Available online at www.sciencedirect.com

ScienceDirect

Transportation Research Procedia 72 (2023) 688–695

Transportation Research Procedia

www.elsevier.com/locate/procedia

Transport Research Arena (TRA) Conference

Self-healing Asphalt Roads: Evaluation of Calcium Alginate Capsules with Bio-Oil

Marina Cabette[a] , Rui Micaelo[b], Jorge Pais[a]*

[a] *University of Minho, Campus de Azurém, Av. da Universidade, 4800-058 Guimarães, Portugal*
[b] *NOVA School of Science and Technology, Largo da Torre, 2825-149 Caparica, Portugal*

Abstract

Incorporating extrinsic self-healing factors in road materials and pavements can transform the road construction and maintenance processes by increasing their life span and eliminating or reducing the need for maintenance. One autonomic self-healing technology available for asphalt pavement is embedding in the material capsules containing rejuvenators. This work presents one production method for encapsulating rejuvenators and assesses capsules characteristics (physical and mechanical). Ca-alginate capsules with Bio-Oil as a rejuvenator were produced in different contents, changing the design parameters, namely the ratio of ca-alginate and rejuvenator. Capsules were characterized based on morphology, size, composition, thermal and mechanical strength.

Keywords: Self-healing; calcium alginate capsule; rejuvenator; bio-oil; compressive test; thermogravimetric test.

Nomenclature

BO	Bio-Oil
N_2	nitrogen
PEMA	poly (ethylene-alt-maleic-anhydride)
Ca	calcium alginate

* Corresponding author. Tel.: +351 253 510 208; fax: +351 253 510 217
E-mail address: jpais@civil.uminho.pt

10.1016/j.trpro.2023.11.456

1. Introduction

Self-healing is a preventive maintenance method as it extends the useful life and durability of pavements, and it also potentially offers favorable economic and environmental effects. The focus of self-healing asphalt pavements is to create and evolve an asphalt pavement material that can heal itself without external intervention. Therefore, the extension of the life of road pavements is a subject of interest for investigating as it allows reducing the cost of rehabilitation and the inconveniences to road circulation. Several studies have been carried out with this objective. Simply heating the upper layers of the asphalt pavement as a self-healing technique could be potentially used in damaged pavements. Besides self-healing through heating, another way to extend the life period of asphalt road pavements is rejuvenation using lubricating oils (Al-Mansoori, Norambuena-Contreras, and Garcia 2018; Micaelo, Al-Mansoori, and Garcia 2016). The rejuvenator encapsulation approach represents a more favourable self-healing method as it allows the aged binder to be rejuvenated; in other words, the asphalt mix can regain some of its original chemical, physical, and mechanical properties. Previous research showed that Ca-alginate encapsulation is a good candidate for this purpose (Xu et al. 2019). Alginates have the ability of self-degradation when exposed to ambient conditions such as the air, so if the crack propagation does not open the capsule, the self-deterioration mechanism will open the capsule and release the rejuvenator (Xu et al. 2018b). The main objective of this research is to optimize calcium alginate capsules for the application in self-healing asphalt. In this study, the calcium alginate capsules are prepared with varying Sodium Alginate solution/Rejuvenator solution (A/R), poly(ethylene-alt-maleic-anhydride) (PEMA) solution/Sodium Alginate (PEMA/A) and de-ionized water/Sodium alginate (W/A) ratios to evaluate the encapsulation of Bio-Oil (BO).

2. Materials and methods

2.1. Materials and preparation process

The production of calcium alginate capsules to encapsulate the rejuvenator requires sodium alginate, de-ionized water, polyethene-alt-maleic-anhydride (PEMA), and calcium chloride ($CaCl_2$). Besides, the rejuvenator used is a bio-oil (BO), which is a residue obtained from the distillation of waste cooking oil and animal fats, and it is composed of the less volatile organics but also contains some residual Fatty Acid Methyl Ester (FAME). Fig. 1 shows the materials used in fabrication.

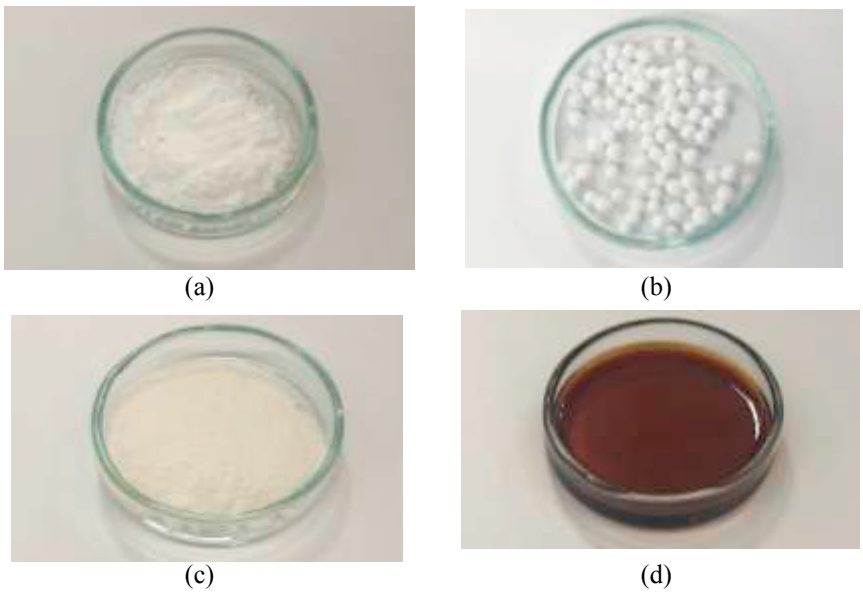


Fig. 1. Capsules materials a) PEMA; b) $CaCl_2$; c) sodium alginate; d) BO.

The calcium alginate capsules were produced following the procedure of Xu et al. (2018a) that is illustrated in Fig. 2. Therefore, to produce calcium alginate capsules, 2.5 wt.% solution of PEMA was mixed with the rejuvenator with a ratio of 40% PEMA and 60% rejuvenator and de-ionized water. Then, the sodium alginate powder was mixed gradually.

To this aim, three ratios were put into account to fabricate the Ca-Alginate capsules of BO (Table 1): Sodium Alginate solution/Rejuvenator (70/30; 75/25; 85/15 and 80/20), Rejuvenator/ Sodium Alginate (3 – 4.29), de-ionized water/Sodium alginate (16.7 – 28.6), poly(ethylene-alt-maleic-anhydride) (PEMA) solution/Sodium Alginate (2 – 16.7) and Rejuvenator/ de-ionized water (0.14 – 0.22) ratios were varied. Each solution was stirred with a mechanical stirrer for 5 minutes at a rate of 600 rpm.

Subsequently, the blend was dropped through pear shape separatory funnel into the $CaCl_2$ solution to allow capsule formation. The CaCl2 solution was stirred at a low speed for the entire duration of the capsule production process. Finally, the calcium alginate capsules are harvested from the recipient, clean with water or alcohol and then dried in an oven at 35- 40ºC. Some produced capsules are shown in Fig 3.

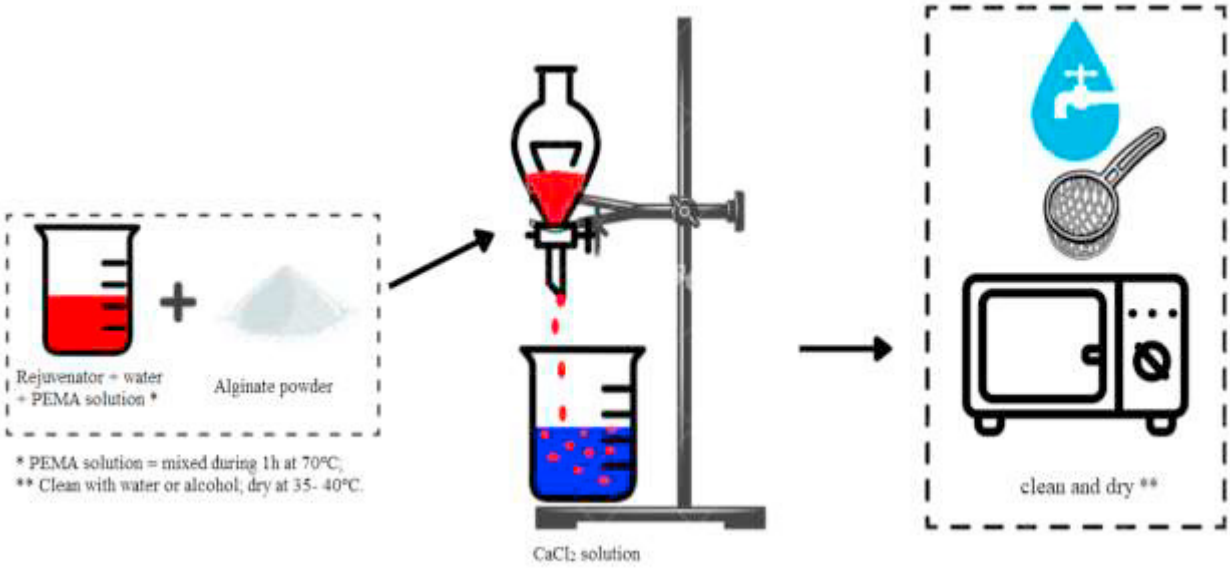
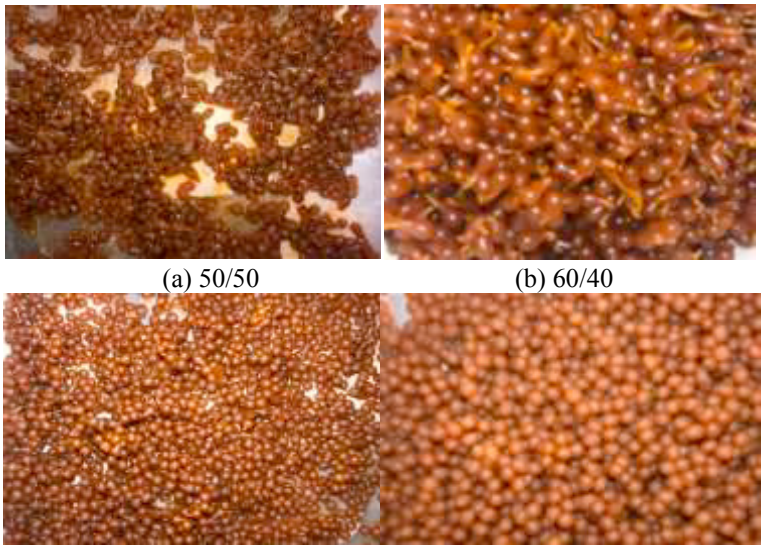


Fig. 2. Production process of ca-alginate capsules.

Table 1. Ca-Alginate ratios.

Sample	Sodium Alginate solution/Rejuvenator solution	Rejuvenator/ Sodium Alginate	de-ionized water/Sodium alginate	PEMA solution/Sodium alginate	Rejuvenator/ de-ionized water
70/30	70/30	4.29	16.7	2.9	0.22
75/25	75/25	4.29	21.4	2.9	0.18
85/15 – w/o PEMA	85/15	4.29	24.3	-	0.18
80/20-A4.29	80/20	4.29	28.6	2.9	0.14
80/20-A3	80/20	3.00	20.0	2.0	0.14
Alginate+PEMAs	-	-	16.7	16.7	-
Alginate	-	-	16.7	-	-



(a) 50/50 (b) 60/40

(c) 75/25 (d) 85/15 – without PEMAs

Fig. 3. Example of the ca-alginate capsules with Bio-Oil as a rejuvenator.

2.2. Characterization of ca-alginate capsules

The capsules were characterized based on the size, morphology, composition and thermal and mechanical strength. The morphology and size were analyzed with the macro lens camera coupled to the mechanical testing machine. To investigate the mechanical strength of prepared calcium alginate capsules, they were subjected to uniaxial unconfined compressive tests at the loading speed of 0.03 mm/s and at room temperature. As shown in Fig. 4, in the force-displacement curve of the compression test, some samples present the yield point before entering the plastic behaviour. In the case of samples that did not clearly show the yield point, the behaviour of the sample during the test was analysed. Therefore, when the curves changed, the intersection point between both lines was chosen as the point before the sample entered its plastic state. Five capsules were tested for each rejuvenator content.

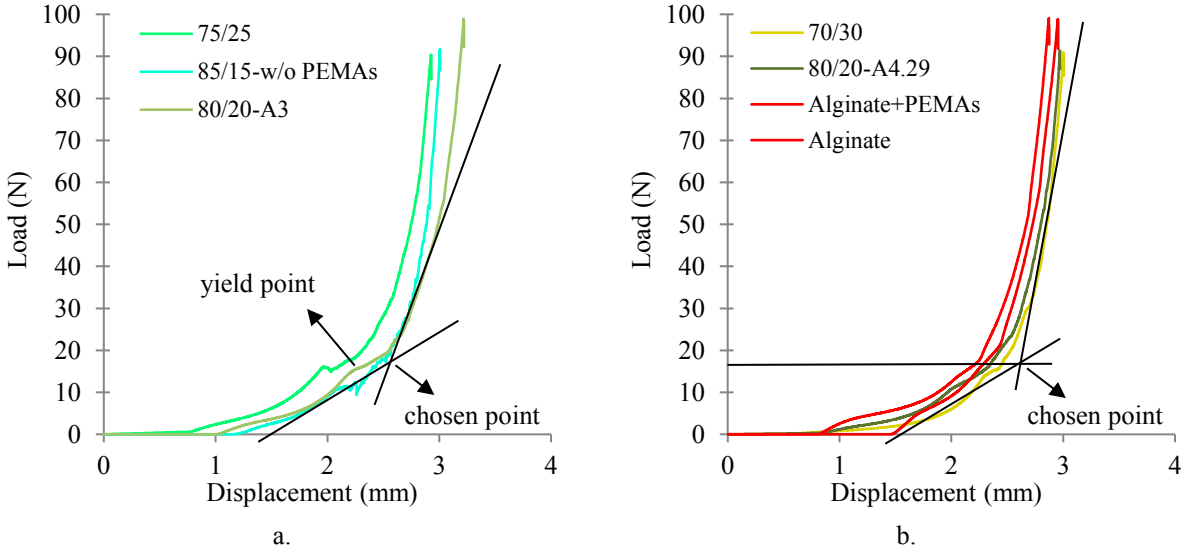


Fig 4. Load-displacement curve from the compressive test: a. sample with the yield point; b. sample without the yield point.

The temperature-dependent mass changes of the calcium alginate capsules were evaluated by Thermogravimetric analysis (TGA). The analysis was performed in a nitrogen (N_2) environment at a flow of 60 ml/min to evaluate the composition and thermal strength. Capsule samples were pre-heated at 30ºC, and then the temperature was increased to 600ºC. Also, the TGA provides to calculate the content of the rejuvenator in ca-alginate capsules. The method is based on the thermogravimetric curve of ca-alginate capsules with and without a rejuvenator. Zhang et al. (2019) developed Equation (1) based on the initial decomposition and complete decomposition of the rejuvenator.

$$x_i = \frac{Z_{1i}+y_2-y_1-Z_{2i}}{1+y_2-y_1} \quad (1)$$

where x_i is the BO content in the capsules (%); y_1 and y_2 are the residual mass percentage of Ca-alginate at the temperature of initial decomposition of the rejuvenator and at the temperature of complete decomposition of the rejuvenator (%); and Z_{1i} and Z_{2i} are the residual mass percentage of capsules at the temperature of initial decomposition of the rejuvenator and the temperature of complete decomposition of the rejuvenator (%).

3. Results and discussions

3.1. Capsule morphology, size and compressive strength

Fig. 5 presents the images of capsules with different compositional ratios. Without a rejuvenator, the calcium alginate capsule has a transparent colour and spherical shape. The Sodium Alginate solution/Rejuvenator solution, poly(ethylene-alt-maleic-anhydride) (PEMA) solution/Sodium Alginate and de-ionized water/Sodium alginate ratios used affect the morphology and properties of calcium alginate capsules. Generally, a higher rejuvenator content results in a more viscous solution that influences the capsule's morphology directly.

Alginate+PEMAs 80/20-A4.29 80/20-A3 70/30

Fig. 5. Images of calcium alginate capsules.

Table 2 summarizes the diameter and compressive strength of capsules fabricated with different rejuvenator content. The results indicate that the diameter of capsules increases with the rejuvenator content. However, the size is influenced by the method used (extrusion drop-wise). If required, capsules can be made smaller by using syringe needles coupled with controlled-pressure pumping systems, as shown by Xu et al. (2019), or by air atomization as used by (Caeiro 2017).

The capsules showed elastic behaviour up to a certain point (yield point) and plastic behaviour above that point during the compressive test, as illustrated in the previous section. The compressive strength value was determined at the intersection point of fitting lines. Table 2 shows the compressive testing results for different ratios. A higher rejuvenator content generally results in higher compressive strength of capsules. Also, PEMA solution addition results in more resistant capsules. And a higher alginate content increased the resistance of the capsule, as shown in the samples with 80/20-A4.29 and 80/20-A3. An increase of 30% of alginate resulted in a resistance increase of 18.75%.

Table 2. Diameter and compressive strength of calcium alginate capsules with different rejuvenator contents.

Samples	Diameter (mm)	Minor axis (mm)	Compressive load (N)
70/30	2.98	2.45	27.8
75/25	2.52	2.45	21.3
85/15 – w/o PEMAs	2.33	2.07	18.1
80/20-A4.29	2.53	2.35	18.2
80/20-A3	2.38	2.35	22.4
Alginate+PEMAs	2.02	1.88	19.7
Alginate	2.52	2.40	19.2

According to the research of García et al. (2010), the mechanical strength of ca-alginate capsules should be higher than 10 N to resist during the mixing and compaction of asphalt mixtures. However, it is noted that the mechanical strength of capsules depends on the fabrication method, loading speed and test temperature. In general, the mechanical strength of produced ca-alginate capsules was well superior to the 10 N limit, which allows expecting the capsules to resist the mixing and compaction processes. In addition, in the literature (Micaelo, Al-Mansoori, and Garcia (2016), Al-Mansoori et al. (2018), Xu et al. (2018a), Zhang et al. (2019), Ruiz-Riancho et al. (2021) and Kargari, Arabani, and Mirabdolazimi (2022) are reported strength values (at 20ºC) in the range of 10-25 N for similar type capsules.

Xu et al. (2019) also found that the optimum A/R ratio of calcium alginate capsules is 30/70 because it demonstrates a higher strength recovery after bending tests, which indicates effective healing due to the release of the rejuvenators from the capsules.

3.2. Composition and thermal strength

The fabrication of hot-mix asphalt mixtures occurs between 150 and 185 ºC, therefore, the weight loss of the thermal degradation of capsules containing rejuvenators should be minimum. Fig. 6 shows the TGA results of the ca-capsules and the constituents. The profiles of weight loss with the temperature increase for the rejuvenator and the polymeric encapsulation structure are very different, which therefore affect the profile of capsules depending on the proportion of these constituents (rejuvenator payload). The BO experiences weight loss between 150 and 450 ºC, at which the remaining weight is null. Differently, the ca-capsules without rejuvenator (with and without PEMA solution) experience mass loss since the test start (25 ºC), and at 450 ºC the remaining mass is approximately 50%. The mass loss of capsules with and without rejuvenator below 100 ºC is related to moisture inside capsules (the polymer is hydrophilic) and then is followed by depolymerization proportional to the temperature increase. The average weight loss at 185 ºC of capsules with rejuvenator was 14.4 %. In the literature, different studies (Al-Mansoori et al. (2018), Zhang et al. (2019) and Ruiz-Riancho et al. (2021) reported mass loss values up to 10% (see Table 3). These authors also reported that, based on different experiments, these capsules survive the mixing and compaction processes, and they break inside the bituminous material due to mechanical loads, releasing the oil to the medium.

In addition, the TGA results were used to determine the composition of capsules because the BO and the polymer structure have significantly different resistance to temperature. To calculate the capsule content, the temperature of initial decomposition and complete decomposition of the BO is 150ºC and 450ºC, respectively. Table 4 reports the composition of capsules. It is concluded that 70/30 capsule had the highest rejuvenator content (53.5%). It can be seen in Fig. 6 and Table 4 that the BO content of the ca-alginate capsules increased with the decrease of the amount of sodium alginate solution on the capsules. Compared to the 80/20-A4.29 and 80/20-A3 capsules, it is shown that with an increase of 30% of sodium alginate, it has a 14.6% increase in BO content on the capsule. PEMAs also influence the BO content on the capsule. If there is no PEMA solution on the capsule, the BO content is higher.

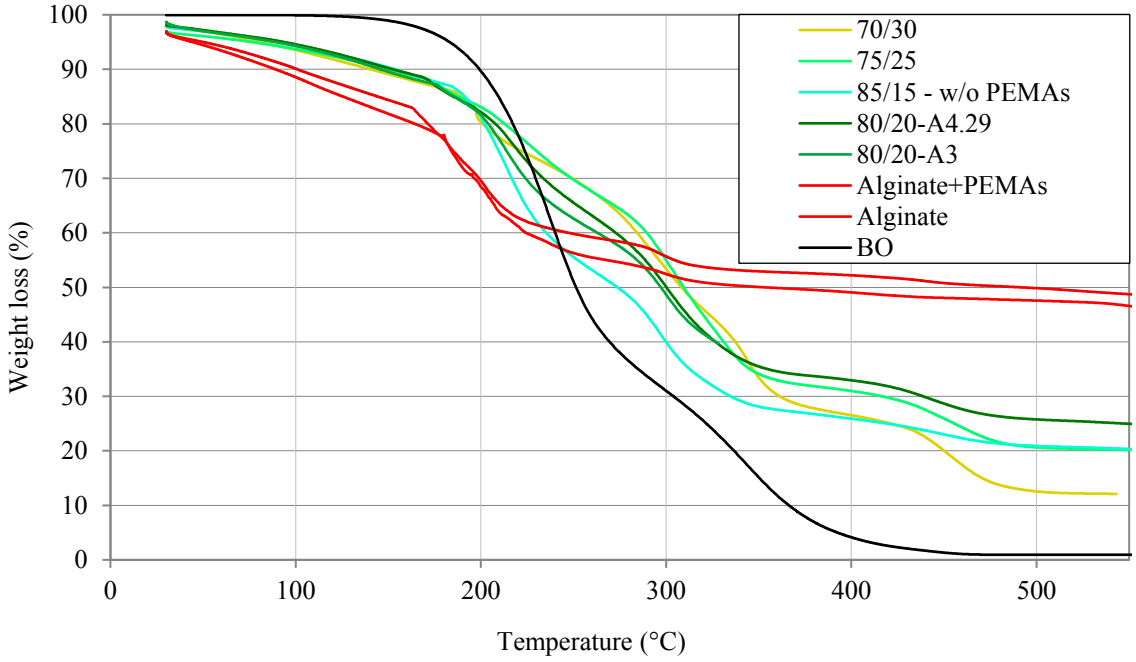


Fig. 6. TGA results of the ca-capsules.

Table 3. Thermal stability of Ca-alginate capsules reported in the literature.

Mass loss	Temperature	Reference
4%	200ºC	Micaelo, Al-Mansoori, and Garcia (2016)
<5%	200ºC	Al-Mansoori et al. (2018)
3.8%	160ºC	Xu et al. (2018a)
10%	200ºC	Zhang et al. (2019)
<5.5%	160ºC	Ruiz-Riancho et al. (2021)
10%	200ºC	Kargari, Arabani, and Mirabdolazimi (2022)

Table 4. Composition of the capsules.

Samples	ca-capsule (%)	BO (%)	Weight total capsule (mg)	BO (mg)
70/30	46.5	53.5	11.2	6.0
75/25	54.2	45.8	10.8	5.0
85/15 – w/o PEMAs	49.3	50.7	7.5	3.8
80/20-A4.29	57.9	42.1	8.3	3.5
80/20-A3	59.6	40.4	7.6	3.1
Alginate+PEMAs	100	-	7.6	-
Alginate	100	-	13.0	-

4. Conclusions

Calcium alginate capsules containing bio-oil were prepared by ionotropic gelation of alginate solutions. Different capsules were prepared by changing the Sodium Alginate solution/Rejuvenator solution, poly(ethylene-alt-maleic-anhydride) (PEMA) solution/Sodium Alginate and de-ionized water/Sodium alginate ratios. The following conclusions were drawn from the study:

- The ratios used in the capsule production process enable better morphology and performance of calcium alginate capsules. Overall, a higher rejuvenator content results in a larger diameter and a higher compressive strength.
- PEMA addition results in more resistant capsules, small capsules, and consequently, a less weight capsule.
- The optimum A/R ratio with Bio-Oil is 70/30. The 70/30 showed a higher resistance and contained more rejuvenator.

Acknowledgements

The authors gratefully acknowledge Fundação para a Ciência e a Tecnologia (FCT) for the financial support (PhD grant reference SFRH/BD/144683/2019).

References

Al-Mansoori, T., J. Norambuena-Contreras, and A. Garcia. 2018. "Effect of Capsule Addition and Healing Temperature on the Self-Healing Potential of Asphalt Mixtures." *Materials and Structures/Materiaux et Constructions* 51 (2): 1–12. https://doi.org/10.1617/s11527-018-1172-5.

Al-Mansoori, T., J. Norambuena-Contreras, R. Micaelo, and A. Garcia. 2018. "Self-Healing of Asphalt Mastic by the Action of Polymeric Capsules Containing Rejuvenators." *Construction and Building Materials* 161: 330–39. https://doi.org/10.1016/j.conbuildmat.2017.11.125.

Caeiro, Andreia Simões. 2017. "Fabrico e Caracterização de Microcápsulas Poliméricas Para Misturas Betuminosas." Master's thesis. NOVA School of Science and Technology.

García, A., E. Schlangen, M. Van De Ven, and G. Sierra-Beltrán. 2010. "Preparation of Capsules Containing Rejuvenators for Their Use in Asphalt Concrete." *Fuel* 184: 603–11. https://doi.org/10.1016/j.fuel.2010.09.033.

Kargari, A., M. Arabani and S. Mirabdolazimi. 2022. "Effect of Palm Oil Capsules on the Self-Healing Properties of Aged and Unaged Asphalt Mixtures Gained by Resting Period and Microwave Heating." *Construction and Building Materials* 316 (February 2021): 125901. https://doi.org/10.1016/j.conbuildmat.2021.125901.

Micaelo, R., T. Al-Mansoori, and A. Garcia. 2016. "Study of the Mechanical Properties and Self-Healing Ability of Asphalt Mixture Containing Calcium-Alginate Capsules." *Construction and Building Materials* 123: 734–44. https://doi.org/10.1016/j.conbuildmat.2016.07.095.

Ruiz-Riancho, N., A. Garcia, D. Grossegger, T. Saadoon, and R. Hudson-Griffiths. 2021. "Properties of Ca-Alginate Capsules to Maximise Asphalt Self-Healing Properties." *Construction and Building Materials* 284: 122728. https://doi.org/10.1016/j.conbuildmat.2021.122728.

Xu, S., A. Tabaković, X. Liu, and E. Schlangen. 2018a. "Calcium Alginate Capsules Encapsulating Rejuvenator as Healing System for Asphalt Mastic." *Construction and Building Materials* 169: 379–87. https://doi.org/10.1016/j.conbuildmat.2018.01.046.

Xu, S., A. García, J. Su, Q. Liu, A. Tabaković, and E. Schlangen. 2018b. "Self-Healing Asphalt Review: From Idea to Practice." *Advanced Materials Interfaces* 5 (17): 1–21. https://doi.org/10.1002/admi.201800536.

Xu, S., E. Schlangen, A. Tabaković, X. Liu, and D. Palin. 2019. "Optimization of the Calcium Alginate Capsules for Self-Healing Asphalt." *Applied Sciences* 9 (3): 468. https://doi.org/10.3390/app9030468.

Zhang, L., Q. Liu, H. Li, J. Norambuena-Contreras, S. Wu, S. Bao, and B. Shu. 2019. "Synthesis and Characterization of Multi-Cavity Ca-Alginate Capsules Used for Self-Healing in Asphalt Mixtures." *Construction and Building Materials* 211: 298–307. https://doi.org/10.1016/j.conbuildmat.2019.03.224.