# A Novel Self-Healing Asphalt by the Action of Polymeric Capsules

Jose Norambuena-Contreras[1,2], Erkut Yalcin[3,4], Samuel Leworthy[5], Alvaro Garcia[6]

（[1] LabMAT, Department of Civil and Environmental Engineering, University of Bío-Bío, Concepción, Chile, jnorambuena@ubiobio.cl）

（[2] Nottingham Transportation Engineering Centre, School of Civil Engineering, University of Nottingham, University Park, Nottingham, UK, ezajn4@exmail.nottingham.ac.uk）

（[3] Firat University, Faculty of Engineering, Department of Civil Engineering, Elazig, Turkey, erkutyalcin@firat.edu.tr）

（[4] Nottingham Transportation Engineering Centre, School of Civil Engineering, University of Nottingham, University Park, Nottingham, UK, Erkut.Yalcin@nottingham.ac.uk）

（[5] Nottingham Transportation Engineering Centre, School of Civil Engineering, University of Nottingham, University Park, Nottingham, UK, Samuel.Leworthy@nottingham.ac.uk）

（[6] Nottingham Transportation Engineering Centre, School of Civil Engineering, University of Nottingham, University Park, Nottingham, UK, Alvaro.Garcia@nottingham.ac.uk）

## ABSTRACT

This paper presents a novel self-healing asphalt mixture by the action of polymeric capsules which will be used by Highways England for the construction of the first self-healing road in the UK. With this purpose, calcium-alginate capsules, with encapsulated sunflower oil have been manufactured and added into the asphalt mixture in three different percentages: 0.5%, 0.75% and 1.00% by total mass of mixture. Furthermore, physical, thermal and mechanical properties of the polymeric capsules have been evaluated. Additionally, self-healing properties of asphalt with, and without, capsules have been assessed at different healing times. The distribution and the integrity of the capsules inside the asphalt mixture were evaluated using X-ray computed tomography. The main results showed that the capsules can resist the mixing and compaction processes without significantly reducing their physical, thermal and mechanical properties. Additionally, capsules showed a good spatial distribution inside the mixture. Finally, it was found that capsules increase the self-healing properties of asphalt when compared to asphalt without capsules.

**Keywords**: Crack-healing; Capsules; Temperature effect; CT scans; Asphalt performance.

## 1. INTRODUCTION

Asphalt mixture is the most used material to build road pavements worldwide. The capacity of road pavements to carry loads depends on the bond between aggregate particles provided by the bitumen. Nevertheless, this bond degrades over time due the most significant issue that bitumen faces, which is the damage from ageing [1]. Ageing results from oxidation and loss of the volatiles from bitumen composition, which causes stiffness and an increase in viscosity. This leads to the appearance of microcracks which evolve to form macrocracks and the detachment or ravelling of aggregates [2]. One recently used technique to resolve the problem of the maintenance of ageing pavement is the use of encapsulated rejuvenators to restore the original properties of the bitumen via self-healing processes [[3]-[6]]. This technique is supported by the fact that bitumen is a self-healing material with the ability to close microcracks by itself [4]. The principle behind this approach is that these capsules containing rejuvenators will remain inactive in the asphalt road for several years until external damage happens to the asphalt pavement [5]. Then, cracks will break the capsule shells at the appropriate time, leading to the release of the rejuvenator into the asphalt, which will diffuse and reduce the bitumen viscosity to allow it to easily flow into the open cracks [6]. With this objective, different methods have been used to manufacture microcapsules, or capsules with encapsulated rejuvenators, for asphalt self-healing. Su et al. [3] prepared microcapsules containing rejuvenator droplets by in-situ polymerisation of urea-formaldehyde making a methanol-melamine-formaldehyde (MMF) prepolymer as a shell. Furthermore, Garcia et al. [6] prepared capsules of a larger size by saturating porous sand with sunflower oil as rejuvenator material, and protected by a hard shell of cement and epoxy resin. Details of another type of polymeric capsule were published by Al-Mansoori et al. [5] and Micaelo et al. [7]. These capsules were made by the ionotropic gelation of sodium alginate in the presence of calcium chloride solution. In these capsules, the encapsulated material was also sunflower oil and their size was a few millimetres. Broadly, these studies demonstrated that the capsules are resistant to asphalt fabrication and release the rejuvenators only when broken, but they did not show the effect on the asphalt self-healing properties for capsule content greater than 0.5% by total weight of mixture.

In this paper, novel polymeric capsules for asphalt self-healing have been designed and tested in asphalt mixtures. These capsules have a greater amount of calcium-alginate structure where the oil is stored, which also improves their mechanical behaviour. Consequently, manufacturing process of the polymeric capsules and their physical, thermal and mechanical characteristics are firstly presented in this paper. Then, the effect of capsule content on the crack-healing properties of asphalt mixtures was quantified at different healing times by using a novel mechanical test. Finally, the spatial distribution and the integrity of the capsules inside the asphalt mixture were evaluated by using X-ray computed tomography (CT scan) tests.

## 2. MATERIALS AND METHODS

### 2.1 Asphalt mixture and polymeric capsules

A standard, dense asphalt mixture AC 20 base (according to EN 13108-1) and polymeric capsules were used in this research. The asphalt mixture consists of virgin bitumen 40/60 pen with a density of 1.030 g/cm$^3$ and a softening point of 49.8ºC, and graded Tunstead limestone aggregate with a density of 2.700 g/cm$^3$. The aggregates' gradation was the following: passing percentages at 20, 10, 2 and 0.063 mm size were 100, 30.3, 2.2 and 1.8, respectively. Additional design properties of the mixture were: binder content of 4.5%$_M$, bulk density of 2.384 g/cm$^3$, air voids of 4.5%, voids in mineral aggregates of 14.9% and voids filled with bitumen of 69.8%. Furthermore, capsules were made of a calcium-alginate polymer that encapsulated the healing agent, which was commercial sunflower oil, with a smoke point of 227ºC and flash point of 315ºC [5]. This type of oil was selected because of the low cost and the fact that extra health and safety procedures are not required for handling in the laboratory [8]. The polymer structure of the capsules was made of sodium alginate ($C_6H_7O_6Na$), which is an anionic polysaccharide widely distributed in the cell walls of brown algae, and a calcium source, provided by Sigma-Aldrich as anhydrous, granular pellets of calcium chloride ($CaCl_2$), of 7 mm diameter, and 93% purity.

### 2.2 Encapsulation procedure

Calcium-alginate capsules of average size 2.5 mm (Figure 1(a)) were prepared at 20ºC by ionotropic gelation of alginate in the presence of calcium [[5],[7]]. To prepare the capsules, first, water and oil in a 0.1 ratio were mixed and stirred to produce a stable emulsion. Then, 55 g sodium alginate were added to a glass container and stirred at 400 rpm for 10 minutes, until complete solution. The amount of sodium alginate used to produce the capsules was defined to obtain an internal structure of calcium-alginate strong enough to hold the oil (Figure 1(b)) and hence with a strength higher than the capsules developed by Al-Mansoori et al. [5] and Micaelo et al. [7]. Simultaneously, a 2% calcium chloride solution was prepared. Capsules were formed by letting the oil-in-water emulsion drop into the calcium chloride solution from a pressure-equalising dropping funnel with 3 mm socket size. During the capsule formation process, the calcium-chloride solution was gently agitated using a magnetic stirrer at 60 rpm. The manufacturing process of the capsules took approximately 2-3 hours. After this time, the capsules were decanted and washed with deionised water and then dried in an electric dryer at 40ºC for 36 hours. Finally, the capsules were stored in a freezer at -18ºC to avoid the release and oxidation of the oil at room temperature.

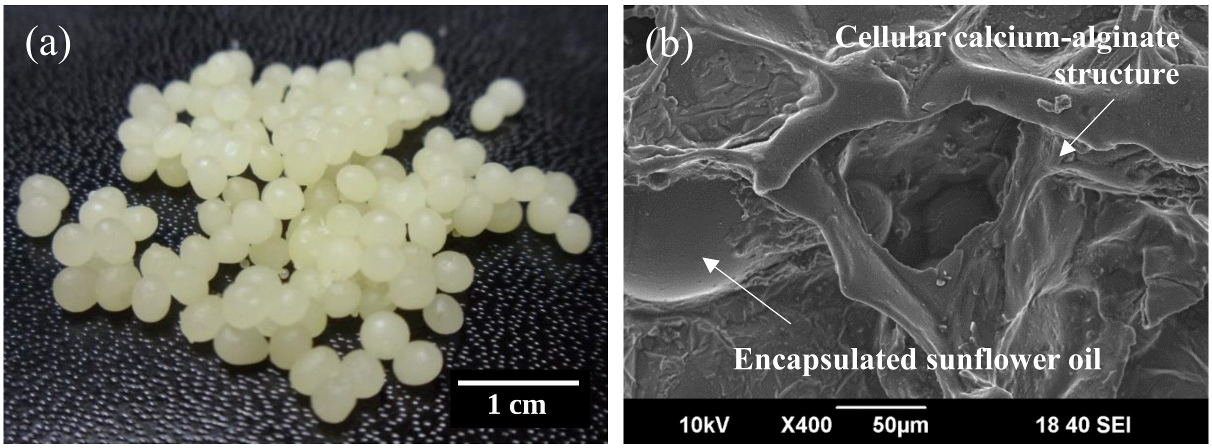


**FIGURE 1 (a) Calcium-alginate capsules, and (b) SEM image of capsule internal structure.**

### 2.3 Manufacturing of asphalt mixture samples

Asphalt mixture beams with, and without, capsules were manufactured. In the asphalt mixture with capsules, three different capsule contents, as a percentage of the total mixture, were used: 0.5%, 0.75% and 1.0%. These contents provided an oil-to-bitumen content by mass in bitumen of approximately 6.97%, 10.46% and 13.95%, respectively. The asphalt mixture was produced in the laboratory in batches of approximately 14 kg, using a lab mixer equipped with a helical horizontal mixing shaft. The aggregates and bitumen were pre-heated at 160ºC for 12 h and 4 h, respectively, while the capsules were left to defrost for two hours at 20ºC prior to the mixing process. The materials were mixed for 2 minutes at 125 rpm at 160ºC, ensuring an adequate dispersion. Then, capsules were added to the drum and mixed for 20 seconds to obtain their uniform dispersion. Then, the mixture was poured into the moulds and compacted to the design for air voids (see section 2.1) by using a roller slab compactor to produce an asphalt slab with dimensions of 306 × 306 × 60 mm. Each slab was cut into six identical asphalt beam samples of 150 × 100 × 60 mm, see Figure 2. Likewise, to facilitate the creation of a single crack surface during crack-healing tests, a transverse notch of 5 × 5 mm was carved at the mid-point, on the bottom surface of the beams. In total, 40 asphalt mixture beams were manufactured in this study, to evaluate the effect of capsule content on asphalt self-healing properties.

### 2.4 Physical, thermal and mechanical properties of capsules

The bulk density, compressive strength and thermal stability of the dry capsules were measured at 20ºC, 80ºC, 160ºC and 180ºC. In all cases, the capsules were pre-conditioned for 4 h at the test temperature. The density was measured using a helium pycnometer. The sample weight of capsules was about 5 g. The mechanical strength was measured by uniaxial compression testing of 10 individual capsules. For that, each capsule was loaded until failure at a loading rate of 0.2 mm/min. In addition, the temperature influence on the mass loss of capsules was evaluated by thermogravimetric analysis (TGA). The TGA tests were performed using nitrogen atmosphere and a heating rate of 10ºC/min. Finally, knowing the density of the capsules and its components, the composition of capsules was calculated based on the rule of mixtures in composite materials [7].

### 2.5 Crack-healing tests and quantification of oil release from capsules

The effect of capsule content on the self-healing properties of asphalt mixtures was measured by using a novel crack-healing methodology published by Al-Mansoori et al. [5]. This method allows the simulation of the capsules' damage resulting from traffic loads. Asphalt self-healing was quantified from the flexural strength recovery of cracked asphalt beams that was measured by means of three-point bending (3PB) tests, after a specified healing time. The asphalt mixture beam used is shown in Figure 2(a). The crack-healing test was carried out according to the following steps, see the schematic diagram in Figure 2(b):

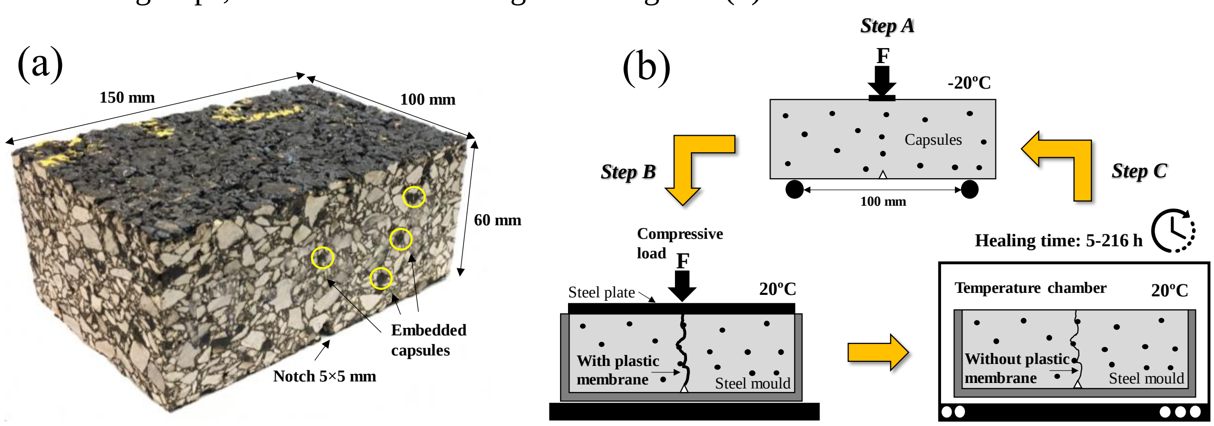


**FIGURE 2 (a) Asphalt beam used, and (b) schematic diagram of the crack-healing test.**

- Step A. Asphalt mixture beams with, and without, capsules, were conditioned at -20ºC for 4 h and 3PB tests were carried out at a loading rate of 2 mm/min until the beams were broken in two pieces;
- Step B. After the 3PB test, a plastic membrane, adaptable to the faces of the crack, was placed between the two broken pieces of the beam. Then, the two pieces were put back together and placed in a steel mould. To break the embedded capsules, a strain controlled compressive load was applied at a rate of 2 mm/min on the top surface of the beam, at 20ºC, until the vertical deformation reached 5 mm. Later, the plastic sheet was removed, and finally the two pieces of the beam were put back together into the steel mould;
- Step C. To start the healing process, the asphalt beams were conditioned in the moulds at 20ºC for ten different healing times ranging from 5 to 216 h. Once the defined conditioning time was reached, the beams were removed from the steel mould, frozen at -20ºC for 4 h, and broken again in two pieces under the 3PB, thus completing a damage-healing cycle.

The healing level, $H_L$, reached for each cracked asphalt mixture beam after a healing time was defined as the quotient between the maximum load of the beam initially tested, $F_0$, and the maximum load measured in the same beam after the healing process, $F_t$. Furthermore, the amount of oil released from the capsules into the mixture after the external compression load was analysed by means of Fourier Transform Infrared Spectroscopy (FTIR) and following the methodology described in Al-Mansoori et al. [5] and Micaelo et al. [7].

## 3. RESULTS AND DISCUSSION

### 3.1 Capsule composition and temperature effect on the capsule properties

The encapsulation procedure presented in this study allowed the manufacturing of polymeric capsules composed of a 75% vol. of sunflower oil and a 25% vol. of calcium-alginate polymer. Additionally, Table 1 presents the average results of the physical, mechanical and thermal properties of the capsules measured at four different temperatures. It was observed that the density of the capsules decreased with the temperature increase, from 1.116 g/cm$^3$ to 0.776 g/cm$^3$ for temperatures of 20ºC and 180ºC, respectively. This density reduction was due to the loss of mass experienced by the capsules when exposed to temperature, as evidenced in TGA results. According to Al-Mansoori et al. [5], the mass loss recorded by the calcium-alginate capsules was attributed mostly to the effect of degradation of polymer structure and water evaporation, and less to the evaporation of the healing agent by oxidation phenomena.

**TABLE 1 Average capsule properties at different temperatures.**

| Property | unit | Temperature value | | | |
|---|---|---|---|---|---|
| | | @20ºC | @80ºC | @160ºC | @180ºC |
| Bulk density | g/cm$^3$ | 1.116 | 1.097 | 1.021 | 0.766 |
| Compressive strength | N | 45.5 | 35.4 | 19.4 | 5.5 |
| Mass loss | % | 0.0 | 3.0 | 4.0 | 5.0 |

Moreover, Table 1 shows the results of compressive strength of the capsules. The stress-strain curves of the compressive tests showed, in general, a ductile behaviour, and the peak load was reached at deformation levels between 0.6 mm and 0.1 mm at 20ºC and 180ºC, respectively. In this way, the capsules reduced their strength and deformation with the increase of temperature. This is because exposure to temperature degrades the polymer capsules making them more brittle, and hence less flexible, to mechanical loads. Previous research [6] had shown that the minimum compressive strength of this type of capsule required to resist the mixing and compaction process was 10 N. Consequently, the measured compressive strength at 20ºC, 45.5 N, and at 160ºC, 19.4 N, showed that the capsules presented in this study can survive the mixing and compaction process.

Additionally, the results of X-ray computed tomography tests (see Figure 3(a)) developed on cylindrical samples (3.5 cm diameter and 60 mm height) of asphalt mixture with capsules, showed that the capsules resist the mixture manufacturing and mainly keep their oil content until they break due to the effect of loading. Furthermore, capsules showed a good spatial distribution inside the mixture, without the presence of capsule clusters due to a poor mixing, see Figure 3(a).

### 3.2 Influence of capsule contents on the crack-healing properties of asphalt mixtures

Figure 3(b) presents self-healing results of asphalt beams containing different percentages of capsules 0.5%, 0.75% and 1.00% by total weight of the mixture. Figure 3(b) shows the healing levels reached for all the asphalt beams with, and without, capsules (WO/C), at different healing times ranging from 5 to 216 h. It can be observed that the healing levels in the asphalt beams with capsules were higher than in beams without capsules, and that the healing level of asphalt mixtures with, and without, capsules increased with the healing time until a maximum value, and then remained constant. Based on the results, maximum healing level value was reached, in general, at 96 h and remained mostly constant until 216 h, see box in Figure 3(b).

The average maximum healing levels were: 49.04%, 54.32% and 54.86% for asphalt mixtures with capsule content of 0.5%, 0.75% and 1.00%, respectively. Likewise, asphalt mixtures without capsules presented an average maximum healing level of 20.44%. These results proved that higher capsule contents in the mixture resulted in higher healing levels for all the healing times studied. This is because higher capsule contents increase the probability of breaking more capsules as a result of external damage, which increases the potential released oil in the mixture. In this study, the percentage of broken capsules measured by FTIR tests after the external compression load were: 35.45%, 45.02% and 60.93% for capsule content of 0.5%, 0.75% and 1.00%, respectively.

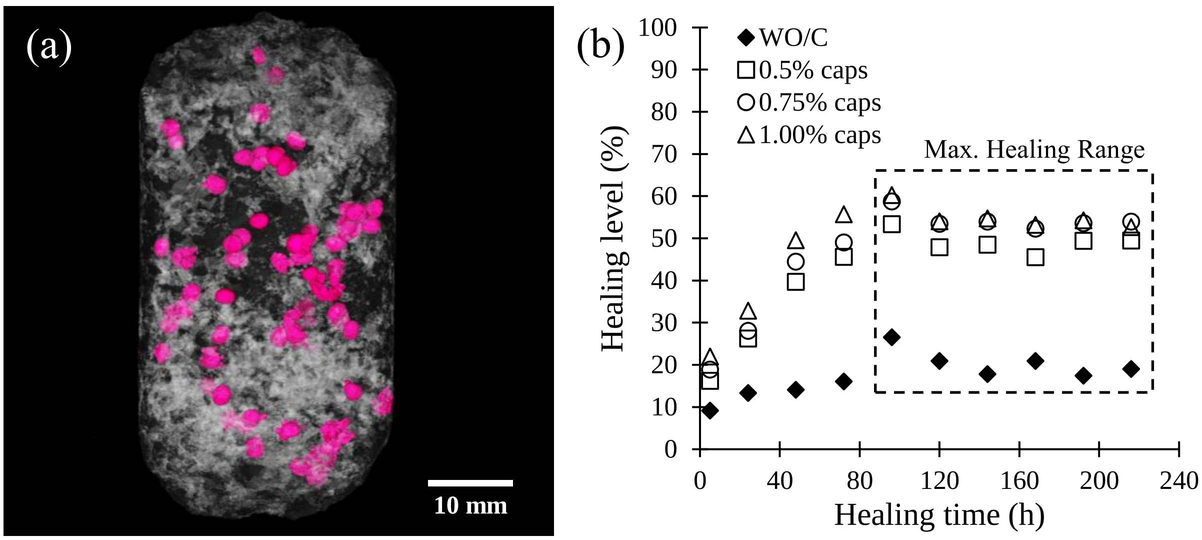


**FIGURE 3 (a) CT Scan 3D image of the capsule spatial distribution inside a cylindrical sample of mixture with 0.5% capsule content, (b) healing level depending on healing time.**

Furthermore, Figure 3(b) also shows that capsule contents higher than 0.5% did not present a significant increase in the maximum healing levels, see results of 0.75 and 1.00% in the maximum healing range. So, although higher contents of capsules increase the healing level of the mixtures, a rejuvenating excess, i.e., oil-to-bitumen content greater than 7.0% by mass, can be detrimental to the properties of the mixture, affecting the rheological properties of bitumen [8]. Therefore, based on the results of this study, 0.5% of capsules was considered as the optimal percentage for asphalt self-healing without affecting the rheological properties of asphalt mixture.

## 4. CONCLUSIONS

- The encapsulation procedure presented in this paper allowed the manufacturing of polymeric capsules with 75% vol. of healing agents, higher than other capsules for asphalt self-healing published in the literature.
- Density and compressive strength of the capsules decreased with temperature, not affecting their mechanical resistance to mixing, and compaction processes during the asphalt mixture manufacturing.

- Thermal stability measurements (TGA), in the temperature range used for asphalt mixture manufacturing, proved that the capsules suffered only a minor mass loss, which was caused by the degradation of calcium-alginate polymer and water evaporation.
- Capsules resisted the mixture manufacturing and, consequently, they can keep their oil content until they break inside the asphalt mixture beams under the effect of loading. Additionally, capsules showed a good spatial distribution inside the mixture.
- Healing levels in the asphalt mixtures with capsules were greater than in mixtures without capsules, and healing levels of asphalt samples with, and without, capsules increased with the healing time until a maximum value where the healing levels remained constant.
- Higher capsule contents in the mixture resulted in higher healing levels for all the healing times studied. Finally, a capsule content of 0.5% by total mass of asphalt mixture was considered as the optimal percentage for asphalt self-healing without affecting the properties of the mixture.

## 5. ACKNOWLEDGMENTS

First author would like to acknowledge the Government of Chile, since this work was partially funded by the CONICYT/BECAS CHILE 74170030. Second author wishes to thank the financial support given by the Scientific and Technological Research Council of Turkey (TUBITAK) (application no. 1059B141600780) for the research scholarship granted. Finally, the authors would like to thank Highways England UK for the funding given, through the Research Project ref. 558065, entitled: Self-healing asphalt using embedded capsules.

## 6. REFERENCES

[1] Airey, G. State of the art report on ageing test methods for bituminous pavement materials. International Journal of Pavement Engineering, 4(3), pp. 165-176. 2003.

[2] Lu, X., and Isacsson U. Chemical and rheological evaluation of ageing properties of SBS polymer modified bitumens. Fuel, 77(9), pp. 961-972. 1998.

[3] Su, J.-F. and E. Schlangen E. Synthesis and physicochemical properties of high compact microcapsules containing rejuvenator applied in asphalt. Chemical Engineering Journal, 198, pp. 289-300. 2012.

[4] Garcia, A., Schlangen., E., and Van de Ven, M. Two ways of closing cracks on asphalt concrete pavements: microcapsules and induction heating. Key Engineering Materials, 417-418, pp. 573-576. 2010.

[5] Al-Mansoori, T., Micaelo, R., Artamendi, I., Norambuena-Contreras, J., and Garcia, A. Microcapsules for self-healing of asphalt mixture without compromising mechanical performance. Construction and Building Materials, 155, pp. 1091-1100. 2017.

[6] García, A., Schlangen, E., van de Ven, M., and Sierra-Beltran, G. Preparation of capsules containing rejuvenators for their use in asphalt concrete. Journal of hazardous materials, 184(1), pp. 603-611. 2010.

[7] Micaelo, R., Al-Mansoori, T., and Garcia, A. Study of the mechanical properties and self-healing ability of asphalt mixture containing calcium-alginate capsules. Construction and Building Materials, 123, pp. 734-744. 2016.

[8] Zargar, M., Ahmadinia, E., Asli, H., and Karim, M.R. Investigation of the possibility of using waste cooking oil as a rejuvenating agent for aged bitumen. Journal of Hazardous Materials, 233, pp. 254-258. 2012.