Journal of Hazardous Materials 184 (2010) 603–611

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Preparation of capsules containing rejuvenators for their use in asphalt concrete

Álvaro García[a,*], Erik Schlangen[a], Martin van de Ven[b], Guadalupe Sierra-Beltrán[a]

[a] Delft University of Technology, Faculty of Civil Engineering and Geosciences, Micromechanics Laboratory (MICROLAB), Stevinweg 1, 2628 CN Delft, The Netherlands
[b] Delft University of Technology, Faculty of Civil Engineering and Geosciences, Road and Railway Engineering, Stevinweg 1, 2628 CN Delft, The Netherlands

ARTICLE INFO

Article history:
Received 8 January 2010
Received in revised form 29 July 2010
Accepted 7 August 2010
Available online 26 August 2010

Keywords:
Asphalt concrete
Rejuvenators
Capsules
Ageing

ABSTRACT

Every year, there is a demand of more than 110 million metric tons of asphalt all around the world. This represents a huge amount of money and energy, from which a good part is for the preservation and renovation of the existing pavements. The problem of asphalt is that it oxidizes with time and therefore its beneficial properties disappear. Traditionally, rejuvenators spread in the road surface, are used to restore the original properties of the pavement. The problem is that, for a rejuvenator to be successful, it must penetrate the pavement surface. Furthermore, application of a rejuvenator will reduce the skid resistance of the pavement and, besides, rejuvenators have many aromatic compounds that can be harmful for the environment. To solve these problems this paper introduces a new concept in road construction: encapsulated rejuvenators. The basic principle is that when the stress in capsules embedded in the asphalt reaches a certain threshold value, the capsules break and some rejuvenator is released, restoring the original properties of the pavement. This paper will show how to prepare such capsules and how to determine their characteristics. This is one of the first steps towards intelligent pavements.

1. Introduction

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 °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 [1]. This mainly happens as a result of oxidation, which is the chemical reaction of the hydrocarbon compounds of bitumen with oxygen [2]. 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) [3]. Liu et al. [4] 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 [5].

Numerous methods are being employed for asphalt pavement preservation, including rejuvenator emulsions, fog seals, and several different thin overlay technologies [6]. Only the first method, rejuvenators, partially restores the original properties of the pavement [7]. Karlsson and Isacsson [7] made a distinction between softening agents and rejuvenating agents. Softening agents are used to lower the viscosity of aged bitumen. Examples of softening agents include asphalt flux oil, lube stock and slurry oil. Rejuvenating agents, on the other hand, have the purpose of reconstituting the binder's chemical composition [8] and consist of lubricating and extender oils containing a high proportion of maltene constituents. The most important goal of rejuvenator products is to restore the asphaltenes/maltenes ratio. In general, rejuvenating agents should be highly aromatic, and if so, both hardening susceptibility and temperature susceptibility are generally improved [9]. They should be composed in such a way that they increase the peptizing power of the maltene phase [10].

Additionally, 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 [11], 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%. Fur-

* Corresponding author. Tel.: +31 15 2782774.
E-mail addresses: a.garciahernandez@tudelft.nl, alvarogarcia007@hotmail.com (Á. García).

0304-3894/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2010.08.078

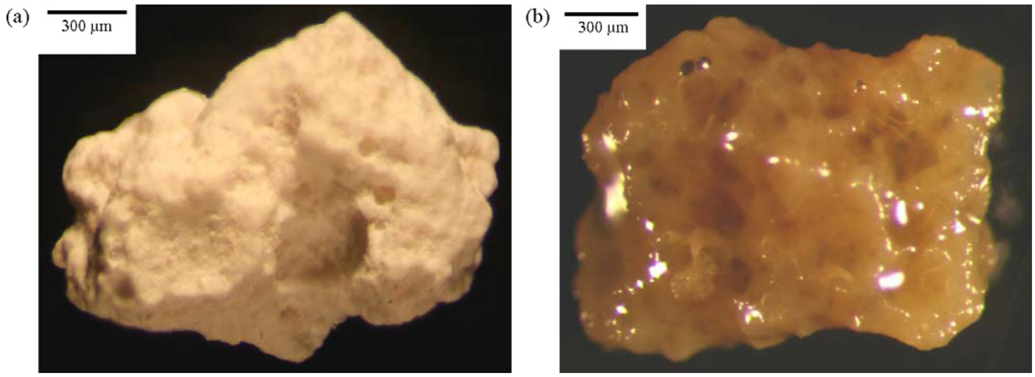


Fig. 1. Optical micrograph of the core materials of the capsules: (a) porous stone used; (b) porous stone with the rejuvenators embedded.

thermore, 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 paper 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 [11–15]. Arshady [15] 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 [16,17], hardeners [18] or solvents [19] is of particular interest for self-healing materials [20–24], coatings [25] and many other industrial applications such as capsular adhesives [18] and protection of catalysis [26]. 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.

Before writing this paper, urea-formaldehyde [17] and melamine-formaldehyde [27] microcapsules containing rejuvenators with an average diameter of 15 μm were made and mixed in asphalt concrete. During the mixing process it became clear that these capsules were not strong enough and therefore preliminary released the rejuvenator into the asphalt concrete mixture. For this reason it was decided to make capsules comprising a hard core made of a porous stone in which the rejuvenators are embedded, surrounded by a hard, impermeable shell. It is assumed that the porous stone gives a higher resistance, by acting as a skeleton for the capsule. 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. Materials and methods

2.1. 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 [28]. The porous sand is shown in Fig. 1(a); the porous sand with the absorbed rejuvenator is shown in Fig. 1(b). 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 10–20 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: Some capsules were introduced in water to see what happened. In these cases, it could be observed that, although the shell was much harder, the oil came out of the capsules. This can happen because of the volumetric changes of this material during the hydration process. The densities for all the materials comprising the capsules are shown in Table 1.

2.2. Size distributions

To investigate the size of the capsules, more than 100 capsules and more than 100 grains of porous sand 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 Fig. 2.

2.3. Encapsulation procedure

Capsules containing rejuvenators have been prepared by a new method developed by the authors (Fig. 3). First, the porous sand was sieved to obtain a fraction between 1 and 1.7 mm (Fig. 4(a)). 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.

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

	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

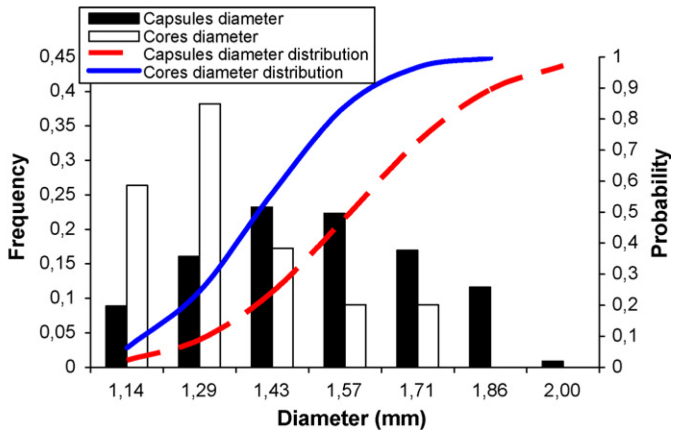


Fig. 2. Capsule sizes distribution.

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 h 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 min 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 shaken by hand to homogenize it (Fig. 1(b)).

To produce the shell, the epoxy and the sand with rejuvenators inside the grains were mixed by hand in a weight ratio 1:2.5 until all soil grains were uniformly covered by a layer of epoxy (Fig. 4(b)). 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 (Fig. 4(c)) 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 (Fig. 4(d)) (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 (Fig. 4(e)). 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 h at 35 °C after which, some more epoxy in a weight ratio 1:20 (1 g of epoxy for each 20 g of capsules) was added to cover the capsules surface (Fig. 4(f)). Once this was done, the capsules were cured during other 8 h at room temperature under a continuous horizontal movement at 400 rpm, to avoid clusters formation.

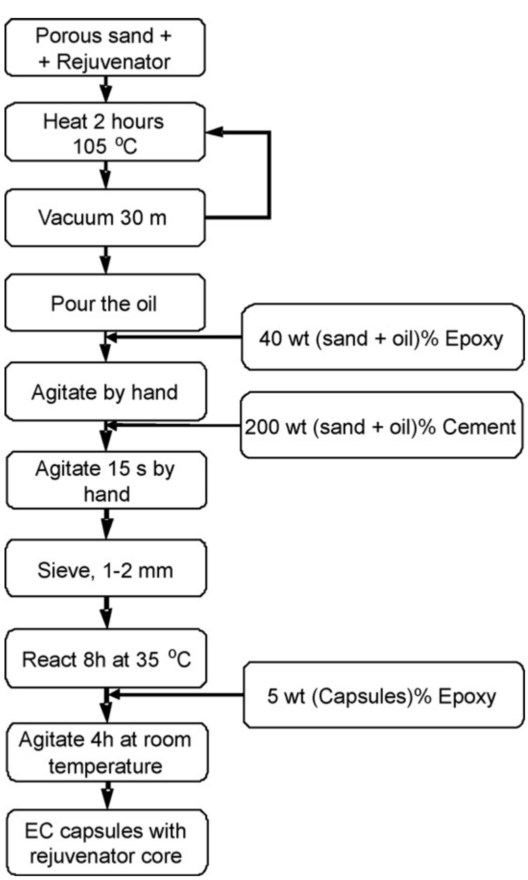


Fig. 3. Capsules recipe.

2.4. Thermal analysis

For the capsules to survive the mixing process of the asphalt concrete, they must resist temperatures between 160 and 180 °C. These temperatures can produce molecular scissions or intermediate compounds in the rejuvenator such as ketones or alcohol [29], 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 °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.

2.5. Mechanical tests

Both tension and compression tests have been performed on the capsules using a Kammrath & Weiss tensile/compression stage. The displacement was applied at a rate of 5 μm/s while load data was acquired from a 500 N load cell with an accuracy of ±1 N. For the tests, the capsules were glued with cyanoacrylate super-glue to the load applicators (Fig. 5).

2.6. 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

Fig. 4. (a–f) Different stages of the fabrication process.

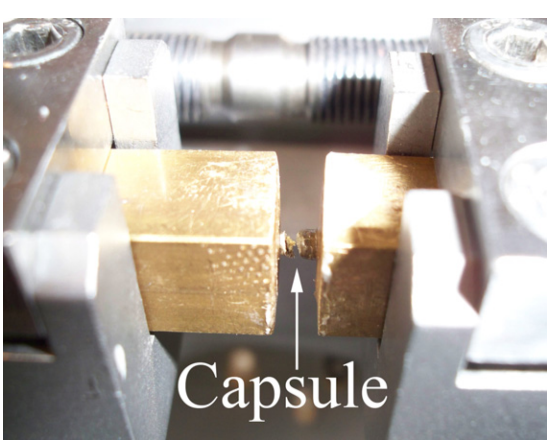


Fig. 5. Photograph of the mechanical experimental setup.

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, which is hydrated lime (size <0.063 mm) (Table 2). 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

3.1. 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 Fig. 3 it is shown that the size of the porous sand used as a core is between 1.0 and 1.7 mm, the most frequent diameter being 1.40 mm. Furthermore, the capsules were sieved between 1.0 and 2.0 mm, and in this figure it can be seen that their most probable diameter is 1.60 mm. The difference between the size of

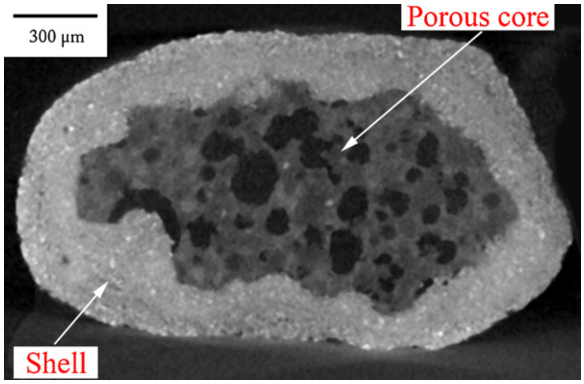


Fig. 6. CT-Scan image of the capsule.

the capsules and the size of the core divided by two will give an approximate value for the shell thickness. From the diameter distribution graphs it can be determined that the mean thickness of the shell is of about 0.10 mm which appears to coincide with what is observed in Fig. 6.

3.2. Thermal analysis

In Fig. 7, 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. Spectra obtained from TGA and DSC are the superposition of the spectra of the decomposition products [30] and therefore the different peaks can be identified with TGA and DSC scans of the different materials in the capsules (Fig. 7).

The first of these endothermic peaks (peak 1 in Fig. 7) corresponds to the loss of two different appearances of water, and comprises two subpeaks as is clearly shown in Fig. 7. The first subpeak (1a) at approximately 100 °C corresponds to the dehydration of pore water while the second subpeak (1b) between 100 and 165 °C corresponds to the dehydration of calcium silicate hydrates. This can be checked in Fig. 8(a) where the TGA curves of the different materials in the capsules are shown. In this figure, it can be observed how there is a large mass loss in the porous sand at these temperatures, but it is not clear where exactly the dehydration of pore water ends and when the dehydration of the calcium silicate granules starts.

As seen in Fig. 8(b) between 350 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 Fig. 7 are very similar to the ones shown for the epoxy in both Fig. 8(a) and [30] for its thermal decomposition. Furthermore, from the comparison of the DSC curve in Fig. 7 with the DSC curve for the rejuvenator in Fig. 8(b) it can be concluded that 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 and 180 °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.

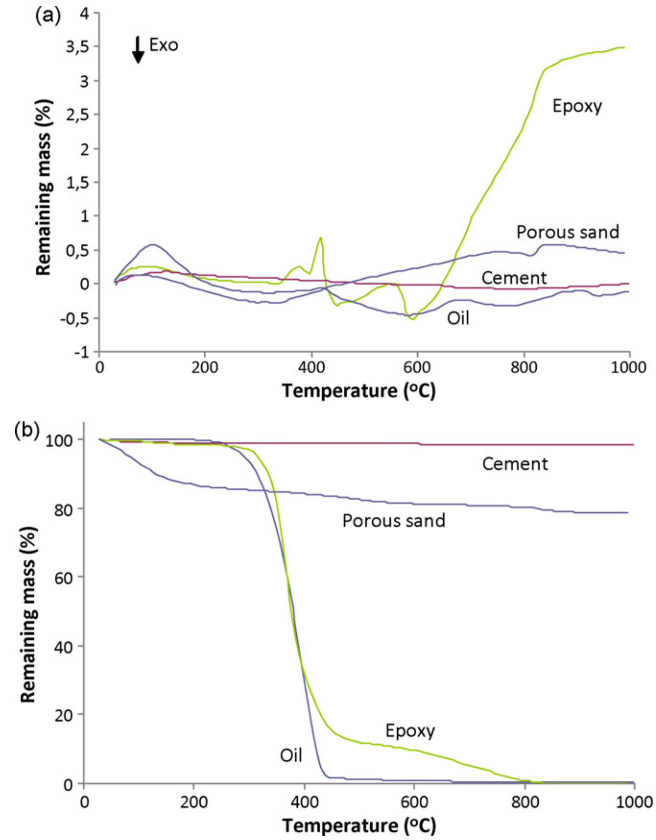


Fig. 8. (a) TGA curves for the capsules and the rejuvenators studied. (b) DSC curves for the capsules and the rejuvenators studied.

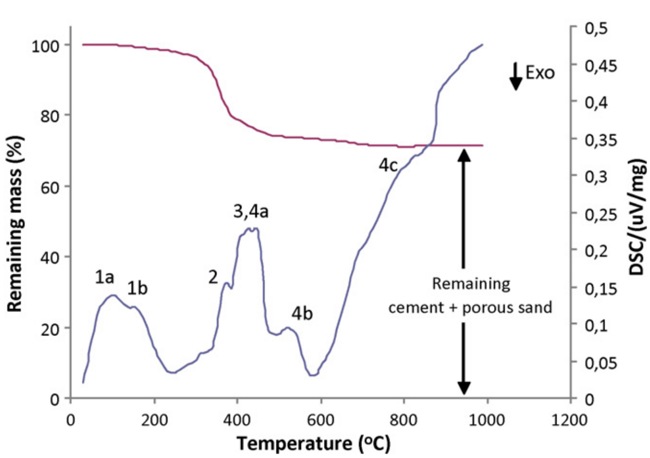


Fig. 7. DSC and TGA curves for the capsules and the rejuvenators studied.

3.3. Capsule composition

The total mass of the capsules consists of four parts: rejuvenator, porous sand, cement and epoxy. 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 five 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%. Sec-

Table 2
Composition of PA 0/16 mixture for Gyratory specimen based on the Dutch standard (RAW 2005).

Sieve size (mm)	Density (g/cm^3)	RAW spec. % retained	Cumm. % ret.	% ret. by weight	Weight (g)
22.4–16.0	2.778	0–7	4	4	48
16.0–11.2	2.774	15–30	25	21	252
11.2–8.0	2.762	50–65	57	32	384
8.0–5.6	2.765	70–85	80	23	276
5.6–2.0	2.781	85	85	5	60
2.0–0.063	2.688	95.5	92.7	7.7	92
Capsules	1.973	–	95.5	2.8	25
<0.063	2.638	100	100	4.5	54
					1191
Bitumen 70/100	1.032	4.5 by wt.			54
				Total wt.	1245

ond, in Fig. 7, after heating the capsules in the TGA at 1000 °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, Fig. 8 shows that the remaining mass of these two materials after heating them at 1000 °C in N_2 atmosphere is 96.75% for the cement and 78.0% for the porous sand.

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

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

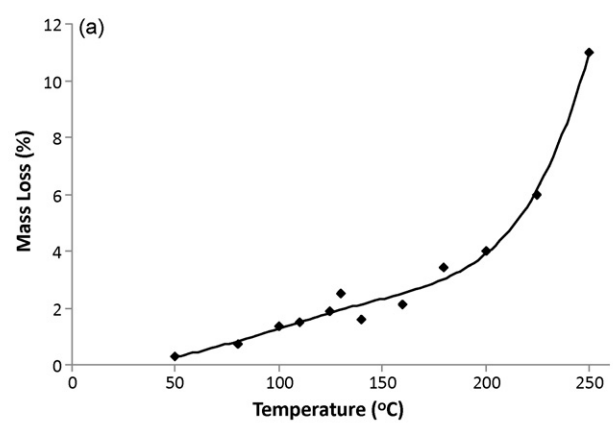
where M_o is the mass of oil in the capsules, M_{ps} is the mass of the porous sand, M_c is the mass of cement, M_e is the mass of epoxy in the capsules, M_r is the remaining mass of the capsules after heating them in N_2 atmosphere at 100 °C, ρ_{cap} is the density of the capsules, ρ_o is the density 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+ps} 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.

3.4. Thermal stability analysis

The capsules must resist very high temperatures during the mixing, transportation and placing process, what alltogether can take about 2 h. Therefore, the thermal stability of the capsules has been investigated by tracking the mass loss of the capsules during different 2 h isotherm temperatures (Fig. 9(a)). From the shape of the curve in this figure it can be seen how it is divided in two different parts. The first one, with linear shape, goes from room temperature 30 to 180 °C and corresponds to the loss of water from the capsules. The total loss of mass of the capsules at 180 °C after 2 h constant heating is about 3%. In Fig. 9(b) the total separated loss of mass of the different capsule materials after 2 h constant heating at 160 °C and at 225 °C can be found. It can be observed that the material with maximum losses at 160 °C is the porous sand. Finally, it can be observed how at this temperature, the mass loss of the other materials is negligible.

Furthermore, in Fig. 9(a) it can be observed that above 180 °C the mass loss rate increases significantly. As seen in Fig. 9(b), for the individual material losses at 225 °C, this is due to an increase in the rejuvenator loss at these temperatures. Additionally, the porous sand materials continue dehydrating and loosing mass. This means that the mass loss of the capsules due to the temperatures during the mixing, transportation and placing (<180 °C) will be at minimum, so that it can be concluded that the capsules can resist the high temperatures at which asphalt concrete is mixed.



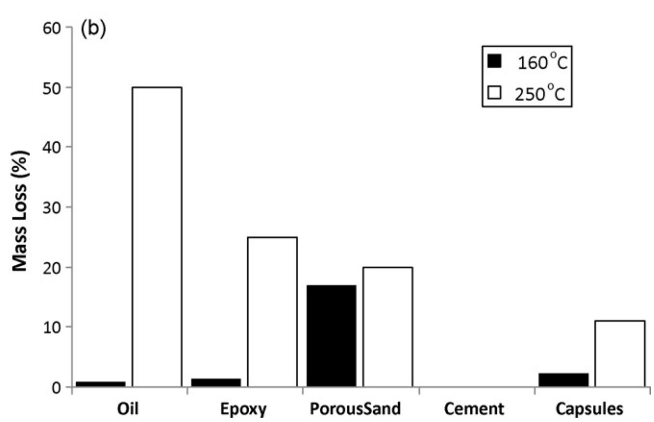


Fig. 9. (a) Mass loss after 2 h isotherm heating at different temperatures. (b) Mass loss after 2 h isotherm heating at 160 and 250 °C of the different materials in the capsules.

3.5. Mechanical resistance

In Fig. 10(a) the force–displacement curves of three capsules broken under tension are shown. In this figure it can be seen that these capsules have a very homogeneous elastic behaviour. The ultimate resistance of the three capsules tested was 11.15, 14.48 and 16.14 N at 13.75, 16.50 and 21.3 μm of deformation, respectively. Furthermore Fig. 10(b) shows the force–displacement curves of three capsules broken under compression. In this case the curves present a different breaking mode compared to the capsules broken under tension. There is a first elastic part where the capsule can be compressed without suffering damage. The maximum resistances here are 7.08, 9.53 and 10.92 N at a deformation of 39.81, 49.16 and 44.02 μm, respectively. It can be seen how the tension resistance of the capsules is higher than the compression resistance. Additionally, from the curves it can be seen that, when the compression continues to be applied the material is much less rigid, probably because the shell material has already been broken and the porous stone is supporting the load. The ultimate resistance of the capsules studied is 11.49, 14.36 and 17.61 N at a deformation of 105.29, 93.06 and 106.92 μm, respectively. The capsules cannot resist any more pressure: at this point they are completely destroyed.

The curves have been obtained at a very low speed, to identify the breaking modes. The maximum resistance of the capsules will change under dynamic loads and should be higher than the maximum stress caused by a vehicle passing after the construction of the road. After some time the bitumen will oxidize and its stiffness will increase. The material will then become more brittle and the capacity to relax the stresses will disappear. Due to the higher stiffness of the binder, the traffic load results in higher stresses on the shell of the capsule. Also, after many loading cycles in the road the capsules will be damaged and the fatigue failure probability increases. One of the advantages of this encapsulation system is that it is possible to give different threshold values for breakage just by increasing the shell thickness. This gives the possibility of

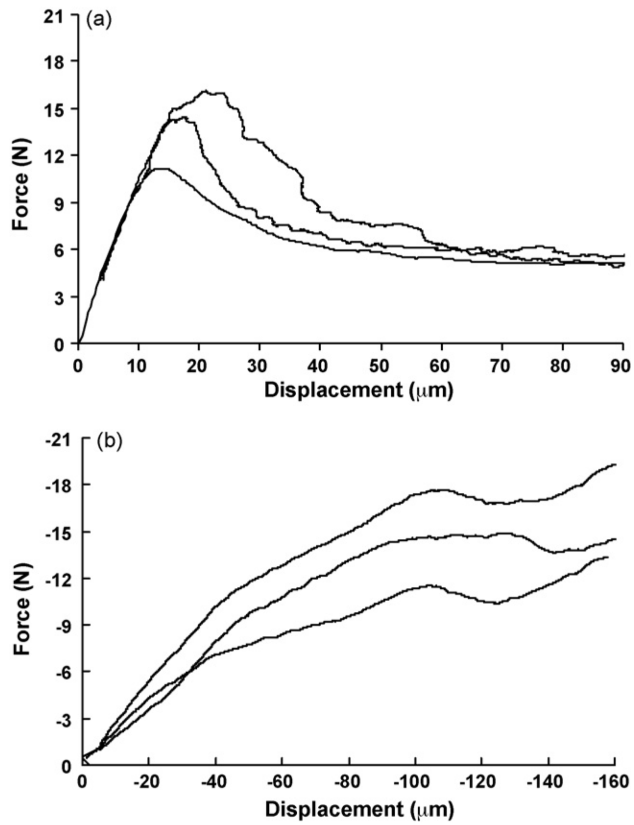


Fig. 10. (a) Force–displacement curves of three capsules broken under tension. (b) Force–displacement curves of three capsules broken under compression.

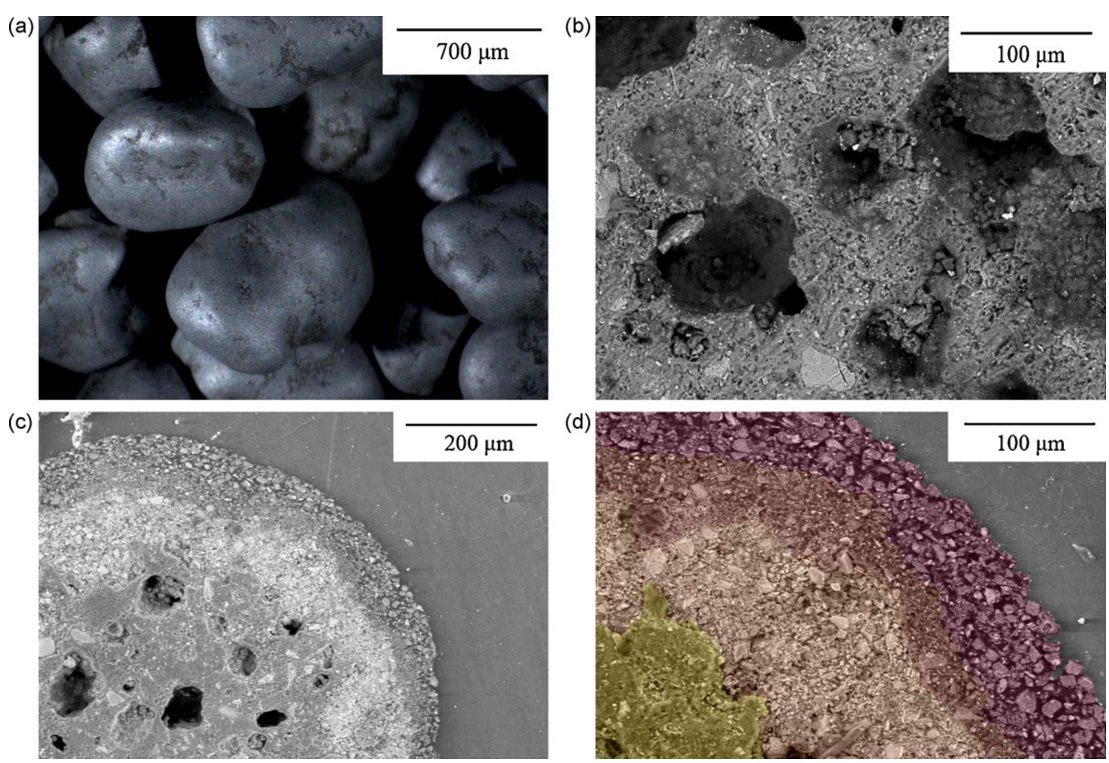


Fig. 11. (a) Optical micrograph of the core materials of the capsules. (b) SEM image of the porous sand used. (c) SEM image of a capsule section showing its different layers. (d) A detail of the shell materials showing the very dense interior wall and the rough exterior of the wall.

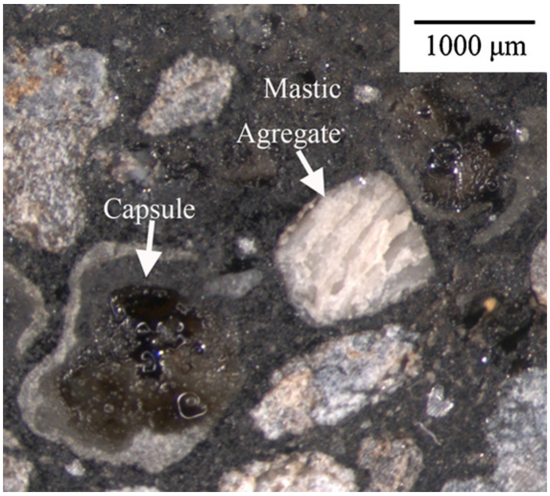


Fig. 12. Section of the capsules embedded in asphalt concrete.

engineering the material in such a way that the time of breakage can be chosen. This means that capsules with different resistances can be designed so that not all the chemicals are released at the same time.

3.6. Capsule morphology

Scanning electron microscopy (SEM) and CT-Scan analysis have been performed to analyze the capsule morphology. In Fig. 11(a) an optical micrograph of the core materials of the capsules is shown. It can be seen that externally they look as aggregates, with their surface very uniform and no external signs of the rejuvenator inside. To allow viewing the capsules morphology they have been embedded in epoxy resin and, once the resin was hardened, it has been polished until some representative sections of the capsules were exposed.

Fig. 11(b) shows a section of the porous sand inside the capsules where multiple micropores can be observed. Fig. 11 (c) shows a section of a capsule which comprises two distinct regions: the core and the shell. In this Figure it can be clearly seen that the shell has three different layers with variable density: the shell is completely made of a mixture of epoxy and cement, but the density changes a lot from the inside to the outside of the capsule. Finally, in Fig. 11(d) a detail of the shell is shown with the very high packaging density of the shell materials close to the porous sand, which prevents the rejuvenator from coming out, and that this density reduces towards a rough surface on the outside of the capsule. This is very positive because the rough surface will increase the bonding level with the binder.

3.7. Incorporation into the 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 min at 285 rpm and a temperature of 160 °C in a 10 l 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. Fig. 12 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, although some of them were broken during the mixing. 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. In a second phase of the work, further investigations will be developed concerning the most critical aspects related to the use of the capsules (breakage of the capsules, failure of the asphalt mixtures, mechanical resistance, maximum lifetime of the pavement), and the results will be subsequently published.

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. Furthermore, the capsules have proven to resist temperatures of 180 °C, common in asphalt concrete, during 2 h with a loss of mass of about 3%. These losses basically come from evaporation of the moisture in the porous stone and not of the rejuvenator. The mechanical behaviour of the capsules has been tested under both tension and compression. The tests show their elastic behaviour as well as their higher resistance to tension than to compression. 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 a second phase of the work, further investigations will be developed concerning the most critical aspects related to the use of the capsules (breakage of the capsules, failure of the asphalt mixtures, mechanical resistance, maximum lifetime of the pavement), and the results will be subsequently published.

Acknowledgments

The authors acknowledge the financial support from the Delft Centre for Materials (DCMat) in the form of project SHM0617, "Unravelling of porous asphalt". Furthermore, the help of INTRON and the helpful discussions with Prof. Andre Molenaar and with Dennis Waterman are gratefully acknowledged.

References

[1] J.F. Branthaver, J.C. Petersen, R.E. Robertson, J.J. Duvall, S.S. Kim, P.M. Harnsberger, T. Mill, E.K. Ensley, F.A. Barbour, J.F. Schabron, Binder Characterization and Evaluation, Vol. 2: Chemistry, SHRP-A-368, National Research Council, Washington, DC, 1993.
[2] R.N. Hunter, Bituminous Mixtures in Road Construction, Thomas Telford, London, 1997.
[3] L.W. Corbett, Composition of asphalt based on generic fractionation using solvent deasphaltening, elution-adsorption chromatography and densimetric characterization, Anal. Chem. 41 (1969) 576–579.
[4] X. Lu, U. Isacsson, Effect of ageing on bitumen chemistry and rheology, Constr. Build. Mater. 16 (2002) 15–22.
[5] R. Karlsson, U. Isacsson, Investigations on bitumen rejuvenator diffusion and structural stability, J. Assoc. Asph. Paving Technol. 72 (2003) 463–501.

[6] R.E. Boyer, Asphalt rejuvenators: “Fact, or Fable”, in: Transportation Systems 2000 (TS2K) Workshop, San Antonio, Texas.
[7] R. Karlsson, U. Isacsson, Material-related aspects of asphalt recycling—state of the art, J. Mater. Civil Eng. 18 (1) (2006) 81–92.
[8] J. Shen, S. Amirkhanian, J.A. Miller, Effects of rejuvenating agents on superpave mixtures containing reclaimed asphalt pavement, J. Mater. Civil Eng. 19 (5) (2007) 376–384.
[9] G.D. Peterson, R.R. Davison, C.J. Glover, J.A. Bulin, Effect of composition on asphalt recycling agent performance, Transport. Res. Rec. 1436 (1994) 38–46.
[10] R.L. Venable, J.C. Petersen, R.E. Robertson, Investigation of Factors Affecting Asphalt Pavement Recycling and Asphalt Compatibility, United States Dept. of Energy, Technical Information Center, Washington, DC, 1983.
[11] C.T. Chiu, M.G. Lee, Effectiveness of seal rejuvenators for bituminous pavement surfaces, J. Test. Eval. 34 (5) (2006).
[12] S.K. Ghosh (Ed.), Functional Coatings: By Polymer Microencapsulation, Wiley-VCH, 2006.
[13] U.R. Pothakamury, G.V. Barbosa-Canovas, Trends Food Sci. Technol. 6 (12) (1995) 397–406.
[14] M.H. Gutcho, Capsule Technology and Microencapsulation, Noyes Data Corp., 1972.
[15] R. Arshady (Ed.), Microspheres, Microcapsules and Liposomes, Vol. 1: Preparation and Chemical Applications, Citus Books, 1999.
[16] J.M. Kamphaus, J.D. Rule, J.S. Moore, N.R. Sottos, S.R. White, A new self-healing epoxy with tungsten(VI) chloride catalyst, J. R. Soc. Interface 6 5 (18) (2008) 95–103.
[17] S. Cosco, V. Ambrogi, P. Musto, C. Carfagna, Properties of poly(urea-formaldeide) microcapsules containing an epoxy resin, J. Appl. Polym. Sci. 105 (2007) 1400–1411.
[18] G.H. Peters, C.K. Schaab, R.D. Hilbelink, T.R. Davis, Development of Multipurpose Capsular Adhesive Systems, NTIS, United States, 1971.
[19] M.M. Caruso, B.J. Blaiszik, S.R. White, N.R. Sottos, J.S. Moore, Full recovery of fracture toughness using a nontoxic solvent-based self-healing system, Adv. Func. Mater. 18 (2008) 1898–1904.
[20] D.N. Little, A. Bhasin, Exploring mechanisms of healing in asphalt mixtures and quantifying its impact, in: S. van der Zwaag (Ed.), Self Healing Materials an Alternative Approach to 20 Centuries of Materials Science, Springer Series in Materials Science, vol. 100, 2007, pp. 205–218.
[21] S.R. White, N.R. Sottos, P.H. Geubelle, J.S. Moore, M.R. Kessler, S.R. Sriram, E.N. Brown, S. Viswanathan, Autonomic healing of polymer composites, Nature 409 (2001) 794–797.
[22] M.W. Keller, N.R. Sottos, Mechanical properties of microcapsules used in a self-healing polymer, Exp. Mech. 46 (2006) 725–733.
[23] S.D. Mookhoek, P.J. Colver, H. Fischer, S.A.F. Bon, S. van der Zwaag, The creation of high aspect ratio capsules to improve the efficiency of self-healing polymer systems, in: A.J.M. Schmets, S. Zwaag (Eds.), First International Conference on Self Healing (1–5), Springer, 2007.
[24] B.J. Blaiszik, M.M. Caruso, D.A. McIlroy, J.S. Moore, S.R. White, N.R. Sottos, Microcapsules filled with reactive solutions for self-healing materials, Polymer 50 (2009) 990–997.
[25] S.H. Cho, S.R. White, P.V. Braun, Self-healing polymer coatings, Adv. Mater. 21 (2009) 645–649.
[26] J.D. Rule, E.N. Brown, N.R. Sottos, S.R. White, J.S. Moore, Wax-protected catalyst microspheres for efficient self-healing materials, Adv. Mater. 2 (2005) 205–208.
[27] J.S. Hwang, J.N. Kim, Y.J. Wee, J.S. Yun, H.G. Jang, S.H. Kim, H.W. Ryu, Preparation and characterization of melamine-formaldehyde resin microcapsules containing fragrant oil, Biotechnol. Bioproc. Eng. 11 (4) (2006) 332–336.
[28] ISO 14688-1:2002, Geotechnical investigation and testing – identification and classification of soil – Part 1: identification and description.
[29] V.F.C. Lins, M.F.A.S. Araújo, M.I. Yoshida, V.P. Ferraz, D.M. Andrada, F.S. Lameiras, Photodegradation of hot-mix asphalt, Fuel 87 (2008) 3254–3261.
[30] K.L. Erikson, Thermal decomposition mechanism common to polyurethane, epoxy, poly(diallyl phthalate), polycarbonate and poly(phenylene sulfide), J. Therm. Anal. Calorim. 89 (2) (2007) 427–440.