Addressing durability of asphalt concrete by self-healing mechanism

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Abstract

Every year a huge amount of energy and economic resources are employed in preservation and renovation of the existing pavements. In the last years, rejuvenators are being used in road maintenance works by restoring the original properties of the aged pavement. The main problem is that once the rejuvenator is spread on the road surface to be effective it must penetrate into the pavement not only in the first centimeters. An innovation procedure to solve this problem is the addition of encapsulated rejuvenators into the asphalt mixes. Once the rejuvenator is released, it will be in contact with the bitumen around restoring the original properties of the binder and increasing the self-healing rate by closing the cracks or limiting its growth. In the present work two encapsulation methods developed by the authors are described. The first one, porous aggregates with the rejuvenator embedded were prepared; the second one polymeric shell microcapsules containing the rejuvenator were synthesized. After preparation and encapsulation of the healing agent, the capsules were embedded into the bituminous matrix. Finally, the autonomous repairing capability was validated through a variety of comparative laboratory tests. Results from this study indicate that the self-healing chemistry developed has a high potential for its use in asphalt pavements by increasing its durability.

Keywords: self-healing, rejuvenator, asphalt concrete, capsules, ageing

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1. Introduction

Road transport is part of the lifeblood of the European economy and single market. It delivers goods across Europe fast, efficiently, flexibly and cheaply. About 44% of goods transported in the EU go by road. People also travel mainly by road, with private cars accounting for 73% of passenger traffic (European Commission, 2013). Road transport is a vital economic sector in its own right, employing about 5 million people across the EU and generating close to 2% of its GDP (European Road Federation, 2012). Therefore, the aim of the European Union’s land transport policy is to promote a mobility that is efficient, safe, secure and environmentally friendly. Also it is estimated that more than 90% of the 5.2 million km of European paved roads and highways are surfaced with asphalt (EAPA, 2012). This represents a huge network that implies a significant amount of economic, human and energy resources, from which a good part is for preservation and renovation of existing pavements. In fact, 50% of the annual construction budget is estimated to be spent on rehabilitation and repair of the existing pavements in Europe (Schlangen E. et al., 2013).

During the service life of a road and before its end of life there are several degradation processes, the stiffness of asphalt concrete increases while its relaxation capacity decreases, and as consequence the binder becomes more brittle causing the development of micro-cracks and in a near future the cracking on the interface between aggregates and binder occurs (Branthaver J.F., 1993). These typical asphalt pavement distresses are the results of the combination of oxidation and traffic loads. The oxidation process starts during the hot-mix process and continues through its service life. During the oxidative aging of the asphalt binder the “solid” part increases (asphaltenes) and the “liquid” or volatile phase decreases (maltenes), so the ratio of asphaltenes/maltenes is reduced, resulting in a dry and brittle pavement (Lesueur, D., 2009; Zhang F. et al., 2011). This aged pavement will lead to pavement failures, such as reflection cracking and surface raveling. These problems increase the expense of renovation and preservation of bituminous pavements and reduce critical parameters such as safety (Asphalt Institute, 2013). Therefore structures that show higher durability and have longer “maintenance free” performance with low repair costs need to be investigated.

In order to prevent this type of pavement failure, numerous methods are being employed for asphalt pavement preservation, including the use of rejuvenator emulsions, fog seals and several different thin overlay technologies (Boyer, R.E., 2000). Only the addition of rejuvenator partially recovers the original properties of the pavements by restoring the original asphaltenes/maltenes ratio to its original balance and reconstituting the binder’s chemical composition (Shen J., et al., 2007; Karlsson D., et al., 2006). The problem is that this type of treatment is superficial, only the first centimetres from the surface are affected, so that the layers below could be equally damaged being the origin of future failures. To address current limitations, embedded capsules containing asphalt rejuvenator are proposed as a promising technique to apply rejuvenator in asphalt mixes in an optimum and efficient way to compensate ageing of asphalt concrete.
2. Background

The concept of self-healing materials is related to their inherent ability to partially reverse damage such as small-crack formation that might have occurred during its service life. It is known that asphalt is a self-healing material by itself, but it only works if there is no traffic circulation. Also it has some limitations: it is a slow process at ambient temperature and non-effective if the cracks are significant (Qiu J., 2012; Garcia A., 2012). The application of microcapsules containing rejuvenator derives from the success observed from some polymer self-healing materials. Encapsulation of active substances as adhesives or solvents is of particular interest for self-healing materials, coatings and many other construction applications (Garcia, A. et al., 2010a; Blaiszka B.J., 2009). The use of embedded capsules, containing asphalt rejuvenator as component of the asphalt mix, is a promising new technique to provide pavements self-healing properties has been developed in the last few years. The main objective is to prevent ageing and oxidation of asphalt mixes in order to increase the lifespan of asphalt pavements and minimise rehabilitation works. Thus, the introduction of these materials into the asphalt mix would avoid operations associated with pavement recycling and could be a remarkable innovation.

Asphalt is a viscoelastic material where two phases can be considered: a phase "liquid" or volatile, formed by maltenes and a “solid” phase composed by asphaltenes. Therefore, theoretically, when a crack appears is closed by itself, but it would do it faster if the "liquid part" of bitumen increases. That can be done by mixing with less dense oil, known as rejuvenator (Garcia A. et al., 2010b). Anyway the inclusion of capsules that release rejuvenator will reduce cracking due to a more balanced maltenes/asphaltenes ratio. Several methods of encapsulating asphalt rejuvenator in microcapsules have been developed in recent studies; some of the more successful were carried out by TUDelf University. These methods are different each other but all of them aim to obtain microcapsules with high thermal stability and high mechanical strength able to withstand the high temperatures and mixing stress of the asphalt. Garcia, A. et al. (2010a and 2010c) reported a method to prepare rejuvenator capsules by using maltenes encapsulated in very porous sand and cover by a composite of resin and fine sand. Su, J.-F. et al. (2012 and 2013) have developed a method to synthetize microcapsules containing rejuvenator by in-situ polymerization using methanol-melamine-formaldehyde (MMF) prepolymer.

Based on the previous studies, ACCIONA in partnership with REPSOL, LAIMAT and TOLSA, has developed more advanced capsules with controlled release mechanism for the self-healing of the asphalt mixes. This work was supported by the Centre for Industrial Development (CDTI) of the Spanish Government within the program supporting the Strategic National Consortiums for Technical Investigation (CENIT) through the development of the TRAINER Project, “Development of a new technology for autonomous, intelligent self-healing of materials”.

3. Test and Results

3.1. Study Approach

The overall aim of this study is the demonstration of the self-healing ability of asphalt mixes with embedded capsules containing rejuvenator in order to increase service life and prevent pavement distresses. Throughout the study, many factors have been evaluated from the encapsulation methods to its final self-healing evaluation.

The study has been divided in four main steps:

1. Development of encapsulation methods for two different types of capsules (porous and polymeric) containing rejuvenator as healing agent.
2. Characterization of the capsules obtained where the main physical and chemical properties has been evaluated.
3. Evaluation of the feasibility of the capsules incorporation into the asphalt mix and determination of its resistance to the manufacturing process of asphalt mixes.
4. Study of the mechanisms for the release of the rejuvenator and evaluation of the self-healing ability.
3.2. Materials used in the investigation

Conventional binder, synthetic binder and rejuvenator, mainly composed of maltenes, were provided by Repsol. Different materials for the formation of the capsule shell were used. Porous aggregate, specifically sepiolite, with different particle size varying from 38 μm up to 6 mm, were supplied by Tolsa. Commercial cellulosic (CE) and polymer (C) used for the formation of the polymeric shell, were provided by Laimat. Aggregates from different origin: limestone, silica, porphyry and andesite, were used for the design of asphalt mixes.

3.3. Experimental results

3.3.1 Encapsulation Methods

3.3.1.1. Polymeric Shell

Different materials were selected for the formation of the microcapsule shell based on the required application. The encapsulating agents studied were: Cellulosic (CE) with high degradation temperatures (about 220 °C), impact strength, flexible, tough and insoluble in aliphatic hydrocarbons and water, and; polymer (C) with thermal stability up to 200 °C. Emulsified and solvent evaporation for CE and C, respectively, were the encapsulation techniques selected taking into account the encapsulating material, the active substance, the functionality of the microcapsules in the matrix in which they are incorporated, the ratio encapsulant-active substance, the final properties of the microcapsules (size, density, dry solid, solid dispersion, ...), and the release mechanism (mechanical action, exposure to environmental influences, ...) etc. The emulsifier was chosen using the HLB (Hydrophyle-Lipophyle Balance). After selecting the emulsifier suitable according to the active substance to be emulsified and the emulsion type to obtain: W/O or O/W or multi emulsion W/O/W, where rejuvenator microcapsules (O) are formed brown droplets into the encapsulant solution (W) Fig. 1.

![Fig. 1. (a) Influence of emulsifier used; (b) microscopic image of O/W emulsion.](image)

Some problems related to the drying process of the CE microencapsulation were observed. So that, C microencapsulation was selected as the most promising material for the formation of the shell achieving a content of rejuvenator of more than 80 %.

3.3.1.2. Porous Aggregate

An impregnation method of rejuvenator in porous aggregates (sepiolites) has been developed. This method consists of a vacuum impregnation process in which the rejuvenator penetrates into the sepiolite porous releasing the air of its internal structure. The method and impregnation system, as well as the capsules obtained are described in Fig. 2.

Once the process finished, the excess rejuvenator was removed by filtration and dried in an oven until all the rejuvenator in excess was released. By using this method of preparation of the capsules, percentages of approximately 40 % of rejuvenator were achieved.
3.3.2 Characterization

3.3.2.1 Polymeric microcapsules

Polymeric capsules containing rejuvenator were characterized and compared with the reference (empty capsules). Particle size and morphology was determined by optic microscopy. A slight increase in particle size in those containing rejuvenator (1-1.3 mm) compared to those empty (0.8-1 mm) was observed. Thermal stability was determined by Differential Scanning Calorimetry (DSC) and thermogravimetry analysis (TGA), Fig. 3 (a, b). Results show that capsules are stable up to 220 °C. Also, capsules filled with rejuvenator show slightly more thermal resistance. In order to simulate the working temperatures of the asphalt mixes manufacture process the microcapsules were subjected to a heating slope of 5°C/min until 180 °C in an air atmosphere, after that they were kept at the same temperature (isothermal) for 4 hours, Fig. 3 (c). Along the test a decrease of 10 % in total mass was recorded, although when temperature was maintained for 4 h at 180 °C, a 5 % of mass loss was observed.

Compression tests have been performed on the capsules using an IR press in order to determine the shell resistance. Loads from 2.5 to 15 tons were applied for 2 minutes. Visual inspections by using an optical microscopy were carried out. As it can be seen in Fig. 4 empty microcapsules are slightly more resistance to compression compared to those containing rejuvenator. Also, at low loads capsules can be compressed without suffering any damage. As the load applied increased part of the rejuvenator is released; however even after applying 15 tons of loads some rejuvenator still remained. Based on the temperature and shell resistance results, it can be concluded that the synthesized polymeric capsules withstand the high temperatures that are necessary for the manufacturing process of the asphalt mixes.

Fig. 3. (a) DSC; (b) TG curves for the capsules studied A) empty capsules B) with rejuvenator; (c) TGA Isotherm at 180 °C 4 h.

Fig. 4. Optical microscopy of the shell of: (a) empty capsules; (b) capsules with rejuvenator. (Tons of load in an IR press a) 2,5 t, b) 5 t, c) 10 t y d) 15 t).
3.3.2.2 Porous aggregates

Thermogravimetry analysis were carried out in an oxygen atmosphere to quantify the percentage of rejuvenator that was adsorbed into the pores of the sepiolite. Sepiolites with different particle size were evaluated: sepiolite A -≤ 4 mm; sepiolite B – 600-250 μm ; sepiolite C – porous sand, Table 1.

| Sepiolite | % Impregnation |
|-----------|----------------|
| A         | 42             |
| B         | 40             |
| C         | 45             |

Following the same procedure than the performed for the polymeric capsules, but increasing the isothermal time, TGA at 180 °C isothermal temperature for 72 hours was carried out in air atmosphere in order to evaluate if they are feasible to withstand high production temperatures. An approximately mass loss of 3 % was observed, which could be linked to the presence of water. Based on the above results it can be concluded that the synthesized capsules resist the high temperatures that are necessary for the manufacturing process of the asphalt mixes.

3.3.3. Incorporation of the capsules into the asphalt mixes.

In this section the resistance of the capsules when incorporated in asphalt mixes was evaluated, as well as, their final properties in two types of asphalt mixes: Very Dense Graded Asphalt Mixes and AC16SurfS 50/70.

3.3.3.1. Very Dense Graded Asphalt Mixes

In order to determine if the rejuvenator releases during the manufacturing process of asphalt mix (mixing process with aggregates and the compaction process), dense graded asphalt Marshall Specimens were made. The Marshall specimens were produced according to the standard UNE-EN 12697-30 and compacted with 75 blows per face. The specimens were composed of 1200 g of asphalt mixes, where the 95 % corresponded to 0/6 limestone aggregates and the 5 % corresponded to synthetic binder. Also, 1 % w/w of capsules was added. Synthetic binder is a light brown binder that allowed analyzing visually the release of rejuvenator during mixing and compaction process. Apparently after the compaction process, it was observed that the capsules of the compacted faces, Fig. 5 (a, b) that have been in contact with the Marshall hammer were slightly deformed; however no release of the rejuvenator was observed. In a second step, the specimens were broken by indirect tensile according to the standard UNE-EN 12697-23, that allowed evaluating them internally and therefore the condition of the capsules. After visual inspection of the core of the specimens, no deformation was detected, Fig. 5 (c).

Duplicate specimens were submitted to a cyclic compression test according to the standard UNE-EN 12697-25 and then broken by indirect tensile (UNE-EN 12697-23). The objective of this study was the evaluation of the condition of the capsules in the core of the asphalt mixes when they were submitted to axial loads. The fluency curves are showed in the Fig. 5 (d, e).

![Fig. 5. (a) Reference very dense grade specimens; (b) 1% Capsules very dense grade specimens; (c) core; (d) Fluency curves; (e) core specimens submitted at maximum load.](image-url)
No differences could be seen after the cyclic compression test between the specimens with capsules and the reference samples. It can be concluded that all the capsules developed were designed to resist working conditions: high production temperatures (170-180ºC), the mixing process with aggregates and the compaction process.

3.3.3.2. AC16SurfS 50/70

AC16SurfS was designed with limestone, silica and andesite aggregates. 4.9% of conventional bitumen 50/70 was used. Their particle size composition is presented in Table 2. Capsules designed were added to the mix by 1% w/w. Marshall specimens were produced according to the standard UNE-EN 12697-30 and compacted with 75 blows per face or 50 blows per face depending on the test carried out.

Table 2. Grading curve of the asphalt mix AC16SurfS 50/70

| Sieve mm | % passing |
|----------|-----------|
| 2        | 100       |
| 22       | 100       |
| 16       | 95        |
| 8        | 67.5      |
| 4        | 42.5      |
| 2        | 31        |
| 0.5      | 16        |
| 0.25     | 11        |
| 0.063    | 5         |

The mechanical tests proposed were: determination of the water sensitivity (UNE-EN 12697-12) and stiffness modulus (UNE-EN 12697-26). Results are shown in Table 3. As it can be seen the addition of capsules to asphalt mixes has no significant influence in the final properties of the asphalt mixes when compared with the reference.

Table 3. Water sensitivity and stiffness modulus results.

| Water sensitivity (%) | Stiffness (MPa) |
|-----------------------|-----------------|
| AC16SurfS             | 93.3            |
| Polymeric capsules    | 87.1            |
| Porous aggregates caps.| 85.3            |
|                       | 6.398           |
|                       | 5.008           |
|                       | 5.163           |

3.3.4. Releasing test and evaluation of self-healing ability

3.3.4.1. Diffusion tests

Fourier Transform Infrared Spectroscopy by Attenuated Total Reflectance (FTIR-ATR) was employed to monitor bitumen rejuvenator diffusion through the capsule shell. With this test, the coefficient of diffusion between the rejuvenator and bitumen through the shell of the capsule can be calculated (Contreras V., et. al., 2012). FTIR-ATR measurements carried out at 100 ºC showed that the rejuvenator diffuses through the shell of the capsule in both porous aggregates and polymeric microcapsules. It should be noted that in the case of polymeric microcapsules the diffusion showed a very rapid initial step due to the remaining rejuvenator content over the shell, then it experienced a stabilization over the measured period of time, Fig. 6 (a). In order to minimize the short-term rejuvenator release and the initial diffusion rate of the polymeric microcapsules, a new synthesis of the polymeric shell may be necessary. The diffusion rate for the porous aggregates capsules showed a more homogenous behaviour as it shown in Fig. 6 (b). This confirms that the rejuvenator will be released in both mechanisms making feasible later the self-healing effect.
3.3.4.2. Ageing Tests

To determine the influence of ageing in both designed capsules, two studies were carried out at binder and asphalt mix level. In a first step, conventional bitumen and bitumen mixed with capsules containing rejuvenator was exposed to a short-term ageing test, RTFOT (UNE-EN 12607-1) and long-term ageing test, RTFOT+PAV (UNE EN 14769). Once the ageing tests were finished, the basic properties of the binders, such as penetration, softening point, viscosity, Fraass breaking point and SARA (saturates, aromatics, resins and asphaltenes) column chromatography, were analysed (Table 4, Table 5). The following tables show the results achieved, where samples 1, 2 and 3 correspond to 50/70 bitumen, 50/70 bitumen (80%) + Rejuvenator (20%) and 50/70 bitumen (78%) + Polymeric microcapsules (22%) respectively. Acronyms UA, STA and LTA correspond to Unaged, Short-Term Ageing and Long-Term Ageing. The obtained results showed that the rejuvenator was released from both porous aggregates and microcapsules mostly during long term ageing. The penetration and Ring&Ball values showed common results after an ageing process (decrease of penetration grade and increasing of the softening point), while Fraass values remained mostly constant. The SARA analysis also validated these results as the original asphaltenes/maltenes ratio was partially restored, which shows that the binder’s chemical composition was mostly recovered. With the sepiolites was impossible to obtain any valid results due to the big influence on bitumen rheology.

Table 4. Penetration, Ring&Ball, Penetration Index and Fraass results.

| Sample | Penetration (dm) | Ring&Ball (ºC) | Penetration Index | Fraass (ºC) |
|--------|-----------------|----------------|------------------|-------------|
|        | UA   | STA | LTA | UA   | STA | LTA | UA   | STA | LTA | UA   | STA | LTA |
| 1      | 59   | 34  | 17  | 50.4 | 52.2 | 67.8 | -0.7 | -0.2 | 0.2  | -9   | -10 | -9  |
| 2      | 208  | 116 | 58  | 38.6 | 43.4 | 51.8 | -0.5 | -0.9 | -0.4 | -14  | -12 | -12 |
| 3      | 77   | 48  | 32  | 50.6 | 56.1 | 62.0 | 0    | 0.1  | 0.4  | -9   | -10 | -10 |

Table 5. SARA column chromatography results.

| Sample | Asphaltenes | Saturates | Naph./Aromatics | Polar/Aromatics |
|--------|-------------|-----------|-----------------|-----------------|
|        | UA   | STA | LTA | UA   | STA | LTA | UA   | STA | LTA | UA   | STA | LTA |
| 1      | 16.8 | 18.9 | 21.8 | 7.3  | 7.9  | 9.3  | 41.1 | 39.4 | 35.4 | 34.8 | 33.8 | 33.4 |
| 2      | 13.4 | 16.2 | 19.6 | 7.6  | 8.1  | 8.0  | 47.9 | 48.0 | 41.7 | 31.2 | 27.7 | 30.7 |
| 3      | 15.3 | 17.1 | 17.5 | 8.9  | 9.0  | 13.4 | 39.4 | 43.2 | 42.9 | 36.5 | 30.7 | 26.2 |

In a second step, a discontinuous asphalt mix for very thin layers, named as BBTM 11B, was designed with porphyry and silica aggregates. 5 % of polymer modified bitumen PMB 45-80/60 was used. Their particle size composition is presented in Table 6. The total amount of capsules, both porous aggregates and polymeric microcapsules, added to the mix were an equivalent of adding 20 % of rejuvenator in relation to the bitumen content. The ageing method proposed was the AASHTO R 30, which consisted on a combination of short and long-term ageing. For short-term ageing the mix was prepared in a mixer and placed in a loose state on tray in a 25 mm thick
layer. The tray was kept in a draft oven at 135 °C for 4 hours and during that time the mix was mixed four times by hand. After that, the mix was compacted by using a gyratory compactor (UNE-EN 12697-31) with 200 cycles. Short-term aged specimens were used later for long-term ageing procedure. For long-term ageing, the specimens were kept in a draft oven at 85 °C for five days. After this process the specimens were cooled down for 16 hours. Reference samples (with no ageing process) were also produced in a gyratory compactor with 200 cycles for comparison. Water sensitivity (UNE-EN 12697-12) and stiffness modulus (UNE-EN 12697-26) tests were carried out in all the samples. Results are shown in Table 7.

Table 6. Grading curve of the asphalt mix of BBTM 11B

| % passing | BBTM 11B |
|-----------|----------|
| 32        | 100      |
| 22        | 100      |
| 16        | 100      |
| 8         | 97       |
| 4         | 66,1     |
| 2         | 23,8     |
| 0.5       | 17       |
| 0.25      | 10,5     |
| 0.063     | 5,3      |

Table 7. Water sensitivity and stiffness modulus results

|                       | Water sensitivity (%) | Stiffness (MPa) |
|-----------------------|-----------------------|-----------------|
| Reference             | 86.88                 | 2.736           |
| Reference Aged        | 98.18                 | 3.398           |
| Porous Aggregates     | 87.71                 | 2.646           |
| Porous Aggregates Aged| 92.76                 | 2.823           |
| Polymeric Microcapsules| 94.6                  | 0.584           |
| Polymeric Microcapsules Aged | 95.9              | 1.018           |

From the above results it can be concluded that mechanical properties in unaged samples were mainly conserved for porous aggregates specimens, while for long-term ageing procedure stiffness modulus decreased and water sensitivity increased, most probably due to the release of the rejuvenator. These conclusions can be confirmed in Fig. 7, where samples with porous aggregates capsules were broken by indirect tensile test and then examined under UV light in order to evaluate visually the release of rejuvenator. These specimens were compared with those produced with the same mix design (BBTM11B) but adding 20 % of rejuvenator directly to the mix. It allowed identifying clearly the rejuvenator from the other components of the asphalt mix (see rejuvenator in green-brown color, Fig. 7 b, d). In the case of polymeric microcapsules, it should be noted that the stiffness results were very low due to the major part of rejuvenator has been released during mixing and compaction process.

![Fig. 7. Specimens containing porous aggregates capsules under UV light. (a) reference unaged; (b) reference with rejuvenator; (c) capsules unaged; (d) capsules aged.](image-url)
4. Conclusions

Main conclusions of the study are presented below:

- Embedded capsules containing asphalt rejuvenator are proposed as a promising technique to apply rejuvenator in asphalt mixes in an optimum and efficient way to compensate ageing of asphalt concrete.
- Two encapsulation methods – porous aggregate and polymeric capsule shell - were successfully developed and designed to resist asphalt mixes working conditions: high production temperatures (170-180ºC), the mixing process with aggregates and the compaction process.
- Percentages of impregnation of 40% for the porous aggregates capsules and more than 80% for the polymeric shell capsules were achieved.
- The incorporation of the capsules into the asphalt mixes doesn’t have influence in the final properties of the developed mixes.
- According to the results the developed microcapsules can release their active agent by both ways: in response to a stimulus (such as mechanical damage or through a controlled released process) and by diffusion.
- Ageing tests confirm that the rejuvenator can be released when exposed to long-term ageing.
- Bitumen rejuvenator diffusion tests show that the rejuvenator is released from the capsule shell along the time. Extrapolation to quantify the time that is needed for the release of the rejuvenator when capsules are exposed under real conditions should be further studied.

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