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Phyto-based sodium chloride hydrogel for highway winter maintenance of porous asphalt pavements

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Abstract

The need of the highway agencies to customize their winter maintenance operations on porous asphalt pavements prompted the authors to develop an innovative anti-icing technology based on the hot liquid spray application of a saline hydrogel. A bio-based (phyto-based) thermo-sensitive sodium chloride (NaCl) brine, that has the ability to form a gel simply by coming into contact with a very cold surface, was conceived. The increase in viscosity and the formation of a gel-like structure would make this anti-icing product able of filling the surface voids without permeating through the mixture (longer residual deicing effectiveness), while maintaining at the same time the pavement frictional resistance. In view of adopting sustainable winter maintenance strategies, this innovative blend was formulated by exploiting the thickening and gelling properties of wall-cell polysaccharides contained in seaweeds fibers. The mechanisms of gel formation were experimentally studied in laboratory, analyzing in detail the thermal and rheological properties of the salt hydrogel during the different phases of preparation, storage and application. On the basis of this characterization, a full-scale validation was carried out on an existing highway porous asphalt pavement. For this purpose, a tank truck prototype was equipped with a heating capacity tank and a customized specific spraying system.

Keywords

Winter road maintenance, permeable pavements, salt brine, antifreeze gel, anti-icing, spray application; sustainability; eco-friendly approach

Highlights

- Permeable asphalt pavements show winter maintenance issues in cold climate environments
- An innovative anti-icing technology based on the hot liquid spray application of a saline gel was developed
- The hydrogel was formulated by exploiting the gelling properties of seaweed polysaccharides
- The blend has the ability to form a gel by coming into contact with a cold pavement surface

- A full-scale validation was carried out on an existing highway porous asphalt pavement

1. Introduction

Ensuring road mobility and improving the accessibility and safety of the traveling public during difficult driving conditions in wintertime represent worldwide critical issues in states with harsh winter climate or in cold regions. In order to effectively face winter road hazards, modern strategies deal on the one hand with integrated and intelligent road weather information systems (RWIS) and maintenance decision support systems (MDSS), based on probabilistic bulletins, road weather models and real-time warning system; on the other hand with the most effective improved operational procedures (equipment and materials) for snow and ice control [1-3]. Operational methods minimize or eliminate weather impacts directly on the road surface, involving the use of mechanical means (plows, brooms, brushes) and the application of chemical agents (salts) and abrasives (sand particles and rock chips) in different phases of a snowstorm [4,5]. The proactive approach to snowfighting, which is often the first in a series of strategies, is called anti-icing. It involves the timely application of freezing-point depressants before or during the early stage of the storm to prevent frost formation and the development of snow and ice stuck to the road surface [6]. Over the last two decades, winter maintenance agencies have gradually transitioned their snow and ice control protocols towards the massive adoption of anti-icing interventions based on the direct liquid application (DLA) in the form of salt brine, i.e. a solution of salt in water, or slurry, i.e. pre-wetted salt at a high solid/liquid ratio (70/30) [7]. Brines with high-concentration (23.3%) of sodium chloride ($NaCl$) are generally sprayed, but brines based on calcium chloride ($CaCl_2$) or magnesium chloride ($MgCl_2$) are sometimes used to speed up the melting process and ensure efficacy down to -21 °C [8]. Once the snowfall has started and snow has accumulated, the reactive operation of deicing, which involves spreading dry or pre-wetted grains of rock or marine salt ($NaCl$), restore safe driving conditions by breaking the bonds that have formed between snow and/or ice and the pavement [9,10]. The technical literature and some scientific experiences have counted for a long time the possibility of using different types of the so-called anti-icing fillers and salt-storage additives, which typically consist of mixtures of inorganic materials whose main component is sodium chloride, directly into asphalt mixtures to develop self-ice-melting pavements [11]. Expectations for the durability of the effectiveness of this anti-icing strategy are not supported by long-term road monitoring data, but diffusional processes, which carry salt from the bulk to the asphalt-water interface, have been observed during laboratory experiments [12,13]. Moreover, abrasives, which do not provide any ice-melting capabilities, are sometimes used to increase the tire-pavement friction [14]. Many inter-related factors influence resource management and the choice or timing of material application: besides the climatic conditions, prevailing weather patterns (ambient temperature and humidity, solar radiation, wind direction and speed, type of precipitation) and topography, road network characteristics, traffic volume and required or accepted level of service (LOS) play a significant role [15,16]. Experience has shown that under the same conditions, some pavement types show durability and functionality issues, as well as winter maintenance issues in cold climate environments.

Permeable asphalt pavements fall into this category. They are pavements in which the surface layer consists of an open-graded asphalt mixture, mainly composed of single size coarse aggregate, with a very high content of interconnected voids (> 16%). They can be built as a full-depth porous asphalt (PA) pavement, in which the single or double porous layer is placed on the top of a stone filter and reservoir, or installed as a thin open-graded friction course (OGFC), also called permeable friction course (PFC), which represents an overlay applied above a dense-graded impervious layer [17,18]. Regardless of the construction technique, the enhanced effectiveness for stormwater management results in several safety and environmental benefits. These kind of pavements can minimize hydroplaning potential by improving the wet pavement frictional resistance and reduce water splash and spray, nighttime surface glare in wet conditions and tire-pavement noise [19-21]. But despite these inherent advantages, the open-graded layout and surface macro-texture of porous asphalt pavements affect their thermo-hygrometric regime at low temperatures, as well as the management of winter maintenance operations [22]. The energy balance based on the pavement heat transfer with the atmosphere and the natural subgrade highlights that the combined effect of night radiation, the low conductivity and the thermal inertia of the porous asphalt surface increase its thermal sensitivity [23]. Specifically, road temperature data recorded in wintertime show that the surface of this kind of pavement tends to be on average a few (2-4 °C) degrees lower than a dense graded layer. Moreover, the water that is entrapped in the interconnected pores in wet conditions is brought by traffic (air pumping effect of vehicle tires) back to the road surface, so that it remains moistened 15% longer [24]. This thermo-hygrometric behavior suggests that open-graded asphalt pavements are very sensitive to freezing in cold and wet climates: ice and snow accumulate faster (earlier and more frequent occurrence of black ice and hoarfrost/rime), thaw more slowly (longer time to recover the bare pavement) and refreeze more quickly [25]. In addition, the coarser surface texture can provide a temporary storage of snow during a storm, which once frozen would be embedded in the pavement and therefore more difficult to remove. Thus, winter maintenance activities require special procedures especially to ensure the effectiveness of anti-icing preventive measures [26]. On the one hand, liquid brine cannot be effectively used because it would quickly drain through the pavement surface; on the other hand, dry granular particles of rock or marine salt, in addition to be subject to scatter and bounce, tend to be trapped into the pore spaces (larger salt grains can minimize this problem) leaving the surface susceptible to icing [27,28]. The best anti-icing solution seems to be the use as soon as the pavement begins to freeze of pre-wetted salt (dry NaCl + $CaCl_2$ brine), especially in some weather events, such as freezing of pre-existing moisture, hoarfrost, freezing rain and black ice [29,30]. In parallel, the use of abrasives as a friction enhancement is not recommended as they tend to clog pores and create additional and costly maintenance to restore the desired porosity of the pavement. Thus, porous pavements require additional maintenance during winter weather both in terms of frequency of spreading and rates of application of deicers ant anti-icing agents. Several European highway agencies have quantified an increase in overall seasonal salt consumption up to 50 percent [31,32], although some US experiences on parking lots and low traffic roads testify to the reduced need for chemicals in intra-storm interventions [33,34]. The use of increasing quantity of salt translates into various drawbacks beyond the economic impact. Salts have negative effects on the road infrastructure, the vehicles (deterioration and corrosion) and the environment by damaging vegetation and polluting water supply sources [35-37].

Therefore, the gradual introduction of green and environmentally friendly alternatives in snow and ice control operations is an ongoing effort towards more sustainable management of road agency operations to generate significant cost savings and increase public benefits. One line of research has investigated the possibility of using organic chemicals, i.e. natural non-toxic co-products, by-products or wastes from different existing processes, to overcome the deleterious effects of chlorides while improving their properties and performances [38,39]. Most of these improved materials, referred to as agricultural-derived products (agro-based or ag-based), have been obtained from the fermentation and processing of agricultural feedstock, including corn, wheat, rice and beet, or from cheese and beer production [40,41]. Recent developments have led to the formulation of several proprietary or patented blends. Each organic compound, applied alone or diluted in deicer formulations, has a specific functionality, but nevertheless has led to positive impacts on the overall effectiveness of winter maintenance operations along with reduced risk to the highway infrastructure and the environment. Specifically, performance enhancers exert their function by providing faster reaction time, improved freezing point depression and ice-melting capabilities, thickeners are used to increase the viscosity of liquid products extending their longevity and residual effects once applied to the pavement, whereas corrosion inhibitors mitigate the corrosive effects of chemicals on metals [42-44].

In view of sustainable highway winter maintenance strategies, the authors developed a bio-based (phyto-based) enhanced sodium chloride brine for anti-icing interventions on asphalt open graded pavements. A hot-applied liquid product, that has the ability to form a gel simply by coming into contact with a very cold pavement surface, was conceived. This blend was formulated by exploiting the thickening and gelling properties of wall-cell polysaccharides contained in seaweeds fibers. In order to pursue a zero-waste model, accumulations of seaweeds removed from beaches and waterfronts during clean-up operations were used. The increase in viscosity and the formation of a gel-like structure would make this anti-icing product able of filling surface voids without permeating through the mixture, while maintaining at the same time the pavement frictional resistance. This thin salt layer would result in a longer residual deicing effectiveness, also becoming an ideal primer (appreciated supplementary effect) for a subsequent dry salt application. The article describes the operational steps that led to the formulation of the optimal blending ratio of the naturally occurring salt (NaCl brine) and thickening agent and the definition of a standardized production procedure. The mechanisms of gel formation were analytically studied on the candidate mixture, analyzing in detail its thermal and rheological properties during the different phases of preparation, storage and application. On the basis of this laboratory characterization, a full-scale validation was carried out on an existing highway porous asphalt pavement, which also required the provision of a prototype tanker truck equipped with a tailor-made specific spraying system.

2. Preparation of seaweed polysaccharides–sodium chloride hydrogel

The phyto-based sodium chloride hydrogel was prepared by adding small quantities of a thickener to a conventional salt brine generally used in winter maintenance operations. A 23.3% wt. NaCl brine, that is the concentration at which it reaches the eutectic point, was made by mixing solar sea/marine salt with water. As far as the gelling agent is concerned, a seaweed fiber (kindly supplied by the B & V - The agar company) in the form of very fine powder with a white to pale straw yellow color, was considered. Specifically, it was obtained by steam explosion, vacuum drying and subsequent milling of marine red algae (*phylum: Rhodophyta*) “ogonori” (*genus: Gracilaria verrucosa*). This is one of the same algal genera from which agar-agar (or simply agar), i.e. a gelatinous phyto-colloid used in the food and pharmaceutical industries as gelling and stabilizing agent, is extracted after various refining processes. The agar forms transparent and stiff thermo-reversible gels, following a hot activation process of the bioactive compound (melting: ≈ 85-95 °C) and a subsequent cooling that sets off the sol-gel transition (gelling: ≈ 35-45 °C). The mechanism of agar gelation involves the transition from a random coil conformation to double-helix associations, followed by their aggregation into a three-dimensional network [45-47].

Several preliminary attempts were made to prepare the most suitable phyto-based salt brine, by varying the amount of seaweed fiber, the solvent temperature and mixing time. The solutions were prepared using a magnetic stirrer, managing the speed to generate a swirling flow. In all tested configurations, gravitational settling of the particles (insoluble fiber fraction) occurred as soon as the stirring was stopped. The gelling agent showed a slight solubility in cold water and NaCl brine, but a better dispersion was detected by increasing the temperature of the solvent. Furthermore, only hot liquid solutions (above 80-85 °C) of seaweed fiber had the ability to form a gel structure on cooling. This process was found to be thermo-reversible and the gelling mechanism could also be activated by heating a cold-prepared blend above its melting point. A wide range of thickener dosages was evaluated from very low to extremely high values, i.e. from 0.2% up to 10% by weight of the solvent (water). The mixtures with a low content of gelling agent (0.2% and 0.5%) retained a liquid character when cooled, i.e. the sample did not produce a firm gel-like structure, whereas a concentration above 5% resulted in a product with a pasty consistency. Refining the analysis in the range 1% to 3 %, the 2% wt. water content in the 23.3% wt. NaCl brine appeared to be the right balance between performances and material addition. This brine exhibited a suitable elastic gel structure upon cooling (similar behavior for the 3%), in contrast to that prepared with 1%, which had a weakened gel strength. Once the optimal mixing ratio of brine and thickening agent was defined, a production protocol was established. The gelling agent (2.3 g) was diluted in 150 g of 23.3% wt. NaCl brine (114.9 g of water), which was preheated and kept on the hot plate of the magnetic stirrer at 90 ± 5 °C. The solution was then stirred for 5 minutes at 1000 rpm in a 350 ml sealed glass container. This time interval and stirring speed, which allowed complete dissolution of the lumps and homogeneous mixing of the particles, refer to the prefixed amount of solvent.

3. Methods

The experimental program on a laboratory scale was set out to evaluate the behavior of the phyto-based anti-icing brine at different stages of pavement application, once a protocol for preparing the mixture had been defined in terms of both ingredient dosage and production procedure. Thermal and rheological analyses were carried out to identify the properties of the anti-icing product both in the production and storage phases and in the road application ones.

3.1 Differential scanning calorimetry

Differential scanning calorimetry tests were performed to rapidly and consistently characterize some thermal properties of the newly designed brine, also assessing the potential freezing point depressant property of the gelling agent. A reference mineral water was used to prepare the brines in order to better limit and control the variables. Measurements were made with a DSC Q100 unit (TA Instruments, USA). A hot droplet (65 ± 1 mg) of product was pipetted into an aluminum test pan, which was weighted after the sealing of the lid. Indium (melting temperature 156.60 °C, $\Delta H_f = 28.45$ J/g) and mercury (melting temperature -38.83 °C, $\Delta H_f = 11.41$ J/g) were used to calibrate the instrument and an empty pan was used as reference. Dry nitrogen was purged into the DSC cell at 50 ml/min. To study the behavior of the brine at low temperatures, the sample was kept at 25 °C for 5 min, cooled to -45 °C at a cooling rate of 2 °C/min, stabilized at -45 °C for 3 min and then heated to 10 °C at the same rate. Water and 23.3% wt. NaCl salt brine were preliminary tested; the measurements were then repeated after adding the seaweed fiber powder to these solvents, according to the production protocol, to analyze the influence of the introduction of the thickener on the freezing temperature. Tests were made on three independent samples of each solution.

3.2 Rheology

In the rheological section, a first part was aimed at characterizing the temperature-sensitive behavior of the liquid blend during the cooling period downstream of the production process. The temperature-dependent complex viscosity (η^*) was measured using an Ares rheometer (TA Instruments, USA) equipped with a coaxial cylinder measuring system in a Couette flow field. The selected geometries consisted of a 32 mm bob (inner cylinder) and a 34 mm cup (outer cylinder). The 15 ml specimen was poured at 80 °C into the cup and the distance from the lower edge of the cylindrical part of the bob to the base of the cup was set to 5 mm. A strain (γ)-controlled transient test was considered, applying a constant shear rate ($\dot{\gamma}$) of 50 s^{-1} and a downward temperature profile in the range 75-35 °C range. The results of this test were also useful in identifying a significant temperature range, i.e. the gelation point at which the transition from liquid to gel character takes place even under continuous mixing conditions, which inevitably influence and govern the most suitable application and transportation techniques.

The second part, which was carried out with a Physica MCR 502 dynamic shear rheometer (Anton Paar, Austria), allowed the properties of the product to be assessed once it had been placed on an asphalt pavement at very low temperatures, in order to better understand its behavior after gelling. A 25 mm parallel-plate measuring system was adopted, using upper and bottom crosshatched surfaces to counteract the wall slip effects. A small quantity of liquid sample was loaded at 50 °C onto the preheated, at the same temperature, lower geometry (both plates were kept almost in contact to avoid thermal shift). A 1.025 mm gap was then set in a controlled configuration with a coupled speed of 0.05 mm/s and a normal force of 10 N. Once the sample was properly compressed, the temperature was reduced to the target one and the excess of material that was squeezed out of the gap was trimmed, before adjusting the final gap to 1 mm. First, shear-strain-amplitude sweep tests were planned to determine the limit of the linear viscoelastic (LVE) region and the yield point. A controlled-shear deformation amplitude ranging from 0.1 to 100% was considered, maintaining a constant angular frequency (ω) of 10 Hz at -12 °C. Frequency sweep tests were then performed to assess the stiffness of the material, in terms of complex shear modulus (G^*) separating the storage (G') and the loss (G'') components, at three very low temperatures equal to 2, -2 and -12 °C, by selecting a decreasing angular frequency logarithmic ramp from 16 to 0.1 Hz at a constant strain amplitude in the LVE range.

4. Results

4.1 Differential scanning calorimetry

Thermal analyses of the seaweed fiber-NaCl hydrogel were performed using the Advantage/Universal Analysis software version 4.5A (TA Instruments, USA). Specifically, (i) the characteristic temperature (T_c), defined as the temperature associated with the peak of the phase transition, and (ii) the latent heat or enthalpy (H_f), represented by the integral area between the peak onset (T_{on}) and offset (T_{off}) temperatures, were determined. Specifically, T_{on} and T_{off} were obtained from the intersection of the tangents to the linear baseline and the peak.

The DSC thermograms, i.e. heat flow versus temperature diagrams, referred to a specimen of the phyto-based modified and of the conventional brine are shown in Fig.1. Only the heating thermogram, i.e. the curve below the baseline, was analyzed as widely suggested in the literature [9,48]. The freezing curve is not as significant and is strongly influenced by the super-cooling effect. Modified and conventional NaCl brines, just like water and thickened water, show almost overlapping heating thermograms, characterized by a well evident phase transition (more diluted NaCl brines generally exhibit two phase transitions with almost equally strong peaks) and very similar thermal properties. Table 1 reports the thermal parameters (T_{on}, T_c and H_f) of each solution calculated as the mean of three independent specimens. These results showed that the gelling agent has no freezing point depressant potential and does not affect the thermal properties of the solvent.

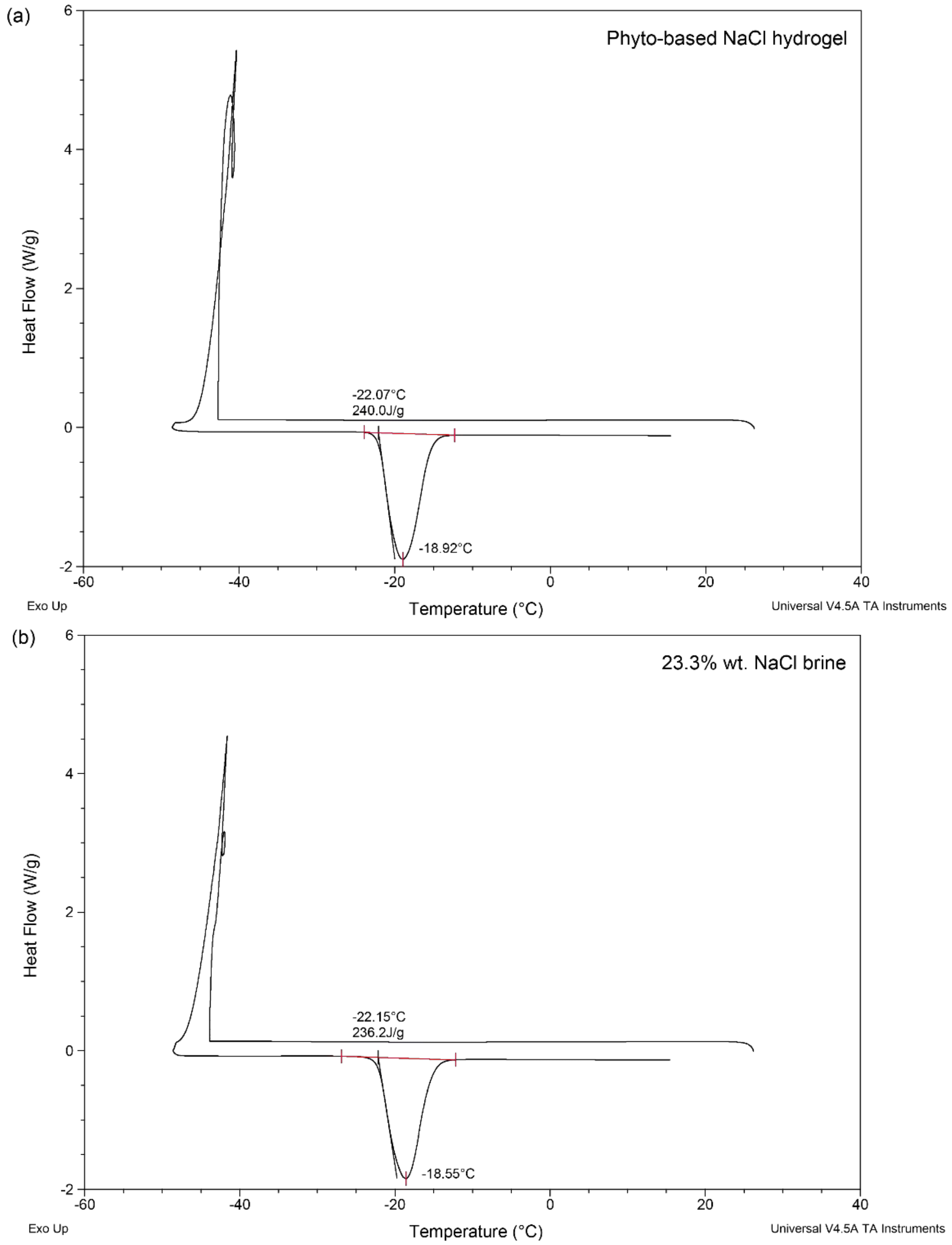

Figure 1 - DSC thermogram of a specimen of the phyto-based NaCl hydrogel (a) and 23.3% wt NaCl brine (b)

Table 1 – Thermal properties of the prepared solutions (Mean and standard deviation of three measurements)

Solution	T_{on} [°C]	T_c [°C]	H_f [J/g]
Water	1.53±0.31	4.29±0.39	332.28±10.32
Water+2%SF[*]	1.20±0.22	3.89±0.31	329.15±11.23
23.3 NaCl	-22.13±0.45	-18.43.±0.59	234.51±7.25
23NaCl+2%SF[*]	-22.15±0.52	-18.64±0.54	243.80±8.69

[*] seaweed fiber/solvent ratio (w/w%)

4.2 Rheology

As far as rheology is concerned, the temperature-dependent viscosity curve is well represented by three fitting lines, defined by different slopes, which highlight the liquid to solid transition of the phyto-based brine (Figure 2). During the cooling process, the material viscosity slowly increased from 5 to 8 mPa·s over the temperature range 75-55 °C, with values 6/7 times higher than in a conventional NaCl brine. As the temperature was reduced, there was a sudden and very substantial increase in viscosity, indicating the start of a rapid gelling process. The temperature of 55 °C, determined by the tangent crossing method, is the gelation point, i.e. the value below which the blend begins to form a gel-like structure. The gel point is significant from an operational point of view as it defines a threshold at which the product can be applied in liquid form. Below 45 °C, the measured points are more dispersed from the straight line, as the specimen has lost its homogeneity within the cup: some jelly macro-particles were unaffected by friction between the coaxial cylinders during the movement, while others were completely crushed.

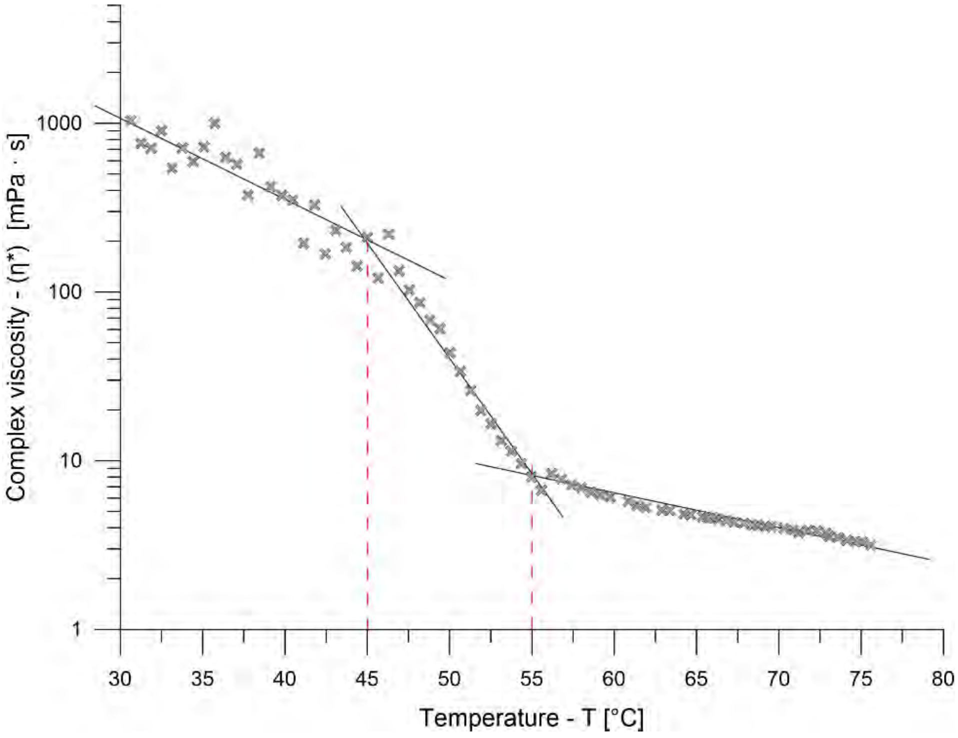

Figure 2 - Temperature-dependent viscosity curve of the phyto-based NaCl hydrogel

Oscillatory tests were planned to study in detail the behavior of the products once applied on the road pavement at low temperatures. The strain amplitude sweep results describe the gel-like character of the enhanced brine: the elastic behavior dominates the viscous one (G'>G") up to the maximum allowable strain limit (γ_L), which defines the LVE region. Unlike the G'(γ) curve, which exhibits a constant plateau followed by an abrupt drop, the G"(γ) curve does not slope downwards as the strain increases, but shows a little evident peak before collapsing (Figure 3a). This behavior, which is very frequent in jelly, may be due to the relative movement between molecules which are not linked or completely fixed in the network. The limits of the LVE region were determined by analyzing the storage modulus function, which was the first to deviate from the plateau value. In particular, a γ_L of 0.25% was identified as the strain value in which the G'(γ) curve deviated from the initial value by more than 5%. From this deformation value, the corresponding limit value of the LVE in terms of shear stress, i.e. the yield stress or yield point (τ_y), was calculated. The graphical representation of the G' and G" functions versus the shear stress τ (Figure 3b), in addition to making the yield stress (τ_y = 8.45 Pa) immediately evident, was also added for determining the flow point (τ_f = 417.23 Pa), defined as the τ-value at the crossover point G' = G", where the gel-like character changes to a liquid state. The moduli traces measured on samples which underwent multiple heating-cooling cycles are substantially overlapping, testifying to the complete thermo-reversibility of the process, which does not affect the thermal behavior of the hydrogel. This behavior offers road operators good flexibility in handling and storing the prepared hydrogel prior to actual application.

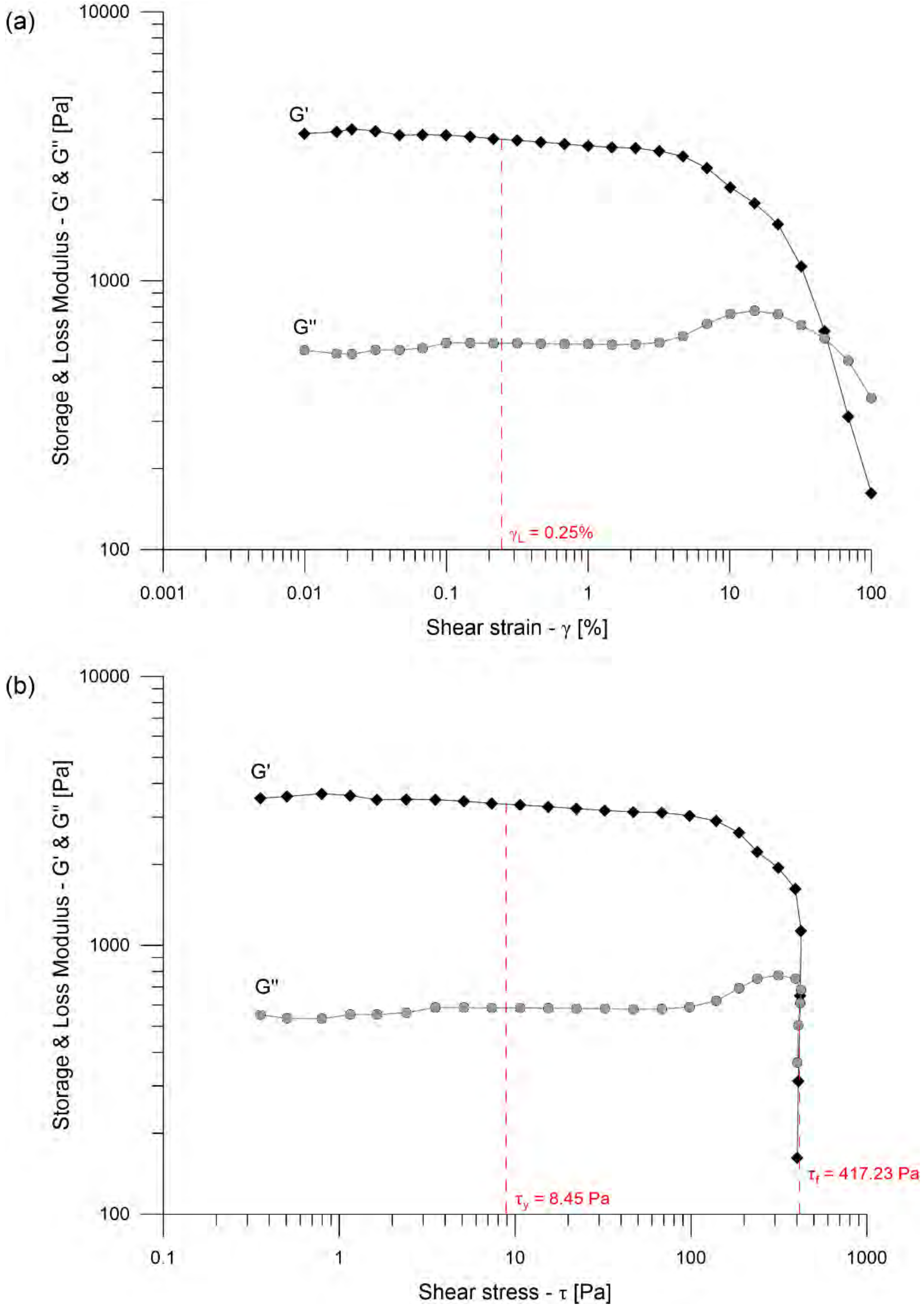

Figure 3 - Strain amplitude sweep results of the phyto-based NaCl hydrogel: G' and G" versus γ (a); G' and G" versus τ (b)

A typical gel structure behavior was also testified by the trend of the shear modulus in the frequency sweep test (Figure 4). Specifically, the two modulus curves follow an almost straight course over the entire frequency range, showing a ratio values G':G" of about 5.5-6.5:1 between 16 and 1 Hz. But, a reduced slope towards lower frequency (f <0.276 Hz) and an incipient decrease at higher frequency (f=16 Hz) were recorded in G'(f) and G"(f) curves, respectively. These trends appear to be insensitive to temperature: the curves for the three temperatures are almost completely overlapping, showing that the product maintains the same structure and consistency at temperatures above freezing.

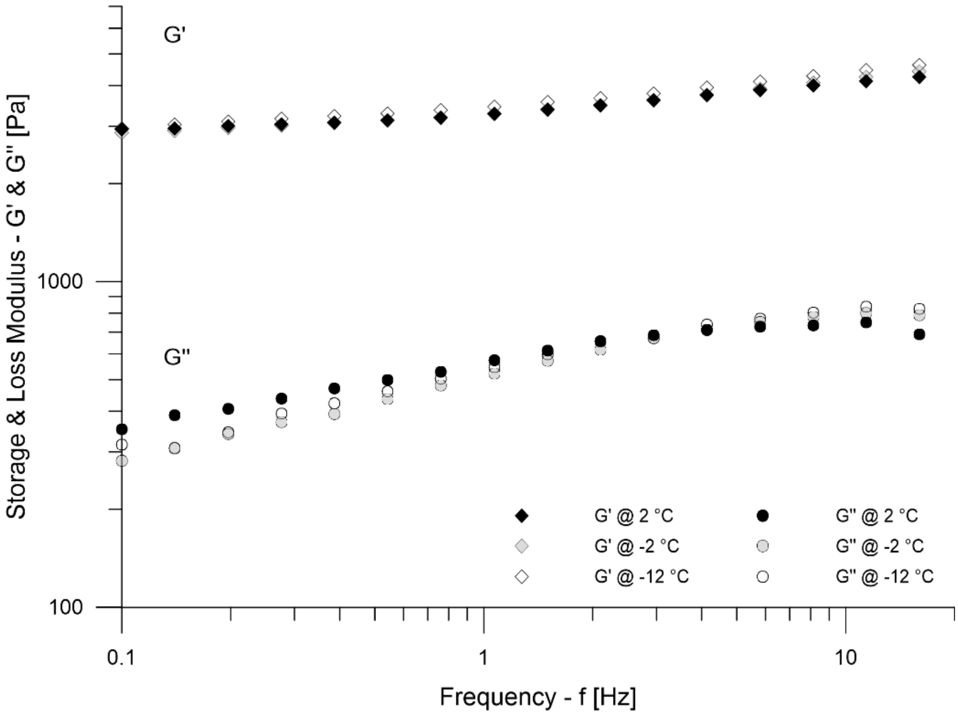

Figure 4 - Frequency sweep results of the phyto-based NaCl hydrogel

5. Optimization of hydrogel transport and application

Testing the feasibility of producing the phyto-based salt brine on a large scale, transporting it from the salt storage site in liquid form and verifying its gelling behavior after application required direct validation on an existing porous asphalt pavement. The enhanced brine was designed as a liquid antifreeze that has the ability to form a gel simply by coming into contact with a very cold surface. Following laboratory characterization, the best performing application method seemed to be the spraying technique. But the successful spray application of a temperature-sensitive product for winter maintenance creates several challenges and issues. In terms of equipment, this requires a vehicle with a bulk liquid tank capable of maintaining heat from loading to delivery and a spray system designed to uniformly release a hot liquid product (65 °C<T<85 °C) at a specific rate during movement. For this purpose, a tank truck prototype equipped with a 500 liters tank with heating capacity and a customized specific spraying system was developed together with the Massenza Srl company (Figure 5).

Figure 5 - Tank truck prototype

Specifically, the sprayer consisted of a rear-mounted double bar (30 cm spacing) capable of vertical and transverse adjustments, including 7+7 (10 cm spacing) flat fan nozzles. The distance between the nozzle orifice and the ground was set at 20 cm during the tests. The theoretical spray pavement coverage was 95.4 cm, assuming a spray angle of 85° and that individual spray patterns did not touch and interfere each other in the longitudinal direction (Figure 6). This system can be operated from the driver’s cab using a control panel to adjust the air pressure and the amount of coating material, the flow of which adapts automatically according to the speed of the vehicle.

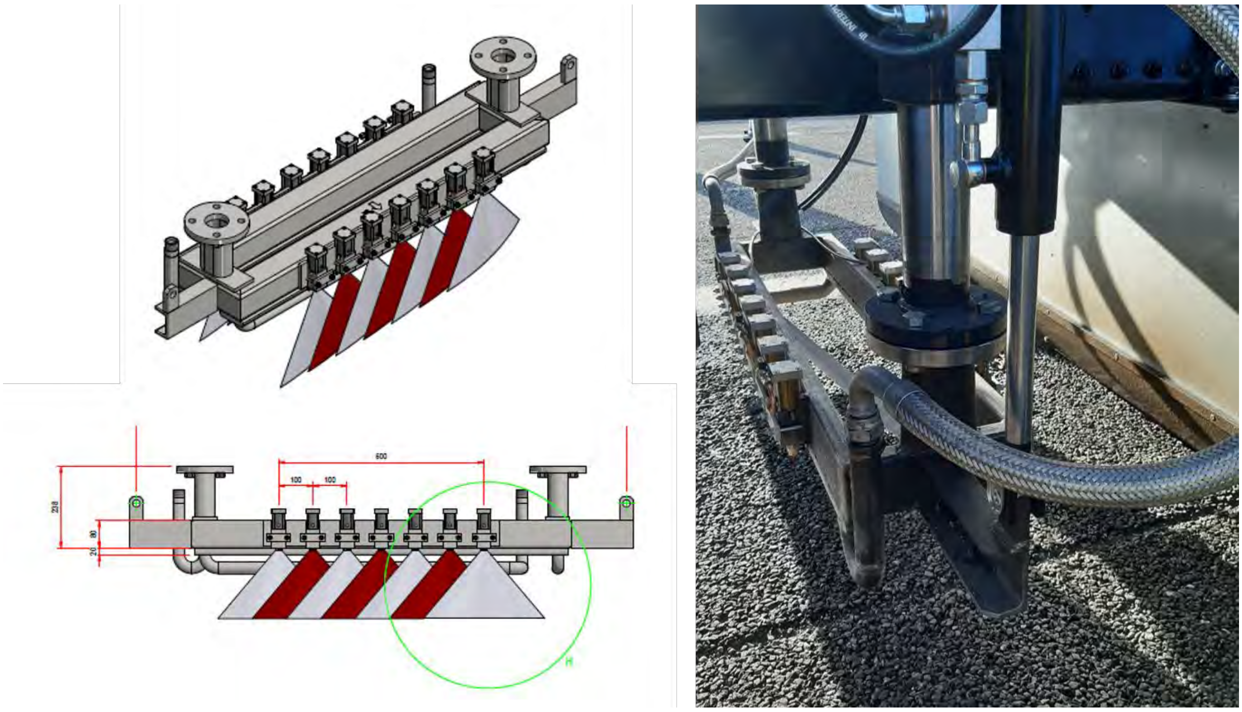

Figure 6 - Designed spraying system

The on-site tests were carried out on the Italian A15 highway “Autocamionale della Cisa” connecting Parma to La Spezia through the valleys of the Taro and Magra rivers. Specifically, a section in the municipality of Medesano (from 17+500 to 19+500 km) in the south carriageway was selected. The pavement in this plain area is characterized by a porous asphalt layer with a maximum nominal size of 10 mm and its gradation contains 66% coarse aggregates (> 12.5/4.75 mm) and 12 % sand (0.075/2 mm). The experimental investigation took place in a winter morning (5.00 to 8.30 a.m.) with ambient and pavement temperatures ranging from -1 to 5 °C, applying the hydrogel brine at 80°±5 °C. A blend nominal application rate of 400 g/m^2 and a forward speed of 20 km/h were chosen. A second pass was also performed on the already treated pavement in some sub-sections, maintaining the same parameters (Figure 7).

Figure 7 - Phyto-based salt brine application on highway porous asphalt pavement

The predicted and analyzed gelling mechanisms, evidenced at laboratory scale, actually occurred even under less controlled boundary conditions and after subjecting the brine to very high shear rates due to passing through nozzles and spray application. The small drops of brine were spread on the cold pavement, where they immediately formed a gel-like structure arranged in very thin film, mainly filling and penetrating the voids but leaving the aggregates almost completely exposed and the surface texture unaltered and recognizable. A thicker gel layer and a more significant coating of the aggregates emerged after the second treatment (Figure 8).

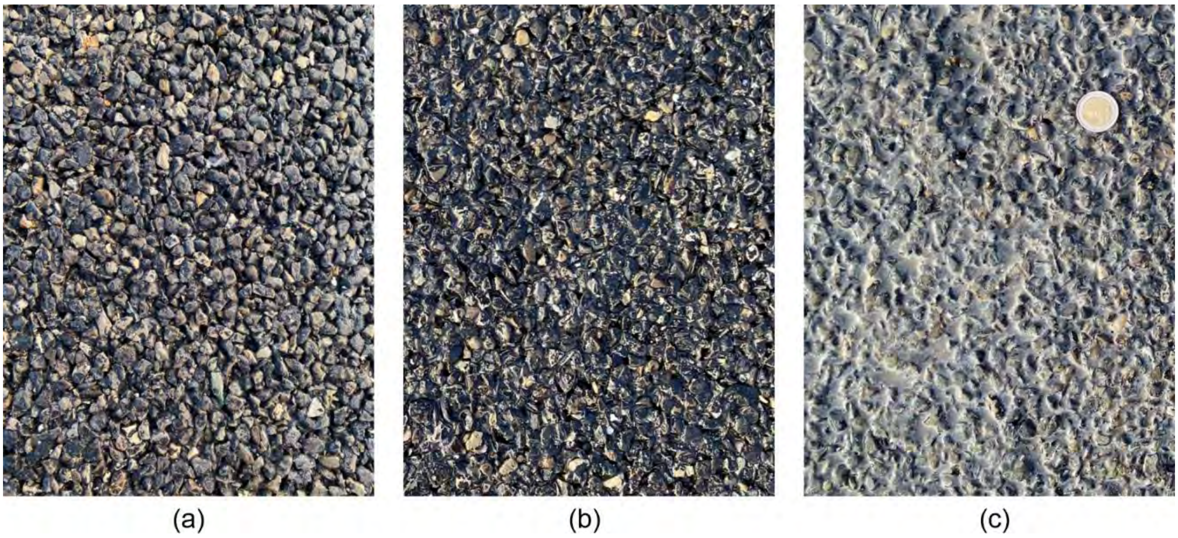
(a) (b) (c)

Figure 8 - Hydrogel layer on the pavement: no treatment (a), single spray (b) and double spay (c)

These visual impressions were also confirmed by the skid resistance evaluation, which was carried out using the portable British Pendulum Tester. The surface friction properties of the porous pavement remained unchanged: no significant differences were found between the British pendulum number (BPN) values measured before and after the salt-enhanced hydrogel application. The product remained embedded in the voids for at least 3 hours after spraying (without traffic), resulting in a longer residual effectiveness on the pavement, reducing the amount of salt in subsequent applications or becoming a pre-treatment for a subsequent treatment with dry granular salt. In any case, within 24 hours in the absence of snowfall and rain, the pavements showed only a slight whitish patina due to the salt residue.

Conclusions

The need of the highway agencies to customize winter maintenance operations on porous asphalt pavements prompted the authors to develop an innovative anti-icing technology based on the hot liquid application of a saline hydrogel. It was conceived as a hot sprayable liquid that has the ability to form a gel by simply coming into contact with a very cold surface. The onset of a gel-like structure in a thin layer would make this product capable of filling surface voids without permeating through the mix but at the same time maintaining the pavement friction resistance. This behaviour translates into a longer residual deicing efficiency, also making it an ideal primer for a subsequent dry salt intervention, allowing a significant reduction in overall salt consumption with consequent economic and environmental benefits. The phyto-based hydrogel has been formulated by exploiting the gelling properties of wall-cell seaweed polysaccharides. In a vision of zero-waste circular economy, a mixture of seaweed fibers, which are now considered as wastes or by-products generated during the processing of marine red algae “ogonori” for the extraction of refined food-grade agar, was used as thickening agent. This dry blend of fibers is a low-cost product that is currently not reused or recycled in the food industry and in other sectors. The hydrogel was prepared adding a small quantity of thickener (2% by weight of the solvent) to a conventional salt brine (23.3% wt. NaCl brine). In addition to optimizing the mixture design and defining a standardized production procedure, the laboratory experimental plan analytically investigated the gel formation mechanism of the enhanced brine. The thermal and rheological analyses revealed that the seaweed fiber acts effectively as a thickener, giving the brine a firm gel-like structure at temperatures below 55 °C and an increased viscosity at higher temperatures, but does not contribute to lowering the freezing point. Once formed, the gel stiffness and consistency appear to be insensitive to the temperature (above -18 °C). The salty seaweed hydrogel showed, like agar, a large hysteresis between its melting (above 80-85 °C) and setting temperature (≈ 55-50 °C). This process resulted to be thermo-reversible and the gelling mechanism could also be activated by heating over the melting point a cold-prepared blend. This behavior offers some food for thought on dosage and application aspects. Firstly, a threshold in which the product can be applied in the liquid form is identified. Secondly, road operators could manage with good flexibility the constituent materials, which can be either kept in different bins or pre-mixed, stored in thermo-controlled silos, possibly equipped with a stirring system to limit the possible gravitational settling phenomena of the insoluble particles, and heat activated when necessary.

Full-scale validation carried out on an existing highway porous asphalt pavement, which required the arrangement of a tank truck prototype equipped with a tailor-made specific spraying system, confirmed the expected gelling mechanisms evidenced in the laboratory scale study, even after subjecting the brine to very high shear rates due to passing through nozzles and the spray application. The heating and recirculation system of the tanker allowed a continuous and progressive mixing of the blend, avoiding the phase separation effects between salt brine and seaweed fiber. The small liquid drops of brine spread onto the cold pavement immediately formed a gel-like structure arranged in a very thin film, mainly filling and penetrating the voids but leaving the aggregates almost completely exposed and the surface texture unaltered and recognizable.

It is important to underline how the surface frictional properties of the porous pavement remained unchanged: no significant differences were found between the British pendulum number (BPN) values measured before and after the salt-enhanced hydrogel application. The product remained embedded in the voids for at least 3 hours after spraying (without traffic), but dissolves in a short period of time (a few hours) leaving a slight whitish patina on the pavement due to the salt residue only in the absence of snow and rain.

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