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RESEARCH ARTICLE-CHEMISTRY

The Effect of Ionic Liquids Incorporation on the Self-healing Behavior of the Bitumen

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Abstract
In the asphalt pavements, which are prepared by mixing bitumen and aggregates, fatigue cracking and thermal cracking failure occur due to continuous loading and climate conditions. Extending the life of asphalt pavements is very important from an environmental and economic point of view. In this study, reactions are conducted to investigate the effects of six ionic liquids (IL) with different side-chain lengths on the self-healing properties of bitumen. Thermogravimetric analysis and differential scanning calorimetry analysis are performed for ionic liquid characterization, while for bitumen characterization, Saturates, Aromatics, Resins, Asphaltenes (SARA) fractionation of bitumen and Gel Permeation Chromatography, Nuclear Magnetic Resonance, Elemental Analysis of these sub-fractions were performed. In addition, two new test methods have been developed to measure the self-healing capacity of bitumen. The first method shows the effects of rest times when intermittent loading is applied to the sample at high temperatures, while the other method was developed to demonstrate the self-healing ability of bitumen at low temperatures with long rest periods. Stripping tests, asphalt fatigue tests and zeta potential measurements are done to investigate the effects of ionic liquids on bitumen and aggregate interactions. The results indicated that different ionic liquids have different effects on asphalt self-healing mechanism. IL improved the self-healing performance of asphalt 40% at high temperatures, and 100% at low temperature while stripping properties 25% and asphalt fatigue life 20% improved. Therefore, it can be concluded that different bitumen-IL modification recipes could be used for self-healing of asphalt pavements, depending on climatic conditions and traffic density.

Keywords Self-healing · Bitumen · Asphalt pavements · Ionic liquids · Asphalt pavement cracking

1 Introduction

Asphalt concrete is one of the most widely used materials in the pavement industry, with about 300 million tones throughout Europe in 2018 [1]. Asphalt is prepared by mixing bitumen and aggregates at temperatures around 190 °C and then compacting them at around 150 °C. Bitumen is a black and viscous hydrocarbon that is obtained as a product of crude oil distillation. Bitumen acts as a binder in the asphalt mixtures to stick the aggregate materials together [2]. Due to continuous loading and varying climatic conditions, fatigue cracking, rutting, and thermal cracking occur on the roads. These are some of the most common reasons for asphalt pavement failure. As a result of the weaknesses in the asphalt pavements, new roads need to be built, or the damaged roads need to be maintained. According to Organization for Economic Co-operation and Development (OECD), around 230 million € was spent on road maintenance in Turkey in 2017. The amount is higher for countries like Japan and Italy, with road maintenance spending around 17.2 and 8.8 billion €, respectively [3].

Since bitumen and aggregates need to be heated to the mixing temperatures for building new roads, road maintenance requires a large consumption of fossil fuels, which has economic and environmental consequences. Greenhouse gas

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emissions occur during manufacturing and the compaction of the asphalt roads, resulting in further negative impacts on the environment [4]. Therefore, extending the service life of asphalt pavements is of paramount importance from an economic and environmental perspective [5]. The asphalt roads' life can be extended by different methods, such as modifying bitumen with different additives, mainly polymers, which is the most common technique. Styrene-butadiene styrene (SBS) is the most widely used polymer for bitumen modification, followed by styrene-butadiene rubber, vinyl acetate, and polyethylene [6]. SBS addition to bitumen results in an increase in strength and elasticity of the bitumen via the physical cross-linking of the molecules into a three-dimensional network. However, modifying the asphalt pavements using SBS has its limitations, and innovative alternative solutions should be implemented to increase the service life of asphalt roads.

An emerging alternative for extending asphalt life is to delay the failure at micro- and macro-level cracks through self-healing property. The self-healing technology has been used in the automotive and aerospace industries for some time [7–9] and recently started to be applied to asphalt concretes. Asphalt concrete already has the intrinsic self-healing property, which can be accelerated artificially. In his work, Phillips explained the self-healing mechanism by a three-step process (TSP). TSP involves closure of macro-cracks due to consolidation of stresses and flow of bitumen, adhesion of two crack surfaces resulting from the surface energy, and complete recovery of the mechanical properties due to diffusion [10]. Other studies have also pointed out that bitumen can recover its mechanical strength by closing the gaps between the cracks at high temperatures or during long rest periods [11–15]. In practice, the features may not always be sufficient. The intrinsic self-healing properties of the bitumen need to be improved to shorten the time or decrease the temperature required for self-healing. Thanks to the self-healing properties of bitumen binders, asphalt pavement has its self-healing functions. Asphalt materials with self-healing properties will reverse the cracking damage and repair the damage in the asphalt. The self-healing mechanism in asphalt is like a zipper, simulating that it first opens (crack formation and propagation) and then closes (healing) [16].

As seen in Fig. 1 in asphalt pavements' adhesive structures have two self-healing mechanisms. These mechanisms are known as adhesive healing and cohesive healing. The healing mechanism resulting from the separation of bonds between the mastic and aggregate surfaces is called adhesive healing. The healing resulting from the healing of micro-cracks in asphalt is called cohesive healing. In both cases, microcracks are self-healing with the rest periods and high temperatures.

There are several technologies in use for improving the self-healing property of asphalt concrete. One approach involves heating the asphalt concrete by adding conductive fibers to enhance the material's conductivity [17, 18]. In their study, Garcia et al. investigated the conductivity of asphalt mortar with different sand-bitumen ratios and volumes of conductive particles. They prepared the specimen by mixing conductive materials, bitumen, and aggregate. Their results indicated that the mixture could be heated with induction energy. They also found that there is an optimum content of additives for different sand-bitumen ratios [19]. In another study aiming to develop inductively heated self-healing asphalt layers, Garcia et al. found that the maximum temperature achieved in a certain period can be controlled by the bitumen-sand ratio and volume of the fibers. They also carried out Gel Permeation Chromatography (GPC) analysis to investigate molecular weight distribution change of heated induction samples found that there is no aging of bitumen during heating [20]. The zeta potential, an expression of the repulsive force between similar and neighboring charged particles in distribution, expresses the electrokinetic potential in colloidal systems. When the pulling force overcomes the driving force, a low zeta potential occurs and clusters form. Therefore, the high zeta potential is known as stability. When we evaluate the zeta potential values, zeta potential between 30 and 40 means averages stability, zeta potential between 40 and 60 means good stability, while values above 60 are shown as excellent results [21].

In another study, Liu et al. studied the effects of different conductive additives on the induction heating speed, bending strength, and induction healing rate. They concluded that the fractured asphalt beams with some conductive additives could regain their bending strength to fresh samples after induction heating [22]. In addition, the effects on the self-healing function of ionic liquids are reviewed, including their ionic diffusion ability and environmental conditions. Also, ionic liquids are defined as basic self-healing agents with their high healing properties, easy healing conditions, and excellent conductivity. Ionic liquids are combined with different materials by reversible reactions, electrochemical and coordination reactions such as Diels–Alder, giving the materials self-healing properties. This property provides self-healing to ionic liquids due to secondary bonds such as ion–dipole interactions, hydrogen bonds, and ionic aggregation [23]. It is seen that the rate constant and extraction kinetics of bitumen decrease with the addition of IL and the contribution of its viscosity. This showed that I.Ls could be an alternative to the Clark hot water-based extraction (CHWE) process. In addition, the electrochemical interactions between oil sands and IL hydrodynamic shear stress affect the kinetic profile of the extraction. Greater surface tension and contact angle are necessary from the thermodynamic point of view. The effect of viscosity significantly influences the release dynamics of bitumen, independent of the interactions between IL and co-solvent and oil sand [24].

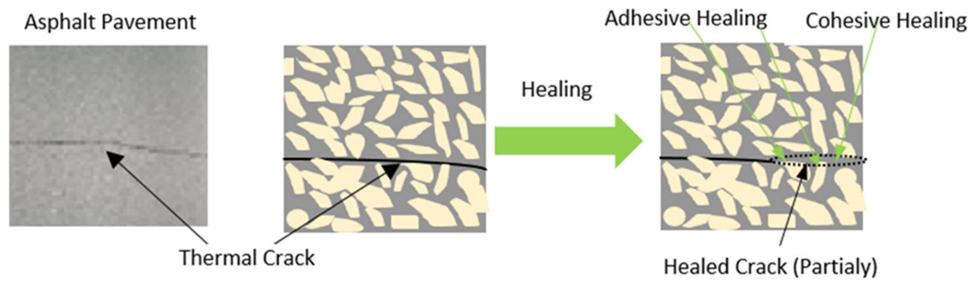

Fig. 1 Schematic illustration of self-healing of thermal cracks in asphalt

The healing effect of induction heating on less commonly practiced porous asphalt was also studied in the literature. Gallego et al. studied the impact of using microwaves instead of electromagnetic induction as an alternative to heating the asphalt concretes. They concluded that microwaves could decrease the optimum amount of steel wool by ten times [25]. The experimental results suggest that induction heating can be successfully applied to porous asphalt with extended [26]. Biological approaches are also employed to increase the self-healing capacity of construction materials. One strategy involves adding bacteria with calcium carbonate to synthesize into the concrete to seal the formed cracks rapidly. In their study, Jonkers et al. investigated the potential of bacteria as a self-healing agent in concrete. They found that specimens produced more crack-plugging minerals than the control specimens after bacteria addition [27]. In another study, Wiktor and Jonkers investigated the crack-healing potential of a two-component bio-chemical self-healing agent embedded in porous expanded clay particles. They concluded that the self-healing agent could improve the durability of the concrete in wet environments [28]. The self-healing ability of asphalt was improved by another method in which healing microcapsules are used. In this method, when the microcapsule encounters the microcrack, it is opened using the fracture energy at the crack's tip, and the healing agent is released into the matrix. In this way, the healing agent diffuses into the microcracks and prevents the crack from spreading [29, 30].

Moreover, the biological approach for self-healing requires certain conditions, such as high pH, for the calcium carbonate synthesizing bacteria to remain viable. Therefore, there is a need for more effective alternative technologies to improve the self-healing capability of bitumen. The use of ionic liquids might be an alternative technology for enhancing the self-healing capability of bitumen. Ionic liquids are made up of an anion and a cation and are usually liquid at room temperature. The ionic liquids have many applications, including catalysis, biological reaction media, and electrochemistry. In studies conducted about Canadian tarsand, the bitumen contained in tarsand is separated using IL and organic solvents. In this method, the mixture form was mixed in the temperature range of 25–55 °C and separated into phases. By this way, it is completely separated from the bitumen sands. Water is not used directly in this process, and then only small amounts of water could be used to separate the entrained sand and clay. The technologies that are mentioned above also have some drawbacks. Self-healing by induction heating technology requires an external heat source, making the application of the technology hard [31–35].

Asphalt self-healing can improve the fatigue cracking performance of asphalt pavements. Asphalt is known as a viscoelastic liquid with its surface wetting and diffusion features. Because of these features, it can close its micro-cracks, regain its strength and hardness, and heal itself. When the self-healing features of asphalt become better, the self-healing process is completed better. In this study, the effects of ionic liquids with different side-chain lengths on the self-healing behavior of bitumen are investigated. The self-healing behavior of bitumen is measured with the newly developed techniques on Dynamic Shear Rheometer (DSR) and Fraass Breaking Point devices.

2 Materials and Methods

50/70 penetration grade bitumen from TUPRAS Izmit Refinery is used in the studies. The ionic liquids, 1-allyl-3-methylimidazolium chloride (IL 1 short) > 98% purity, 1-hexadecyl-3-methylimidazolium bis-trifluoromethylsulfonyl)imide (IL 1 long) > 98% purity, 1-butyl-3-methylimidazolium chloride (IL 2 short) 99% purity, 1-hexadecyl-3-methylimidazolium chloride (IL 2 long) > 98% purity, 1-butyl-3-methylimidazolium bromide (IL 3 short) 99% purity and Methyltrioctylammonium bis(trifluoromethylsulfonyl)imide (IL 3 long) 99% purity are purchased from IOLITEC Inc. Agilent 1200 series GPC performs molecular weight analysis with 300 × 7.5 mm sized mixed gel Zorbax column. Tetrahydrofuran is used as solvent and carrier phase. Twenty μ injections with a 1 ml/min volumetric rate are applied for the measurements.

Elemental analysis of bitumen is carried out by a Thermo Finnigan Flash EA 1112 Series model elemental analyzer using 3 − 4 mg samples. The thermal behavior of ionic liquids over specific temperature ranges is studied by a Mettler Toledo 822e Differential Scanning Calorimeter. DSC

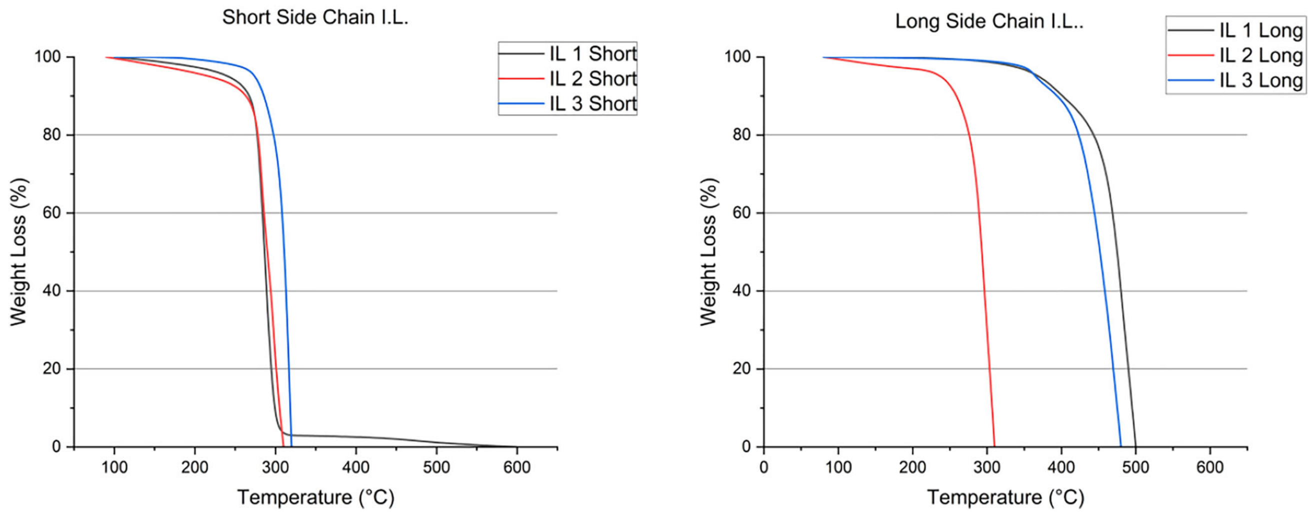

Fig. 2 TGA results of ILs

analysis for bitumen and ILs is carried out under the N_2 atmosphere. The temperature range used in the studies is from −50 to + 300 °C with a heating rate of 10 °C/min. Zeta potential measurements of the distributions were made on the Malvern 2000 Zetasier instrument. For their measurement, the dispersions need to be diluted. So, the dispersions were subjected to precipitation at 600 rpm for 30 min. The zeta potentials of the non-precipitated fractions were measured ten times in two consecutive series, and these measurements were averaged. Nuclear magnetic resonance (NMR) analysis of bitumen is carried out by a Varian Unity Inova 500 MHz NMR model analyzer using 1–2 mg samples.

The self-healing measurements at high temperatures are carried out on an Anton Paar SmartPave 102 Dynamic Shear Rheometer. The self-healing behavior of bitumen during long resting periods at low temperatures is studied by an Anton Paar BPA5 Fraass Breaking Point device. The asphalt performance of the developed formulations is studied on the Cooper Universal Testing Machine device according to the EN 12697-24 E standard.

The effect of ionic liquid addition on bitumen aggregate interactions is studied by using a modified version of the method given in the work by Painter et al. [36]. Tar sand, toluene, and ionic liquids are used in a weight ratio of 1:2:3. The ionic liquid is added to tar sand, and toluene is added to tar sand-ionic liquid mixture. The final mix is mixed at 55 °C with a magnetic stirrer. The phase separation is investigated via visual investigation. The effects of ionic liquid addition on bitumen- aggregate affinity are further investigated by stripping tests. 100 g of 6.3–10 mm aggregate is mixed with 5 g of bitumen until the aggregate surface is fully covered with bitumen. The aggregates are taken into a petri dish, and water is added. The petri dish is placed in an oven at 60 °C for 24 h. At the end of 24 h period, the percentage of the aggregate area covered with bitumen is investigated.

3 Results and Discussion

3.1 Ionic Liquid Characterization

The ionic liquids were characterized by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA investigations are carried out to determine the thermal stability of the ionic liquids. Thermal stability is critical for the additives since asphalt mixing, and compaction temperatures are high (~ 180 °C). The TGA results for the ionic liquids are given in Fig. 2.

Looking at Fig. 2, it is seen that the temperatures at which mass loss of long-chain ionic liquids is higher than that of short-chain ionic liquids. The results indicate that all of the ionic liquids used in this study have high thermal stabilities. It can be concluded that these ionic liquids can be bitumen additives since they will remain in the mixture at asphalt mixing and compaction temperatures.

In addition to the TGA studies, DSC analysis is carried out to investigate the possibility of endothermic or exothermic reactions at asphalt mixing and compaction temperatures and results are shown in Fig. 3. According to literature results, the boiling points of ILs are generally below 100 °C. The results of DSC analysis of ILs indicate that the ILs have boiling points in the range 60–80 °C. These results are in agreement with the literature results. The results indicated that five ionic liquids have only one peak within the investigated temperature range, indicating the melting temperature. In contrast, no peaks were obtained for the last ionic liquid since it is already a liquid at the lower limit of the temperature range (°C) used in the investigations.

3.2 Bitumen Characterization

Bitumen chemistry is an essential parameter in bitumen modification. Gaestel et al. found that the relative amounts of

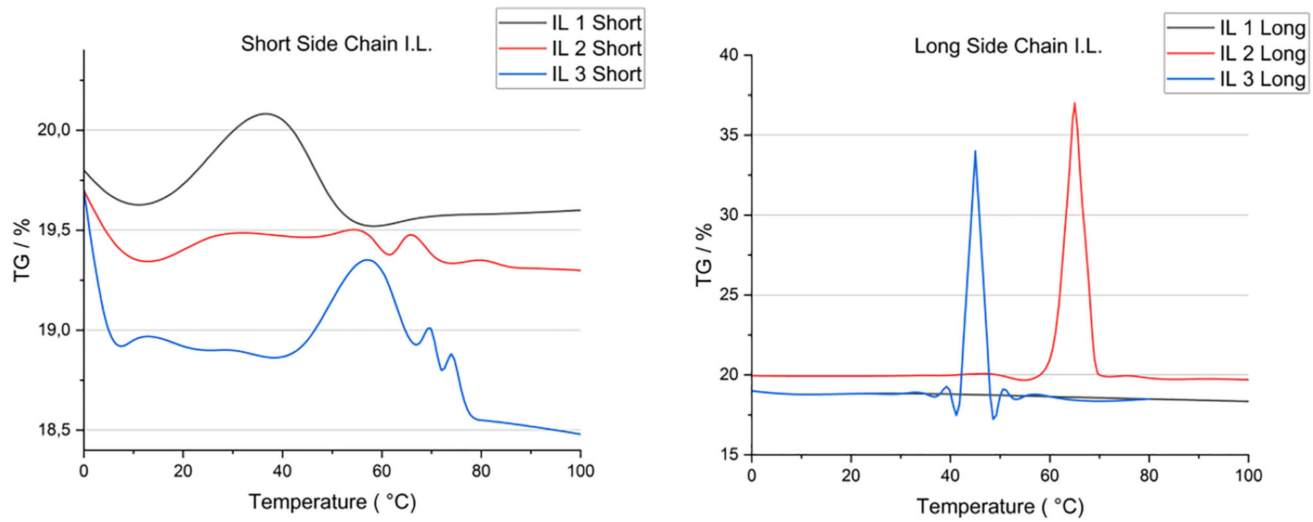

Fig. 3 DSC results of ILs

Table 1 Characterization results of bitumen and SARA fractions

	Bitumen	Saturate	Aromatic	Resin	Asphaltene
Sara analysis (%)	–	27	40	21	12
Elemental analysis					
% C	83.67	86.34	84.82	81.72	82.84
% H	10.95	11.90	9.23	9.03	5.68
% S	3.17	1.59	3.34	2.52	3.68
% N	0.85	–	–	1.06	1.05
H/C ratio	1.57	1.65	1.31	1.33	1.40
GPC analysis					
Mw (g /mole)	803	724	674	719	1460
% Molecular weight	803	195	270	151	175
	Calculated % Molecular Weight for Bitumen 791				
H-NMR results (%)					
Methyl ends (CH_3)	1.27	0.97	5.26	1.10	6.72
Methylene chain(CH_2)	19.94	20.21	19.85	20.79	–
Saturated rings or hydroaromatic rings (CH_2,CH)	66.98	73.96	60.95	62.85	86.12
α-aromatic branches (CH_2, CH)	9.98	3.78	11.31	11.35	2.68
Single aromatic ring(C_6H_6)	1.93	1.09	2.63	–	4.48
Diphenyl methane bridge(CH_2)	–	–	–	0.15	–
Single, double or triple aromatic rings	–	–	–	3.76	–

Saturates, Aromatics, Resins, Asphaltenes (SARA) fractions of the bitumen are of primary importance for the compatibility between the polymer and the bitumen [37]. Since bitumen chemistry is an essential parameter in bitumen modification, the amounts of SARA fractions and their elemental composition of the SARA fractions in bitumen are determined. The results are given in Table 1.

Table 1 indicates that the aromatic fraction is the most common subgroup in the bitumen structure of this study. Furthermore, it is seen that asphaltene and resin fractions contain most of the sulfur and the whole nitrogen that is present in the bitumen. After separating the subgroups, the molecular weight of bitumen and SARA fractions was measured using gel permeation chromatography (GPC), and results are also given in Table 1. Asphaltene has the highest molecular weight among the fractions, as expected. The measured bitumen molecular weight in GPC is 803, and the calculated molecular weight of bitumen by multiplying percentages of each fraction with their molecular weight was found as 791. Comparing the measured and calculated bitumen molecular weights is reasonably close to each other, indicating high extraction performance. The H/C ratios for the saturate and the asphaltenes fractions are given as 2 and 1, respectively, in the literature [38, 39]. However, the H/C ratio for saturate fraction is found as 1.65, whereas for asphaltenes, it is seen as 1.4. H-NMR studies are carried out to explain the disagreement between the results. An investigation of Table 1 indicates that saturates contain high amounts of saturated rings or hydroaromatic rings. This arrangement of carbons decreases the hydrogen content in saturates, which explains the slightly lower H/C results. On the other hand, asphaltene fractions have α-aromatic alkyl chains with a higher H/C mole ratio.

3.3 Preparation of Bitumen and ILs Mixtures

Based on our preliminary studies and observations in the laboratory, a method has been developed to mix bitumen and ionic liquids. According to the developed method, the bitumen is first heated up to 100 °C, rendered fluid. The heated bitumen was added to the reactor and mixed for 5 min at 250 rpm. Then ILs are added to the reactor. After each addition of 1% additive IL, the mixture is mixed at 250 rpm for 3 min. At the end of the ILs addition, mix bitumen and ionic liquids are mixed at 250 rpm for 30 min.

3.4 Self-Healing Capability Measurements

There is no standard test method for measuring the self-healing capability of bitumen. Therefore, new test methods are developed to carry out the measurements for quantifying the self-healing capabilities of the formulations.

The Multiple Stress Creep Recovery (MSCR) test is modified to measure the self-healing characteristics at high temperatures. In the MSCR test, a load is applied to the specimen for a certain period, followed by a relaxation period with no load on the specimen. At the end of the test, the non-recoverable creep compliance (Jnr) is measured, which measures the amount of strain the specimen cannot recover. It is known that the resting period has a significant effect on the self-healing capability of bitumen. Therefore, as part of method design studies, the resting period in the MSCR test is varied. The non-recoverable compliance value is measured to see the effects of resting periods. The results obtained with base bitumen are given in Table 2.

The results in Table 2 indicate that the Jnr value decreases with increasing resting periods. This decrease can be related to the enhancement of self-healing to occur at more extended rest periods, meaning that the developed method can be used to investigate the self-healing capability of bitumen. After determining the adequacy, the technique is used to elaborate on the effects of ionic liquid addition on the self-healing properties of bitumen. For this purpose, six different ionic liquids are mixed with bitumen at two different ratios (1% and 5% bitumen to ILs, % wt) to prepare a total of 12 specimens. The specimens are then tested with the newly developed technique, and the Jnr values are compared with the base bitumen. The results indicated that ionic liquid incorporation could improve the self-healing properties of bitumen at high temperatures. In particular, IL 1 short chain and IL 2 short chain yielded excellent results with a nearly 40% improvement compared to base bitumen. This improvement results from the lower viscosity values of the modified bitumen, which increases the mobility of the molecules and results in the closure of the microcracks.

In addition to MSCR studies, a Fraass Breaking Point tester was used as a part of test design studies to determine the self-healing capabilities of bitumen at low temperatures

Table 2 Modified MSCR results for bitumen and bitumen + ILs, at 64 °C

	% IL	Resting Period (sec)	Non-recoverable compliance (Jnr) (1/kPa)
Bitumen		9	6.81
		18	0.68
Bitumen + IL 1 short	1	9	5.47
		18	0.6
	5	9	4.46
		18	0.48
Bitumen + IL 2 short	1	9	5.65
		18	0.64
	5	9	4.06
		18	0.46
Bitumen + IL 3 short	1	9	5.01
		18	0.58
	5	9	6.71
		18	0.72
Bitumen + IL 1 long	1	9	7.65
		18	0.86
	5	9	8.26
		18	1.17
Bitumen + IL 2 long	1	9	5.45
		18	0.61
	5	9	7.44
		18	0.8
Bitumen + IL 3 long	1	9	6.83
		18	0.74
	5	9	8.91
		18	2

Table 3 Time to breakage in base and ionic liquid added bitumen with different rest periods

% IL	Fatigue time (min.) (at −4 °C)	Resting period (day)	Failure temperature (°C)	Load exposure time until failure (min)
Bitumen	30	0	−7	50
		2		80
		4		240
Bitumen + IL 1 short	30	0	−7	250
		2		233
		4		333
	30	0	−7	Failure at first twist
		2		214
		4		Failure at first twist
Bitumen + IL 2 short	30	0	−7	144
		2		150
		4		81
	30	0	−7	130
		2		168
		4		95
Bitumen + IL 3 short	30	0	−7	3
		2		50
		4		70
	30	0	−7	6
		2		162
		4		112
Bitumen + IL 1 long	30	0	−7	81
		2		616
		4		140
	30	0	−7	123
		2		240
		4		333
Bitumen + IL 2 long	30	0	−7	80
		2		48
		4		100
	30	0	−7	450
		2		116
		4		166
Bitumen + IL 3 long	30	0	−7	43
		2		45
		4		410
	30	0	−7	31
		2		42
		4		Failure at first twist

during very long resting periods. The idea of the test is to apply a load, which will not fail, on the specimen, then give a rest period to allow the sample to heal itself, use a load once more until failure and measure the time of load exposure. The results indicate that as the resting period increases, the specimen can withstand loading for longer without failure. This means that the specimen can heal itself during the resting periods, indicating that the developed technique can be used

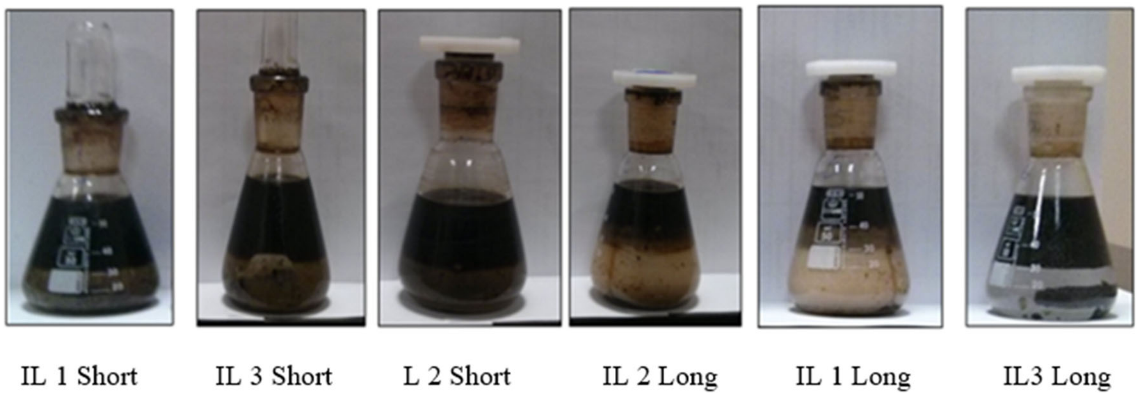

Fig. 4 The effect of ionic liquids on bitumen–filler interactions after one week

to measure the self-healing capability of bitumen during very long resting periods. Results are shown in Table 3.

The developed technique is used on ionic liquid-modified bitumen samples to investigate the effect of ionic liquid addition on the self-healing properties of bitumen at low temperatures and very long resting periods. When the results obtained for additive-free and ionic liquid added bitumen are compared, it has been determined that longer bending times are required for a fracture to occur in bitumen modified with 1% IL1 short and 5% IL 1 long ionic liquid. In this context, positive results have been obtained with bitumen modified with these two ionic liquids. The results indicate that ionic liquid addition can extend the loading time until failure two times more than base bitumen. IL 1 long is the ionic liquid that gives the best results in this test. The ionic part of the ionic liquids allows the formation of dipole–dipole and H bonds. In contrast, the hydrocarbon part makes it possible to form van der Waals forces within bitumen. These non-covalent bonds can explain the improvements compared to base bitumen.

3.5 Measurement of Ionic Liquid on Bitumen–Aggregate Interactions

Visual investigations were used to study the effect of ionic liquids on bitumen-filler interactions in this study. The results obtained with mixtures involving six different ionic liquids at the end of one week are given in Fig. 4.

An investigation of Fig. 4 reveals that the addition of ionic liquid can trigger or prevent phase separation, depending on the properties of the ionic liquid. The results indicate that the IL-3 short side chain prevents phase separation between the bitumen and filler materials. This is indicated by the almost homogeneous mixture that is obtained at the end of 1 week period. On the other hand, complete phase separation is obtained with the IL-3 long side-chain combination. However, zeta potential measurements were also made to determine the stability of these phases. The results obtained as a result of the zeta potential measurements are given in Fig. 5.

The zeta potential results obtained support the observational analysis results given in Fig. 4. Figure 5 shows that the highest zeta potential was obtained with IL 3 short, while the lowest zeta potential value was obtained with IL 3 long. According to these results, the stability of the mixture prepared with IL 3 short is the highest, and the stability of the mix prepared with IL 3 long is the lowest. The bitumen–aggregate interactions are further studied by stripping tests. The binding between bitumen and 6.3–10 mm aggregate particles in the presence of water is measured in this test. The obtained results are given in Table 4.

The results in Table 4 indicate that the addition of 1% IL results in a high stripping performance with all ionic liquids. However, further addition of some ILs decreases the bitumen viscosity to such an extent that the bitumen can no longer cover the aggregate surface effectively. This is indicated by the 20–25% results obtained for IL 1 short chain and IL 2 short chain.

3.6 Asphalt Performance

Fatigue tests are carried out on compacted asphalt specimens that are prepared by the base and ionic liquids-modified bitumen. In fatigue tests, a loading-resting cycle is applied on the asphalt specimens, and the number of cycles until failure is determined. The results for fatigue tests are given in Fig. 6.

The results indicate that the addition of IL 1 long improves the fatigue performance of the asphalt by around 30% compared to base asphalt. The long hydrocarbon chain of the ionic liquids improves the solvation power of the bitumen, thus making the binding between the bitumen and the aggregates stronger.

These stronger bonds between the bitumen and the aggregate molecules make the material more robust, explaining the 30% improvement in resistance to fatigue property compared to the base bitumen.

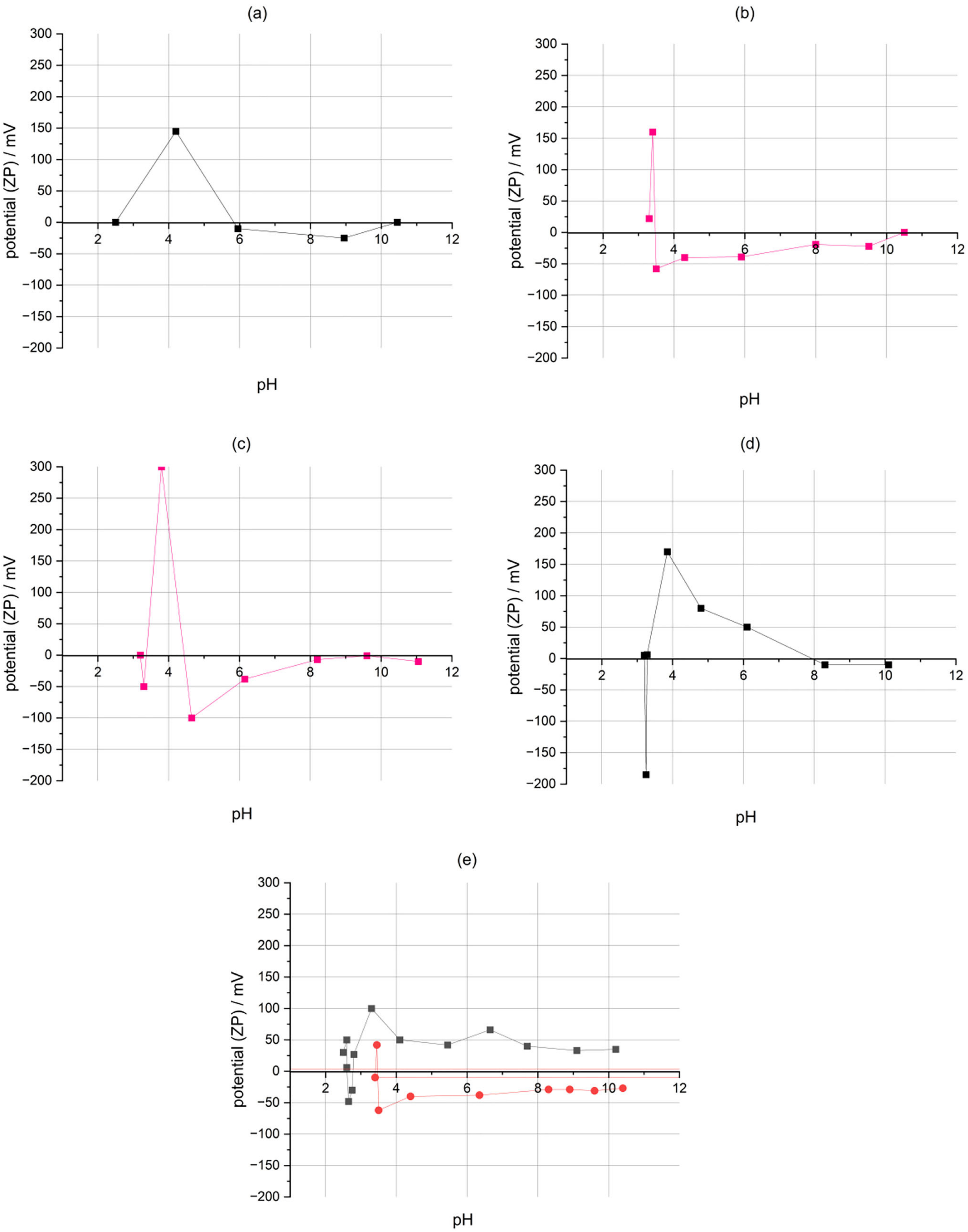

Fig. 5 Z potential of ILs-oil sand mixtures, IL-1 short (**a**), IL-2 short (**b**), IL-3 short (**c**), IL-2 long (**d**), IL-1 long (**e**) (red line), IL-3 long (**e**) (black line)

Table 4 Stripping test results

% IL	% Stripping strength					
	Bitumen + IL 1 short	Bitumen + IL 2 short	Bitumen + IL 3 short	Bitumen + IL 1 long	Bitumen + IL 2 long	Bitumen + IL 3 long
1	95–100	95–100	95–100	95–100	95–100	95–100
5	20–25	20–25	50–55	95–100	80–90	95–100

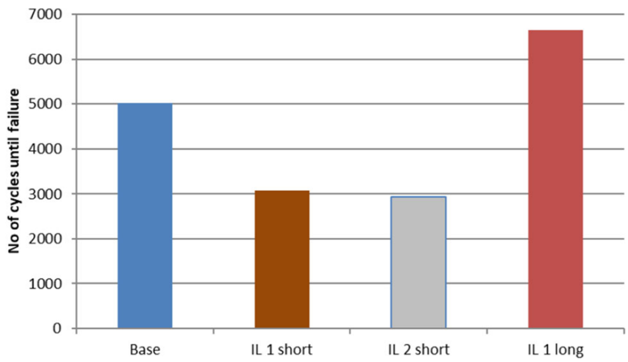

Fig. 6 Fatigue test results

4 Conclusions

This study aimed to investigate the effects of ionic liquids with different side-chain lengths on the self-healing behavior of bitumen. Ionic liquids, with their ionic parts and hydrocarbon parts, are considered good candidates for improving the self-healing capability of bitumen. The thermal stability examination of ionic liquids is of great importance since bitumen needs to be heated up to 150 °C for mixing and compaction. The thermogravimetric analysis results obtained from the studies with long- and short-chain ionic liquids indicate that these ionic liquids could remain stable at asphalt mixing temperatures between 150 and 160 °C. In addition to those, from the DSC analyses it was determined that no unexpected reaction was observed during heating in the tested ionic liquids; therefore, ionic liquids could be used safely in bitumen/asphalt mixtures.

Two test methods are developed to measure the self-healing capability of bitumen at high and low temperatures. With the help of the developed new self-healing determination techniques, IL 1 short chain and IL 2 short chain gave excellent results in high-temperature self-healing measurements with a nearly 40% improvement compared to base bitumen. Ionic liquid incorporation improved the self-healing capability of bitumen during long-resting periods at low temperatures, with almost 100% improvement with IL 1 long side chain. In addition to the self-healing measurements at high and low temperatures, stripping tests are carried out to study the effect of ionic liquid incorporation on bitumen–aggregate interactions under wet conditions. The results indicated that ILs with long side-chain yielded results around 95–100% for all 1% addition and 5% addition for ILs 1 and IL 3.

In the observational analyses, while almost no phase separation is observed in the mixture prepared with IL 3 short, phase separation is observed with IL 3 long, which indicates a high separation performance. In this context, IL 3 short increases the interaction between bitumen and fine aggregate/filler. Increasing the attraction between bitumen and aggregate will have a positive effect, especially on the healing of adhesive cracks.

Each of the mentioned tests is used to measure a certain property of the bitumen. For example, the self-healing test developed on DSR predicts bitumen performance in regions with high temperatures. In contrast, the stripping test is used to predict the performance of the formulations in areas that receive large amounts of rain. The results obtained with different ionic liquids indicate that different ionic liquids are suitable for improving different qualities of the bitumen. Therefore, ionic liquid-bitumen formulations should be prepared for road applications depending on the climatic conditions and traffic loading.

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Declarations

Conflict of interest The authors declare that there is no conflict of interest.

References

1. EAPA, Asphalt in Figures 2018. 2020
2. Baumann, B.: Polarization sensitive optical coherence tomography: a review of technology and applications. Appl. Sci. **7**, 474 (2017). https://doi.org/10.3390/app7050474
3. OECD: Infrastructure maintenance (indicator) (2023). https://doi.org/10.1787/c73dc965-en
4. Rubio, M.C.; Moreno, F.; Martinez-Echevarria, M.J.; Martinez, G.; Vazquez, J.M.: Comparative analysis of emissions from the manufacture and use of hot and half-warm mix asphalt. J. Clean. Prod. **41**, 1–6 (2013). https://doi.org/10.1016/j.jclepro.2012.09.036

5. Behnood, A.; Gharehveran, M.M.: Morphology, rheology, and physical properties of polymer-modified asphalt binders. Eur. Polym. J. **112**, 766–791 (2019)
6. Airey, G.D.: Styrene butadiene styrene polymer modification of road bitumens. J. Mater. Sci. **39**, 951–959 (2004). https://doi.org/10.1023/B:JMSC.0000012927.00747.83
7. http://www.nissan-global.com/EN/TECHNOLOGY/OVERVIEW/scratch.html (Access year 2017).
8. Kumar, M.H.; Moganapriya, C.; Kumar, A.M.; Rajasekar, R.; Gobinath, V.K.: Self-healing materials in aerospace applications. Self-Heal. Smart Mater. Allied Appl. (2021). https://doi.org/10.1016/B978-0-08-100037-3.00011-0
9. Khan, N.I.; Halder, S.: Self-healing fiber-reinforced polymer composites for their potential structural applications. In: Thomas, S.; Surendran, A. (Eds.) Self-Healing Polymer-Based Systems, pp. 455–472. Elsevier, New York (2020)
10. Phillips, M.C. Multi- step models for fatigue and healing, and binder properties involved in healing. in Eurobitume Workshop on Performance Related Properties for Bituminous Binders 1998. Luxemburg (Paper Number 115). DOI:https://doi.org/10.1617/2912143772.051
11. Raithby, K.D.; Sterling, A.B.: The effect of rest periods on the fatigue performance of a hot-rolled asphalt under reversed axial loading. Assoc Asphalt Paving Technol Proc **39**, 134–152 (1970)
12. Shen, S.; Chiu, H.; Huang, H.: Characterization of fatigue and healing in asphalt binders. J. Mater. Civ. Eng. **22**(9), 846–852 (2010). https://doi.org/10.1061/(ASCE)MT.1943-5533.0000080
13. Little, D.N., Lytton, R.L., Williams, A.D., Chen, C.W.: Microdamage Healing in Asphalt and Asphalt Concrete", Volume I: "Microdamage and Microdamage Healing, Project Summary Report, in Publication No: FHWA-RD-98–1412001, Texas Transportation Institution, College Station: Texas
14. Little, K.Y.; Lytton, R.: Fatigue and healing characterization of asphalt mixtures. J. Mater. Civ. Eng. **15**(1), 75–83 (2003). https://doi.org/10.1061/(ASCE)0899-1561(2003)15:1(75)
15. Daniel, J.S.; Kim, Y.R.: Laboratory evaluation of fatigue damage and healing of asphalt mixtures. J. Mater. Civil Eng. **13**, 434–440 (2001). https://doi.org/10.1061/(ASCE)0899-1561(2001)13:6(434)
16. Brochu, A.B.; Craig, S.L.; Reichert, W.M.: Self-healing biomaterials. J. Biomed. Mater. Res. Part A **96**(2), 492–506 (2011)
17. Behnia, B.; Reis, H.: Self-healing of thermal cracks in asphalt pavements. Constr. Build. Mater. **218**, 316–322 (2019). https://doi.org/10.1016/j.conbuildmat.2019.05.095
18. Kim, Y.R.; Little, D.N.; Lytton, R.L.: Use of dynamic mechanical analysis (DMA) to evaluate the fatigue and healing potential of asphalt binders in sand asphalt mixtures. J. Assoc. Asphalt Paving Technol. **71**, 176–199 (2002)
19. Garcia, A.; Schlangen, E.; van de Ven, M.; Liu, Q.: Electrical conductivity of asphalt mortar containing conductive fibers and fillers. Constr. Build. Mater. **23**, 3175–3181 (2009). https://doi.org/10.1016/j.conbuildmat.2009.06.014
20. Garcia, A.; Schlangen, E.; van de Ven, M.; van Vliet, D.: Induction heating of mastic containing conductive fibers and fillers. Mater. Struct. **44**, 499–508 (2011). https://doi.org/10.1617/s11527-010-9644-2
21. Greenwood, R.; Kendall, K.: Selection of suitable dispersants for aqueous suspensions of zirconia and titania powders using acoustophoresis. J. Eur. Ceram. Soc. **19**, 479–488 (1999). https://doi.org/10.1016/S0955-2219(98)00208-8
22. Liu, Q.; Wu, S.; Schlangen, E.: Induction heating of asphalt mastic for crack control. Constr. Build. Mater. **41**, 345–351 (2013). https://doi.org/10.1016/j.conbuildmat.2012.11.075
23. Zhang, W.; Jiang, H.; Chang, Z., et al.: Recent achievements in self-healing materials based on ionic liquids: a review. J Mater Sci. **55**, 13543–13558 (2020). https://doi.org/10.1007/s10853-020-04981-0
24. Tourvieille, J.N.; Larachi, F.; Duchesne, C.; Chen, J.: NIR hyperspectral investigation of extraction kinetics of ionic-liquid assisted bitumen extraction. Chem. Eng. J. **308**, 1185–1199 (2017). https://doi.org/10.1016/j.cej.2016.10.010
25. Liu, Q.; Garcia, A.; Schlangen, E.; van de Ven, M.: Induction healing of asphalt mastic and porous asphalt concrete. Constr. Build. Mater. **25**, 3746–3752 (2011). https://doi.org/10.1016/j.conbuildmat.2011.04.016
26. Gallego, J.; del Val, M.A.; Contreras, V.; Paez, A.: Heating asphalt mixtures with microwaves to promote self-healing. Constr. Build. Mater. **42**, 1–4 (2013). https://doi.org/10.1016/j.conbuildmat.2012.12.007
27. White, S.R.; Sottos, N.R.; Geubell, P.H.; Moore, J.S.; Kessler, M.R.; Sriram, S.R.; Brown, E.N.; Viswanathan, S.: Autonomic healing of polymer composites. Nature **409**, 794–797 (2001)
28. Su, J.F., Qiu, J., Schlangen, E.: Self-healing bitumen by microcapsules containing rejuvenator, in ICSHM 20132013: Gent. p. 494–497. https://doi.org/10.1038/35057232
29. Jonkers, H.M.; Thijssen, A.; Muyzer, G.; Copuroglu, O.; Schlangen, E.: Application of bacteria as self-healing agent for the development of sustainable concrete. Ecol. Eng. **36**, 230–235 (2010). https://doi.org/10.1016/j.ecoleng.2008.12.036
30. Wiktor, V.; Jonkers, H.M.: Quantification of crack-healing in novel bacteria-based self-healing concrete. Cement Concr. Compos. **33**, 763–770 (2011). https://doi.org/10.1016/j.cemconcomp.2011.03.012
31. Olivier- Bourbigou, H.; Magna, L.: (2002) Ionic liquids: perspectives for organic and catalytic reactions. J. Mol. Catalysis A: Chem. **182–183**, 419–437 (2002). https://doi.org/10.1016/S1381-1169(01)00465-4
32. Seddon, K.R.: Ionic liquids for clean technology. J. Chem. Tech. Biotechnol. **1997**(68), 351–356 (1997)
33. Vekariya, R.L.: A review of ionic liquids: applications towards catalytic organic transformations. J. Mol. Liq. **227**, 44–60 (2017). https://doi.org/10.1016/j.molliq.2016.11.123
34. Zhu, S.; Wu, Y.; Chen, Q.; Yu, Z.; Wang, C.; Jin, S.; Ding, Y.; Wu, G.: Dissolution of cellulose with ionic liquids and its application: a mini-review. Green Chem. **8**(4), 325 (2006). https://doi.org/10.1039/B601395C
35. Frade, R.F.M.; Afonso, C.A.M.: Impact of ionic liquids in environment and humans: an overview. Hum. Exp. Toxicol. **29**(12), 1038–1054 (2010). https://doi.org/10.1177/0960327110371259
36. Painter, P.; Williams, P.; Mannebach, E.: Recovery of bitumen from oil or tar sands using ionic liquids. Energy Fuels **24**(2), 1094–1098 (2010). https://doi.org/10.1021/ef9009586
37. Gaestel, C.; Smadja, R.; Lamminan, K.A.: Contribution à la connaissance des propriétés des bitumes routiers. Revue Générale Routes Aérodromes **466**, 85–92 (1971)
38. Spiecker, P.W.; Gawrys, K.L.; Kilpatrick, P.K.: Aggregation and solubility behavior of asphaltenes and their subfractions. J. Colloid Interface Sci. **267**, 178–193 (2003). https://doi.org/10.1016/s0021-9797(03)00641-6
39. Akmaz, S.; Iscan, O.; Gurkaynak, M.A.; Yasar, M.: The structural characterization of saturate, aromatic, resin, and asphaltene fractions of batiraman crude oil. Pet. Sci. Technol. **29**(2), 160–171 (2011). https://doi.org/10.1080/10916460903330361