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Synthesis, characterisation and mechanical impact of novel capsules using porous aggregates containing asphalt rejuvenator as an effective way to restore aged binder properties

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Abstract

Roads, due to use and time, become aged and as a result, they require maintenance. This paper presents a promising technology to compensate ageing. The method uses porous aggregates as capsules containing rejuvenator. The rejuvenator will be released during the asphalt pavement's service life, reversing the impact of ageing on asphalt performance, properties and, thus, extending pavement's durability. This paper describes the properties of two porous aggregates, the encapsulation method and the properties of the capsules. The capsules were incorporated into an asphalt mix and their fundamental properties analysed. Finally, the recovery potential of the aged binder was evaluated using ageing tests. The results demonstrate the effectiveness of the technology, a change in binder properties was observed over time, but to a lesser extent for the bitumen when capsules were included than for the reference. The solution also highlights the benefits of using encapsulated rejuvenator over the use of rejuvenator directly added to the mix.

Keywords: porous aggregates, capsules, bitumen, rejuvenation, rejuvenator, durability, maintenance.

Highlights

- A new type of capsule was developed as an efficient solution to incorporate rejuvenators into asphalt mixes.
- The encapsulation method consisted of a vacuum impregnation process at a controlled temperature.
- The capsules were characterised using some well-established methods alongside some more novel tests.
- The benefits of using encapsulated rejuvenator to compensate ageing were demonstrated.

1. Introduction

Roads play a main role in developing countries and societies by providing essential links between the different regions, thus facilitating the transport of goods and the movement of people [1]. The EU-27 road network was estimated to be around 3.9 million km in length in 2017, being dominant compared to other transport modes [2], so keeping it in good working condition is critical.

Roads become damaged and deteriorate over time, requiring maintenance, without which roads would continue deteriorating, requiring significant repairs or even replacement after just a few years. The costs of maintenance of pavements are not negligible. For example, for OECD countries, the maintenance to overall expenditure ratio on roads was 33% in 2005, but it has been reduced since the global economic crisis (e.g: 27% in 2011), while the age of the roads increases [3]. Hence, investing in maintenance at the right time extends the service life of roads and saves significant future costs [4].

Extending the service life of asphalt pavements is a promising field of study within the road sector. This can be done by improving the quality of the asphalt when laying it or improving the quality of the asphalt mixes throughout their service life. On the one hand, the use of better quality materials together with the addition of some additives to the bitumen or asphalt mix (polymers [5], fibres [6], nano-based additives [7], among others) are good examples for improving the quality of the asphalt during the pavement construction stage. On the other hand, adequate maintenance is a good solution for improving the properties of the mix throughout their service life [8]. In this scenario, a promising technology that has captured the attention of some researchers in the last years is self-healing [9].

In recent years, the design of materials with healing ability has become more and more popular in a wide range of materials and applications. In the particular field of asphalt-based materials, it is well known that asphalt pavements can heal themselves. The asphalt-healing phenomenon was first reported by Bazin in 1967 [10]. However, the natural healing of asphalt pavement requires higher temperatures and enough rest periods [11], which are difficult to achieve in practice due to the continuous traffic load and changing temperature. Other researchers focused on the development of extrinsic healing methods in asphalt to recover the asphalt pavement from its damage. There are two main methods to promote asphalt self-healing: 1. Induction healing of asphalt mixtures and 2. Microcapsules filled with a healing agent [12,13].

The first method has been extensively investigated in the last years [14]. It consists of heating the damaged area of the asphalt pavement locally with induction or microwave energy to increase its healing capacity by adding conductive particles [15-19]. In this method, the high temperatures may accelerate the ageing of the asphalt binder, which may result in crack formation and pavement failure.

The second method provides an alternative solution for self-healing asphalt, in which capsules containing rejuvenator as a healing agent are prepared for their incorporation into a bituminous matrix. For the capsules to be successful, they should release the rejuvenator agent when a crack appears, so that the rejuvenator diffuses into the aged binder and fixes the cracks.

Rejuvenators are used to restore the loss of certain properties of the aged (oxidised) bitumen, avoiding that asphalt embrittles. However, the overall effects of rejuvenators on the properties of asphalt binders have not been well studied [20, 21]. Recent studies demonstrate that there is a point beyond which the asphalt binder may not be rejuvenated [22]. Other studies show that proper rejuvenator will improve cracking and durability without compromising on rutting resistance and at the same time restore the "healing" ability [23].

The application of asphalt rejuvenators has also proved to be an effective method of pavement preservation [24]. Some studies concluded that by using rejuvenators effectively, the pavement life could be extended by up to 8 years, resulting in savings of 29% on the life cost of the treated pavement [25]. More recently, rejuvenators have also been used for asphalt mixtures containing large percentages of reclaimed asphalt pavement, since they can reduce the performance grade of the bitumen to the level of the virgin asphalt binder [26]. Rejuvenators are effective when, spread over the road surface, they fully penetrate into the pavement, not accumulating only in the first centimetres [27]. Encapsulation is a promising way to solve this problem.

There are different methods to prepare capsules in the literature: encapsulation of rejuvenator inside a polymeric shell, usually prepared by in-situ polymerisation of methanol-melamine-formaldehyde (MMF) pre-polymer [28], epoxy capsules [29], using alginate fibres [30] and calcium alginate [31,32]. These methods have some limitations; in the first, formaldehyde in high concentration can be dangerous for human health. The capsules developed by the second method are strong enough to survive the mixing and compaction, but the breaking mechanism is difficult to control. The third method can only repair small micro-cracks and the content of the rejuvenator is very limited. In the last one, calcium calcinate capsules have low strength and tend to release the healing agent too fast [33].

With a similar idea, but a different mechanism of work, Casado et al [34] demonstrated the potential of using porous aggregates as a carrier of the rejuvenator to improve the quality of the asphalt mixes throughout the service life. In contrast to the encapsulation methods described before, in which, when external damage occurs to the pavement, cracks break the capsules making them to release the rejuvenator into the bitumen and fix the cracks, in this method, the capsules do not break. The rejuvenator is released over time from the pores of the aggregates, due to the compatibility between the rejuvenator and the bitumen that is around it, to compensate binder ageing. In other words, this technology is an effective solution for preventive maintenance. This method helps to recover the loss properties of the aged bitumen in the asphalt mix, preventing minor cracks from becoming major ones.

The objective of this paper is to demonstrate the potential use of novel capsules using porous aggregates containing rejuvenator, as an efficient way to improve the properties of the aged binder when compared with a reference sample (with no capsules) after different ageing levels. To this end, two types of porous aggregates with different particle size and morphology were examined and their properties analysed. Capsules were prepared using a vacuum impregnation process and temperature and their main properties were evaluated. Moreover, thermal stability and the impregnation efficiency were studied using thermogravimetic analysis (TGA) and the rejuvenator diffusion capacity in the bituminous matrix was evaluated through Fourier Transform Infrared Spectroscopy (FTIR). The developed capsules were added to an asphalt mix and their impact on the mechanical properties was investigated. In particular, a very thin asphalt concrete was designed, and the air voids content, water sensitivity and plastic deformation were examined to check if the addition of capsules and rejuvenator can affect the mix performance compared to that of the reference mix.

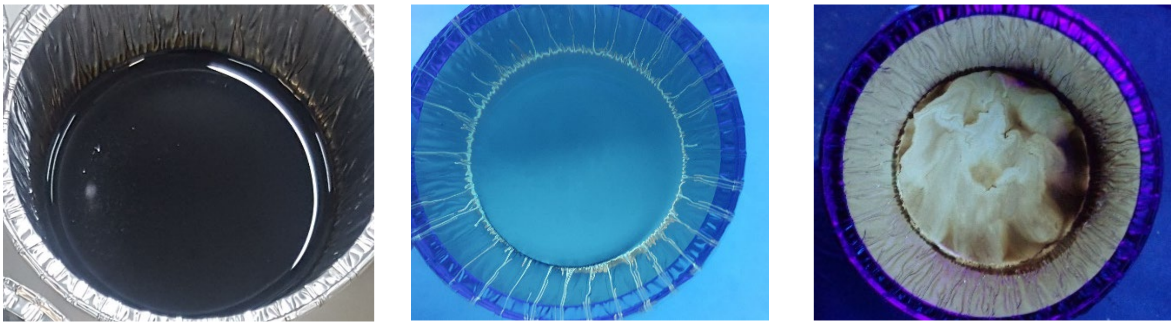
Finally, the effect of capsule addition on the recovery potential of the properties of aged binder was investigated by quantification of changes in the asphalt binder before and after ageing treatment in an oven. In the research, the benefits of using encapsulated rejuvenator instead of adding it directly to the asphalt mix were also investigated.

2. Materials and methods

2.1. Raw materials

2.1.1. Asphalt rejuvenator

A commercial asphalt rejuvenator was selected due to its capacity to partially recover the original properties of oxidised asphalt by restoring the asphaltenes/maltenes ratio to its original balance and reconstituting the chemical composition of the binder. Figure 1 shows the rejuvenator used in this research. The coloration of rejuvenator under visible light is similar to the asphalt binder's; however, when examined under ultraviolet light (UV) it turns greenish-blue, due to the fluorescent component of rejuvenator, which facilitates the differentiation of rejuvenator from the asphalt binder.



(a) (b) (c)

Figure 1. (a) Rejuvenator sample under visible light, (b) under UV light and (c) bitumen sample with some drops of rejuvenator

2.1.2. Porous aggregates

Two types of porous aggregates with particle size equal to or smaller than 4mm were selected as carriers for the rejuvenator. In particular, sepiolites and vermiculites were the substrates used in the investigation. Both clays possess a great surface area and have good absorptive properties. They show low density, with values of 1800-2300 kg/m^3 for sepiolites and 90-130 kg/m^3 for vermiculites.

Other properties, such as particle size, microscopy, thermogravimetric analysis characteristics and specific surface area were investigated, and the results are presented below.

Particle Size Distribution

Vermiculite is finer-grained than sepiolite (Figure 2). A grading analysis confirmed this. The particle size distribution according to EN 933-1, in which the percent passing each sieve was calculated, is shown in Table 1. Sepiolite has a more homogenous grading, being mostly particles with a diameter of 2-4 mm. Vermiculite has a more varied grading, having a significant proportion of finer particles with particle size smaller than 2 mm.

Figure 2. Detail of porous aggregates: sepiolite (left); vermiculite (right)

Table 1. Particle size distribution of the porous aggregates used in the study

	Sepiolite	Vermiculite
Sieve size (mm)	**% Passing**	
5.6	100	100
4	97.9	88.7
2	3.7	25.5
1	0	9.1
0.5	0	3.8
0.25	0	1.9
0.125	0	0.6
0.063	0	0.2

Microscopy

The texture and morphology of the substrates used in the study were also analysed by scanning electron microscopy. The selected fraction for sepiolites and vermiculites corresponds to the minerals observed in Figure 3 and Figure 4, both at low and high magnification (x 400 and x 1000, respectively). The porosity of the samples is observed in both figures. Sepiolites show intraclastic textures. A typical lamellar morphology with a uniform thickness distribution is observed in Figure 4 for the vermiculite mineral. Moreover, two phases can be identified, the main one in a lighter shade and a second darker one.

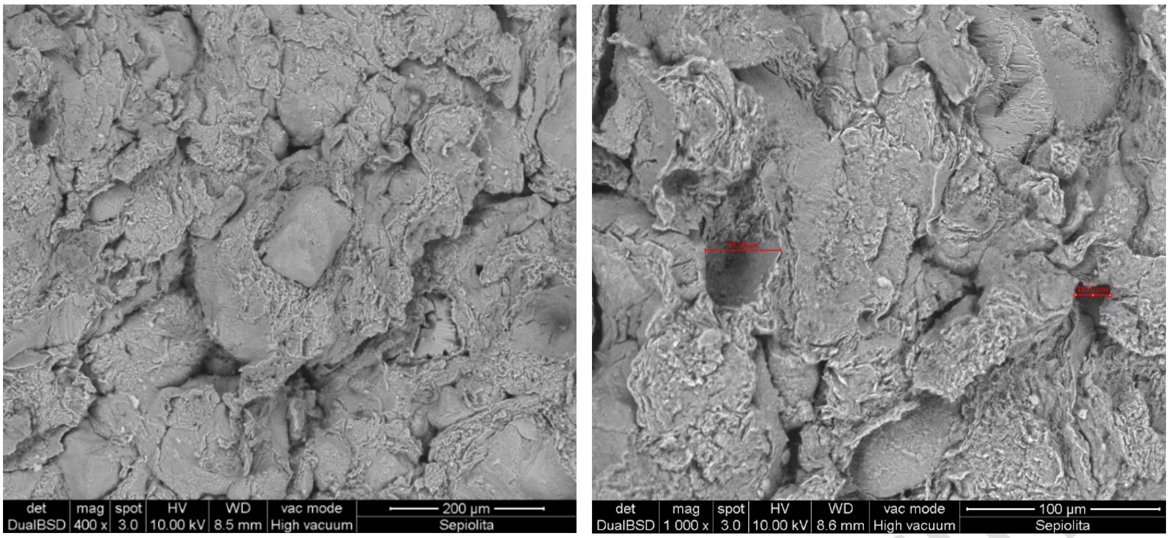


Figure 3. SEM image of sepiolite (Left: magnified 400 times; right x 1,000 times)

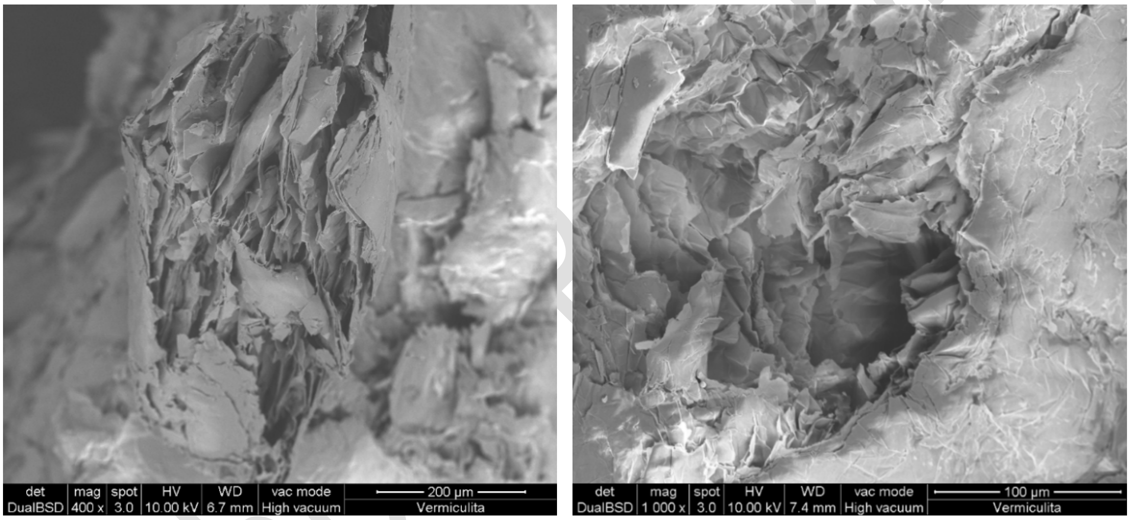


Figure 4. SEM image of vermiculite (Left: magnified 400 times; right x 1,000 times)

Thermogravimetric analysis

Both porous aggregates were characterized by thermogravimetric analysis (Figure 5 and Figure 6) in an atmosphere of air. The thermogravimetric curves (TG) of sepiolite are shown in Figure 5, where a total weight loss of 16.46% is distributed in four phases. Taking into account that the sepiolite is a hydrous magnesium silicate with the formula $Mg_8Si_{12}O_{30}(OH)_4(H_2O)_4.8H_2O$, the mass losses for phases 1 to 4 correspond to: (1) The first most noticeable is registered at 85.76 °C, which corresponds to the loss of water physically bonded to the sepiolite, adsorbed on the external surface, also known as moisture (10.11%). (2)

At approximately 284 °C, there is another peak with a weight loss of 1.6%, attributed to the loss of two of the four crystallisation water molecules which are more weakly bonded. (3) The third peak is observed at 472°C, showing a weight loss of approximately 2%, due to the elimination of the other two, more strongly bonded, crystallisation water molecules. (4) The last peak appears at about 830 °C, which is attributed to the loss of hydroxyl groups [35].

Figure 6 shows the TG of vermiculite, a layered mineral with general formula $(Mg,Fe,Al)_3(Al, Si)_4O_{10}(OH)_2.4H_2O$. From the TG results, a broad peak recording a weight loss of 3.65% can be seen at 61.63°C. This is associated with the release of physically adsorbed water on the surface (moisture). The second peak registered at 160 °C corresponds to the decomposition of some hydrates in the vermiculite interlayer [36]. The small loss at about 850°C is due to the loss of water by dehydroxylation [37].

The capacity to retain water in the structure makes these substrates suitable for their use as absorbents. Considering that the traditional manufacturing temperature of hot mix asphalt is about 175 °C and, according to the TG curves, thermal degradation of the porous aggregates is not expected in any case.

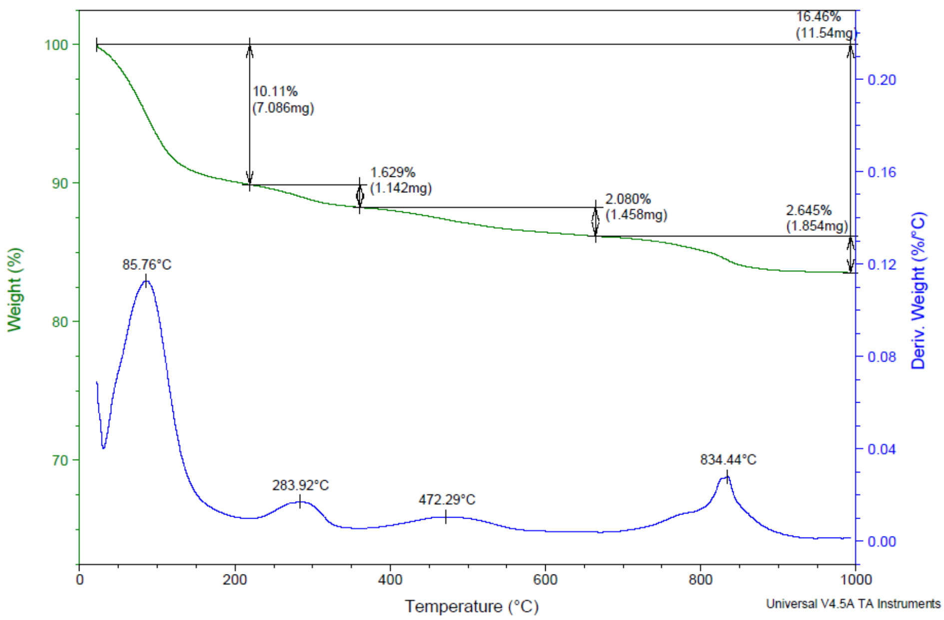


Figure 5. Thermogravimetric curve of sepiolite

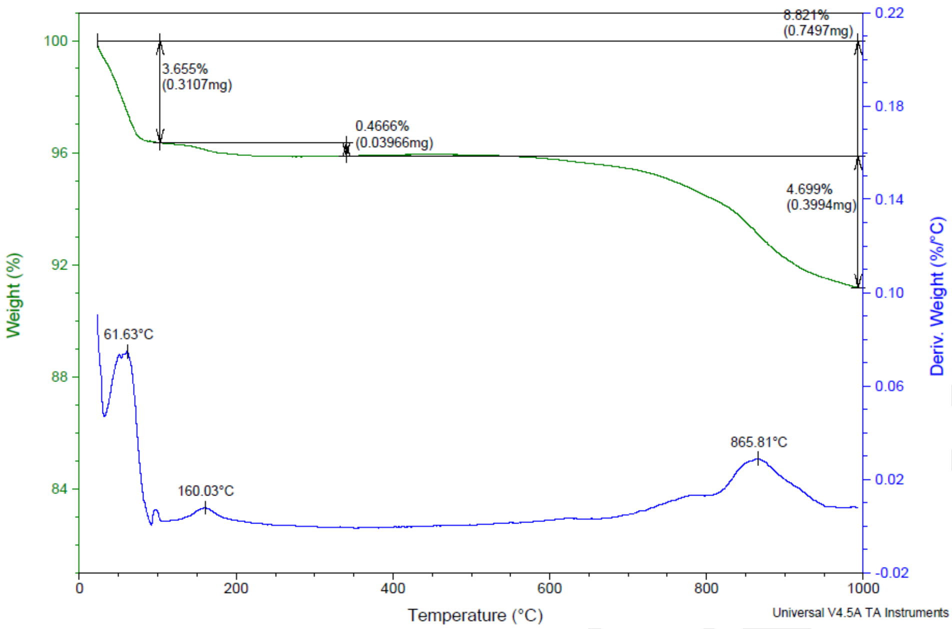


Figure 6. Thermogravimetric curves of vermiculite

Specific Surface Area

The specific surface area of the porous aggregates used in the study was determined by adsorption of N_2, which is a suitable approach to determine the specific area of solid materials, especially for those with open porosity [38].

Nitrogen adsorption-desorption isotherms at the liquid nitrogen temperature (77 K) were analysed using a Micromeritics ASAP 2010 analyser by increasing the pressure or concentration of the adsorbing gas. Data recorded was presented in a graph, where the x-axis is the relative pressure of the gas and the y-axis is its volume adsorbed onto the sample. Figure 7 and Figure 8 show the N2 adsorption/desorption isotherms of sepiolite and vermiculite. Their adsorption isotherms are classified as type II and IV, respectively, of the IUPAC (International Union of Pure and Applied Chemistry) classification. The type II isotherm (Figure 7) is characteristic for macroporous materials where only a very small increase in nitrogen adsorbed volume occurred in the range of partial pressure from 0.1 to 0.25. The type IV isotherm (Figure 8) is characteristic of mesoporous materials with three-dimensional interconnected pore geometry and high energy of adsorption. From these findings and according to the IUPAC nomenclature, sepiolite is a macroporous material, which means the pores are larger than 50 nm in diameter; meanwhile, vermiculite is a mesoporous material; i.e., the pore diameters are between 2 and 50 nm.

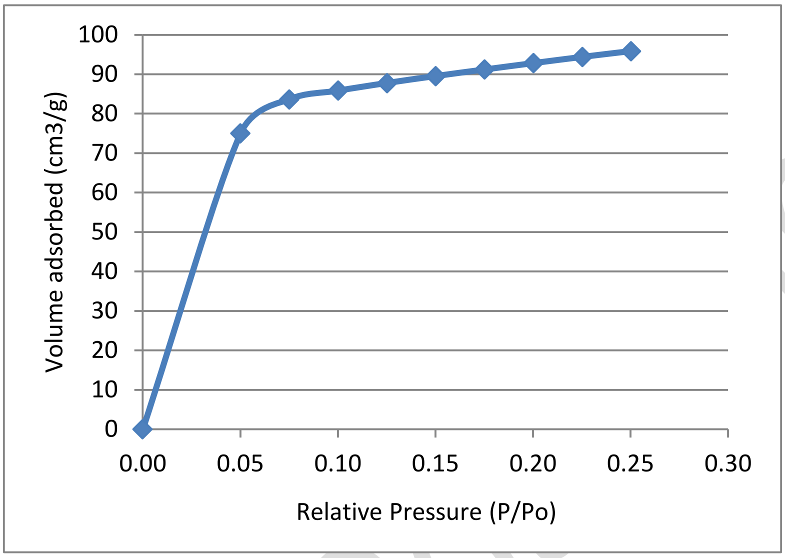


Figure 7. N_2 adsorption-desorption isotherms of sepiolite sample

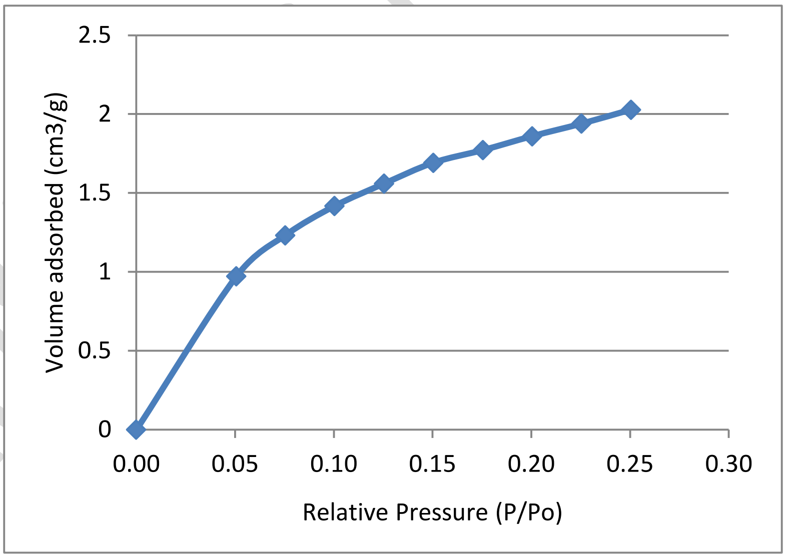


Figure 8. N_2 adsorption-desorption isotherms of vermiculite sample

The specific surface area was calculated based on the BET method [39] in N2 adsorption. The BET equation (Equation 1) describes the relationship between the number of gas molecules adsorbed (W) at a given relative pressure (P/P_0), where C is the BET constant.

$$\frac{1}{W\left[\left(\frac{P_0}{P}\right)-1\right]} = \frac{1}{W_m C} + \frac{C-1}{W_m C}\left(\frac{P}{P_0}\right) \qquad (1)$$

This equation describes a linear plot of 1/ W [(P_0/P) – 1] vs. P/P_0. This plot is known as the BET plot (Figure 9). This plot should usually yield a straight line in the approximate relative pressure range 0.05 to 0.35. The value of the slope and the intercept of the line are used to calculate the monolayer adsorbed gas quantity (W_m) and the BET constant (C). The BET specific surface area can be calculated from equation 2 and 3:

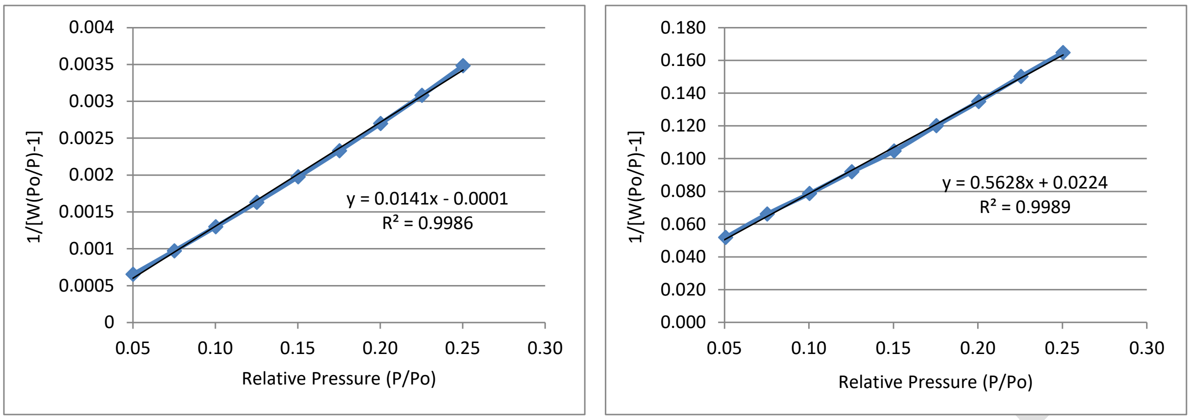
$$S_{total} = \frac{Wm\, N_A\, S}{W} \qquad (2)$$

$$S_{BET} = \frac{S_{total}}{mass\ sample} \qquad (3)$$

where N_A is Avogadro's number and S is the adsorption cross section of the adsorbing species.

From the BET plot (Figure 9) and taking into account the equations described above, the BET surface area was determined to be 311 m^2/g for sepiolite and 7.4 m^2/g for vermiculite. This means a BET surface area 40 times greater for sepiolite than for vermiculite. This could be expected given the porosity of each material. This data is consistent with the values found in the literature for these materials [40, 41]. The small specific surface area of vermiculite observed can be attributed to the strong hydrogen bonds between the tetrahedral sheet and the water of interlayer cations in vermiculite, which keep the interlayer zone obstructed and thus could reduce superficial nitrogen adsorption considerably [42].

It can also be observed that the linear fit of the BET equation applies satisfactorily to the entire adsorption isotherm (P/P_0 = 0.05 – 0.35) in both samples, with the R^2 values greater than 0.995.



(a) (b)

Figure 9. BET plot (a) Sepiolite (b) Vermiculite sample

2.2. Encapsulation method

The method developed by the authors consists of a vacuum impregnation process at temperature, in which the rejuvenator penetrates into the pores of the aggregate, releasing the air from its internal structure. As the system returns to atmospheric pressure, the pores are filled with the surrounding fluid. The process is completed by filtration and drying of the excess rejuvenator (Figure 10).

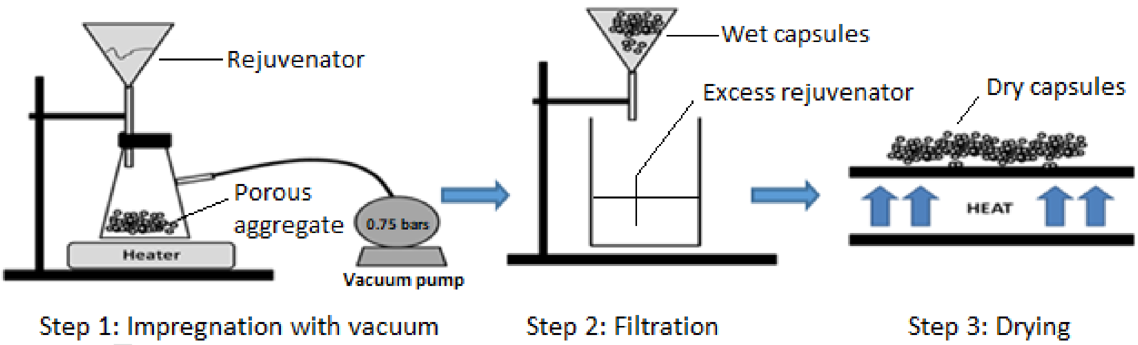
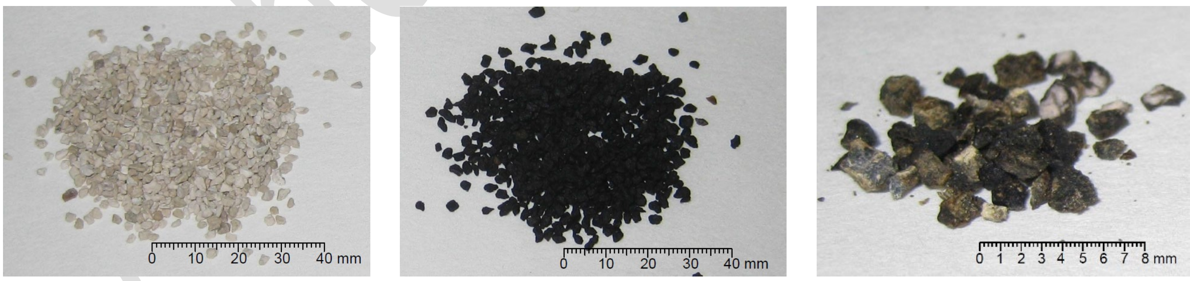


Figure 10. Schematic representation of the encapsulation method

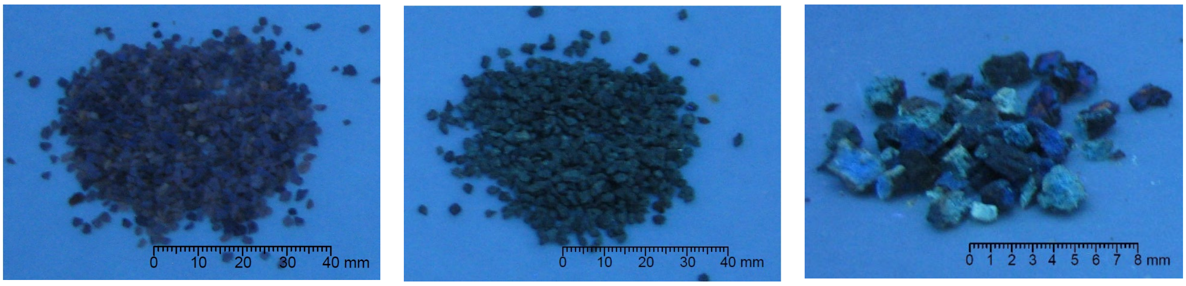
Different trials on vacuum impregnation were carried out to achieve the maximum amount of rejuvenator penetration into the pores of the substrates. The procedure of the most effective experiment is reported next. Before the impregnation process, the materials were prepared. Porous aggregates were heated to 80 °C for 8 hours to remove moisture content. The rejuvenator was heated to 100 °C for 2 hours, time enough to reduce its viscosity, which facilitates its penetration into the aggregate air voids. 100 g of porous aggregate was placed into a flask, which was connected to a vacuum pump. The rejuvenator was then added until the porous aggregate was fully submerged. The mix - rejuvenator and aggregate - was kept warm at 100 °C for the whole process. This is the optimal temperature for rejuvenator penetration into the porous aggregate's voids. After the porous aggregate were covered with rejuvenator, a vacuum was applied for approximately 60 minutes at 0.75 bars to remove the air. This process continued as long as air bubbles keep appearing under vacuum. Then, the vacuum was released and the flask returned to ambient pressure. Any excess rejuvenator was recovered by filtration for reuse in future vacuum impregnation processing and the capsules were dried in an oven to constant weight.

This three-step process was carried out with the two substrates described in section 2.1, sepiolite and vermiculite. As an example, details of the sepiolite examined under visible and ultraviolet light, in three different configurations: empty, filled with rejuvenator and broken, are shown in Figure 11 and Figure 12, respectively.



(a) (b) (c)

Figure 11. (a) Empty capsules (b) filled with rejuvenator (c) broken sepiolite under visible light



(a) (b) (c)

Figure 12. (a) Empty capsules (b) filled with rejuvenator (c) broken sepiolite under UV light

2.3. Testing methods for the characterisation of capsules containing rejuvenator

2.3.1. Impregnation capacity and thermal stability

The impregnation efficiency and thermal stability of the capsules were evaluated by thermal analysis using a thermogravimetric analyser. This analysis measures the amount of weight change of a material with increasing temperature. The test is run up to the thermal degradation of the sample. The percentage residue obtained from the TGA curves indicates the quantity of rejuvenator that is adhered inside the pores of the aggregates.

The thermogravimetric analysis was performed at a heating rate of 10 °C/min from ambient temperature to 1000 °C in an air atmosphere using a Thermal Analyser TG Rheometric instrument. This TGA is provided with an internal balance that automatically tares and weighs in samples.

2.3.2. FTIR and diffusion analysis

The encapsulation process of the rejuvenating agent requires suitable temperature conditions for the impregnation to take place with maximum efficiency. It is thus important to evaluate the influence of temperature on the properties of the rejuvenating agent, so that it does not lose its properties due to inadequate ageing.

Fourier Transform Infrared Spectroscopy (FTIR) was the method adopted to investigate changes in the chemical composition of the rejuvenator due to oxidative ageing, where carbonyl and sulfoxide functional groups were used to characterise the level of oxidation that may occur during the encapsulation process [43, 44]. These groups are considered as relevant markers for qualifying bitumen ageing. The peaks at wavenumbers of approximately 1030 cm^{-1} and 1740 cm^{-1} represent the sulfoxides (S=O) and carbonyls (C=O), respectively. These peaks are normalised against reference aliphatic functional groups (peaks at 1376 cm^{-1} and 1460 cm^{-1} representing methyl (CH_3) and ethyl (CH_2) groups), since it is anticipated that these structures are stable and not affected by applied ageing procedures. The use of a reference group is done to remove any variation in the absorbance spectra due to a variation of the IR [45].

Carbonyl and sulfoxide indices are calculated as follows:

$$ICO = \frac{V_{CO}}{V_{ref}} \qquad (4)$$

$$ISO = \frac{V_{SO}}{V_{ref}} \qquad (5)$$

Where V_{CO} is the carbonyl peak value (height or area), V_{SO} is the sulfoxide peak value (height or area), V_{ref} = Ethyl + methyl peak values.

In addition, FTIR by attenuated total reflectance (FTIR-ATR) was applied to monitor the diffusion rate of rejuvenator absorbed inside the pores of the substrates into the bituminous matrix by placing the capsules and a film of bitumen in contact. Diffusion in bitumen was previously studied using FTIR-ATR, to investigate the influence of specific parameters (temperature, viscosity, etc.) on diffusion characteristics [46], and to evaluate the rejuvenation level in bitumen [47].

In this study, the diffusion coefficient (D) of the different functional groups was determined from the intensity variation of the bands and equations based on Fick's second law, according to the procedure described by Contreras et al. [48]:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (6)$$

where c: concentration in molar ratio, t: time, D: diffusion coefficient, x: position.

The definition of these coefficients helps better to understand the evaluation of the bitumen rejuvenation process.

2.4. Evaluation of the technical feasibility of the use of capsules for asphalt.

2.4.1. Asphalt mix design

An asphalt concrete for very thin layers, BBTM 11B type according to the Spanish standard, and commonly used for surface courses, was designed following CEN EN 13108-2, using commercial polymer-modified bitumen 45/80-65, whose main characteristics are shown in Table 2, porphyry aggregates, limestone filler and the experimental capsules. Polymer-modified bitumen was selected instead of the conventional one (unmodified) because it is mandatory for this type of asphalt mixtures for medium and high traffic intensity in Spain [49]. Likewise, a BBTM 11B mix was selected for the study since asphalt surfaces with high voids content are more susceptible to oxidative ageing due to greater exposure of the binder to air and higher temperatures.

The bitumen accounted for 5% of the mixture by weight while aggregates accounted for the remaining 95%. Capsules were added to the asphalt mix as an additive, which means that they were not taken into account for the mix grading. The aggregate grading and proportions of each component are shown in Table 2.

The percentage of capsules incorporated into the mix was 1% for the capsules using vermiculite and 1.5% for the ones with sepiolite. These values result from the impregnation efficiency achieved in the encapsulation process to prepare asphalt samples with approximately the same amount of rejuvenator for both substrates, which is 0.70% by weight of the total asphalt mix.

Table 2. Characteristics of the Polymer-Modified Bitumen 45/80-65

Property	Test Method	Result	Units
Penetration at 25°C	EN 1426	45-80	0.1 mm
Softening Point	EN 1427	≥ 65	ºC
Elastic Recovery at 25°C	EN 13398	≥ 70	%

Table 3. Aggregate grading and proportioning

Aggregate type	% Aggregate	Sieve (mm)							
		22	16	11.2	8	4	2	0.5	0.063
Coarse aggregate 6/12	73	100	100	99.01	49.77	0.15	0.14	0.10	0
Fine aggregate 0/6	21.6	100	100	100	100	79.82	47.89	12.77	0.07
Filler	5.4	100	100	100	100	100	100	99.0	98.3
Sepiolite capsules	1	100	100	100	100	80.59	37.83	0.09	0
Vermiculite capsules	1.5	100	100	100	100	89.11	42.45	1.42	0

The production of the asphalt test specimens containing capsules was similar to the standard process for the manufacturing of hot mix asphalt, with the difference that the capsules were incorporated into the mixer just after the aggregates and before the bitumen was added. The laboratory mixing and compaction temperatures were 165 °C and 150 ºC, respectively. Mixing temperature was defined according to experience and was confirmed by the bitumen supplier recommendations.

2.4.2. Physical and mechanical characterisation of the asphalt mix samples

Asphalt mixes (unaged) were characterised and the impact on the three main properties, air voids (EN 12697-8), water sensitivity (EN 12697-12) and wheel tracking test (EN 12697-22), was investigated. The first determines the structure of the mixes, the second the asphalt mixture cohesion between binder and aggregates in the presence of water and the last determines the permanent deformation behaviour of asphalt based on the low-stiffness response of the asphalt; that is, its response at high temperature and long loading time. These tests were selected as good indicators of the performance of the samples after the mixing and compaction process, since any release of the rejuvenator would significantly affect their properties.

For the water sensitivity test, four cylindrical specimens for each conditioning (wet and dry) with a diameter of 101.6 ± 0.1 mm and a height of 63.5 ± 2.5 mm were prepared. The compaction energy was 2 x 50 blows (50 blows per face) using an impact compactor (EN 12697-30). For the wheel tracking test, two 40 x 30 x 5 cm specimens were prepared by a roller compactor (EN 12697-33).

In addition to the asphalt mixtures with capsules, three more mixes were analysed and results were compared to each other: a reference asphalt mixture (without capsules), another with rejuvenator to which the equivalent amount of rejuvenator contained in the capsules was directly added to the bitumen, and finally one with empty capsules.

Results from the tests were also compared with the specifications defined in Article 543 of the Spanish Specifications for Road and Bridge Construction [49].

2.5. Evaluation of the recovery potential of the aged bitumen with embedded capsules in asphalt using ageing tests.

Ageing tests are a good metric to evaluate the change of asphalt properties in the field over the life of a pavement. Asphalt ageing can be simulated in the laboratory by conditioning the asphalt mix in an oven for different periods and at different temperatures [50]. The most commonly used one is a two-step method, which includes a short-term ageing and a long-term ageing. The short-term ageing is associated with the loss of volatile components and oxidation of the bitumen during asphalt mixture construction, while the long-term ageing represents the progressive oxidation of the in-place material in the field.

The standard protocol AASHTO R-30 developed within the Strategic Highways Research Programme (SHRP) [51] with some modifications was adopted in this research. The standardised method consists of curing loose mixture for 4 hours at 135°C for short-term ageing. Then the mix is compacted and conditioned for 5 days at 85°C for long-term ageing. However, in this research, the short-term oven ageing (STOA) was followed by a modified long-term oven ageing (LTOA) with lower temperature and during a prolonged period (50 °C for up to 90 days).

Table 4 shows the ageing protocol. A temperature of 50 ºC was selected as it was considered more appropriate to accomplish the research objectives (longer periods and smoother temperature, which could represent what occurs in the field).

Table 4. Ageing programme

Ageing Protocol	Curing time and temperature
Short-term ageing (STOA)	135 ºC, 4 h
Long-term ageing (LTOA)	STOA + 50 ºC, 15, 30, 45, 60, 75, 90 days

After the ageing treatment, the binder recovered (EN 12697-3) was studied to quantify changes in the asphalt binder properties before and after the LTOA ageing treatment, referred to as the ageing index. The properties examined during ageing studies were penetration (EN 1426) and softening point (EN 1427).

Results of the test can demonstrate the technical feasibility of this technology, by measuring the change in properties of the bitumen blends over time. An improvement in the penetration and softening point temperature over the values exhibited for the reference sample (with no capsules added) suggests that a rejuvenation process is taking place. It means that the rejuvenator is being released to some extent from the capsules.

3. Results and discussion

3.1. *Impregnation capacity and thermal stability*

The test was performed at a constant rate of 10 °C/min in an oxidative environment using air from ambient temperature up to 1,000 °C. The TGA sample preparation procedure for the capsules filled with rejuvenator is quite simple and it does not differ from the conventional one for other types of materials. A small representative sample of capsules of about 10 mg was put in the crucible handling box and the equipment automatically tared and weighed in using the TGA's internal balance. Examples of the thermogravimetric (TG) curves for sepiolite and vermiculite filled with rejuvenator are shown in Figure 14 and Figure 15, in which the peaks in the figures represent temperatures of combustion. The TG curve of the rejuvenator was also included in the study as a reference (Figure 13).

Asphalt rejuvenator TG (Figure 13) showed good thermal stability up to a temperature around 300 °C, a temperature high enough to guarantee its properties are maintained during the manufacturing process of asphalt mixes. Above this temperature, the rejuvenator started thermally decomposing at an increasing rate. The maximum rate of mass loss (79.33%) occurred at a temperature of 393 °C, denoting thermal decomposition of asphalt constituents. The mass loss continued to take place at a decreasing rate until 542 °C, where a mass loss of 21.03% was recorded, which was due to the combustion of the sample under oxygen. Beyond this temperature, the rate of decomposition started to drop until it reached a near zero value, where no significant mass loss took place. The entire sample was thermally degraded at the end of the temperature programme leaving no residue behind.

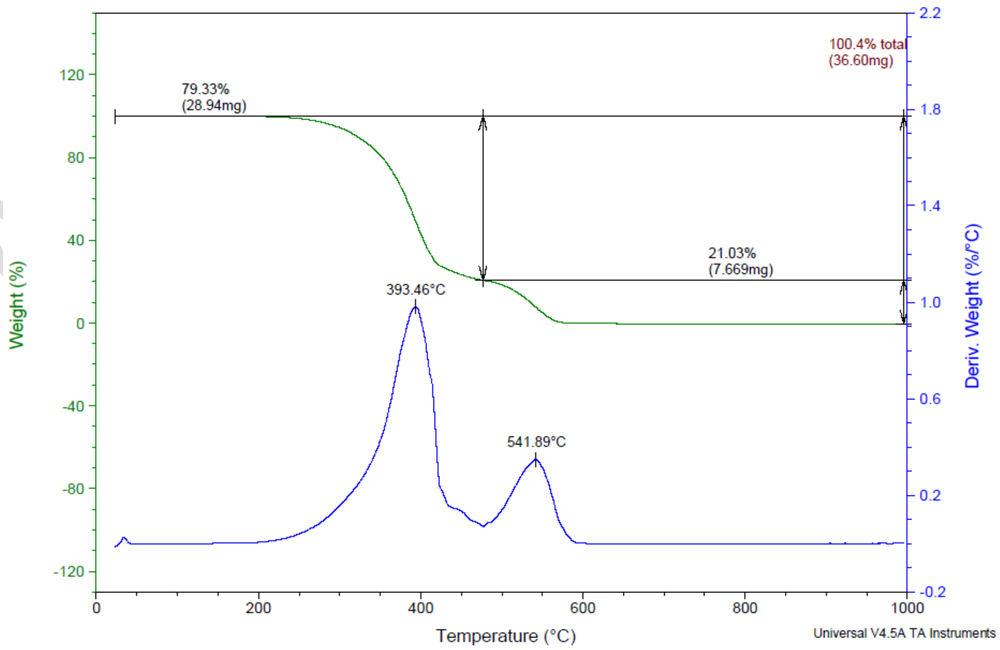


Figure 13. TG curve of asphalt rejuvenator

Given that rejuvenator is totally thermally degraded under the test conditions due to its organic nature, the percentage residue obtained from the TGA curves of sepiolite and vermiculite filled with rejuvenator represents very closely the impregnation efficiency of the method; that is, 44.40% and 78.14%, respectively in Figure 14 and Figure 15.

In the particular scenario of sepiolite capsules (Figure 14), the peaks associated with loss of water observed in Figure 5 disappeared, the two first peaks in the TG curve being an indicator of the presence of rejuvenator, as suggested by the comparison with the reference TG curve of the rejuvenator (Figure 13). The last two peaks in the curve are due to the nature of the sepiolite itself. The one at 743 °C indicates the formation of a transient amorphous phase, the other at 833 °C, showing a minimal loss of 0.80%, represents the loss of constituent water. An analysis of this data indicates that the real quantity of rejuvenator absorbed in the pores of sepiolite is around 40%. This number is the sum of the rejuvenator mass loss in the figure (27.34% and 13%).

Looking at the TG curve of vermiculite (Figure 15), it is noticeable that the peaks observed in Figure 6 corresponding to the reference vermiculite are not shown; therefore, the percentage residue in Figure 15 corresponds entirely to the presence of rejuvenator, which is 78%.

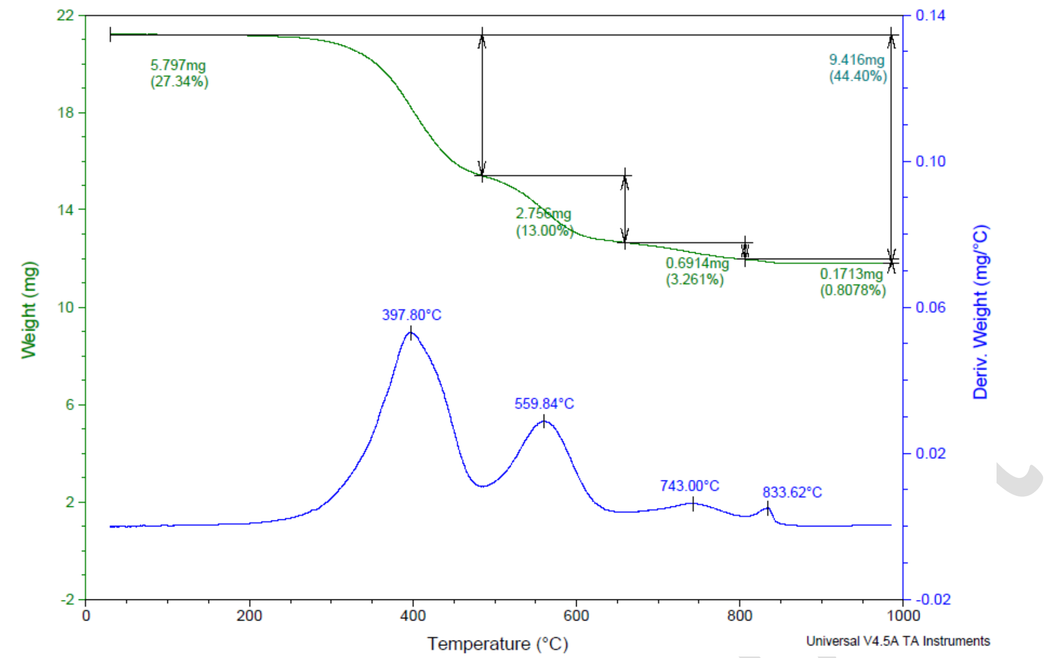


Figure 14. TG curve of sepiolite filled with rejuvenator

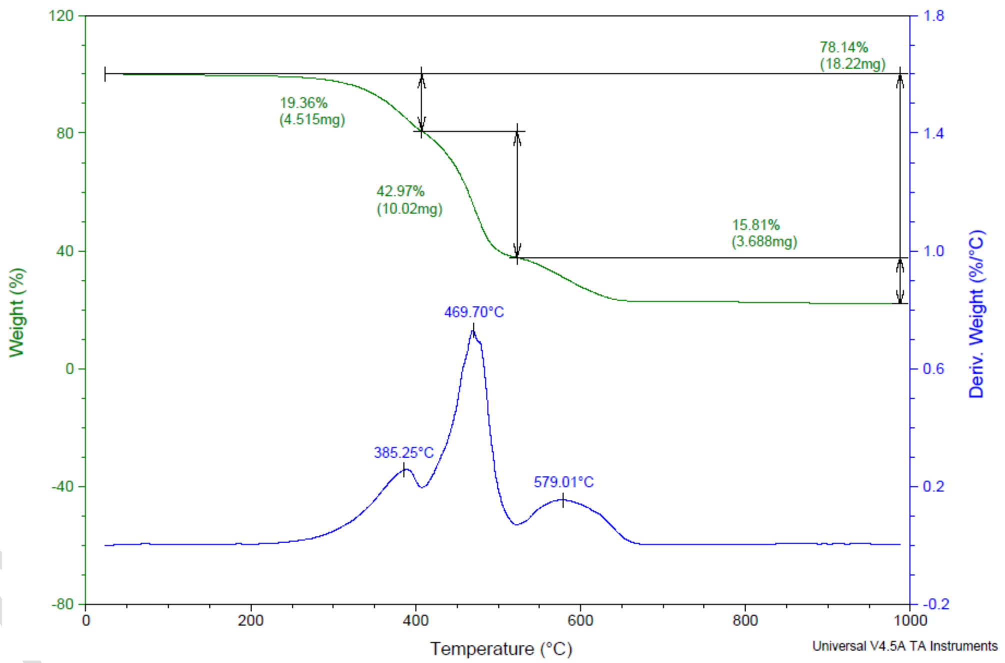


Figure 15. TG curve of vermiculite filled with rejuvenator

These data were compared with those obtained from the calcination test using a muffle furnace on 50-100 mg samples, submitted to the same test conditions: temperature was increased up to 1,000 °C at a constant rate of 10 °C/min in an atmosphere of air. The residue obtained was weighed and recorded. Results are shown in Table 5, which are really close to the ones from the thermogravimetric analysis.

Table 5. Calcination results of the samples studied

Substrate type	**Impregnation capacity, %**	**Average of Impregnation Capacity, %**	**Standard deviation, %**
Sepiolite	40.05 40.11 40.42	40.19	0.20
Vermiculite	77.94 78.16 78.00	78.04	0.11

Using vermiculite–instead of sepiolite significantly affects the absorption efficiency, from 78% wt % to 40 wt %. This difference may be due to the different specific surface area, pore diameter and morphology of the porous aggregates, as shown in the previous Materials section.

3.2. FTIR and diffusion analysis

The FTIR method was used to analyse the influence of temperature on the chemical characteristics of the capsules, taking into account the values of the indices of the carbonyl (ICO) and sulphoxide compounds (ISO), measured in the rejuvenating agent recovered from the capsules.

The recovery procedure of the rejuvenator was simple, the capsules were crushed in a mortar and immersed in dichloromethane, the solid particles were filtered out and the dichloromethane was evaporated. The recovered rejuvenator was then characterised by FTIR.

Carbonyl (ICO) and sulfoxide (ISO) indices were calculated according to equations 4 and 5, respectively. The results of those indices are reported in Table 6. Fresh rejuvenator used in the study was included for comparison purposes.

The results in Table 6 show that initially the rejuvenating agent does not contain carbonyl and sulfoxide compounds, while the values of the rejuvenator recovered from the two types of substrates do show values for both parameters, indicating that the rejuvenating agent is slightly oxidised, with the vermiculite capsules showing the highest values. The reason for this is most likely the preparation process of the capsules, especially the drying step with temperature, which took considerably longer than the used for sepiolite.

Table 6. Carbonyl and Sulfoxide Indices

	ICO	**ISO**
Fresh rejuvenator (reference)	0.000	0.007
Rejuvenator recovered from sepiolite	0.000	0.001
Rejuvenator recovered from vermiculite	0.036	0.006

Once the capsules were prepared, an analysis of the diffusion capacity of the rejuvenating agent in the bitumen when the two come into contact was performed by measuring the diffusion coefficients.

For this measurement, the FTIR with attenuated total reflectance (FTIR-ATR) was applied to monitor the diffusion of the rejuvenator from the pores of the capsules to the bitumen matrix. As this test depends largely on concentration and temperature, all the samples were prepared with the same number of capsules and the same amount of bitumen and at a temperature of 100 °C. This temperature was selected considering that diffusion is a slow occurring process and it can be accelerated with temperature.

The diffusion coefficients of all the functional groups identified in the samples, both for sepiolite and vermiculite, are shown in Figure 16 and Figure 17. Of all of them, the infrared spectral absorption band of CH2 was taken as a reference, which corresponds to those that are diffused very quickly, together with the SO2 band, corresponding to just the opposite, those that are diffused more slowly, which could indicate the end of the diffusion process. Bearing in mind that the higher the diffusion coefficient, the higher the diffusion rate, the results show that the sepiolite containing rejuvenator diffused at a slightly slower rate than the vermiculite one.

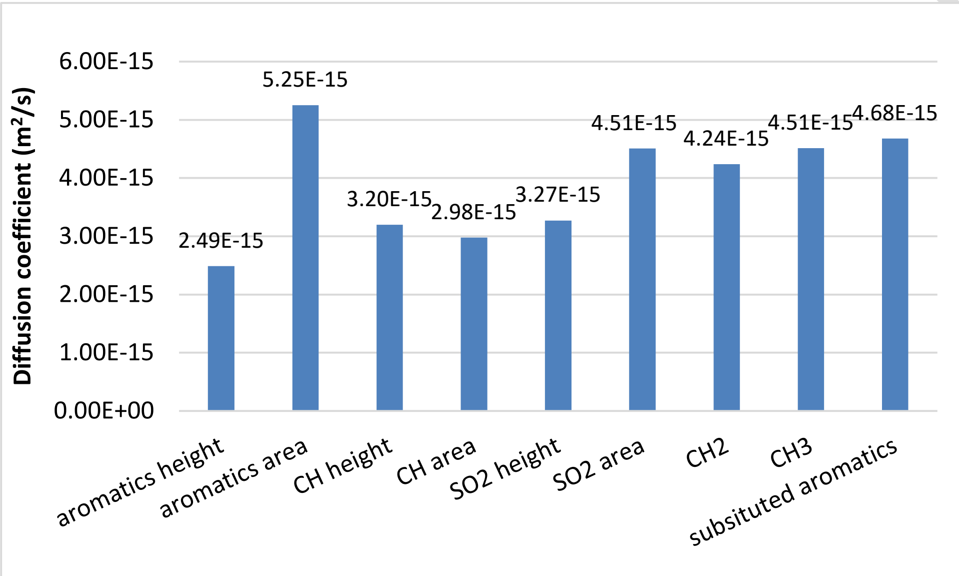


Figure 16. Diffusion coefficients of rejuvenator (from sepiolite capsules) into the bituminous matrix

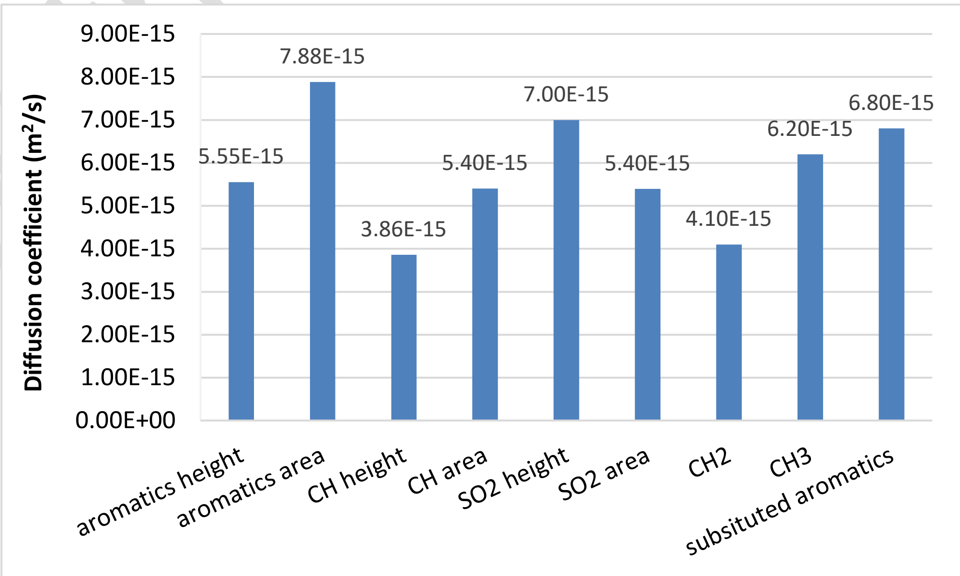
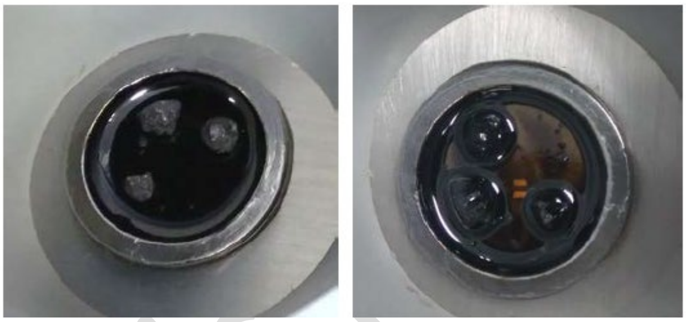


Figure 17. Diffusion coefficients rejuvenator (from vermiculites capsules) into the bituminous matrix

This test provides a good measure of the ability of the encapsulated rejuvenator to be mixed with the bitumen, reducing the negative impact of ageing over time. However, it is also noted than according to the photographs from the samples analysed before and after the test (Figure 18), the capsules containing rejuvenator work as a kind of sponge, absorbing the bitumen film that is underneath. This probably indicates that the presence of the capsules interferes in some way with the normal procedure followed for assessing diffusion between two fluids using FTIR-ATR techniques.



(a) (b)

Figure 18. Detail of the diffusion process before (a) and after (b) the test

3.3. Effect of the capsules containing rejuvenator on the mechanical properties of the asphalt mixes.

A BBTM11B asphalt mix was designed with aggregates accounting for 95% of the mix and polymer-modified binder for the remaining 5%. A known percentage of capsules, both using sepiolite and vermiculite with rejuvenator, was added to the mix and the properties in relation to air voids, water sensitivity and wheel tracking test were evaluated.

The asphalt mixes included for comparison purposes were: a reference asphalt mix (without capsules), another with rejuvenator added directly to the bitumen, representing 100% of rejuvenator release from the capsules, and finally one with empty capsules. In total, six asphalt mixes were studied. The mixes with added rejuvenator, both in the form of capsules and directly incorporated into the bitumen prior to mixing, contained approximately the same amount of rejuvenator.

The results were statistically analysed with Minitab software to determine whether the differences in the mechanical behaviour were significant. In all the cases, a 95% confidence interval (p-value 0.05) was applied. The T Student test was employed when a normal distribution of the results and homogeneity of the variances were observed, and the Mann–Whitney U test was used otherwise. In this analysis, when the significance level is lower than 0.05, it is assumed that the asphalt mixes significantly differ, and if it is higher than 0.05 there are no differences between the mixes investigated.

Figure 19 and Figure 20 show the volumetric properties of the asphalt mixes. In particular, density and air voids were the properties evaluated. A slight decrease in the densities and an increase in the air void content was noticed in the four asphalt mixes with capsules, both empty and filled with rejuvenator, due to the low density of the porous aggregates. This was less noticeable in the capsules filled with rejuvenator, since most of the pores were occupied with the rejuvenating agent. Table 7 shows the p-values of each experimental mixture compared to the reference. In this case, the differences are significant, although they are quite small. In any case, all the analysed samples are within the acceptable limits for this type of asphalt mix according to the Spanish specifications (12-18% air voids). This is the main reason why the bitumen content was set at 5% in all the asphalt mixes.

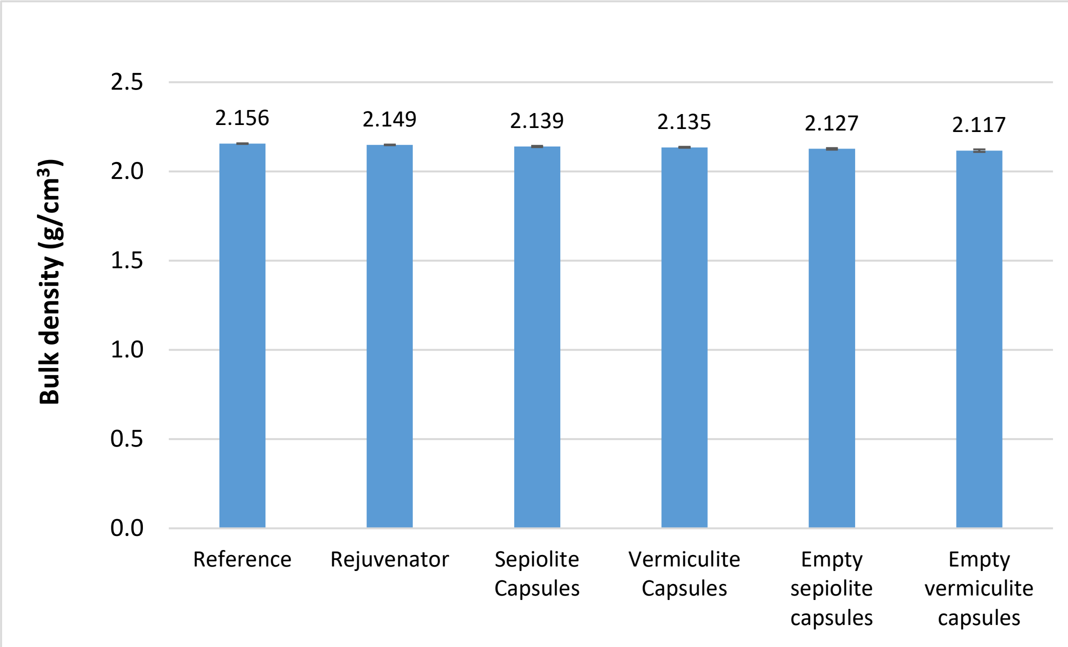


Figure 19. Bulk density results BBTM11B asphalt mixes

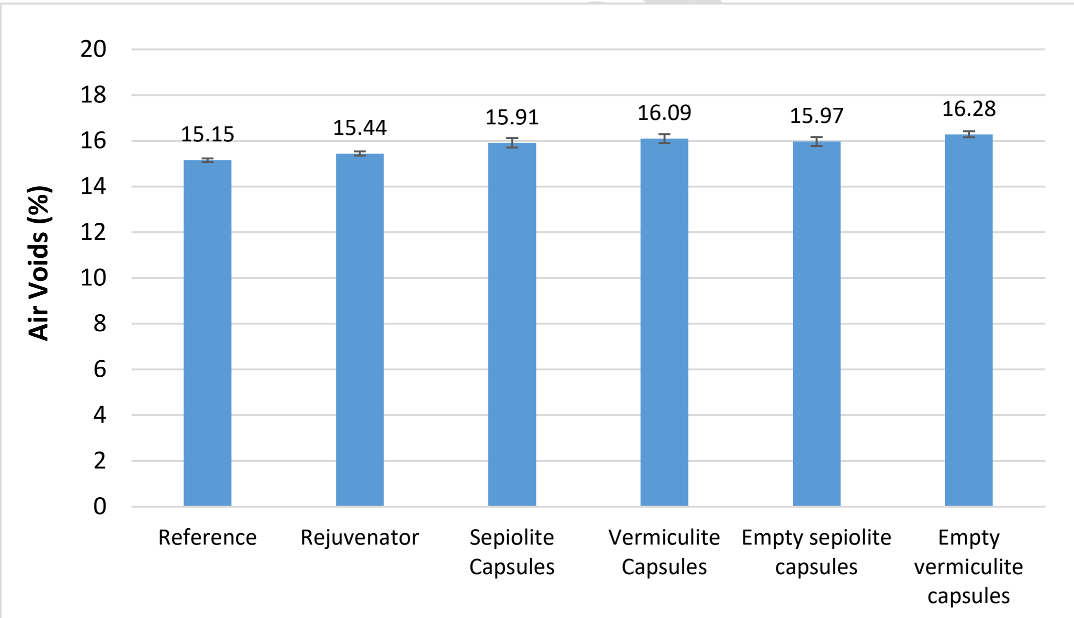


Figure 20. Air voids results BBTM1B asphalt mixes

The resistance to moisture damage was evaluated using the water sensitivity test following EN 12697-12 for the indirect tensile strength ratio (ITSR). Eight specimens were tested, 4 immersed in water at 4ºC for 72 hours and the other 4 kept in a dry environment at 20 ºC. After that, all specimens were brought to a test temperature of 15ºC for 3 hours and the indirect tensile strength was measured (EN 12697-23). The results obtained are shown in Figure 21. Figure 22 shows the water sensitivity test results expressed as the indirect tensile strength ratio.

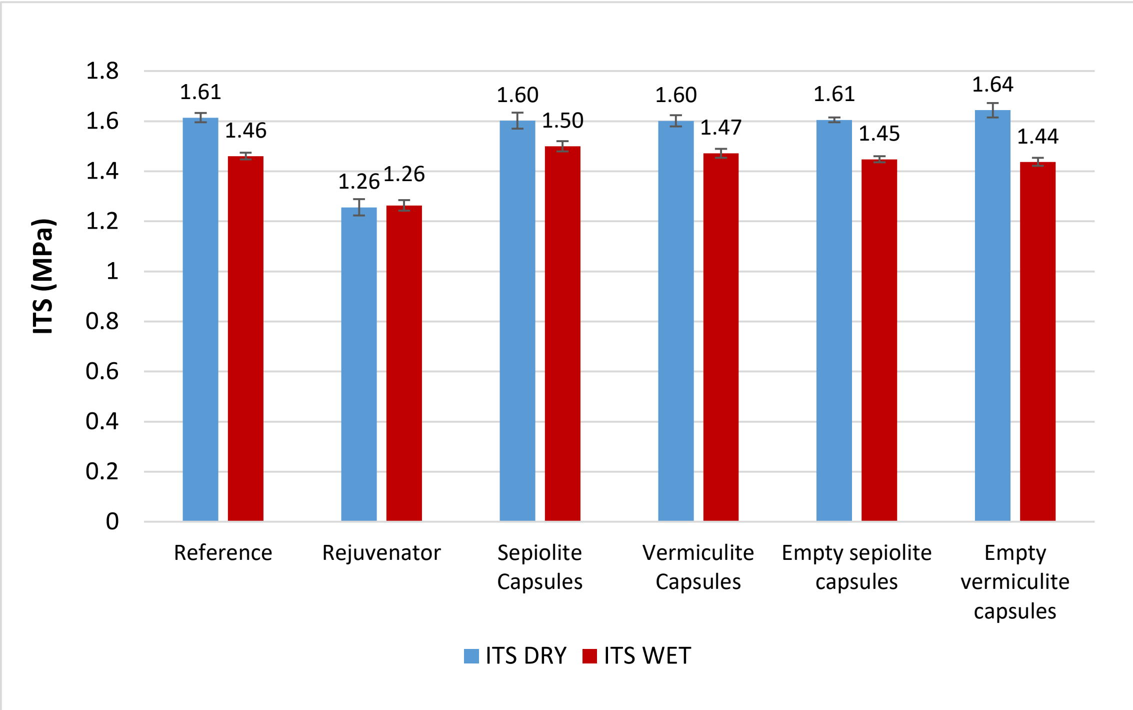


Figure 21. Indirect Tensile Strength (dry and wet) of the asphalt mixes

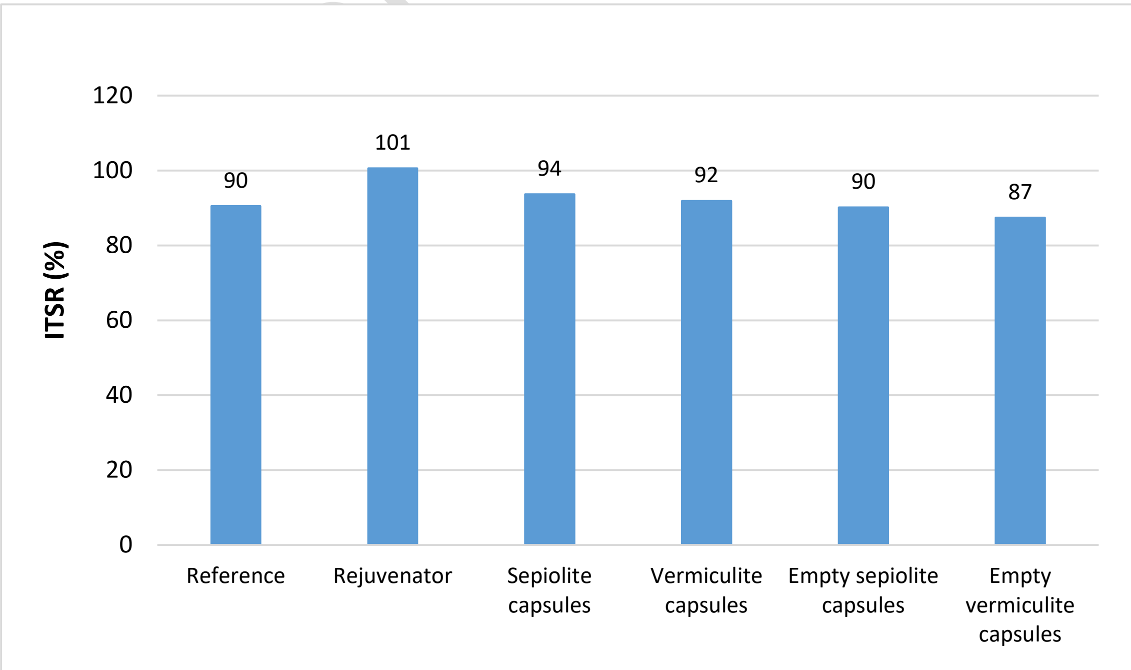


Figure 22. Water sensitivity test results

The resistance to the indirect tensile strength for all the samples, excluding the one with rejuvenator, was at the same level, both for dry and wet conditions. The cohesion for the experimental samples with the capsules filled by rejuvenator immersed in water was slightly higher than for the reference mix. In fact, the only significant difference was obtained for the mix with sepiolite capsule, showing a higher resistance (Table 7).

The ITSR values for almost all the mixtures, except for the one with empty vermiculite capsules, met the specified values of being over 90%, indicating an adequate resistance to water damage. The sample with rejuvenator exhibits the highest value as expected, as the higher the binder content, the better resistance to water damage. By comparing the ITSR of the vermiculite and sepiolite containing rejuvenator and their control samples (empty capsules), an improvement of the cohesion between binder and aggregates in the presence of water was observed.

These results indicate that the performance of the experimental mixes (with capsules filled with rejuvenator) achieved a level of performance comparable or better than the reference mix. This indicates that the capsules did not affect the properties of the asphalt in terms of water sensitivity.

The plastic deformation of the BBTM mixtures was evaluated by the wheel tracking test (EN 12697 – 22) using Procedure B, tested in air at 60°C. The results for the mean wheel tracking slope (WTS) are shown in Figure 23. It can be observed that the sample with rejuvenator added to the mix shows the highest plastic deformation. This makes sense since the rejuvenator softens the binder. In contrast, the values of the capsules with the rejuvenating agent remain at similar levels to the reference, proving that the rejuvenator is not prematurely released by the fracture of the capsules during the asphalt mix production process. This highlights the advantages of using encapsulated rejuvenator as a useful method to incorporate the additive.

An improvement in the performance of the asphalt samples with empty capsules compared with the reference mix is also shown in Figure 23. These small differences could be attributed to the small film of rejuvenator covering the capsules after the impregnation process or to the effect of the experimental particles in the mix particle size distribution. In any case, Table 7 shows that only the mix with the rejuvenator directly added is significantly different.

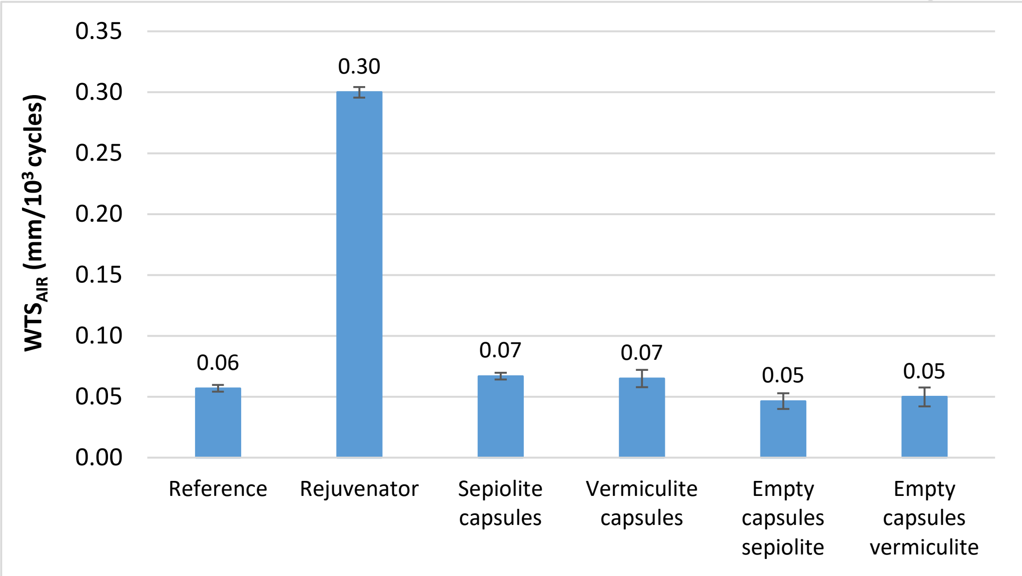


Figure 23. Wheel tracking test results

Table 7. Significances of the mechanical tests

p-value (reference)	Rejuvenator	Sepiolite Capsule	Vermiculite Capsule	Empty sepiolite capsule	Empty vermiculite capsule
Air Voids	0.005	0.005	0.005	0.005	0.005
ITS Dry	0.000	0.538	0.421	0.442	0.146
ITS Wet	0.000	0.022	0.353	0.206	0.074
Wheel tracking	0.000	0.004	0.124	0.066	0.157

Based on the results, it can be concluded that the addition of capsules with rejuvenator does not compromise the mechanical properties of the asphalt mixtures and that these capsules are able to withstand the asphalt manufacturing process. Moreover, the benefit of introducing rejuvenator using the capsules instead of adding it directly to the asphalt mix was proven, reducing therefore the risk of plastic deformations during the first years of service.

3.4. Influence of the ageing test on the recovery potential of the aged bitumen with capsules incorporated into the asphalt mix.

Ageing of bituminous binders is manifested as an increase in its penetration and reduction in its ring and ball temperature. Therefore, the penetration value at 25 °C, according to EN 1426, and softening point temperature, as stated by EN 1427, were measured on the recovered binders from the aged asphalt mixes as a first approach.

Although the extraction process with a dissolvent could slightly affect the results, there is a coherent trend when comparing the recovery of the penetration and softening temperature of the samples investigated (with capsules, with the rejuvenator directly added and the reference mixture).

Figure 24 and Figure 25 show the change in penetration and softening values after long-term ageing after different periods. In all the binders tested the penetration value increases and the softening point temperature decreases. The binder with rejuvenator (in red in Figure 24) exhibits the lowest ageing in contrast to the reference mix (in blue) which shows the lowest penetration values. The penetration of the binder recovered from the samples with the capsules, both sepiolite and vermiculite, after short periods is between those shown for samples with rejuvenator and the reference mix. As long as the ageing is more prolonged, the values approach those for the rejuvenator, being almost at the same level after 90 days of ageing.

A similar trend is observed for the softening point (Figure 25), with the difference that the values of the binder recovered from the vermiculite capsules are closer than sepiolite to the ones of the bitumen with rejuvenator. This seems to indicate that vermiculite capsules are able to release the rejuvenator more easily than sepiolite. This is in line with the observed behaviour in the diffusion test by FTIR-ATR, which revealed that vermiculite diffused at a faster rate than sepiolite.

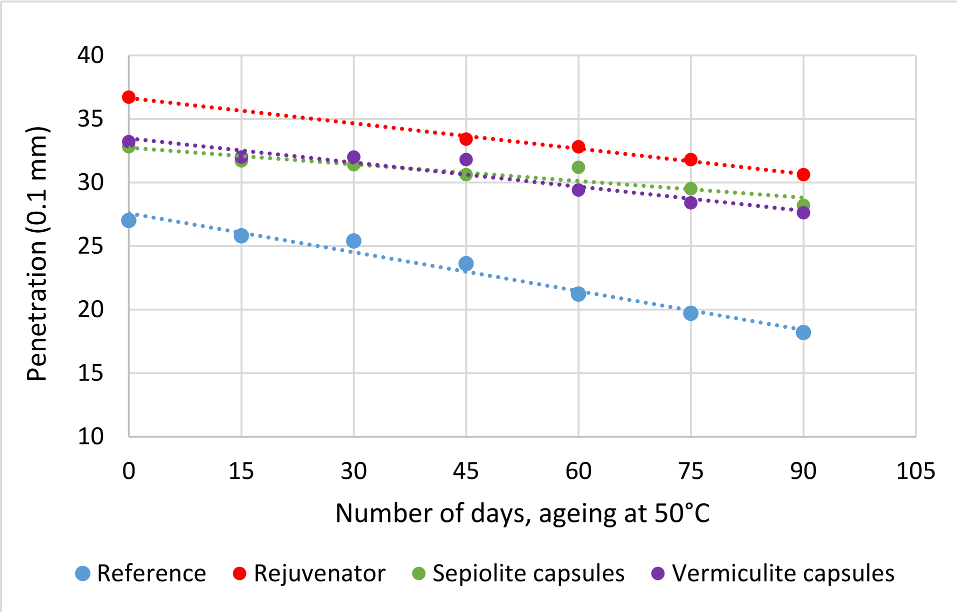


Figure 24. Penetration of the recovered binder for the asphalt mixes after long-term ageing

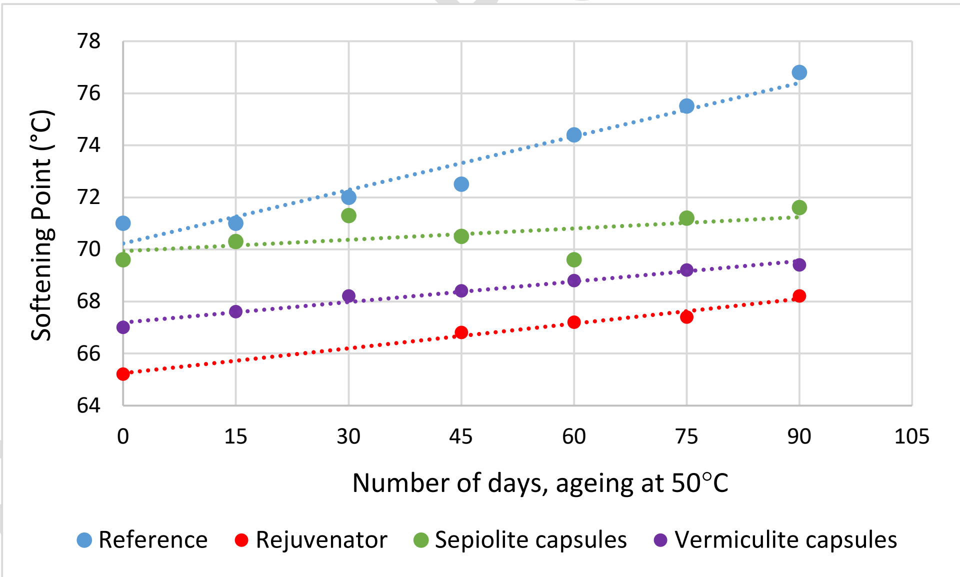


Figure 25. Softening point of the recovered binder for the asphalt mixes after long-term ageing

From Figure 24 and Figure 25 it can also be seen that after 90 days conditioning at 50 °C, in both sepiolite and vermiculite capsule some rejuvenator remained inside the capsule, as values for penetration and softening point are close, but not at the same level than those for the samples with just rejuvenator. This guarantees the rejuvenation process over time.

The change in behaviour of asphalt due to ageing was also evaluated by establishing the Ageing Index (AI). AI for a given performance parameter is defined as the ratio of the value of the performance parameter after LTOA ageing to the value of that parameter in the STOA. The IAs for penetration and softening point are reported in Table 8.

For these two parameters, the most noticeable change was in penetration. Again, binder from the recovered asphalt mix with rejuvenator shows the lowest values for penetration and the highest values for softening point. Binder from the reference mix shows the opposite trend. Values of binder recovered from the capsules are roughly equal to those with the rejuvenator.

Table 8. Ageing Indices

Parameter	Reference	Rejuvenator	Sepiolite capsules	Vermiculite capsules
Penetration	0.67	0.83	0.86	0.83
Softening Point	1.08	1.05	1.03	1.04

Results from this test reveal the potential effectiveness of the capsules developed. A change in the binder properties over time is observed in all the samples analysed, but to a lesser extent for the capsules than for the reference sample.

4. Conclusions

This study explores the potential use of porous aggregates as capsules containing rejuvenator as an effective way to restore aged binder properties. Although the promising results of this technology, complementary tests to evaluate the performance on the aged asphalt mix would be highly advisable. Based on the results the following conclusions have been obtained:

- A new type of capsules, using porous aggregates as encapsulation material and asphalt rejuvenator as a rejuvenating agent, was presented. The recommended method of capsule preparation is vacuum impregnation at 100 ºC. In this method, the rejuvenator penetrates into the pores of the aggregates releasing the air from their internal structure.

- Two different types of porous aggregates, sepiolite and vermiculite, with different particle size and morphology were studied. These aggregates have a high pore content, making them highly suitable for their use as encapsulation material.
- TGA is an effective method to quantify the amount of rejuvenator introduced into the aggregate's pores. In this method, vermiculite is more favourable than sepiolite, since the impregnation capacity of the two was 75% and 44%, respectively. This increment may be due to the differences observed in the texture and morphology of the porous aggregates. TGA analysis also proved the good thermal stability of the capsules, being resistant up to 300 °C. This temperature is high enough to guarantee the integrity of the capsules during the asphalt manufacturing process, which usually takes place below 200 ºC.
- FTIR, through an analysis of the carbonyl and sulfoxide indices, was the method used to quantify any changes in the chemical composition of the rejuvenating agent recovered from the capsules due to the temperature used in the encapsulation process. Results from this test indicate that the rejuvenator was slightly oxidised for the vermiculite and remained at similar levels as pure rejuvenator for sepiolite. FTIR was also used to evaluate the level of diffusion of the rejuvenating agent from the capsules into the bituminous matrix. Findings from this test show that the oil contained in vermiculite diffused at a faster rate than the oil contained in sepiolite. This method is a good approach to understand the releasing process of rejuvenator; however, the setup of the test by placing the capsules in contact with a film of bitumen, together with the complexity of bitumen composition, makes it difficult to study the diffusion process in

depth. Further research may be needed to better understand the diffusion rate of rejuvenator absorbed in the pores of the substrates into the bituminous matrix.

- Results for mechanical properties of the asphalt mixes reveal that the capsules survived the asphalt manufacturing process, as there were no big differences between the results shown for the mechanical tests in comparison with a reference sample with no capsules added. Moreover, the addition of a rejuvenator directly to the mix may lead to a highly deformable mix. This highlights the benefit of encapsulating the rejuvenator rather than mixing it directly in the asphalt.
- The binder recovered from the asphalt mixes with capsules showed higher penetration and lower softening point than the reference sample. In addition, the ageing index of the asphalt mix with capsules was almost at the same level as the asphalt mix with rejuvenator directly added to the asphalt mix. This demonstrates the potential of using these capsules to restore the properties of aged binder.
- Overall, the research results indicate that the capsules presented are a promising alternative to reduce the premature ageing of asphalt pavements, improving the quality of the asphalt over the service life. This process stands out both for its simplicity and for its economic feasibility.

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