Effect of encapsulated pyrolytic rejuvenator derived from end-of-life mining tyres on the self-healing properties of aged bitumen

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ABSTRACT: This study aimed to evaluate the use of biopolymeric capsules based on alginate and a pyrolytic rejuvenator derived from end-of-life mining tyres to enhance the self-healing properties of aged bitumen in asphalt pavements. Capsules were produced using the jet vibrating technique settled with nozzle sizes of 300, 450, 750 µm and $CaCl_2$ hardening solutions at 2%, 5%, and 8% by total weight (wt.) of bitumen. Their morphological, thermal, and mechanical properties were analysed. Self-healing performance was evaluated by incorporating 0.5%, 1.0%, and 2.0% wt. capsules into long-term aged bitumen and testing healing efficiency through cyclic fracture-healing tests over 6 and 24-hour periods. The main results showed that capsules presented mechanical and thermal stability for the paving conditions. An optimal capsule design was achieved using a 750 µm nozzle size and 2% wt. $CaCl_2$ solution. Finally, a dosage of 1% wt. of the optimal capsule design optimised the self-healing property.

1 INTRODUCTION

The oxidative damage of asphalt bitumen, driven by environmental factors and traffic conditions, presents a significant challenge to the long-term durability of asphalt pavements. This challenge has spurred advancements in technologies designed to enhance the extrinsic self-healing of bituminous materials through the use of encapsulated rejuvenators (Gonzalez-Torre and Norambuena-Contreras 2020).

Encapsulated rejuvenators are typically spherical additives, such as polynuclear or core-shell capsules, which enclose asphalt rejuvenating liquids (oils). These capsules are incorporated into asphalt mixtures to restore the original physical and rheological properties of aged bitumen (Xu et al., 2018).

During the service life of asphalt pavements, the bitumen undergoes oxidation due to traffic loads and environmental exposure, leading to microcrack formation and propagation. When a microcrack intersects with a capsule or is subjected to pressure from traffic loads, the capsule can rupture or deform, releasing the rejuvenator. The rejuvenator subsequently diffuses into the cracked area, softening the aged bitumen, which then flows and seals the microcrack (Al- Mansoori et al., 2018). The success of this healing process depends on factors such as the duration of healing time and the number of activated capsules.

Recent research has emphasised the sustainable synthesis of polynuclear biocapsules as rejuvenators, promoting the use of biopolymers like alginate and rejuvenating agents derived from industrial waste, including pyrolytic oils (PO) from End-of-Life tyres (ELTs) (Norambuena-Contreras et al., 2021). Studies, such as those by Xu et al., 2019, suggest that capsules with polynuclear morphology allow a controlled release of rejuvenators, supporting multiple healing cycles in the bituminous material. Additionally, Chávez-Delgado et al., 2024a concluded that the addition of 3% wt. of PO derived from ELTs in long-term aged bitumen restored its rheological properties to an unaged bitumen state. Chávez-Delgado et al., 2024b explored the pyrolysis of ELTs from mining tyres to produce asphalt rejuvenators. So, its encapsulation could be used for asphalt self-healing purposes.

Despite advancements, research gaps remain in the encapsulation of pyrolytic rejuvenators, especially in their thermal-mechanical stability and impact on aged bitumen's self-healing performance. This study evaluates the effect of varying dosages of a patented encapsulated pyrolytic rejuvenator and rest periods on the self-healing capacity of long-term aged bitumen. Polynuclear biopolymeric capsules were synthesised and analysed for thermal and mechanical properties, while laboratory tests measured the healing efficiency of aged bitumen with these capsules.

2 MATERIALS AND METHOD

2.1 *Materials*

The polymeric structure of the capsules consisted of low-viscosity sodium alginate (density 1.02 g/cm^3, viscosity ≤ 300 mPa·s in a 2% wt. solution), provided by Buchi (Switzerland) and calcium-chloride dihydrate ($CaCl_2 \cdot 2H_2O$) at 77% purity, provided by Winkler (Chile). The pyrolytic oil (PO) presented density 0.86 g/cm^3, viscosity 1.7 mPa·s and pH 8.9. Virgin asphalt bitumen specified as CA-24 (PG 64-22) was long-term aged using the Pressure Air Vessel (PAV) method, according to ASTM D 6521-19.

2.2 *Synthesis and characterisation of the capsules*

Capsules with polynuclear internal morphology were synthesised based on the ionic gelation principle by electrostatic interactions between sodium alginate and the Ca^{2+} ions form the Calcium solution, following the method proposed by Concha et al., 2024. First, a 2% wt. sodium alginate solution was prepared by using a magnetic stirrer (SCI550-S) at 250 rpm for 24 h. Next, the PO was incorporated in the alginate solution at a biopolymer:oil mass (B:O) ratio of 1:5, resulting in a stable emulsion. Then, the emulsion was pumped using an encapsulator Buchi (B-390) through nozzles of 300, 450, and 750 µm diameter. The emulsion was then separated into droplets and collected in $CaCl_2 \cdot 2H_2O$ hardening solution prepared at three concentrations: 2%, 5%, and 8% wt. Finally, the capsules were filtered from the $CaCl_2$ solution and rinsed with deionised water later dried in an oven at 30ºC for 24h.

The morphological, physical, thermal, and mechanical properties of each capsule design were determined as proposed by Norambuena-Contreras et al., 2021. The diameter of 100 random capsules was measured using an optical microscope (Leica EZ4) with 35x magnification and the software ImageJ®. The physical property of encapsulation efficiency (EE), i.e., the proportion of PO encapsulated, was determined as the average of three measurements. Thermogravimetric analysis (TGA) was carried out using a NETZSCH STA 409 PC equipment in a range of temperatures 20-600ºC, and constant N_2 flow of 50 mL/min. The average compressive strength of 10 capsules per design was evaluated using a Universal Testing Machine (UTM) Zwick/ Roell Z005 with a load cell of 1kN and a load speed of 0.2 mm/min. Capsules were tested at preconditioning temperatures of 20, 50, 80, 120, and 150ºC.

2.3 *Self-healing of PAV-aged bitumen with capsules*

The effect of the PO capsule dosage (0.5%, 1.0%, 2.0% wt. of bitumen) on the self-healing ability of PAV-aged bitumen samples was evaluated on ductility samples through a mechanical cyclic process of 3 steps described as follows. *Step 1. Conditioning*. Ductility samples were conditioned at -5°C for 2 h (Figure 1(a)), ensuring a brittle fracture. *Step 2. Fracture*. The samples were fractured into two pieces at 5°C under uniaxial tensile test using a Zwick/Roell Z05 universal testing machine with 1 kN load cell and a loading speed of 5 mm/min (Figure 1(b)). *Step 3. Healing*. The fractured pieces were placed back into the mould and secured with bolts at the ends of the sample. The fractured samples were conditioned at 20°C in a thermal chamber for two healing (rest) times: 6h and 24h, (Figure 1(c)). After this, steps 1 and 2 were repeated, determining a healing level (HL) as:

$$HL\ (\%) = \left(\frac{F_h}{F_i}\right) \times 100 \tag{1}$$

Where F_i and F_h are the maximum forces resisted by a sample before and after the healing process, respectively. For each healing time, an effective average healing level (HL_e) was calculated by comparing the maximum average HL of each test sample (HL_{po}) with capsules and the ones without capsules (HL_{ref}):

$$HL_e = HL_{po} - HL_{ref} \tag{2}$$

For each healing condition, three measurements were made. Finally, statistically significant differences in the morphological, physical, and mechanical properties were evaluated by Analysis of Variance (ANOVA) with a significance of 95% (α:0.05) and the Tukey's pairwise mean comparisons.

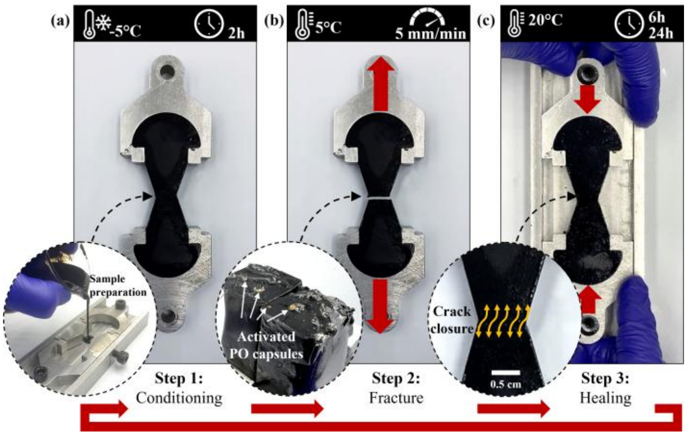

Figure 1. Healing test method on bitumen samples showing the steps of: (a) Conditioning, (b) Fracture, and (c) Healing.

3 RESULTS AND DISCUSSION

3.1 *Characterisation of the biopolymeric capsules*

Figure 2 shows representative optical microscopy images for each of the PO capsule designs. Overall, the capsules presented average values of size ranging from 0.61–1.1 mm and EE values between 96.5%–98.9%. Additionally, ANOVA and Tukey tests revealed that the higher the nozzle diameter, the higher the capsule size was. Nonetheless, the nozzle size had no effect on the EE. Regarding the $CaCl_2$ content, ANOVA and Tukey tests revealed no statistical differences for both size and EE. Consequently, a low $CaCl_2$ can be primary selected reducing its use.

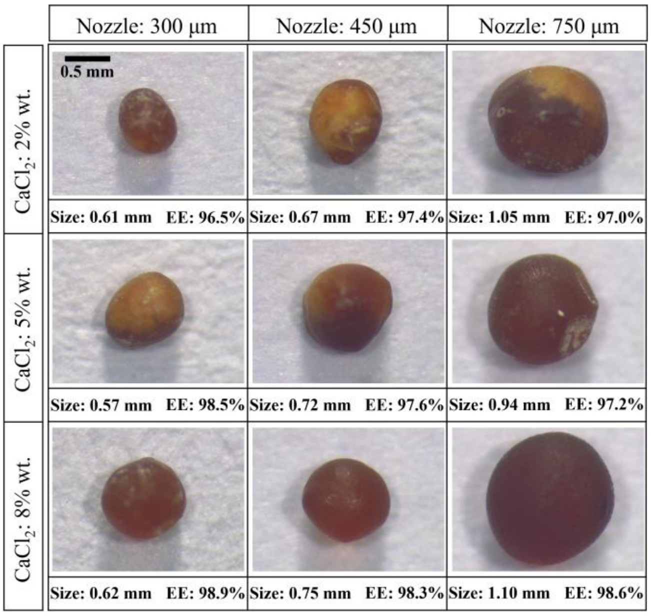

Figure 2. Optical images for each capsule design, showing their representative average sizes and encapsulation efficiency.

Figure 3 shows the average results of compressive strength for each capsule design, ranging between 5.1–15.1 MPa. Overall, these values were higher than the maximum compacting pressure during paving (Sac) of 0.7 MPa (Delgadillo et al., 2008) or the contact pressure for light-duty truck, around 1.0 MPa (Yu et al., 2022). These high compressive strength values could make capsule activation difficult. Consequently, to decide a proper capsule design, ANOVA revealed that the lower compressive strength values were reached for the capsule designs of 750 µm - 8% $CaCl_2$ (5.1 MPa) < 300 µm-8% $CaCl_2$ (7.5 MPa) < 750 µm-2% $CaCl_2$ (8.8 MPa). Based on these results and the previous selection of capsule designs based on 2% $CaCl_2$, the optimal capsule design was that based on a nozzle diameter of 750 µm and 2% $CaCl_2$.

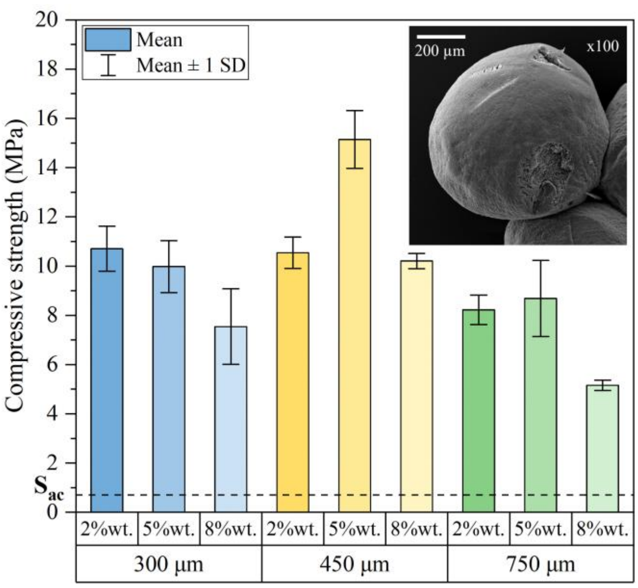

Figure 3. Average capsule compressive strength based on nozzle size (300, 450, 750 µm) and $CaCl_2$ content (2%, 5%, 8% wt).

Figure 4 shows the effect of thermal degradation on the average compressive strength of the optimal capsule design. Overall, the compressive strength was reduced with the temperature increase from 20°C to 150°C (temperature of asphalt mixing) resulting in average values between 8.2 MPa and 2.1 MPa, respectively. It can be noticed that, at 150°C, the compressive strength of the optimal capsule design is higher than the Sac, potentially ensuring their stability during paving. The high mechanical stability of the capsule at this temperature can be explained by its low thermal degradation as proved by the TGA analysis, where the optimal capsule design presented a mass loss lower than 5% at 150°C, mostly attributed to the loss of initial moisture and partial damage on the alginate matrix structure of the capsule, not compromising their mechanical stability.

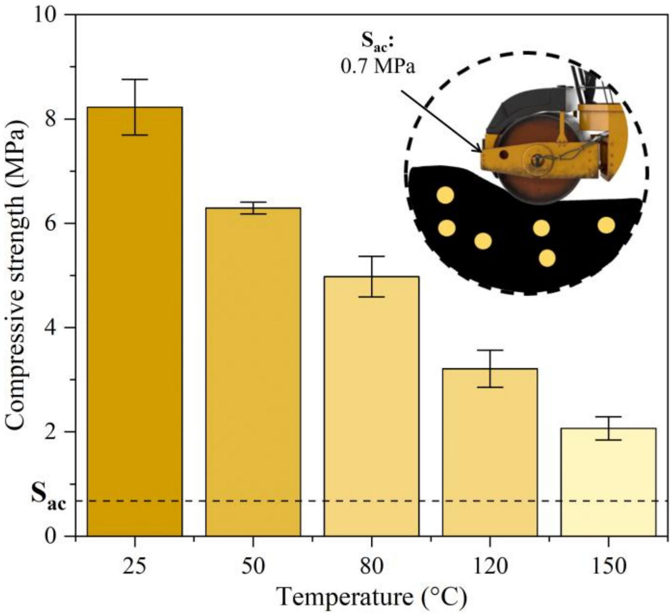

Figure 4. Average compressive strength of the optimal capsule (750 µm nozzle size, 2% wt. $CaCl_2$) at different temperatures.

Based on these results, it is concluded that the optimal capsule design was a mechanically and thermally stable additive to be incorporated into bituminous materials for asphalt self-healing purposes. These Ca-alginate PO capsules can be potentially activated by fatigue damage during the service life of the asphalt pavement similarly as proposed by García-Hernandez et al., 2020 in alginate capsules with sunflower oil.

3.2 *Effect of capsule addition on the self-healing properties of aged bitumen*

Figure 5 presents the average results of *HL* depending on the capsule content and the healing time. Overall, the *HL* was increased with the capsule addition, and healing time. ANOVA analysis developed on each individual variable showed statistically significant differences for i) the healing time of 6 h (average *HL*: 32.1%) and 24 h (average *HL*: 61.7%), and ii) the capsule dosage of 0%, 0.5%, 1%, and 2%, with average HL values of 28.5%, 44.3%, 55.3%, and 59.5%, respectively. These results suggest that higher HL values are obtained with a healing time of 24 h, and a capsule content of 2% wt.

With respect to the combined analysis of each factor on the HL, Figure 5 revealed that, at low healing time of 6h, no statistically significant effect was detected for samples with 0.0%, 0.5% and 1% capsule content. Consequently, the HL evaluated at shorter healing times was only sensitive to a capsule content of 2%. While, for a healing time of 24 h, 0.5% of capsule dosage showed statistically significant differences with respect to a reference sample. Capsule contents of 1% and 2% did not yield statistically significant differences in the HL.

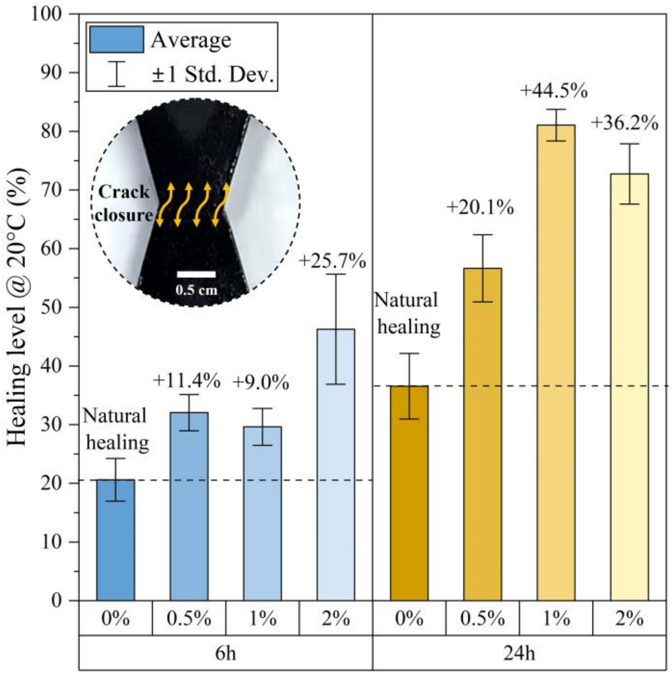

Figure 5. Average HL results for bitumen samples depending on the capsule dosage (0, 0.5, 1, 2% wt.) and healing time (6, 24 h).

Additionally, the effective healing provided by effect of the capsule (HL_e) are shown above each healing bar. It is observed that capsule contents of 1% or higher, combined with a healing time of 24 h, resulted in HL_e values exceeding 30%. Specifically, for 24 h healing, a 1% capsule content led to an increase of 44.5%. Since no statistically significant differences were observed in the HL between 1% and 2% capsule contents, it can be concluded that long healing times using a capsule content of 1% optimised the healing level of the asphalt binder is used in the production of asphalt mixtures. Future research proposes the use of a capsule design based on 750 um and 2% $CaCl_2$.

4 CONCLUSIONS

- The synthesised capsules designs containing pyrolytic liquid derived from end-of-life mining tyres presented high encapsulation efficiency, over 95% and mechanical stability. The optimal design was a capsule synthesised with a nozzle size of 750 µm and 2% wt. $CaCl_2$.
- Thermal-mechanical laboratory tests proved that the capsules were stable to the simulated mixing temperature and compaction load, without affecting the capsule integrity.
- A capsule content of 1.0% wt. and 24-hour healing time optimised self-healing properties in PAV-aged bitumen, resulting in an effective healing level of up to 44.5%.

5 ACKNOWLEDGMENTS

The authors acknowledge the funding from the National Agency for Research and Development of Chile (ANID) through the FONDEF IdeA 21I10127 and the University of Bío-Bío FAPEI FP2441850.

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