Encapsulated rejuvenators: Increasing the lifetime of asphalt pavements

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ABSTRACT: After some years of use, the stiffness of asphalt concrete increases, its relaxation capacity decreases, the binder becomes more brittle, micro-cracks develop in the binder and cracking of the interface between aggregates and binder occurs. This mainly happens as a result of oxidation. There are numerous methods being employed for asphalt pavement preservation, including rejuvenator emulsions, fog seals, and several different thin overlay technologies. Only the first method, rejuvenators, partially restores the pavement original properties. However, for a rejuvenator to be successful, it must penetrate the pavement surface. Besides, application of a rejuvenator will also reduce the skid resistance of the pavement, which may be significant for runways or other areas where high aircraft speeds are likely to occur. To solve these problems, in this paper it is proposed to encapsulate the rejuvenators and mix them in the asphalt concrete. When the binder oxidizes, due to higher stiffness of the binder the traffic load will result in higher stresses on the shell of the capsule. When the stress reaches a certain threshold, the particles break and the rejuvenator is released. For that, capsules comprising a hard core made of a porous stone surrounded by a hard, impermeable shell have been developed. In this paper we will show how to make these capsules and some preliminary results of the research.

KEY WORDS: Capsules, asphalt, rejuvenation, maltenes, ageing.

1 INTRODUCCTION

Asphalt concrete is one of the most common types of pavement surface materials used in the world. It is a porous material made at very high temperatures (~180 ^{o}C) consisting of a mixture of asphalt binder (bitumen), aggregate particles and air voids. After some years of use, the stiffness of asphalt concrete increases while its relaxation capacity decreases, the binder becomes more brittle causing development of micro-cracks and ultimately cracking of the interface between aggregates and binder occurs (Branthaver et al., 1993). This mainly happens as a result of oxidation, which is the chemical reaction of the hydrocarbon compounds of bitumen with oxygen (Hunter, 1997). This process already begins during the hot-mix process and continues throughout the lifetime of the pavement. Asphalt binders are usually simplified in two subdivisions: a solid one called asphaltenes and a liquid one called maltenes. Maltenes can be further divided into polar aromatics (PAs), naphthalene aromatics (NAs) and saturates (paraffins, PAs) (Corbett, 1969). Liu et al., 2002, state that during the oxidative aging of the asphalt binder, PAs transform to asphaltenes, and NAs convert into PAs, which subsequently oxidize and become asphaltenes as well. During this process, the asphaltenes content increases, while PAs and NAs decrease: the solid part increases and the liquid part decreases, resulting in an increase of the rigidity of the pavement. The viscosity of the maltenes, however, does not change significantly (Karlsson et al., 2003).

For a rejuvenator to be successful, it must penetrate the pavement surface. However, application of a rejuvenator may reduce the skid resistance of the pavement, which can be significant for instance runways or other areas where high aircraft speeds are likely to occur. In Chiu et al., 2007, three rejuvenators, one cutback asphalt and two emulsions (one tar based and the other asphalt based), were applied on a 12-year-old parking lot pavement to assess their effectiveness. It was found that none of them penetrated more than 2 cm into the pavement, in spite of the void content being 9.7 %. Furthermore, this paper shows how the application of the rejuvenators causes a high reduction in the surface friction of pavements with high macro-texture depth. Also, when applying these materials, the road must be closed for some time after their application. Finally, a not unimportant aspect of these rejuvenators is that they may be dangerous for the environment.

To solve these problems, this research proposes to encapsulate the rejuvenators in the asphalt concrete. This encapsulation process enables mixing incompatible compounds in a wide range of applications from fragrance and cosmetics to advanced coating (Vebable et al., 1983). Arshady, 1999, defines the microcapsules as "particles, spherical or irregular, in the size range of about 50 nm to 2000 μm or larger, and composed of an excipient polymer matrix (shell or wall) and an incipient active polymer (core substance)". Encapsulation of active substances as epoxy resins (Kamphaus et al., 2008), hardeners (Cosco et al., 2007) or solvents (Caruso et al., 2008) is of particular interest for self-healing materials (Little et al., 2007), coatings (Cho et al., 2009) and many other industrial applications such as capsular adhesives 0 and protection of catalysis (Rule et al., 2005). The capsules developed for this paper can break due to constant fatigue loads as well as increasing stiffness of the binder during oxidization: traffic loads will result in higher stresses on the shell of the capsule due to the increased stiffness. When the stress finally reaches a certain threshold value, the capsules break and the rejuvenator will be released. Some conditions these capsules must have are that the shell material should be strong enough to resist the mixing process, the high temperatures, and all the years in the road until the capsule is necessary. The objective of this paper is to show how to make these capsules filled with rejuvenators and explain their main characteristics.

2 EXPERIMENTAL METHOD

4.1 Capsule materials

Core materials used in the encapsulation includes porous sand and the rejuvenator. The porous sand is made of calcium silicate granules forming a microporous structure (Catsan hygienic litter, Effem company, Verden) with a particle size between 1 and 1.7 mm. This material has thousands of micropores specially designed to absorb liquid and is therefore from here on referred to as "porous sand". It has a density of 2.08 g/cm^3 and 87 % by weight of water absorption. This size of porous sand was chosen with the idea of substituting part of this fraction of aggregates in asphalt concrete with the capsules, to maintain the original specific surface of the aggregates; besides, 2 mm is the maximum size of the sand within the ISO 14688. The material used as a rejuvenator is a very dense, aromatic oil obtained from Petroplus Refining Antwerp (800 DLA).

The materials forming the capsule wall are particles of cement Type I 52.5R bonded by a liquid epoxy resin (Struers Epofix resin, bisphenol A-epichlorhydrin and hardener, triethylenetetramine, in a 10.7 wt.-% proportion). The average particle diameter of cement Type I typically is about 10 to 20 µm. Cement was chosen because of its fineness, but it could have been any other type of crushed filler (cement was chosen because it is a material relatively easy to find in the laboratory). It is important to avoid the cement hydration: if hydration takes place after the encapsulation, the capsules obtained will be porous because of the volumetric changes of this material. The densities for all the materials comprising the capsules are showed in Table 1.

	Rejuvenator	Porous sand	Cement	Epoxy
Density (g/cm^3)	0.922	2.315	3.141	1.127
Mass (%)	9.4	11.7	64.2	14.7
Volume (%)	20.9	13.1	24.9	13.0

Table 1: Composition of the capsules (by mass and by volume).

4.1 Size distributions

To investigate the size of the capsules, more than 100 capsules have been checked by taking photographs under the optical microscope and by measuring their size using ImageJ analysis software. This results in the distributions shown in Figure 1.

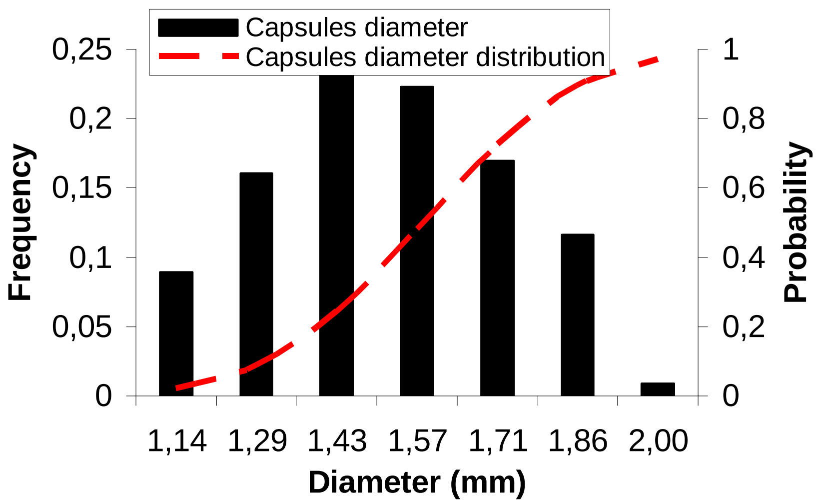

Figure 1: Capsule sizes distribution.

4.1 Encapsulation procedure

Capsules containing rejuvenators have been prepared by a new method developed by the authors (Figure 2). First, the porous sand was sieved to obtain a fraction between 1 and 1.7 mm. These sizes were chosen as appropriate ones to replace this aggregate fraction in asphalt concrete. The sand was dried in a stove at 70 °C during 24 h to remove as much moisture as possible.

To make the core of the capsules the porous sand was put in a tall container. Then, the rejuvenator was added until the sand was covered up to a level of twice the height of the sand and everything was heated during 1 hour at 105 °C to reduce the viscosity of the oil. After this, the recipient with the sand and the rejuvenator was brought into a vacuum chamber during at least 30 minutes to remove the air and force the oil to penetrate into the sand grain voids. The heating and the vacuum process has been repeated twice to remove as much air as possible. Finally, the excess rejuvenator was removed and the porous sand, now with rejuvenator inside the grains, was shaked by hand to homogenize it.

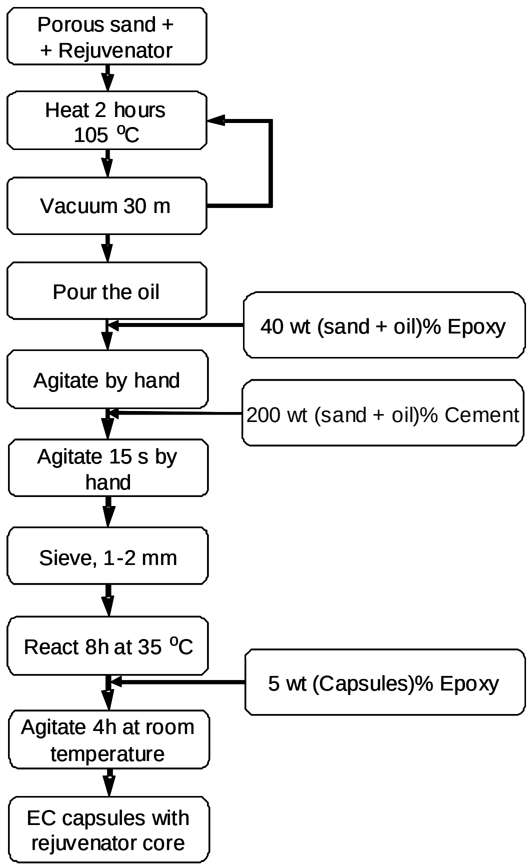

Figure 2: Capsules recipe

To produce the shell, the epoxy and the sand with rejuvenators inside were mixed by hand in a weight ratio 1:2.5 until all soil grains were uniformly covered by a layer of epoxy. In another container a number of steel balls with a diameter of 2 cm in a volumetric ratio of 1:54 to the total volume of the container have been added to 4 parts of cement CEM I 52.5 R (by weight) and 1 part of sand with rejuvenator and the epoxy. Then, the container was energically moved in circles for no more than 15 s (this time is appropriate for the numbers of balls added. Fewer balls would mean longer shaking times. More balls would mean shorter shaking times). Due to this movement, the cement binds to the epoxy surrounding the soil particles forming a shell of epoxy-cement around the porous sand particles. From here on, these particles will be referred to as capsules. To finish the process, the capsules have been sieved between 1 and 2 mm to separate them from the excess cement. It is important to maintain these rates. If for example, the amount of cement is more than mentioned above, the capsules would be drained of the rejuvenator (cement particles tend to be covered by epoxy until a certain thickness, if there is an excess of cement, it absorbs all the epoxy and the oil inside the porous sand). However, if it there is less cement the shell would not form. Furthermore, if more epoxy than indicated is added, clusters of capsules will form; while if less epoxy is added, the shell would be weak and the capsules would loose rejuvenator. Finally, if more steel balls are added, the shell of the capsules will break, and if there are less steel balls, clusters of capsules will form.

After separating the capsules from the excess cement, the fresh capsules were let to cure for 8 hours at 35 ^{o}C after which, some more epoxy in a weight ratio 1:20 (1 gram of epoxy for each 20 grams of capsules) was added to cover the capsules surface. Once this was done, the capsules were cured during other 8 hours at room temperature under a continuous horizontal movement at 400 revolutions per minute, to avoid clusters formation.

4.1 Thermal analysis

For the capsules to survive the mixing process of the asphalt concrete, they must resist temperatures between 160 ^{o}C and 180 ^{o}C. These temperatures can produce molecular scissions or intermediate compounds in the rejuvenator such as ketones or alcohol (Lins et al., 2008), as well as mass loss due to the evaporation of these products. This was determined by performing thermogravimetric analysis (TGA) on the capsules. Furthermore, to study energy changes and phase transitions in the capsules, differential scanning calorimetry (DSC) has been used. Both thermogravimetric analysis and differential scanning calorimetry tests were performed on a NETZSCH, TG 449 F3 Jupiter Thermo-Microbalance, using nitrogen atmosphere and a heating rate of 10 ^{o}C/min.

In order to obtain thermal stability curves, a mass of capsules was measured in an aluminium crucible. Finally, the loss of mass was recorded after heating during 2 h at different isothermal temperatures.

4.1 Porous asphalt concrete materials

To prove that the capsules will resist the mixing process of asphalt concrete, they were added to a common porous asphalt concrete mixture. In this mixture, the aggregates used were quarry material (Bestone, Bremanger Quarry, Norway) (size between 2.0 and 22.4 mm), crushed sand (size between 0.063 and 2 mm), and filler type Wigro 60K, (size < 0.063 mm). Finally, the bitumen used was 70/100 pen, obtained from Kuwait Petroleum, in a 4.5 % by weight. To check if the capsules resisted the mixing process, the asphalt core obtained was sawn and examined under the optical microscope.

3 RESULTS AND DISCUSSION

4.1 Capsule size and distribution

Apart from producing very strong and heat resistant capsules, the method described in this article allows for the creation of capsules of different sizes and shapes only by changing the type of porous sand. In Figure 1, it is shown that the most probable diameter of the capsules obtained is 1.60 mm, being the size of the porous sand used as a core between 1.0 and 1.7 mm. From the capsule observed in Figure 3, it can be determined how the mean thickness of the shell is of about 0.10 mm.

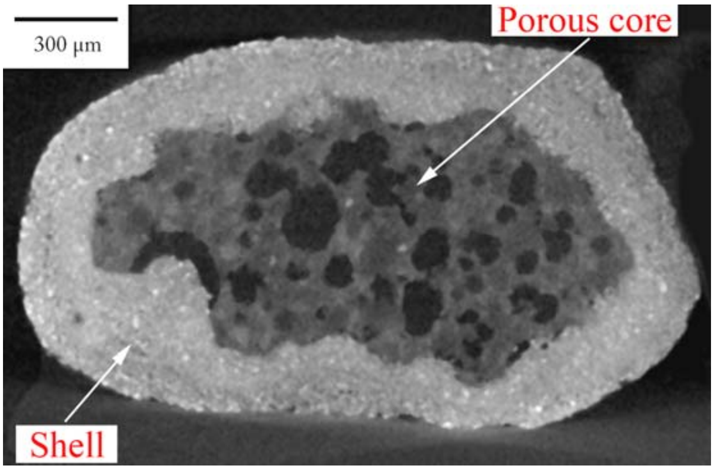

Figure 3: CT-Scan image of the capsule

4.1 Thermal analysis

In Figure 4, representative DSC (Differential Scanning Calorimetry) and TGA (Thermogravimetry Analysis) scans of the rejuvenator and of the capsules are shown. In the DSC plot of the capsules there are three different main endothermic peaks. The first of these endothermic peaks (Peak 1 in Figure 4) corresponds to the loss of two different appearances of water, and comprises two subpeaks as is clearly shown in Figure 4. The first subpeak (1a) at approximately 100 °C corresponds to the dehydration of pore water while the second subpeak (1b) between 100 °C and 165 °C corresponds to the dehydration of calcium silicate hydrates.

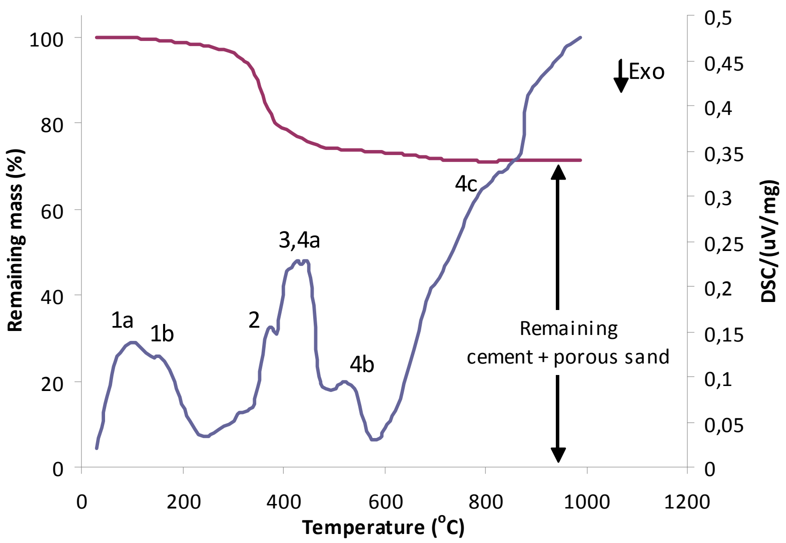

Figure 4: DSC and TGA curves for the capsules and the rejuvenators studied.

Between 350 °C and 450 °C most of the epoxy degradation occurs. Though with the data available the individual decomposition products cannot be identified, minor peak 2 and peak 4a in Figure 4 are very similar to the ones shown for the epoxy in (Erikson, 2007) for its thermal decomposition. Furthermore, peak 3 corresponds to the thermal decomposition of the rejuvenator. The major decomposition rates of both epoxy and rejuvenator coincides at about 440 °C. Finally, peaks 4b and 4c corresponds to the final epoxy degradation.

As mentioned above, the bitumen mixing temperatures are between 160 ^{o}C and 180 ^{o}C. At these temperatures, the losses in the capsules are between 0.8 % and 1.3 % respectively. These losses correspond to the pore water in the porous sand and to the dehydration of its materials. In order to increase the volume content of rejuvenator inside the capsules it would be necessary to beforehand dry the porous sand, but it needs further investigation at which temperature and for how long drying would be needed. Therefore, a topic of future study will be to determine the heating temperature and the time to maximize the volume of oil in the capsules without reducing their resistance by degrading the porous sand materials.

4.1 Capsule composition

The total mass of the capsules consists of four parts: rejuvenator, porous sand, cement and epoxy (Figure 3). To find the mass exact composition of the capsules different techniques have been used. First, the volumetric relationship between the core and the shell of the capsules was found through CT-Scan analysis of 5 capsules. The core of the capsules was assumed to be composed of porous sand and rejuvenator; its total volumetric percentage within the capsules being 31.25 %. The shell was assumed to consist of cement and epoxy; and its total volume inside the capsules is 68.75 %. Second, in Figure 4, after heating the capsules in the TGA at 1000 ^{o}C, it is showed how the remaining mass of the capsules is about 71 % of the original mass. If these heated capsules are investigated under the optical microscope, it can be observed that the only remaining materials are cement and porous sand. Additionally, Figure 4 shows that the remaining mass of these two materials after heating them at 1000 ^{o}C in N2 atmosphere is 96.75 % for the cement and 78.0 % for the porous sand.

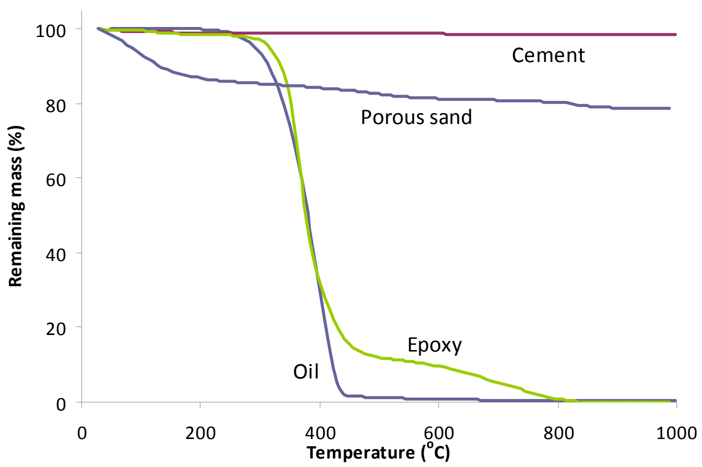

Figure 5: DSC curves for the capsules and the rejuvenators studied.

With this data it is possible to make a system of four equations with the masses of the four capsules components as unknowns:

$$\left\{\begin{array}{l} M_o + M_{ps} + M_c + M_e = 1 \\ \rho_{cap} \cdot \left(\dfrac{M_o}{\rho_o} + \dfrac{M_{ps}}{\rho_{ps}} \right) = V_{o+ps} \\ \rho_{cap} \cdot \left(\dfrac{M_c}{\rho_c} + \dfrac{M_e}{\rho_e} \right) = V_{c+e} \\ 0.967 \cdot M_c + 0.780 \cdot M_{ps} = M_r \end{array}\right\} \begin{array}{l} M_o = 0.094 \\ M_{ps} = 0.117 \\ M_c = 0.642 \\ M_e = 0.147 \end{array} \quad (1)$$

Where M_o is the mass of oil in the capsules, M_{ps} is the mass of the porous sand, M_c is the mass of cement, M_e is the mass of epoxy in the capsules, M_r is the remaining mass of the capsules after heating them in N_2 atmosphere at 100 ^oC, ρ_{cap} is the density of the capsules, ρ_o is the density of the rejuvenator, ρ_{ps} is the density of the porous sand, ρ_c is the density of cement, ρ_e is the density of the epoxy, V_o+p_s is the volume of the core of the capsules and V_{c+e} is the volume of the shell measured with the CT-Scan.

The solution is the total mass percentage of each component inside the capsules. It can be seen that approximately 9 % of the mass content of the capsules is rejuvenator. If the mass of rejuvenator is divided by the mass of porous sand it is found that the porous sand can absorb about 80 % of its own weight, which is very similar to what was found for the water absorption of the porous sand. Furthermore, if the quantity of compounds in the capsules is expressed in terms of volume (Table 1), it can be seen how 20.9 % of the total volume in the capsules is rejuvenator. Finally, one interesting remark about these capsules is the relatively high volume of epoxy needed. Epoxy is a very expensive material so in the future different polymers will be studied to decrease the price of the capsules.

4.1 Incorporation into porous asphalt concrete

To prove that the capsules resist the mixing process, they were incorporated into a porous asphalt concrete mixture as an additional aggregate. The mixture was blended during 15 minutes at 285 r.p.m and a temperature of 160 ^oC in a 10 litter mixer and compacted in a gyratory compactor to simulate a real porous asphalt pavement. Then, the sample was sawn in half and the cross section was examined under the optical microscope.

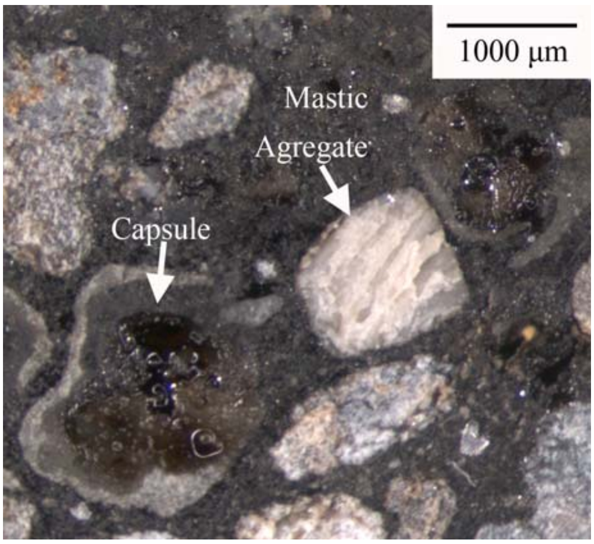

Figure 6: Section of the capsules embedded in asphalt concrete.

Figure 6 shows that the capsules resist the mixing process and still have lots of oil in them. In this Figure it can be seen that the capsules are integrated in the matrix as an additional aggregate. As shown above, the capsules look very well bonded to the binder, which will help for the force transfer to the capsules. Furthermore, during the mixing process the capsules are evenly distributed, which will greatly benefit the rejuvenation process, as it will occur in the whole pavement, when and where it is necessary, not just in the surface. Future research should be done to show the effect of the capsules on the ageing of the pavement.

4 CONCLUSIONS

In this paper an encapsulation system for asphalt concrete has been designed. These capsules are designed to contain rejuvenators and have the objective of reverting the asphalt concrete ageing. This is the first time that an encapsulation system has been designed for asphalt concrete and it potentially has many advantages over the traditional rejuvenation systems such as a whole volumetric penetration, it has no negative effect on the skid resistance of the pavement and also a better environmental performance, avoiding the use of oils on the road surface. The capsules comprise a porous stone in which the rejuvenator is embedded surrounded by a hard shell made of an epoxy-cement matrix with a volume percentage of 20.9, 13.1, 24.9 and 13.0 % of rejuvenator, porous sand, cement and epoxy respectively. This gives a hard capsule that is able to resist the high temperatures and stresses during the mixing and the compaction of asphalt concrete with a very dense shell in the areas in contact with the porous sand and a very rough shell in the areas in contact with the asphalt binder.

The capsules obtained have a medium size of 1.60 mm. The idea is to substitute part of the sand aggregates in asphalt concrete by the capsules. Finally, the capsules were mixed in porous asphalt concrete. The asphalt concrete was sawn and it showed that the rejuvenators were intact inside the asphalt concrete mixture. In the future, the effect of these capsules on the asphalt concrete ageing will be investigated in order to proof their effect.

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