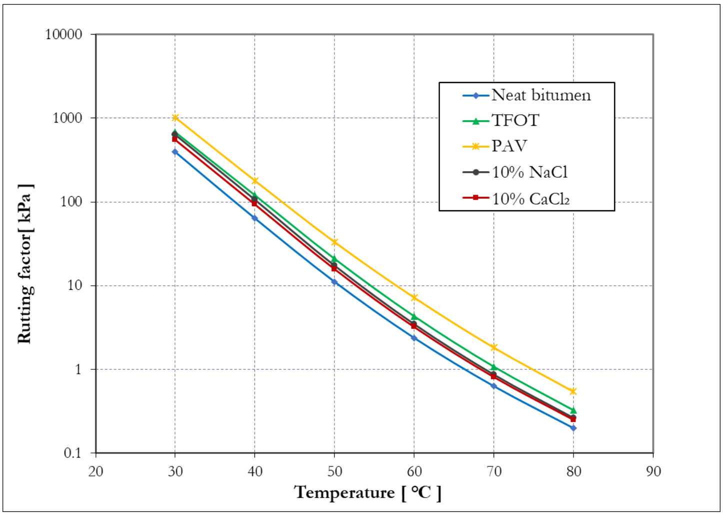

Figure 10. The rutting factor of bitumen before and after aging.

Table 6. The failure temperature of five kinds of bitumen.

Bitumen Type	Neat Bitumen	TFOT Aged Bitumen	PAV Aged Bitumen	10% NaCl Aged Bitumen	10% $CaCl_2$ Aged Bitumen
Failure temperature (°C)	65	70	74	69	68

3.5. Comparison of Bitumen Aging Degree Caused by Thermal-Oxidative Aging and Salt Solution Aging

The above test results showed that salt solution would also lead to bitumen aging. In order to systematically compare thermal-oxidative aging and salt solution aging, the aging degree of bitumen caused by different aging methods was characterized by the aging factor of the main property parameters [42]. In this research, the aging factor (AF) of oxygen content, penetration, softening point, and complex viscosity; the average value of AF of flexural creep stiffness and stress relaxation ability (at −12 and −18 °C); complex shear modulus $|G^*|$; phase angle δ; and rutting factor (at 30, 40, 50, 60, 70, and 80 °C) were calculated according to Formula 1 and shown in Table 7. The positive and negative values of AF indicate that the parameters increase or decrease after different aging methods.

$$\text{Aging factor (AF)} = \frac{\text{Parameter}_{\text{after aging}} - \text{Parameter}_{\text{neat bitumen}}}{\text{Parameter}_{\text{neat bitumen}}} \tag{1}$$

where $\text{Parameter}_{\text{after aging}}$ indicates the property parameter of bitumen after aging, and $\text{Parameter}_{\text{neat bitumen}}$ indicates the parameter of neat bitumen.

As seen from Table 7, salt solution aging had the same varying trend with thermal-oxidative aging, leading to negative AF values of penetration, m-value, phase angle, and positive AF values of the rest of the parameters. However, PAV aging resulted in the highest value of the sum of absolute values of all AF, followed by 10% NaCl, and TFOT aging; 10% $CaCl_2$ had the smallest value of the sum of absolute values of all AF. These results indicate that PAV aging leads to the most severe aging on bitumen, followed by 10%

NaCl, and TFOT aging; 10% $CaCl_2$ causes the least aging on bitumen. Meanwhile, the sum of absolute values of all AF of salt solution aged bitumen is close to that of TFOT aged bitumen, which indicates that the influence of salt solution aging on bitumen performance is comparable to that of TFOT aging (short-term aging).

Table 7. The aging factor of four kinds of aging methods.

Aging Method	TFOT	PAV	10% NaCl	10% $CaCl_2$
AF-Oxygen content	1.33	3.37	2.19	1.93
AF-Penetration	−0.23	−0.51	−0.50	−0.27
AF-Softening point	0.12	0.21	0.13	0.07
AF-Complex viscosity	2.00	9.05	3.71	2.29
$\overline{AF}$-S	0.86	1.01	0.87	0.24
$\overline{AF}$-m-value	−0.11	−0.21	−0.17	−0.11
$\overline{AF}$-Complex shear modulus $\lvert G^* \rvert$	0.75	1.75	0.49	0.35
$\overline{AF}$-Phase angle δ	−0.05	−0.10	−0.03	−0.02
$\overline{AF}$-Rutting factor $\lvert G^* \rvert/\sin\delta$	0.78	1.84	0.50	0.36
Sum of absolute value of all AF	6.23	18.05	8.59	5.64

4. Conclusions

This paper compared the effect of thermal-oxidative aging and salt solution aging on the bitumen performance of laboratory samples.

Bitumen showed the same varying trends under salt solution aging and thermal-oxidative aging in terms of oxygen element, physical properties and low-temperature properties, and high-temperature properties, resulting in the aging of bitumen. However, different effects on the morphology of bitumen caused by salt solution aging compared to thermal-oxidative aging were observed, i.e., salt solution aging led to sharp angles of bitumen pieces, while thermal-oxidative aging induced the rough surface of bitumen with certain cracks.

The aging degrees caused by thermal-oxidative aging and salt solution aging were different, arranging the aging degree caused by four kinds of aging methods in descending order: PAV aging, 10% NaCl aging, TFOT aging, and 10% $CaCl_2$ aging. These differences in morphology and aging degree of bitumen caused by thermal-oxidative and salt solution aging are attributed to the different conditions and mechanisms of aging methods.

The aging effect of salt solution aging on bitumen performance is almost equivalent to that of TFOT aging, except for morphology.

This research revealed that salt solution aging had a similar aging effect on bitumen performance with TFOT aging. The experimental design and comparison results can provide a theoretical basis for the establishment of bitumen solution aging standards. However, the results in this research are only valid for neat bitumen, and it should be followed by further investigations on the effect of different aging methods on modified bitumen and the mechanism of salt solution aging on bitumen in future studies.

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