RILEM Technical Letters (2021) 6: 1-7
https://doi.org/10.21809/rilemtechlett.2021.129

Biocapsules containing low-cost rejuvenators for asphalt self-healing

Jose L. Concha[1o]*, Luis Arteaga-Pérez[2], Irene Gonzalez-Torre[1], Jose Norambuena-Contreras[1]

[1] LabMAT, Department of Civil and Environmental Engineering, University of Bío-Bío, Concepción, Chile
[2] LPTC, Department of Wood Engineering, University of Bío-Bío, Concepción, Chile

° Jose L. Concha was invited for submission of this letter as an awardee of the RILEM PhD Grant for the 74th RILEM Annual Week, 2020

Received: 04 November 2020 / Accepted: 28 January 2021 / Published online: 15 March 2021

Abstract

This study aimed to characterise polynuclear biocapsules containing low-cost rejuvenating agents for asphalt self-healing. Capsules consisted of a biopolymeric matrix of calcium alginate containing cooking oil and mineral oil as rejuvenating agents, synthesised using ionic gelation through the pumping dripping technique. The physical-chemical properties of the oil-in-biopolymer emulsions and their stability over time were studied. The morphological and thermophysical properties of the biocapsules and the encapsulation efficiency of the rejuvenating agents were quantified and characterised by microscopic techniques and laboratory tests. Main results showed that emulsions should be used for encapsulation purposes within a period no longer than 2h, reducing the effect of instability phenomena. Besides, the biopolymer-based polynuclear capsules presented uniform size, internal multicavity microstructure resulting in high encapsulation efficiencies and thermal stability at high temperatures, proving that cooking oil and mineral oil can be potentially used as low-cost rejuvenating agents and thermally stable additives for asphalt self-healing purposes.

Keywords: Oil rejuvenators; Oil-in-water emulsion; Emulsion instability; Biocapsules; Asphalt self-healing

1 Introduction

Nowadays, intense research has been carried out to promote the autonomic healing of cracked asphalt pavement by means of microencapsulated rejuvenating agents [1]. Encapsulated rejuvenators are spherical particles that contain about 70% of low-viscosity oils and are added to the asphalt mixture as an additive to recover the original properties of aged bitumen [2,3]. When microcracks in propagation encounter capsules, they trigger to rupture, and the rejuvenator fills the cracks by capillarity reconstituting the chemical composition of bitumen caused by ageing [4]. For this, low-cost and low-environmental impact rejuvenators such as cooking oil [5] and bio-oil [6] have been encapsulated using alginate, a biopolymer presenting nontoxicity, excellent biocompatibility, easy gelation, and long-term stability [7-9].

Currently, in-situ polymerisation [10-12] and ionic gelation [13,14] techniques have been widely used for the synthesis of core-shell and polynuclear capsules, based on the preparation of oil-in-water (O/W) emulsions containing a rejuvenating agent (disperse phase) in an aqueous solution (continuous phase). Nevertheless, O/W emulsions are usually affected by physical instability phenomena, such as gravitational separation (creaming or sedimentation), flocculation, or coalescence [15-18], reducing their long-term stability during the encapsulation process and negatively affecting the synthesis of the capsules. To evidence the occurrence of these phenomena, the measurement of the droplet coarsening of the disperse phase over time is a simple and effective method to evaluate the instability of the O/W emulsions [15].

To prevent the occurrence of instability in the O/W emulsions, authors such as Su et al. [4,10,12] and Sun et al. [11] have proposed the incorporation of surfactants during the synthesis of capsules via in situ polymerisation, reducing the interfacial tension between the continuous and disperse phases. Su et al. [12] concluded that the incorporation of styrene-maleic anhydride, between 1.5-2.0 wt.% is a proper amount to stabilise the emulsions. Meanwhile, Sun et al. [11] proposed the incorporation of sodium dodecyl sulfate, resulting in microcapsules with high yield and regular shape.

On the other hand, authors such as Garcia et al. [3], Micaelo et al. [13] and Norambuena-Contreras et al. [2,6,14] have recently proposed the preparation of O/W emulsions incorporating a biopolymer of alginate for the synthesis of capsules, based on the ionic gelation principle. These emulsions, containing sunflower oil as a rejuvenator, are expected to be stabilised by the thickening effect of the alginate used as an encapsulating agent, as proposed by Micaelo et al. [13]. Thus, the movement of the oil droplets is reduced, preventing them from coalescing. However, the factors influencing the occurrence of instability phenomena in O/W emulsions synthesised to develop encapsulated

* Corresponding author: Jose L. Concha, Email: jlconcha@ubiobio.cl

rejuvenators in asphalt pavements have not been reported yet. Thus, the study of these factors in emulsions incorporating low-cost rejuvenators could promote their use as a feasible alternative to conventional ones and improve the current methods used for the synthesis of capsules with asphalt self-healing purposes.

This study presents the synthesis and characterisation of polynuclear biocapsules containing two low-cost rejuvenating agents encapsulated in a biopolymeric matrix with asphalt self-healing purposes. With this objective, polynuclear biocapsules were synthesised using cooking oil and mineral oil as rejuvenators, encapsulated in a biopolymeric matrix of sodium alginate. The physical stability of the O/W emulsions containing the rejuvenators and the morphological and thermophysical properties of the polynuclear biocapsules were evaluated in laboratory.

2 Materials and methods

2.1 Materials

Biopolymeric capsules, containing fresh Cooking oil (CO) coming from sunflower and Mineral oil (MO) as rejuvenators, were synthesised in this study. The polymeric structure of the capsules consisted of calcium-chloride dihydrate ($CaCl_2 \cdot 2H_2O$) with 77% purity, provided by Winkler and low-viscosity biopolymer sodium alginate powder (density 1020 kg/m^3, viscosity ≤ 0.3 Pa·s in a 2% w/w solution), provided by Buchi. CO presented density 850 kg/m^3, viscosity 0.07 Pa·s @ 20°C, and pH 5.3-5.5 @ 25°C. MO presented density 730 kg/m^3, viscosity 0.274 Pa·s @ 20ºC, and pH 7.9-8.1 @ 25°C.

2.2 Synthesis and characterisation of oil-in-water emulsions

Two types of O/W emulsions were synthesised in this study, based on the incorporation of 1) cooking oil (CO) and 2) mineral oil (MO). Firstly, for each type of emulsion, 250 mL of a 2% w/w sodium alginate solution were prepared, being continuously agitated by a magnetic stirrer (Scilogex, model SCI550-S) at 250 rpm for 24h. Next, the alginate solution was stirred at 950 rpm for 40 min. using a mechanical stirrer (Scilogex, model OS40-Pro-LB Pro). During this process, 25 g of the CO and MO rejuvenators were incorporated into the alginate solution, resulting in two oil-in-water (O/W) emulsions.

The stability of each O/W emulsion was evaluated through the creaming index (CI) [16,17], indicating the extent of separation of the O/W emulsion components over time, as represented by Figure 1. For this, first, 15 mL of each freshly emulsion was poured into a glass vial, measuring its initial total height (h_e) in cm, associated to an initially homogeneous O/W emulsion without phase separation, as described by Figure 1a. To evaluate the rate at which the components of the emulsions experienced phase separation, the height of the serum layer (h_s) in cm was measured for each emulsion at different resting times: 0h, 1h, 2h, 3h, 6h, 12h, and 24h. The measurement of the serum layer with time is an indicator of the extent of separation of the disperse phase (CO and MO used as rejuvenators) from the continuous one (alginate solution), by the ascension of the oil droplets to the top of the O/W emulsion, known as the creamed layer (h_c).

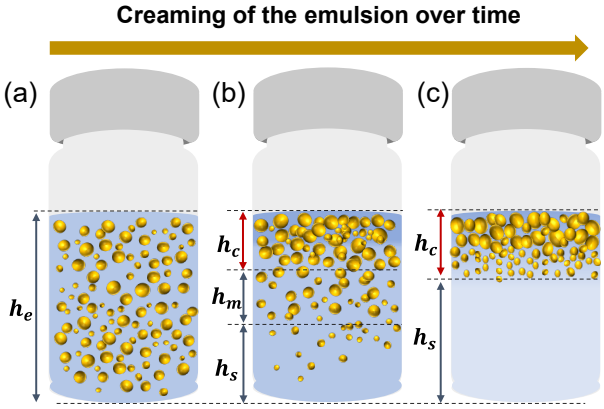

Figure 1. Representation of the creaming of an O/W emulsion over time. (a) First, the oil is dispersed into the aqueous phase, resulting in a homogeneous O/W emulsion of initial height h_e. (b) With time, the emulsion becomes physically unstable, and the oil progressively ascend to the top of the emulsion, identifying three layers: a serum (h_s), a middle (h_m), and a creamed (h_c) layer. (c) In the end, the continuous and disperse phases of the emulsion are completely separated in a serum (h_s) and a creamed (h_c) layers.

Thus, CI was determined according to Equation 1:

$$CI(\%) = \frac{h_s}{h_e} \times 100 \quad (1)$$

CI was reported as the average of three measurements for each resting time. In addition, for each of the after-mentioned times, an aliquot of the O/W emulsion was extracted to evaluate the droplet size (diameter) of the disperse phase by fluorescence microscopy (ICOE IV 5100FL) and the image processing software ImageJ® (Fiji, version 1.52p). The number-weighted (d_{10}), surface-weighted (d_{32}) and volume-weighted (d_{43}) mean diameters, as well as the droplet size distribution of the disperse phase, were determined, as proposed by Grumenezcu [15] and McClements [17], respectively.

2.3 Synthesis and characterisation of biocapsules

Polynuclear biocapsules were synthesised based on the ionic gelation principle using the pumping dripping technique described by Norambuena-Contreras et al. [6]. For this, a syringe containing 60 mL of each O/W emulsion (Figure 2a) was placed in an automatic syringe pump configured at a rate of 2 mL/min. The outgoing emulsion drops from the syringe were let down into a $CaCl_2$ hardening solution of 5% w/w calcium chloride in deionised water, continuously agitated by a magnetic stirrer (SCI550-S) at 250 rpm, see Figure 2b. The distance between the outgoing drops and the $CaCl_2$ solution was 0.35 m. Then, freshly capsules were filtered and dried in an oven at 35°C for 24h (Figure 2c) and then stored in a freezer at -10°C, avoiding possible oxidation of the rejuvenating agents.

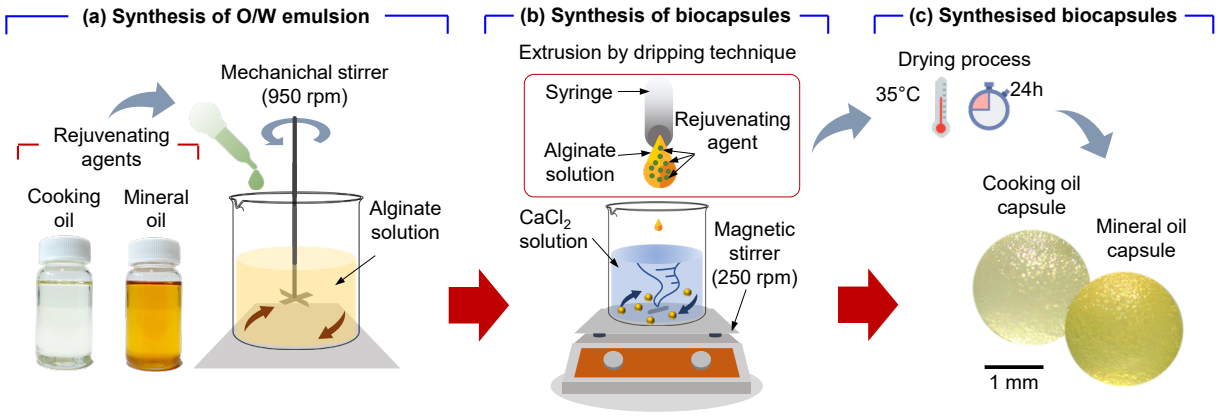

Figure 2. Representation of the synthesis of the: (a) CO and MO emulsions; and (b) CO and MO biocapsules. (c) Synthesised CO and MO biocapsules.

The encapsulation efficiency (E_e) of CO and MO capsules was determined based on the method proposed by Guadarrama-Lezama et al. [19]. First, 2 g of capsules were added into 10 mL of hexane and stirred for 10 min. at 100 rpm, using a magnetic stirrer. Next, the hexane containing the non-encapsulated rejuvenating agent was filtered from the capsules and stored in a 25 mL glass beaker, previously weighted.

The filtered capsules were distributed in two 15 mL Falcon tubes incorporating 8 mL of sodium citrate solution in a concentration of 8% w/w, being periodically agitated for 24h until the complete dissolution of the capsules. Then, 5 mL of hexane: isopropanol solution in a volume proportion of 3:1 were incorporated to each Falcon Tube and then centrifugated at 5000 rpm for 10 min. in a Hermle Z207A centrifuge. The dissolvent solution containing the encapsulated rejuvenator was extracted from the Falcon tubes and stored in other 25 mL glass beaker, previously weighted.

Both beakers were placed in an oven at 30°C for 24 h. Once completed this process, the residual mass in the beakers was measured each 10 min. until no difference was registered in two consecutive measures. The beaker with the residual mass from the filtered capsules corresponded to the rejuvenating agent (R_s) on the surface of the capsules, in g. While, the beaker with the residual mass after the dissolution of the capsules, corresponded to the encapsulated rejuvenating agent (R_e), in g. This way, E_e was calculated according to Equation 2:

$$E_e(\%) = \frac{R_e}{R_s + R_e} \times 100 \quad (2)$$

Thus, E_e was represented as the average of three measurements. Additionally, the size and mass distribution of 100 capsules were determined by optical microscopy (Leica EZ4) and an auto-balance (PerkinElmer AD 6000), respectively. The internal structure of the capsules was characterised by SEM (Hitachi SU 3500). Finally, the thermal stability of the capsules and their components was measured by TGA-DTG between ambient temperature and 600ºC at 10ºC/min in N_2 (10 mL/min) in a TA Tech Q50 thermobalance.

3 Results and discussion

3.1 Influence of the rejuvenating agents on the instability of oil-in-water emulsions

The freshly prepared CO and MO O/W emulsions presented d_{10}, d_{32}, and d_{43} values of 49.47 µm; 58.90 µm; and 63.67 µm, and 56.62 µm; 75.40 µm; and 82.56 µm, respectively. Thus, the synthesised emulsions can be categorised as macroemulsions, for which the diameter of the droplets range between 0.1µm-100µm [15]. As stated by Grumenezcu [15], this category of emulsion is particularly affected by instability phenomena associated to the physical-chemical properties of their components, such as the droplet size of the disperse phase. For instance, based on the above-mentioned mean diameter values, both emulsions presented $d_{10}<d_{32}<d_{43}$, meaning a polydisperse nature with a tendency to creaming and coalescence instability phenomena. The particularly highest d_{10}, d_{32}, and d_{43} values for the MO emulsion indicate a tendency to be more unstable than CO emulsion.

To prove this, Figure 3a shows the average results of creaming index for both O/W emulsions over time, observing an increase of their value in two stages. The first stage, defined from 0h to 3h, CO and MO emulsions presented a high creaming rate with CI values of 58.5% and 71.8% at the end of this period, respectively. During this stage, the initially homogeneous emulsions (h_e) developed phase separation of their components in three layers; h_s, h_m, h_c; as described by Figure 1b. From 3h to 24h, a second stage was defined and characterised by the increase of the CI at a significantly lower rate than the first stage. After 24h, CO and MO emulsions reached CI values of 73% and 80%, respectively. At the end of this period, the emulsions presented a total separation of their components in two layers; h_s, corresponding to the aqueous phase; and h_c, corresponding to the disperse phase (see Figure 3b). Overall, the above results evidenced that emulsions were affected by the gravitational separation of their components by creaming, becoming unstable over time.

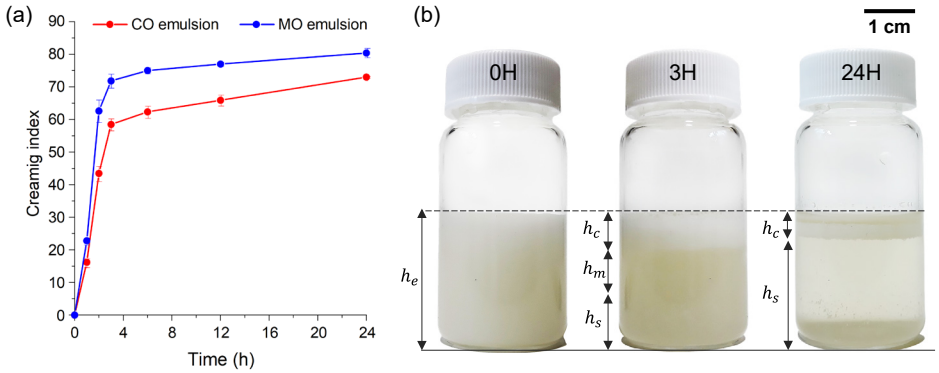

Figure 3. (a) Average creaming index results over time for the CO and MO O/W emulsions; (b) Evolution of the creaming process occurring in an O/W emulsion with CO as rejuvenator agent at 0h, 3h, and 24h of response.

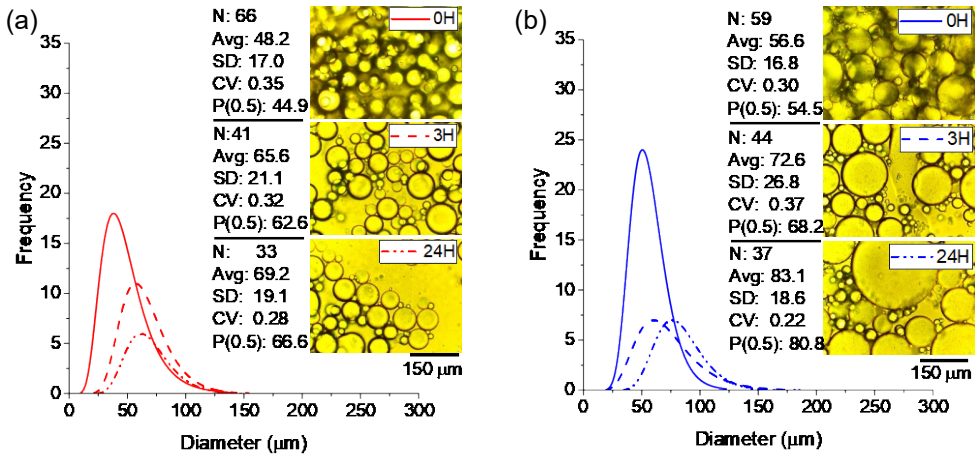

Figure 4. Frequency histograms of the diameter of the droplets fitted to a log-normal distribution(N: number of samples, Avg.: Average value, SD: Standard deviation, CV: coefficient of variation, and P(0.5): 50th percentile for the diameter measurement) and fluorescence microscopy images of the oil droplets at 0h, 3h, and 24h for the O/W emulsions containing: (a) Cooking oil (b) Mineral oil as rejuvenating agents.

The particularly high CI for the emulsion containing MO could be attributed to the following three factors:

- The density difference between the continuous and disperse phase (Δρ) promotes the creaming phenomenon based on Stokes's law [16]. Thus, the more the density difference between these phases, the more the creaming velocity. Therefore, MO presented a Δρ higher than CO; 290 kg/m^3 and 170 kg/m^3, respectively.
- The increment of the droplet size of the disperse phase over time by coalescence, as seen in the fluorescence microscopy images in Figure 4a and b. Thus, the greater the droplet size of the disperse phase, the greater the velocity at which the droplets ascend to the top of the emulsion, facilitating the creaming process. For instance, after 24h response, the average droplet diameter for CO and MO emulsions increased to 69.2 µm and 83.1 µm, being in-line with their respective CI tendency, and so, with the velocity of ascending of the rejuvenators to the top of the emulsion, favouring the phase separation.
- Another factor facilitating the creaming of the emulsions is the fact that alginate is an anionic polysaccharide with no emulsifying activity, promoting instability phenomena in O/W emulsions [20]. To reduce the effect of the creaming, current researches have explored the chemical functionalisation of alginate, providing it with an amphiphilic nature to stabilise O/W emulsions [21].

Finally, although it is possible to decrease the instability of the O/W emulsion by incorporating surfactants or by keeping the emulsion under agitation, these alternatives could potentially increase the economic cost of the capsules. Thus, considering the above discussion and the current state of fabrication of the emulsions, they should be used for encapsulation purposes within a period no longer than 2h, reducing the effect of instability phenomena.

3.2 Morphological and physical properties of the biocapsules

Figure 5a and b show that the encapsulation process of the O/W emulsions resulted in biocapsules with regular spherical and external rough morphology. From these images, it is also appreciated that MO capsules presented a size visibly larger than the CO capsules. This was confirmed by the frequency histograms sowed in Figure 5c, where the average diameter of CO and MO capsules were 1771.49 µm (SD: 79.21 µm) and 1800.47 µm (SD: 94.58 µm), respectively. The slightly higher diameter for the MO capsules was attributed to its high viscosity compared to CO, retarding the release of the outgoing O/W emulsion drops from the needle tip. Overall,

the encapsulation of each oil rejuvenator resulted in capsules with homogeneous size as evidenced their low coefficient of variation (CV) in the histograms. Additionally, representative SEM images taken from the cross-sectional area of both biocapsules (Figure 5d-f) reveals that the rejuvenators were encapsulated in an internal polynuclear microstructure, also reported by Zhang et al. [22] and Xu et al. [23]. They hypothesise that a polynuclear internal microstructure can provide: (1) a controlled liberation of the rejuvenating agent, providing multiple healings on aged bitumen, and (2) good thermal and mechanical stability. Moreover, the frequency histograms of mass in Figure 5g show that the MO capsules presented an average mass higher than CO capsules; 2.75 mg (SD: 0.56 mg) and 3.14 mg (SD: 0.59 mg), respectively. Thus, the MO biocapsules could store an amount of rejuvenator higher than CO biocapsules.

To prove the previous hypothesis, Figure 5h shows the average E_e results for both type of capsules, showing that the MO capsules increased the amount of encapsulated rejuvenating agent presenting a higher encapsulation efficiency compared to the CO capsules; 93.4% (SD: 2.65%) and 88.1% (SD:1.86%), respectively. Based on these results, the higher E_e for the MO capsules was attributed to their larger size compared to the CO capsules, extending their internal polynuclear microstructure to store a greater amount of rejuvenator inside them. A reason for a E_e not being 100% was attributed to the encapsulation mechanism. When the outgoing emulsion drops impacted on the $CaCl_2$ solution in agitation, part of the rejuvenating agent could have been separated from the emulsion, as proposed by Martins et al. [24]. As a consequence, when extracted the capsules from the hardening solution, a remanent amount of rejuvenator was remained on the surface of the capsules, being then identified as non-encapsulated rejuvenator (R_s). Thus, reducing the distance between the drops and the hardening solution could increase E_e. Although this, the higher encapsulation efficiency obtained for both types of biocapsules indicates their potential use as additives for asphalt self-healing purposes.

Nonetheless, for a successful incorporation of encapsulated rejuvenators into asphalt pavements, the biocapsules should meet a series of specifications related to the manufacturing of asphalt mixtures. From a thermal point of view, capsules should resist the temperature of fabrication of HMA around 160° C, as stated by Xu et al. [23]. While, from a mechanical point of view, Yamaç et al. [25] stated that capsules should at least resist a compressive strength value of 10 N to prevent breaking during mixing and compaction.

3.3 Thermal stability of the biocapsules

Figure 6(a-c) shows the TGA and DTG curves, recorded for biopolymeric capsules with and without the rejuvenating agents. As evidence of the thermal decomposition of the encapsulating biopolymer of alginate, the Figure 6a shows that a polynuclear biocapsule without rejuvenating agent reached its higher rate of decomposition at 183°C, resulting in a loss of mass of 14.04%. This phase decomposition has been attributed to the removal of physically and chemically bounded water and the limited devolatilisation of some fractions of the alginate. Vincent et al. [26] reported a similar tendency, witnessing the drying and volatilisation of hydroxy-compounds (including water bound to organic groups) in the same order of temperature. In the present study, the recorded mass loss was below 5% at the temperature of the fabrication of asphalt (around 160°C), proving that alginate can be potentially used as an encapsulation material for the different rejuvenating agents.

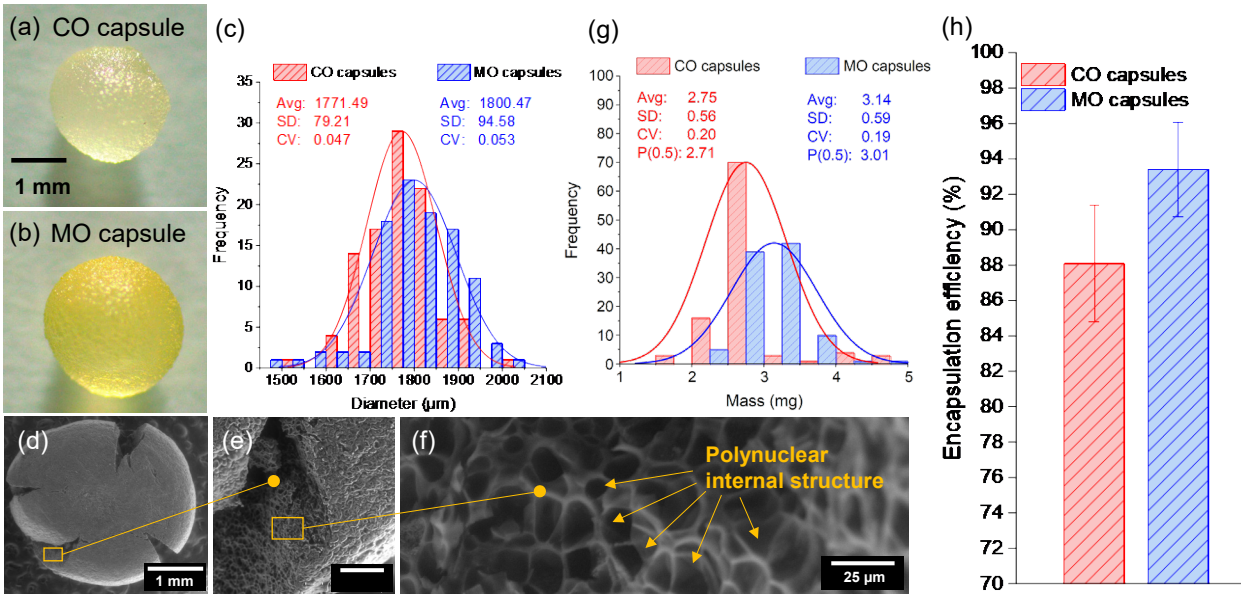

Figure 5. (a-b) Optical images of CO and MO biocapsules, respectively; (c) Frequency histograms of the diameter of the CO and MO biocapsules fitted to a normal distribution; (d-f) SEM images showing the polynuclear internal microstructure of the biocapsules; (g) Frequency histograms of the mass of the CO and MO biocapsules fitted to a normal distribution; and (h) Average results of the encapsulation efficiency of CO and MO biocapsules.

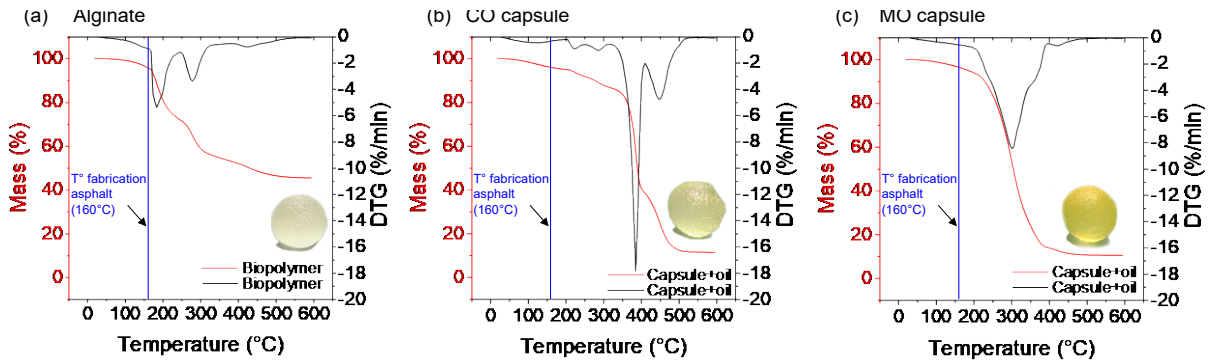

Figure 6. Thermogravimetric results for: (a) the alginate biopolymer used as encapsulating agent; (b) CO capsule; and (c) MO capsule.

To confirm this, Figure 6b and c show the thermal decomposition curves of the CO and MO biocapsules incorporating the respective oils in the biopolymer matrix of alginate. From these Figures, it can be noticed that the alginate extended its thermal stability when containing the CO and MO oils, with low degradation rates (DTG below 1%/min) at temperatures up to 339°C and 209°C, respectively. Particularly, for the CO and MO capsules, the thermal degradation occurred in a single step with a maximum decomposition rate at 384.8°C and 294.6°C, respectively. Although the lower temperature at which the MO capsules were significantly degraded, this temperature is still considerably higher to that at which asphalt mixtures are manufactured.

Finally, it can be concluded that the synthesis of polynuclear biocapsules using alginate as encapsulating material and CO and MO oils as rejuvenating agents can be potentially used as a thermally stable additive for asphalt self-healing purposes.

4 Conclusions

Based on the previous discussion, the following conclusions can be drawn:

- The cooking and mineral oil-in-water emulsions were categorised as macroemulsions, since d_{10}, d_{32}, and d_{43} mean diameters were in the range from 0.1µm to 100µm. They also presented a polydisperse character, which meant both types of oil-in-water emulsions were susceptible to instability phenomena, with a greater effect on the MO due to its higher droplet sizes attributed to the higher viscosity of the oil.
- The physical stability results of the emulsions indicated that both cooking and mineral oil-in-water emulsions were totally creamed after 24h. The particularly higher creaming index value for the mineral oil-in-water emulsion was attributed to the increase of the droplet size over time, the low density and coalescence of the disperse phase, and the non-emulsifying activity of alginate. To reduce the creaming effect in the emulsions, they should be used with encapsulation purposes within a period of 2h.
- The encapsulation of the cooking and mineral oil-in-water emulsions in the alginate biopolymer matrix resulted in biocapsules with spherical morphology, uniform size, and internal polynuclear microstructure. The particularly higher viscosity for the mineral oil promoted the synthesis of the largest biocapsules with average sizes of 1.8 mm.
- The larger size of the mineral oil-in-water emulsion allowed to keep more rejuvenator inside them, with an average encapsulation efficiency of 93.4%. Overall, the encapsulation efficiency over 85% reached by both emulsions suggests their use as a suitable solution for asphalt self-healing.
- TGA results proved that the biopolymer of alginate used as encapsulating material provided high thermal stability to the cooking and mineral oil biocapsules, which presented residual mass over 96% at the temperature of asphalt manufacturing, proving that cooking oil and mineral oil can be potentially used as low-cost rejuvenating agents and thermally stable additives for asphalt self-healing purposes.

Finally, future research could be focused on the synthesis of thermophysical and mechanical optimised capsules in asphalt mixtures, determining: (1) the best method of incorporation of the capsules during the fabrication of an asphalt mixture, without affecting their structural integrity (e.g., during compaction process at high temperatures), (2) the release mechanism and (3) diffusion of the rejuvenating agent through a cracked asphalt mixture, and finally (4) the study of the self-healing properties of the optimised capsules on aged asphalt mixtures.

CRediT Authorship statement

José L. Concha: Formal analysis, Methodology, Writing – original draft, Visualisation. Luis Arteaga-Pérez: Formal analysis, Methodology, Writing – review & editing. Irene Gonzalez-Torre: Conceptualisation, Methodology, Supervision, Writing – review & editing. Jose Norambuena-Contreras: Conceptualisation, Funding acquisition, Methodology, Supervision, Resources, Writing – review & editing.

Acknowledgements

The authors want to thank the financial support given by the National Research and Development Agency (ANID) from Chile, through the Research Project FONDECYT 1190027 and FONDEQUIP EQM-140088 for the acquisition of the Hitachi Scanning Electron Microscope (ESEM). Additionally, the first author wishes to thank the financial support given by the

University of Bío-Bío for his internal PhD scholarship granted, and the RILEM association for the PhD Grant given to attend the 74th Annual RILEM Week in Sheffield, UK.

References

[1] I. Gonzalez-Torre, J. Norambuena-Contreras, Recent advances on self-healing of bituminous materials by the action of encapsulated rejuvenators. Constr Build Mater (2020) 258: 19568. https://doi.org/10.1016/j.conbuildmat.2020.119568

[2] J. Norambuena-Contreras, E. Yalcin, R. Hudson-Griffiths, A. García, Mechanical and self-healing properties of stone mastic asphalt containing encapsulated rejuvenators. J Mater Civil Eng (2019) 31(5) https://doi.org/10.1061/(ASCE)MT.1943-5533.0002687

[3] A. Garcia-Hernández, S. Salih, I. Ruiz-Riancho, J. Norambuena-Contreras, R. Hudson-Griffiths, B. Gomez-Meijide, Self-healing of reflective cracks in asphalt mixtures by the action of encapsulated agents. Constr Build Mater (2020) 252: 118929. https://doi.org/10.1016/j.conbuildmat.2020.118929

[4] J. Su, S. Han, Y. Wang, E. Schlangen, N. Han, B. Liu, X.L. Zhang, P. Yang, W. Li, Experimental observation of the self-healing microcapsules containing rejuvenator states in asphalt binder. Constr Build Mater (2017) 147: 533-542. https://doi.org/10.1016/j.conbuildmat.2017.04.190

[5] S. Shirzad, M.M. Hassan, M.A. Aguirre, L.N. Mohammad, W.H. Daly, Evaluation of sunflower oil as a rejuvenator and its microencapsulation as a healing agent. J Mater Civil Eng (2016) 28 (11). https://doi.org/10.1061/(ASCE)MT.1943-5533.0001625

[6] J. Norambuena-Contreras, L.E. Arteaga-Perez, A.Y. Guadarrama-Lezama, R. Briones, J.F. Vivanco, I. Gonzalez-Torre, Microencapsulated bio-based rejuvenators for the self-healing of bituminous materials. Materials (2020) 13(6). https://doi.org/10.3390/ma13061446

[7] M.D. Eqbal, V. Gundabala, Controlled fabrication of multi-core alginate microcapsules. J Colloid Interf Sci (2017) 507: 27-34. https://doi.org/10.1016/j.jcis.2017.07.100

[8] L. Yu, Q. Sun, Y. Hui, A. Seth, N. Petrovsky, C. Zhao, Microfluidic formation of core-shell alginate microparticles for protein encapsulation and controlled release. J Colloid Interf Sci (2019) 539: 497-503. https://doi.org/10.1016/j.jcis.2018.12.075

[9] Z. Wu, J. Wu, R. Zhang, S. Yuan, Q. Lu, Y. Yu, Colloid properties of hydrophobic modified alginate: Surface tension, ζ-potential, viscosity and emulsification. Carbohydr (2018) 181: 56-62. https://doi.org/10.1016/j.carbpol.2017.10.052

[10] J. Su, Y. Wang, N. Han, P. Yang, S. Han, Experimental investigation and mechanism analysis of novel multi-self-healing behaviors of bitumen using microcapsules containing rejuvenator. Constr Build Mater (2016) 106: 317-329. https://doi.org/10.1016/j.conbuildmat.2015.12.120

[11] D. Sun, B. Li, Y. Tian, T. Lu, X. Zhu, G. Sun, F.A. Gilabert, Aided regeneration system of aged asphalt binder based on microcapsule technology. Constr Build Mater (2019) 201: 571-579. https://doi.org/10.1016/j.conbuildmat.2018.12.167

[12] J.F, Su, E. Schlangen, Synthesis and Physicochemical Properties of High Compact Microcapsules Containing Rejuvenator Applied in Asphalt. Chem. Eng J (2012) 198-199: 289-300. https://doi.org/10.1016/j.cej.2012.05.094

[13] R. Micaelo, T. Al-Mansoori, A. Garcia, Study of the mechanical properties and self-healing ability of asphalt mixture containing calcium-alginate capsules. Constr Build Mater (2016) 123: 734-744 . https://doi.org/10.1016/j.conbuildmat.2016.07.095

[14] J. Norambuena-Contreras, Q. Liu, L. Zhang, S. Wu, E. Yalcin, A. Garcia, Influence of encapsulated sunflower oil on the mechanical and self-healing properties of dense-graded asphalt mixtures, Mater Struct (2019) 52(78). https://doi.org/10.1617/s11527-019-1376-3

[15] A.M. Grumenezcu, Emulsions. Nanothecnology in the Agri-Food Industry, Volume 3. Elsevier USA, 2016.

[16] D.J. McClements, Critical review of techniques and methodologies for characterisation of emulsion stability. Crit. Rev. Food Sci. Nutr (2007) 47(7): 611-649. https://doi.org/10.1080/10408390701289292

[17] D.J. McClements, Food emulsions. Principles, practices, and techniques, third edition. CRC Press, USA, 2016. https://doi.org/10.1201/b18868

[18] T. Tadros, Emulsions. Formation, stability, industrial applications. DeGruyter, Germany, 2016. https://doi.org/10.1515/9783110452242

[19] A.Y. Guadarrama-Lezama, L. Dorantes-Alvarez, M.E. Jaramillo-Flores, C. Pérez-Alonso, K. Niranjan, G.F. Gutiérrez-López, L. Alamilla-Beltrán, Preparation and characterisation of non-aqueous extracts from chilli (Capsicum annuum L.) and their microencapsulates obtained by spray-drying. J Food Eng (2012) 112: 29-37. https://doi.org/10.1016/j.jfoodeng.2012.03.032

[20] P. Shao, J. Feng, P. Sun, N. Xian, B. Lu, D. Qiu, Recent advances in improving stability of food emulsion by plant polysaccharides. Food Res Int (2020) 137: 109376. https://doi.org/10.1016/j.foodres.2020.109376

[21] Y. Li, Y. Feng, G. Yu, J. Li, Y. Zhou, Y. Liu, Preparation and characterisation of oil-in-water emulsion based on eco-friendly emulsifiers. Colloids Surf A Physicochem Eng Asp (2020) 602: 125024. https://doi.org/10.1016/j.colsurfa.2020.125024

[22] L. Zhang, Q. Liu, H. Li, J. Norambuena-Contreras, S. Wu, S. Bao, B. Shu, Synthesis and characterisation of multi-cavity ca-alginate capsules used for self-healing in asphalt mixtures. Constr Build Mater (2019) 211: 298-307. https://doi.org/10.1016/j.conbuildmat.2019.03.224

[23] S. Xu, A. Tabaković, X. Liu, D. Palin, E. Schlangen, Optimisation of the calcium alginate capsules for self-healing asphalt. Appl Sci (Switzerland) (2019) 9(3). https://doi.org/10.3390/app9030468

[24] E. Martins, D. Poncelet, R.C. Rodrigues, D. Renard, Oil encapsulation techniques using alginate as encapsulating agent: Applications and drawbacks. J. Microencapsul (2017) 34(8): 754-771. https://doi.org/10.1080/02652048.2017.1403495

[25] Ö. E Yamaç, M. Yilmaz, E. Yalçın, B.V. Kök, J. Norambuena-Contreras, A. Garcia, Self-healing of asphalt mastic using capsules containing waste oils. Constr Build Mater (2021) 270. https://doi.org/10.1016/j.conbuildmat.2020.121417

[26] T. Vincent, C. Vincent, L. Dumazert, B. Otazaghine, R. Sonnier, E. Guibal, Fire behavior of innovative alginate foams. Carbohydr. Polym (2020) 250: 116910. https://doi.org/10.1016/j.carbpol.2020.116910