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ORIGINAL ARTICLE

Influence of cement content and environmental humidity on asphalt emulsion and cement composites performance

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Abstract Asphalt and cement concrete are the most popular materials used in the construction of roads, highways, bridge deck surface layers and pavements in airports and other areas with heavy wheel roads. Whereas asphalt possesses, compared to concrete, the advantages of a short curing period, high skid resistance and easy maintenance, it also shows lower fatigue durability, ravelling and rutting due to repeated concentrated loads and susceptibility to temperature changes and moisture. On the other hand, concrete pavements are initially more expensive, have lower driving comfort and are susceptible to cracking due to volume changes and to salt damage. A material with low-environmental impact and with advantages of both asphalt and concrete may be obtained by combining bitumen emulsions and a cementitious material. In this paper, cold asphalt mixtures with different amounts of cement were tested with Marshall stability tests. Selected mixtures were also cured at different environmental relative humidity (35, 70 and 90 % RH). By monitoring the mass of the specimens and estimating the water bound by the cement, the total water remaining in the mixtures was calculated. Details of the microstructure in the mixtures were examined with X-ray microtomography. According to the results of the present study, cement contributes to the hardening of cold asphalt mixtures both by creating cement paste bridges between the aggregates and by removing water from the mixtures through cement hydration. Asphalt and cement composites appear to be promising materials for implementation in real pavements, although their rate of hardening needs to be improved further.

Keywords Bitumen emulsion · Portland cement · Environmental relative humidity · Cement asphalt composite · Hydration

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1 Introduction

Asphalt and cement concrete are a mixture of binder (bitumen or cement paste, respectively) and aggregates. They are the most popular materials used in the construction of roads, highways, bridge deck surface layers and pavements in airports and other areas with heavy wheel roads. These road materials are subjected to a variety of mechanical and environmental loads that might ultimately impair their integrity. Examples of these loads are moisture, which softens subgrade soil, destroying the structural capacity of pavements [1], or continuous traffic loads that induce damage such as fatigue cracks [2]. It is often difficult to choose the right material for a pavement [3]. Asphalt has many advantages against concrete, such as low curing period, relatively good point-load carrying capacity, skid resistance and besides, it is easy to maintain [4]. Moreover, concrete pavements are initially more expensive [5], and they are susceptible to cracking due to volume changes and to salt damage [6], due to de-icing salts used on roads in cold weather zones. On the other hand, asphalt concrete pavements have many other disadvantages compared to cement concrete pavements, such as a poor fatigue resistance, ravelling and rutting due to repeated concentrated loads, high susceptibility against temperature changes, lower lifetime [7] and higher maintenance cost [8]. It is a common belief that concrete is more suited for heavy traffic and asphalt for lower traffic, although asphalt pavements can be designed for any environment [9].

With this in mind, a material showing advantageous properties of both asphalt and concrete could be obtained by combining asphalt emulsions and a cementitious material. The purpose of this combination is to reach higher compressive strengths and lower temperature susceptibility than hot mix asphalt concrete and higher tensile strength and flexibility than cement concrete [10]. Additionally, it would not be necessary to heat up the materials for mixing. For this reason, cold mix asphalt concrete would also have the advantage of reducing the energy consumption and the CO_2 emissions [11]. Finally, the composite could be used both for pavement recycling [12] and for new mixtures [13].

Without cement additions, cold mixes have poor mechanical performance and high moisture susceptibility [13]. The addition of cement improves the Marshall stability of the mixtures, the compressive strength, the stiffness [13] and the hardness of the interface between cement asphalt emulsion mastic and aggregates [14]. For these reasons, between 1 and 3 % of ordinary Portland cement by mass of aggregates may be added to cold mix asphalt concrete [15]. Additionally, cement helps the emulsion to break faster [16], with shorter curing time, as it absorbs water from the emulsion. It is noted that different types of cement have a distinct effect on the curing rates of the mixture [14].

The fine particle size of the cement and their partial dissolution upon contact with an aqueous solution induce a faster breaking of the emulsion after placement [17]. The use of very fine particles may however impact the mixture negatively, because water from the emulsion will coat the fine particles and will be consumed in early hydration products. As a result, not all aggregates may be covered with emulsion. The presence of asphalt emulsion may also have a negative effect on the hydration of cement [18], as the emulsion stops the formation of a dense and well-connected cementitious binder. Moreover, surfactants (which confer stability to the emulsion) are known to retard cement hydration [19]. In the end, cement hydrates form an integral part of the binder, increasing the resistance to permanent deformation and improving moisture and temperature susceptibility of cold mixed asphalt [20].

It has been reported in the literature that cold mix asphalt concrete with cementitious additions could have comparable properties to hot mixtures after curing [13], which makes it very promising for its use as a road material. However, these mixes harden too slowly for use in bulk asphalt and it is still necessary to improve the rate of water removal from the mixture. This study aims at investigating the rate of hardening in different environmental conditions and obtaining a better understanding of the behaviour of cold mix asphalt concrete. A series of mixtures with different amounts of cement and cured at a constant temperature (20 °C) but at different environmental humidity levels (35, 70 and 90 % RH) have been investigated in this study.

2 Experimental method

2.1 Materials

A dense asphalt concrete mixture was used in this research. This type of mixture was chosen because it is the most commonly used in Switzerland. The aggregates distribution is shown in Fig. 1. The aggregates used to make cold mix asphalt concrete specimens were quarry material (size between 2 and 16 mm and density 2,770 kg/m^3), crushed sand (size between 0.063 and 2 mm and density 2,688 kg/m^3), and filler (size <0.09 mm and density 2,638 kg/m^3). The total

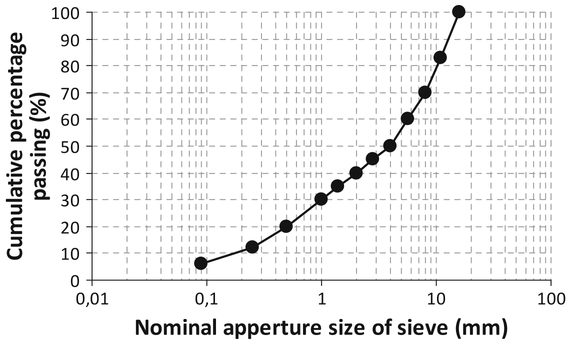

Fig. 1 Aggregates distribution (0/16) in the cold mix asphalt concrete

amount of filler in the mixture was 6 % of the total mass of aggregates.

The bitumen emulsion used was Webacid C60OBO, from CTW Strassenbaustoffe AG (Switzerland), an unmodified cationic and fast breaking emulsion with approximately 60 % of bitumen concentration, density 0.99 g/cm^3 and pH 2.5. A cationic emulsion was chosen because cold mixtures with the same type of aggregates as the ones used in this research and based on cationic emulsions showed superior mechanical properties when combined with Portland cement [18]. Additionally, to facilitate the mixture preparation, tap water was added to the mixture.

Ordinary Portland cement was added to the mixture in different amounts, by replacing different masses of filler with cement, from 0 % (no cement in the mixture) to 6 % (all filler replaced). The cement was a CEM I 42.5 N with a modified Bogue-calculated composition [21] (by wt%): C_3S: 60.8, C_2S: 12.5, C_3A: 4.76, C_4AF: 9.8, free CaO: 0.5, Na_2O eq.: 0.81 and Blaine fineness of 277 m^2/kg.

The percentages of materials in the mixture, by mass, were 2.52 % of water, 13.44 % of bitumen emulsion and 84.03 % of aggregates. The initial water-to-cement ratio (w/c) in the mixtures with cement varied from 3.13 in the mixture with 1.5 % cement to 0.78 in the mixture with 6 % cement; these figures do not take into account the water absorption by the aggregates.

2.2 Test samples preparation

The materials were mixed in a laboratory planetary mixer with a 20 kg bowl. The amount of materials in each mixture was 12 kg and the temperature during the mixing process was 20 ± 1 °C. The raw materials were added to the bowl in this order: first the emulsion and the water, then the coarse aggregates, then the sand and finally, the filler and cement. Materials were mixed during approximately 1 min.

One mix was used to make 9 cylindrical Marshall specimens with 10 cm diameter, approximately 6 cm height and approximately 1,190 g of mass. Immediately after placing the specimens in the mould, they were compacted with 100 blows of the Marshall hammer, 50 for each side of the specimens. A picture of a typical specimen is shown in Fig. 2a.

Additionally, 3 hot mix asphalt specimens were prepared for comparison purposes. Bitumen was obtained by evaporating the water from the bitumen emulsion at 110 °C, during 2 h. After this, aggregates and bitumen, without water, were heated to 160 °C and mixed in the same laboratory mixer used for making the cold mix asphalt concrete. The exact mass of materials for each specimen before compaction was 1,190 g. Finally, the specimens were compacted using 100 blows of the Marshall hammer, 50 for each flat face of the specimens.

2.3 Isothermal calorimetry

The rate of heat release was measured on two duplicate specimens of the mixture with 3 % cement with isothermal calorimetry at 20 °C using a TAM Air Isothermal Calorimeter by Thermometric AB. About 20 g of freshly-mixed material was inserted into glass vials of internal diameter 22.5 mm, closed and placed in the measuring cell [22]. The rate of heat release was then integrated to obtain the cumulative heat release. By dividing the cumulative heat release with the potential heat of hydration of the cement, an estimation of the degree of hydration reached by the cement was obtained [23].

2.4 Curing

The specimens were cured at three different environmental relative humidity levels: 35 ± 3 %, 70 ± 3 %, 90 ± 3 %, at a constant temperature of 20 ± 0.5 °C. Moreover, some specimens were wet cured, also at a constant temperature of 20 ± 0.5 °C. After compaction, the moulds containing the test specimens were left to cure for 1 day in their respective

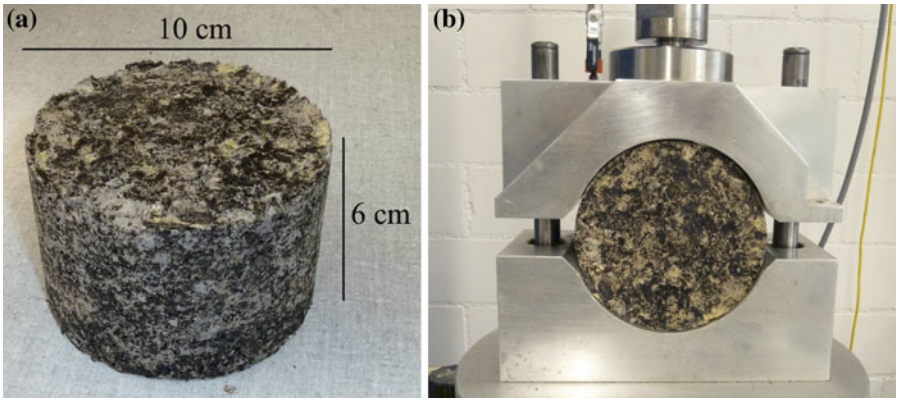

Fig. 2 **a** Test specimen. **b** Marshall test setup

humidity-controlled rooms. While in these moulds, water could evaporate through the specimens' upper face only.

After the first day, the specimens were demolded and left in the humidity-controlled room where they had been curing during the previous day. For curing, they were placed on a flat surface. Water could evaporate through the lateral and the top faces of the specimens, but not from the bottom one. This method was chosen because according to preliminary tests it is able to guarantee uniform curing for all the specimens. The specimens were let to harden for 1, 3, 7, 14, 21 and 28 days, respectively.

2.5 Marshall stability tests

The Marshall stability of more than 190 specimens, with different amounts of cement and cured at different environmental humidity levels, was tested. Marshall tests were run according to the EN 12697-34 Standard; the speed of the compression applied in the specimens was 50 mm/min. Every Marshall stability value was obtained from the average results of 3 specimens.

The Marshall stability test was chosen because it gives an indication of the compressive resistance of the mixture, and additionally, it shows the capacity of the mixture for flow, which will change depending on the amount of cement and on the curing conditions. The Marshall test setup can be seen in Fig. 2b.

In Fig. 3a, the force–displacement curve for a typical sample is shown. In Fig. 3b, the derivative of this curve is shown, which could be considered as an indication of the test sample stiffness. For this reason, this parameter will be called *rigidity* in the following. It has been calculated as

$$\mathrm{FD} = \frac{\Delta F}{\Delta D} = \frac{F(i) - F(i-1)}{D(i) - D(i-1)} \quad (1)$$

where FD is the force derivative, i is the number of data analysed, F is the force measured in the test sample and D is the displacement.

Accordingly, the *force* that the samples resist is defined as the force measured when the material has the highest rigidity (the inflection point in the force–displacement graph).

2.6 Moisture loss

Moisture loss was measured daily in the specimens cured for 28 days, by weighing them. Additionally, after the 28-days Marshall stability test, the specimens were dried at 90 °C during 12 h and weighed, for measuring the amount of evaporable water still present in the mixture. This was of particular interest in the case of mixtures with cement, where part of the water became bound in the hydration products of cement. The temperature of 90 °C was chosen because at the higher temperatures normally used for measurements of evaporable water in concrete (105–110 °C), also the bitumen present in the mixture might have been affected.

2.7 X-ray microtomography

To have an indication of the microstructure in the asphalt-cement composites, X-ray microtomography was employed. A small piece of asphalt concrete, with

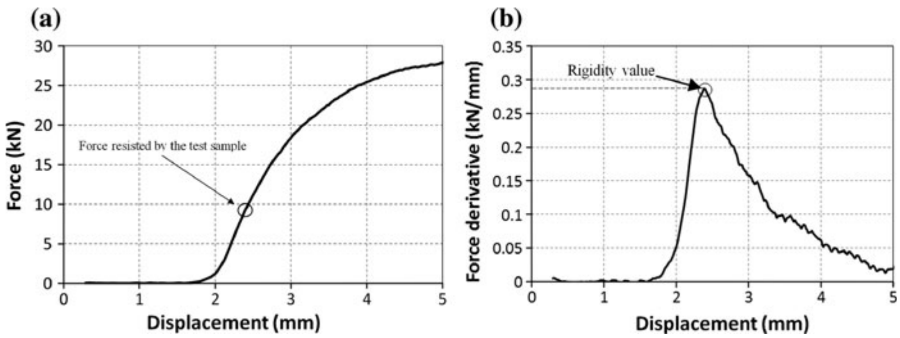

Fig. 3 **a** Force–displacement curve for the reference hot mix asphalt. **b** Derivative of the force displacement curve for the reference hot mix asphalt

approximately 2 mm length, was extracted from a specimen with 6 % of cement that had been curing during 28 days at 90 % relative humidity. This specimen was chosen because all of the filler that could be observed would be cement and the high relative humidity would help to reach the highest cement hydration, but also because water evaporation would happen in the mixture.

The X-ray microtomography scans were executed at the micro computed tomography facility at EMPA. The X-ray source ("XT9160-TXD" from Viscom) was operated with an acceleration voltage of 80 kV and a current of 120 µA. A tungsten transmission target on a diamond support was used. The sample was mounted on a rotational table ("UPR-160F air" from Micos) in a distance of 11.8 mm from the X-ray source and the distance between the X-ray source and the X-ray detector was 1,155 mm. It was ensured that the focal spot size of the X-ray tube was about 2 µm and therefore a spatial resolution of 4 µm was achieved. 720 projection images with 1,024 × 600 pixels and an exposure time of 2.8 s were taken at angles uniformly distributed over 360° with the help of flat panel X-ray detector ("XRD 1621 CN3 ES" from Perkin Elmer, 2 × 2 binned). The detector was calibrated with the help of a dark field and flat fields recorded at different X-ray beam intensities. The projection images were corrected for bad pixels, beam hardening and ring artefacts before a standard filtered back projection algorithm was used for reconstructing the three-dimensional distribution of the absorption coefficient (1,024 × 1,024 × 600 voxels 3D image) [24].

A reconstruction of the cementitious part of the binder was prepared by segmenting the materials found in a specific volume, based on simple thresholding. With this simple method, aggregates, cement paste, bitumen and voids could be readily separated. The software used for this reconstruction was ImageJ, DeVIDE and Meshlab.

3 Results

3.1 Mechanical properties of the reference hot mix asphalt concrete

In Fig. 3, representative curves for the force and rigidity from one of the hot mix asphalt test samples are shown. In these test specimens, the average force resisted by three test samples, measured at maximum stiffness, is 9.23 kN. Additionally, the maximum average stiffness of three specimens is 0.28 kN/mm.

3.2 Effect of different amounts of cement in samples cured at 90 % relative humidity

In Fig. 4a, the evolution of the force resisted by samples with different amounts of cement (0, 1.5, 3, 4.5 and 6 %), and cured during 1, 3, 7, 14, 21 and 28 days, at 90 % ambient relative humidity, is represented.

In Fig. 4, it can be observed that just after compaction, the portable capacity of the mixture was close to 0 kN, while the force resisted by the test samples increased with curing time. In case of adding 3 % of cement, the force increased from 1.87 kN after 1 day curing to 7.63 kN after 28 days curing. Additionally, it can be observed that the mixtures hardened faster when the amount of cement was increased. For example, the force resisted by the samples after 28 days curing, was 5.72 kN in the case that no cement was added to the mixture, and 14.7 kN in the case that 6 % cement was added to the mixture. The force resisted was higher than the force resisted by the reference hot mix asphalt (9.23 kN) only in the cases where more than 4.5 % of cement was added and after more than 10 days curing.

In Fig. 4b, the evolution of the rigidity in these test samples is shown. It can be observed that the rigidity increased with the curing time. For example, in samples with 3 % of cement, it increased from 0.03 kN/mm after 1 day curing to 0.11 kN/mm after 28 days curing. The rigidity increased also with the amount of cement in the mixture (0.05 kN/mm for a material without cement vs. 0.22 kN/mm for a material with 6 % cement, after 28 days curing), however the rigidity was never higher than the one from the reference hot mix asphalt (0.28 kN/mm).

3.3 Effect of curing at different relative humidity levels in samples with 3 % of cement

In Fig. 5a, the evolution of the force resisted by the samples is represented. These tests were done on specimens with 3 % of cement, cured at 20 ± 0.5 °C and at different relative humidities (35 ± 3 %, 70 ± 3 %, 90 ± 3 % and wet curing). Additionally, in Fig. 5b, the evolution of the rigidity in these test samples has been represented.

In Fig. 5a, b it can be observed that the force and rigidity in these materials improved with time, for all the relative humidity levels studied. For example, in test specimens cured at 35 %, the force increased from 1.93 kN after the first day curing, to 9.33 kN after 28 days curing. This increase in force and rigidity happened even when the specimens were submerged in water, where the force increased from 1.8 kN after the first day to 4.6 kN after 28 days. No significant difference in the force increase was observed between samples cured at 35 % relative humidity and samples cured at 70 % humidity. However, samples cured at 90 % relative humidity hardened slower than samples cured at low relative humidities. Besides, it was found that in samples cured under water, the resistance did not increase further after 7 days curing, when the force resisted was 4.57 kN. The force resisted by specimens with 3 % of cement was higher than the force resisted by the reference hot mix asphalt (9.23 kN), when the humidity was lower than 70 % and after more than 15 days curing.

In the case of test samples cured at 35 % relative humidity, the rigidity increased from 0.03 kN/mm

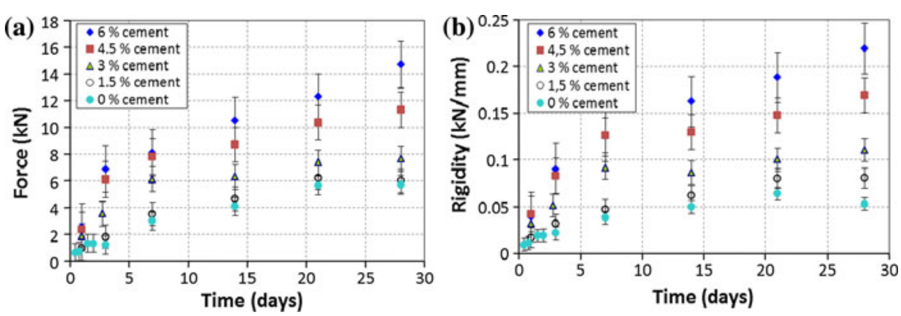

Fig. 4 **a** Evolution of the mechanical resistance with time and different amounts of cement. **b** Evolution of the relationship (kN/mm) with time, for samples cured at 90 % environmental humidity and different amounts of cement

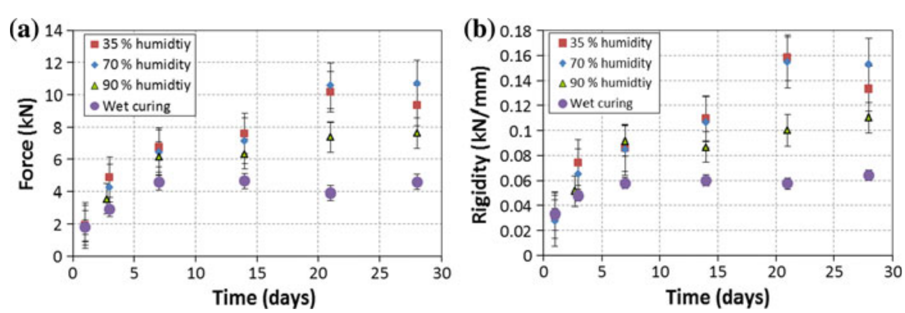

Fig. 5 **a** Evolution of the mechanical resistance with time, for samples with 3 % of cement. **b** Evolution of the rigidity (kN/mm) with time, for samples with 3 % of cement

after 1 day curing to 0.13 kN/mm after 28 days curing (Fig. 5b). On the other hand, when the test samples were submerged in water, the rigidity increased from 0.03 kN/mm after 1 day to 0.06 kN/mm after 28 days. Moreover, there was not much difference in the rigidity gains between samples cured at 35 % relative humidity (0.13 kN/mm, after 28 days curing) and samples cured at 70 % relative humidity (0.15 kN/mm, after 28 days curing). Finally, the rigidity was never higher than the one from the reference hot mix asphalt (0.28 kN/mm).

3.4 Effect of curing at different relative humidity levels in samples with 0 % of cement

In Fig. 6a, b, the evolution of the force and rigidity resisted by cold mix asphalt concrete, without cement, cured at cured at 20 ± 0.5 °C and at different relative humidities (35 ± 3 %, 70 ± 3 %, 90 ± 3 % and wet curing) is shown. As in the cases cited above, the force resisted by the test specimens, as well as their rigidity after compaction, was practically negligible, however it increased progressively with time. For example, in the case of asphalt test samples cured at 35 % relative humidity, the force resisted after 1 day was 2.03 kN, while the force resisted after 28 days curing was 5.98 kN. During the first days, specimens cured at low relative humidities hardened faster than specimens cured at high humidities. In addition, the force resisted by these test specimens and their rigidity were always substantially lower than the force resisted by the reference hot mix asphalt (9.23 and 0.28 kN/mm, respectively).

Specimens cured under wet conditions did not acquire any measurable mechanical resistance during the curing process. In fact, these test samples were too loose for being tested and crumbled into pieces during handling.

3.5 Relationship between the rigidity and the force resisted by the test specimens

In Fig. 7 the relationship between the rigidity and the force, for all the samples studied, is shown. It can be observed that the rigidity of the test samples increased linearly with the force resisted. Also, it can be seen that this curve is the same for all the samples studied, independently of the amount of cement in the mixture and of the environmental relative humidity at which the test specimens were cured. Moreover, it can be seen that after compaction, when the force resisted tends to 0 kN, the rigidity of the test samples tended to 0 kN/mm.

When these results are compared with those obtained for hot mix asphalt, it can be observed that even when both materials could resist the same force, the rigidity of cold mix asphalt concrete was always lower than that of the reference hot mix asphalt. Moreover, if the same linear tendency continues, a cold mix asphalt concrete mixture with a rigidity of 0.28 kN/mm would resist approximately 20 kN,

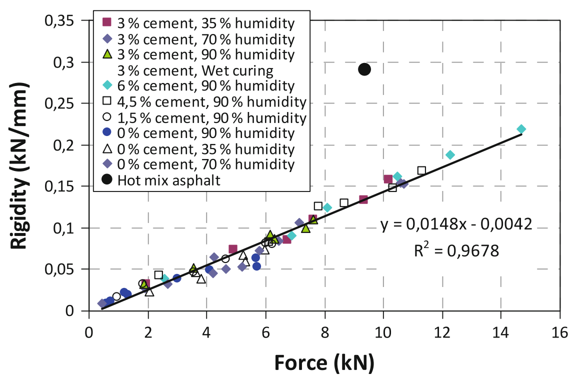

Fig. 7 Rigidity (kN/mm)–force (kN) relationship for test samples with different amounts of cement, cured at 90 % humidity

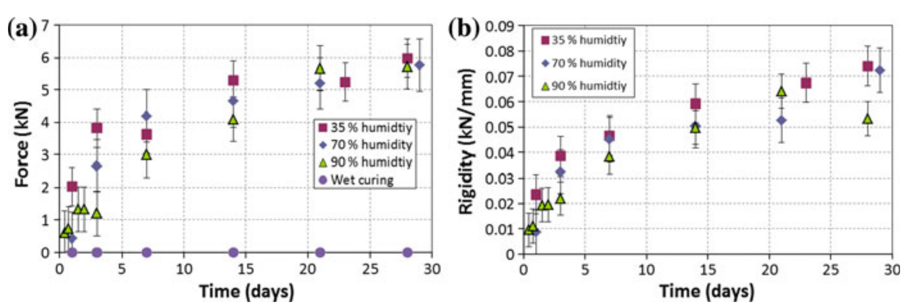

Fig. 6 **a** Evolution of the mechanical resistance with time, for samples without cement. **b** Evolution of the rigidity (kN/mm) with time, for samples without cement

which is a much higher value than the reference hot mix asphalt.

3.6 Degree of hydration from isothermal calorimetry

The degree of hydration (Fig. 8) of the cement was calculated by integrating the rate of heat release measured with isothermal calorimetry in the first 72 h after mixing and then dividing the cumulative heat release by the calculated potential heat of the cement, 443 J/g [23]. In this calculation it was assumed that all the heat release of the mixture occurred due to hydration of cement, an assumption supported by literature [18]. Figure 8 shows that the cement reaches a degree of hydration of about 0.7 in the first 3 days. Based on the slope of the degree of hydration versus time curve, it is likely that a degree of hydration of about 0.9 or higher will be reached after a few days. As explained in Sect. 2.3, the samples for isothermal calorimetry hydrated in sealed conditions (no water loss) in the calorimetry vial. Considering that the mixture with 3 % cement had a w/c of 1.57, it can be concluded that the degree of hydration of this sample is representative at least of the samples that were either wet cured or cured at 90 % RH.

3.7 Water loss in specimens cured at different humidities, with 0 % and 3 % of cement

The evolution the water content in mixtures with 3 % of cement and without cement during the curing process at different relative humidities, is shown in Fig. 9a, b, respectively. This water content includes only the evaporable water. The amount of water in the mixture, compared with the initial amount of water, has been calculated as:

$$M_{EW} = M(t) - M_d \quad (2)$$

where $M(t)$ (g) is the mass of the test specimens at curing time t and M_d (g) is the mass of the test specimens, dried at 90 °C after 28 days curing.

In Fig. 9, it is noted that approximately 35 % of the water was lost during the first curing day. This happened mainly due to the compaction process of the test specimens, which reduced the total space available for water in the mixture. Additionally, it can be observed that the main mass loss happened during the first 5 days, when the total amount of water in the mixture was reduced to about 25 % of the initial value.

Additionally, in Fig. 9a it can be observed that the amount of water after 28 days curing was 8.86, 6.11 and 3.94 %, in test samples with 3 % cement, when they were cured at 90, 70 and 35 % humidity, respectively. Furthermore, in Fig. 9b, it can be observed that the amount of water was 11.05, 6.82 and 4.94 % for samples without cement, cured at 90, 70 and 35 % humidity, respectively. Cold mix asphalt concrete without cementitious additions was much more sensitive to the environmental humidity than when cement was added. Finally, there was a minimum amount of water that could not be eliminated through the evaporation in the air.

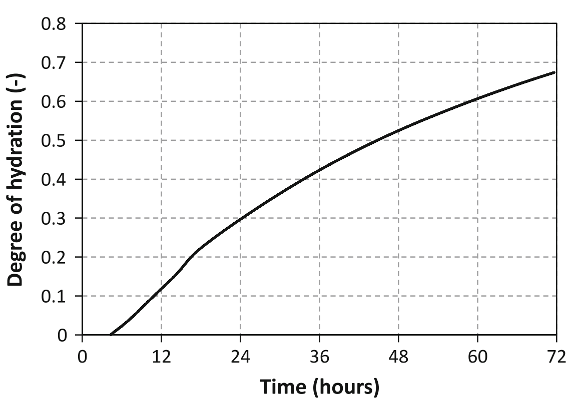

Fig. 8 Degree of hydration of the cement in the first three after mixing in a mixture with 3 % of cement in sealed conditions at 20 °C

3.8 Evolution of water to solids ratio

In the mixtures with cement, while part of the initial mixing water is lost to evaporation (Fig. 9a), another part is bound to the hydration products of cement. As the mechanical properties of the mixture depend on the amount of water that is still present, the amount of water bound by the cement needs to be taken into account as well. The simple approach adopted in this study is to calculate the amount of bound water in the mixtures with Powers' model [25]. According to this classical model, an average Portland cement will chemically bind at full hydration about 0.23 g water per g of cement. In addition to this amount, another about 0.19 g water will be adsorbed onto the calcium silicate hydrate gel, which has a high surface area and nanometer-sized pores. While the water bound in the

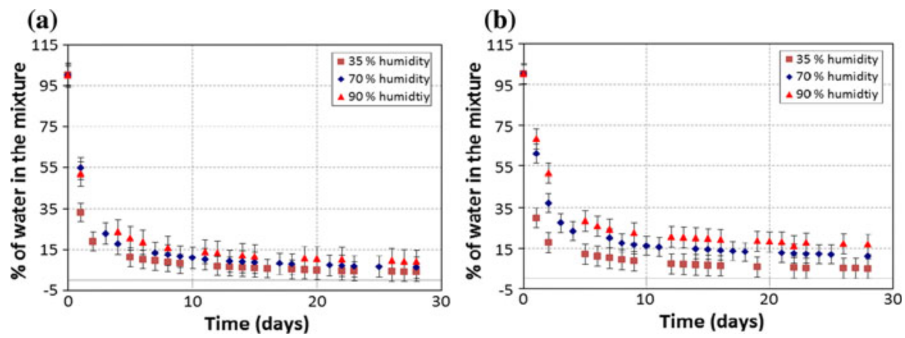

Fig. 9 **a** Percentage of evaporable water in the mixture through the curing process, for samples with 3 % cement. **b** Percentage of evaporable water in the mixture through the curing process, for samples with no cement

hydration product is considered non-evaporable water and will be retained when drying at 90 °C (see Sect. 2.6), the adsorbed water will be lost by either drying at very low RH or at high temperature. To apply this approach for the calculation of the amount of non-evaporable water in the mixtures with cement at 28 days, M_{NEW}, one needs to know the degree of hydration α of the cement. Based on the calorimetry results (Fig. 8), one can assume at 28 days a degree of hydration of about 0.9. The bound water in the mixtures with cement can then be calculated as:

$$M_{NEW} = 0.23 \cdot \alpha \cdot C \quad (3)$$

where C is the mass of cement in the mixture divided by the total initial mass of the mixture.

The water-to-solids ratio of the cold asphalt mixtures at 28 days of curing, where the water is further divided into evaporable water, non-evaporable water and water lost by evaporation, are plotted in Figs. 10 and 11. In this calculation, the aggregate and the bitumen are both considered as solids. Figure 10 shows the results of mixtures with different amounts of cement (0–6 %) cured at 90 % RH. It is evident that while the amount of evaporable water (by drying at 90 °C) decreased with an increasing addition of cement, the amount of evaporable plus non-evaporable water was roughly similar. Cement contributed therefore to consume a part of the water that would have remained in the mixture even after curing and thereby it increased the mechanical properties of the mixture (see Fig. 4).

Figure 11 shows the results of mixtures with either no cement or 3 % cement cured at different relative humidity levels (35, 70 and 90 %) for 28 days. Here it can be noticed that while the amount of water remaining in the mixture depended on the ambient relative humidity, the presence of cement in the mixture contributed to reduce the evaporable water at all levels, and especially at higher relative humidities. Mixtures containing cement are thereby less sensitive to the ambient humidity than mixtures without

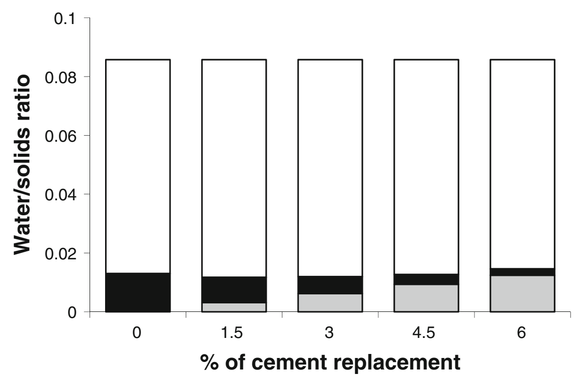

Fig. 10 Water to solids ratio of the mixtures with different amount of cement (0–6 % by mass of aggregate) cured for 28 days at 90 % humidity. The water lost by evaporation is shown in *white*, while the evaporable water still present in the mixture is *black* and the water bound into the hydration products of cement is *gray*

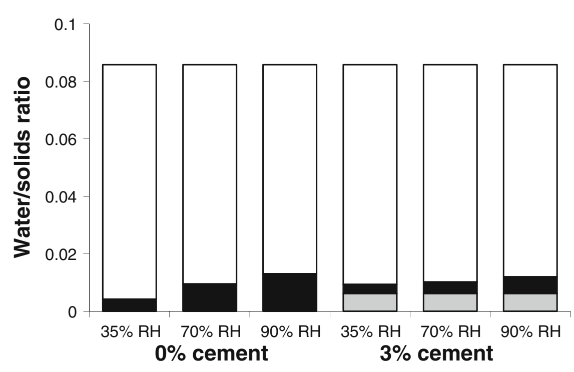

Fig. 11 Water to solids ratio of the mixtures with no cement and 3 % of cement by mass of aggregates cured at different relative humidity levels (35, 70 and 90 %) for 28 days. The water lost by evaporation is shown in *white*, while the evaporable water still present in the mixture is *black* and the water bound into the hydration products of cement is *gray*

cement, which is confirmed by the mechanical properties development (compare Figs. 5, 6). A particularly striking case is that of mixtures curing under water, which achieved some strength only in the case cement was present.

3.9 Evolution of stiffness as a function of the evaporable water content

As discussed in the previous sections, the removal of the evaporable water in the mixture and the increase in the mechanical properties appear to be closely linked. In Fig. 12 the relationship between the rigidity of the test specimens and the total amount of water present in the material is plotted. This figure has been obtained from the results of samples without cement cured for 1, 3, 7, 14, 21 and 28 days at different relative humidity. In addition, values for samples containing 1.5, 3, 4.5 and 6 % cement cured for 28 days have also been inserted in the graph. For the value containing cement, the amount of evaporable water was calculated by subtracting the bound water corresponding to a degree of hydration of the cement equal to 0.9 (see Sect. 3.8 for details). In Fig. 12 it can be observed that the rigidity of the test specimens appears to be related to the percentage of evaporable water present in the mixture. Moreover, the mixtures containing cement were more rigid and resisted higher loads (see also Fig. 7) than mixtures without cement, and the rigidity and force resisted increased proportionally to the amount of cement added to the mixture. This is supposed to be a product of both the water consumption due to cement hydration (Sect. 3.8) and the direct

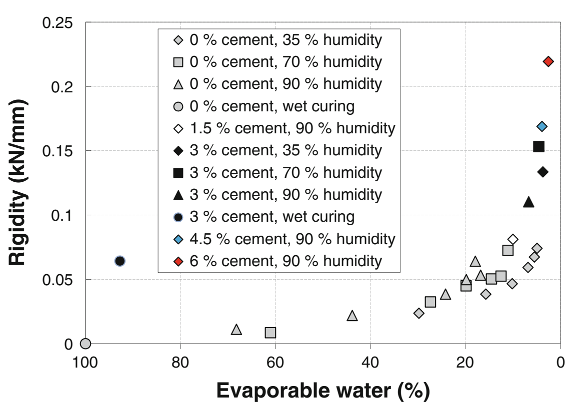

Fig. 12 Relationship between the rigidity of the test specimens and the total amount of evaporable water in the mixture

contribution of the cement hydration products that decrease porosity and bind the aggregates together.

4 Discussion

In Fig. 13, a schematic representation of the hardening process of an asphalt and cement composite is shown. Just after mixing the materials, a homogeneous mixture composed of aggregates, water, bitumen droplets and cement is expected to be formed (Fig. 13a). At that moment, each aggregate and the cement particles are wet with water, and there is no contact between aggregates and bitumen droplets as the asphalt emulsion has not yet broken.

Once the test samples were exposed to low ambient relative humidities, the mixtures started drying. The evaporation rate from the mixtures depends on a number of factors, including the ambient temperature and relative humidity, the porosity and the permeability of the mixtures and the competition between drying and binding of water into hydration products of cement [26–28]. During the drying process, the distance between bitumen droplets decreases and these start collapsing into larger conglomerates. At some point during this process, the emulsion breaks. Additionally, air will penetrate in the specimens and some aggregate surfaces will become available to be wetted by bitumen. Other aggregates surfaces may become hydrophobic when the surfactant contained in the emulsion adsorbs onto them. Moreover, bitumen will start a sort of capillary flow through the empty spaces left by water [29, 30], and the mechanical properties of the mixture will improve with time, as seen in Figs. 6 and 12. Especially in this last figure, it is very obvious that there is a relationship between the amount of evaporable water and the mechanical properties of the mixture: This happens because the amount of bitumen bridges between the aggregates increases with the amount of water removed from the material.

The evaporative process will continue until the gravity exceeds the maximum capillary pressure difference between the surface and the interior of the test specimen: In Fig. 9a, b, it can be observed that there is a limit for the water percentage reduction which clearly depends on the environmental relative humidity. The curing process can be significantly accelerated by adding a material that binds part of the

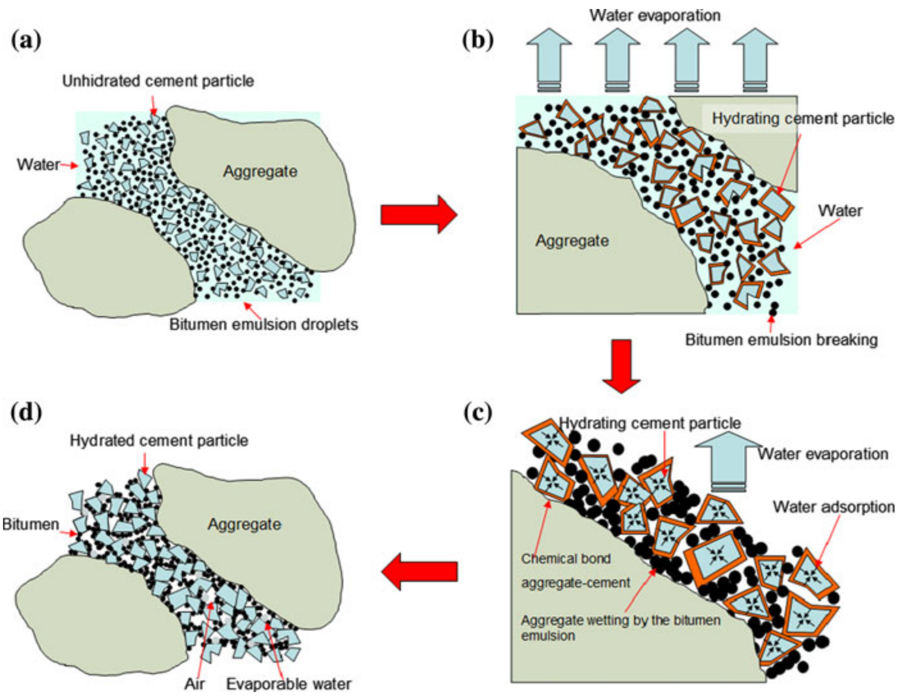

Fig. 13 Schematic representation of the hardening process of an asphalt-emulsion composite

water in, like Portland cement in the present case (Fig. 4).

In case where cement is added to the mixture, it will have two effects. First, it will remove part of the evaporable water from the mixture, using it for its hydration. And second, it will change the pH of the emulsion, breaking it (Fig. 13b). On contact of cement with water, the pH of the aqueous phase increases up to 12–13 within a few minutes and remains at those levels afterwards [31, 32]. As it was explained in the methods section, a cationic emulsion was used in this research. These emulsions are positively charged, and when they enter in contact with the aggregates, which tend to be negatively charged, emulsified bitumen particles tend to agglomerate in the surface of the aggregates. As hydrating cement particles have a high negative charge and high surface area, they will make that the bitumen emulsion break very fast in presence of cement hydration products. This can be observed in Fig. 5, where the amount of cement in the mixture accelerates greatly the setting process and the development of the mechanical properties. These results coincide with the ones obtained by previous authors [10, 13]. In any case, although there are some fundamental studies on the topic [14, 33], it is still unclear which is the exact effect of using cationic or anionic emulsions in the mixture, or which is the effect of the emulsion in the cement hydration. At low concentrations, neither anionic not cationic emulsions interfered substantially with cement hydration [18], while at higher concentration it was shown that anionic emulsions retard the hydration peak and decrease the total amount of heat produced [33]. In the present case, a retarding effect of the cationic emulsion was observed, but the total amount of heat produced appears not to be affected (see Fig. 8 and discussion thereof). Another issue that does not seem to be completely solved is the interaction of cement and bitumen in the mixture. Whereas the cement hydration products do not seem to be affected by the presence of the emulsion [33, 34], little knowledge is available about the microstructure formed and about how cement and bitumen interact in binding the aggregates [14, 34].

As discussed in the results section, based on the calorimetry results (Fig. 8) and on the high w/c of the mixture, it is reasonable to assume that most cement will be hydrated after the first few days of curing, especially in the case where the samples were cured at 90 % RH or wet cured. The more cement is added to the mixture, the more water will be adsorbed (Fig. 10). An increase of the cement content also increases proportionally the amount of hydration products formed and thereby the volume of cementitious bridges between aggregates and filler [35]. As a result, the force resisted by the mixture and its stiffness is higher, because the deformability of the cement phase is much lower than the deformability of the bitumen phase. Another result is that cement improves the moisture resistance of the mixture, as cement creates a chemical bond between the aggregates (Fig. 13c) that is not affected by the presence of water, even when the cold mix was cured in wet conditions (compare Figs. 5, 6).

Different authors (e.g. [13]) have pointed out that already small amounts of cement (2–3 %) added to cold mixes would make the mixture stiffer than hot mix asphalt and that replacing more than 3 % of cement in the mixture creates a brittle material [36]. This was not observed in the mixes studied in this paper, where the force and rigidity of the material were linearly related, independently of the amounts of cement used or the curing conditions (Fig. 7) and where in all cases studied, the rigidity of the cold mix asphalt concrete was lower than for the corresponding hot mix asphalt. Based on these results, an ideal cementitious material for improving the properties of cold mix asphalt concrete will need to:

1) bind a high amount of water into its hydration products, in order to remove water from the mixture and for improving the wettability of aggregates by bitumen;
2) form hydration products that have large volume and fill space, in order to create a number of bonds with the aggregates;
3) hydrate rapidly, in order to decrease the hardening time of cold mixes from weeks to several hours.

Other types of cementitious materials may be more efficient than Portland cement in this respect. For instance, calcium sulfoaluminate cements hydrate rapidly compared to Portland cement, bind a greater amount of water (about twice as much) during hydration, and their main hydration product, a hydrous calcium aluminium sulfate mineral called ettringite, fills porosity and contributes to fast strength gain [22, 37]. In fact, quick-hardening cold asphalt mixes containing a mixture of calcium aluminate and calcium sulphate minerals, which also will react to form ettringite, have already received some attention in the past [38].

As mentioned before, the exact way how the microstructure forms in these mixtures is still poorly understood. Figure 14 shows a detail of the inner microstructure of a mixture containing 6 % of cement cured at 90 % RH. The bubbles evident in the figure possibly appeared due to a suboptimal compaction of the mixture. There might be scope for improving the compaction method of these mixtures, which is different both from hot mix asphalt and from concrete; a possibility would be application of pressure and vibration at the same time. Another possible cause of these bubbles is air entrainment caused by the surfactant in the emulsion, a phenomenon that has been observed before [18]. Another feature visible in the microstructure shown in Fig. 14 is some degree of aggregate debonding, which may be improved with a different compaction method and with the use of adhesion promoters. Bonding of cement paste and aggregates could also be improved by reducing the amount of water in the mixture and the w/c using superplasticizers. This would help in minimizing the initial porosity and the water content of the mixture, thereby also increasing the rate of setting and curing. Finally, the non-homogeneous areas where the binder is only composed of bitumen (Fig. 14) may occur due to an inappropriate mixing method and to a premature

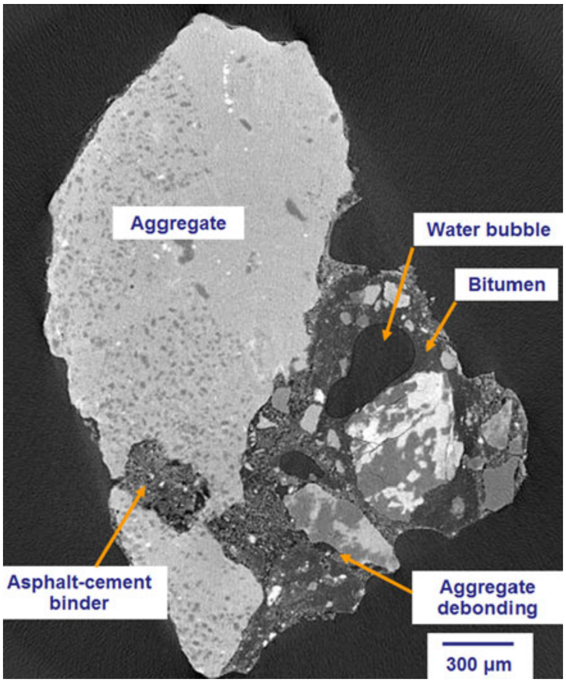

Fig. 14 Microtomography detail of an asphalt and cement composite, taken from a test sample, cured during 28 days, at 90 % RH and with 6 % of cement

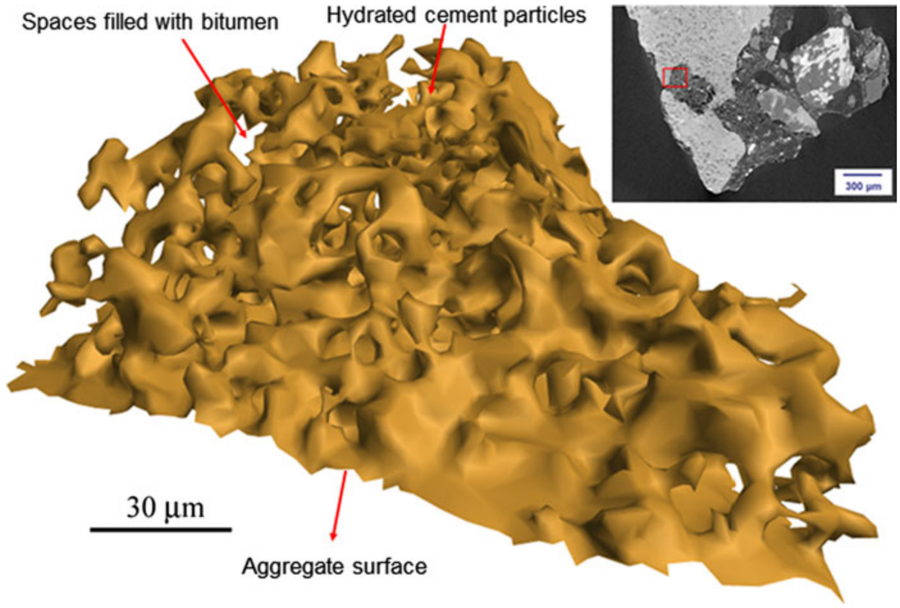

Fig. 15 3D reconstruction of a section of the asphalt and cement binder. The *red square* represents the approximate point from where this image was reconstructed. (Color figure online)

breaking of the emulsion, which might also be influenced by the cement presence (see discussion above).

The ultimate objective of cement-asphalt composites studies would be to obtain a material where the binder microstructure looks like Fig. 15, where a 3D reconstruction of a detail of asphalt and cement binder is shown. Figure 15 shows a foam-like structure, where hydrated cement particles create an interconnected structure that binds the aggregates, but at the same time where bitumen adheres to aggregates and intimately imbricated with the cementitious structure. In this particular microstructure, cement paste will help supporting much higher loads than in hot mix asphalt and at the same time bitumen will offer the flexibility needed for a soft riding that cement concrete roads are lacking. This structure is somehow similar to dry shake treatments in industrial concrete pavements, where soft inclusions are added to improve impact resistance [39], or to the porous structure of a human bone.

5 Conclusions

This paper confirms that asphalt and cement composites may be suitable for being used as a road material. Cold mix asphalt concrete test samples, made with different amounts of cement (0, 1.5, 3, 4.5 and 6 %), were cured for different times (1, 3, 7, 14, 21 and 28 days) at different environmental relative humidities (35, 70, 90 % and wet curing) and tested with Marshall stability tests. It was found that cold mix asphalt concrete without cement additions resists much lower forces and it is less rigid than hot mix asphalt concrete, even after 28 days curing at a very low relative humidity. However, when part of the filler (1.5–6 % by mass) is replaced by Portland cement, the force resisted by the material and its rigidity increase progressively. Although the rigidity of the cold mix asphalt concrete specimens tested was always below the rigidity of the corresponding hot mix asphalt, the total force resisted could be higher, depending on the amount of cement added.

Moreover, it was observed that there is a clear relationship between the environmental humidity during curing, the water losses and the speed at which cold mix asphalt concrete gains resistance. Indeed, the force and rigidity of the mixtures were inversely proportional to the amount of water present in the mixture. Cement hydrated almost completely in the mixture and the final amount of free water in the mixture was reduced when the amount of cement was increased. However, even when the composite was cured for 28 days and contained 6 % of cement, a small amount of evaporable water still remained in the mixture.

Additionally, X-ray microtomography revealed that these mixtures had a number of inhomogeneities and cracks. Water bubbles, debonded aggregates, zones with high porosity and segregation of bitumen and cement were observed. These defects can be caused by inappropriate mixing and compaction methods, or by an excessive amount of water in the mixture. An extensive study on the microstructure of asphalt and cement composites will follow, as there is clearly scope for optimizing this type of mixtures.

Based on the results of this study, it can be concluded that asphalt and cement composites have the potential for being used as road materials, although they are still at an early stage of development. As suggested by this research, by mixing asphalt emulsion and cement, it should be possible to obtain a material with higher compressive resistance than a traditional asphalt concrete, but with the same flexibility. The main handicaps of these composites are that it is still unclear how they should be mixed and compacted and especially the long time needed for the curing process. This last problem could be addressed in the future by using cementitious materials different from Portland cement.

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References

1. Marienfeld L, Guram K (1999) Overview of field installation procedures for paving fabrics in North America. Geotext Geomembr 17(2):105–120
2. Liang R, Zhou J (1997) Prediction of fatigue life of asphalt concrete beams. Int J Fatigue 19(2):117–124
3. Conway-Schempf N (2000) Case study: economic input-output life cycle assessment of asphalt versus steel reinforced concrete for pavement construction. Carnegie Mellon University, USA
4. Brown ER (1988) Preventive maintenance of asphalt concrete pavements. NCAT Report No 88-1
5. DECICORP (1996) Economic research on continuously reinforced concrete pavement. Report of the Steel Reinforcement Institute of Australia, SRIA, Construction Industry and Economic Research, 2nd stage
6. Litvan GG (1976) Frost action in cement in the presence of De-Icers. Cem Concr Res 8(3):351–356
7. Yoder EJ, Witczak MW (1975) Principles of pavement design. Wiley, New York
8. Concrete pavement maintenance/repair. Cement Concrete & Aggregates Australia 2009 http://www.concrete.net.au/publications/pdf/PavementRepair.pdf, 15 p
9. FHWA-SA-98-079, Life-cycle cost analysis in pavement design
10. Li G, Zhao Y, Pang SS, Huang W (1998) Experimental study of cement-asphalt emulsion composite. Cem Concr Res 28(5):635–641
11. Thenoux G, González A, Dowling R (2007) Energy consumption comparison for different asphalt pavements rehabilitation techniques used in Chile. Resour Conserv Recycl 49(4):325–339
12. Jenkins KJ, van de Ven MFC, Derbyshire R, Bondietti M (2000) Investigation of the early performance properties of a pavement, recycled with foamed bitumen and emulsion through field testing. Action in transport for the New Millennium. 19th Annual South African transport conference
13. Oruc S, Celik F, Akpinar MV (2006) Effect of cement on emulsified asphalt mixtures. J Mater Eng Perform 16(5): 578–583
14. Wang Z, Sha A (2010) Micro-hardness of interface between cement asphalt emulsion mastic and aggregates. Mater Struct 43:453–461
15. Head RW (1974) An informal report of cold mix research using emulsified asphalts as a binder. Proc Assoc Asph Paving Technol 43:110–131
16. Terrel RL, Wang CK (1971) Early curing behaviour of cement modified asphalt emulsion mixtures. Proc Assoc Asph Paving Technol 40:108–125
17. Nataatmadja A, Chowdhury SH, Liu L, Fragomeni S (2002) Development of a bitumen-bound high performance base course material. In: Loo Y-C (ed) Proceedings of advances in mechanics of structures and materials. Taylor & Francis, pp 413–418
18. Pouliot N, Marchand JD, Pigeon M (2003) Hydration mechanisms, microstructure and mechanical properties of mortars prepared with mixed binder cement slurry-asphalt emulsion. J Mater Civ Eng 15(1):54–59
19. Weiss WJ, Lura P, Rajabipour F, Sant G (2008) Performance of shrinkage reducing admixtures at different humidities and at early ages. ACI Mater J 105(5):478–486
20. James AD, Needham D, Brown SF (1996) The benefits of using ordinary Portland cement in solvent free dense graded bituminous emulsion mixtures. International symposium on asphalt emulsion technology (AEMA), October 3–6, 1996, Washington DC, pp 179–188
21. Taylor HFW (1989) Modification of the Bogue calculation. Adv Cement Res 2:73–77
22. Lura P, Winnefeld F, Klemm S (2010) A method for simultaneous measurements of heat of hydration and chemical shrinkage on hardening cement pastes. J Therm Anal Calorim 101:925–932
23. Wyrzykowski M, Lura P (2012) Controlling the coefficient of thermal expansion of cementitious materials—a new application for superabsorbent polymers. Cement Concr Compos. doi:10.1016/j.cemconcomp.2012.08.010
24. Feldkamp LA, Davis LC, Kress JW (1984) Practical cone-beam algorithm. J Opt Soc Am A: 1:612–619
25. Powers TC, Brownyard TL (1947) Studies of physical properties of hardened Portland cement paste. J Am Concr Inst 43:984–987

26. Lehmann P, Or D (2009) Evaporation and capillary coupling across vertical textural contrasts in porous media. Phys Rev E Stat Nonlin Soft Matter Phys 80:046318. doi: 10.1103/PhysRevE.80.046318.
27. Scherer GW (1990) Theory of drying. J Am Ceram Soc 73(1):3–14
28. Lura P, Pease BJ, Mazzotta G, Rajabipour F, Weiss WJ (2007) Influence of shrinkage reducing-admixtures on the development of plastic shrinkage cracks. ACI Mater J 104(2):187–194
29. García A (2012) Self-healing of open cracks in asphalt mastic. Fuel 93:264–272
30. Liu Q, García A, Schlangen E, van de Ven MVD (2011) Induction healing of asphalt mastic and porous asphalt concrete. Constr Build Mater 25(9):3746–3752
31. Birchall JD, Howard AJ, Bailey JE (1978) On the hydration of Portland cement. Proc R Soc Lond Ser A Math Phys Sci 360(1702):445–453
32. Jonsson B, Wennerstrom H, Nonat A, Cabane B (2004) Onset of cohesion in cement paste. Langmuir 20(16):6702–6709
33. Yang J, Yan P, Kong X, Li X (2010) Study on the hardening mechanism of cement asphalt binder. Sci China Technol Sci 58(5):1406–1412
34. Brown SF, Needham D (2000) A study of cement modified bitumen emulsion mixtures. In: Proceedings of the 2000 annual meeting of the association of asphalt paving technologies
35. García A, Castro-Fresno D, Polanco JA (2008) Evolution of penetration resistance in fresh concrete. Cement Concr Res 38(5):649–659
36. Wang Z, Wang R (2011) Influences and mechanisms of ordinary Portland cement on properties of asphalt emulsion composites. Adv Mater Res 160–162:235–240
37. Winnefeld F, Lothenbach B (2010) Hydration of calcium sulfoaluminate cements—experimental findings and thermodynamic modeling. Cement Concr Res 40(8):1239–1247
38. Higuchi Y, Harada Y, Nakagawa K, Kawaguchi I, Kasahara Y (1978) Quick hardening cement-asphalt composition, US Patent 4084981
39. García A, Castro-Fresno D, Polanco JA (2007) Effect of dry-shaking treatment on concrete pavement properties. Constr Build Mater 22(11):2202–2211