Effects of surfactants on the formulation, cohesion build-up and moisture resistance of virgin and recycled cold bituminous mixtures and relationship to emulsion breakup

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Abstract

The use of bitumen emulsion in pavement structures, coupled with the introduction of reclaimed asphalt pavement (RAP), is an effective approach to preserve non-renewable resources and save energy. The formulation of virgin and recycled cold mix asphalt (CMA) requires the compatibility of the emulsion with the aggregates and RAP, according to their respective physicochemical characteristics. The objective of this research was to investigate the influence of parameters related to the bitumen emulsion and asphalt mixture composition on the implementation and durability of virgin and recycled CMA.

The study focused on granite-based CMA with recycling rates of 0 and 50 %. Six emulsions were produced by varying the nature and content of the surfactant (0.9, 1.2 and 1.5 wt%). The mixtures were fabricated with different total water contents. The cohesion build-up and the compressive strength of the optimized mixtures were assessed.

The results showed that the optimal total water content of virgin and recycled CMA differed with the surfactant type and decreased when the surfactant content increased, regardless of the composition. Likewise, the kinetics of cohesion build-up of mixtures is influenced by the amount of added water, surfactant nature and content. The moisture resistance of the mixtures is related to their short-term cohesion and is the highest at an optimum emulsifier content. Finally, the recycled asphalt mixes exhibited better compaction properties, higher mechanical strength (+ 0.5-0.7 MPa) and water resistance than those of virgin asphalt mixes.

Keywords: Cold mix asphalt, bitumen emulsion, recycling, cohesion build-up, moisture sensitivity

1. Introduction

The consideration of energy savings and the reduction of environmental impacts and non-renewable resources in asphalt mix industry have conducted to lower production temperatures and to use reclaimed asphalt pavement (RAP) during the manufacture. With the bitumen emulsion cold mix asphalt (CMA) technique, energy consumption is drastically decreased because no heating is required.

At present, the numerous applications of virgin and recycled cold mixtures in road pavement remain the expertise of constructors (Syndicat des fabricants d'émulsions routières de bitume et de liants anhydres 2006). Some research has been undertaken to develop a rational mix design approach (Lesueur and Potti 2004; Ojum 2015; Serfass et al. 2011) and to obtain materials with high mechanical performance close to that of hot mixes. The issue also lies in the complexity of the emulsion itself.

Bitumen emulsion is a dispersion of bituminous binder (40-75 wt%) in fine droplets in an aqueous phase (25-60 wt%) and stabilized by chemical components called emulsifiers (0.1-2.5 wt%), which are generally surfactants (Salomon 2006) These emulsifiers present affinity both with water and oil according to the two parts of their molecules: a lipophilic hydrocarbon chain and a hydrophilic polar head. In its use for asphalt mixes, the bitumen emulsion breaks in contact with the mineral surface to release the binder in the granular matrix (Rodríguez-Valverde et al. 2008). Bitumen droplets merge to form a continuous film; thus, the binder is reconstituted to ensure the cohesion and coating properties required for aggregates and RAP. This breaking process is very complex and its kinetics is still poorly understood and uncontrolled.

2. Background and goal

The influence of surfactants on the stability of emulsions has already been the subject of numerous studies (Mercado et al. 2012, 2014; Rodríguez-Valverde et al. 2008; Ziyani et al. 2014). The different theories of emulsion breaking mechanisms on the mineral surface are known:

- Breakage by adsorption of surfactants and bitumen droplets on the mineral surface;
- Rupture by rising pH of the aqueous phase (case of cationic emulsions);
- Rupture by volume reduction of water (due to absorption, drainage and evaporation).

These steps can occur independently, probably simultaneously, and are strongly linked to the mineralogical composition of aggregates, as well as the surfactants. These will be decisive for the emulsion breaking process until coalescence, as well as for the performance of cold mix asphalt.

The flocculation and coalescence phenomena have been elucidated without clearly addressing the question of their impact on the final properties of the mix. The type of interactions between the mineral surface and bitumen emulsion depends, among others, on the presence in a high proportion or not, of alkaline or alkaline-earth elements in the mineral, on the emulsifier nature and content. Khan *et al.* (Khan et al. 2018) showed that for certain types of bitumen in the emulsion, a dosage of surfactants above a given concentration compromises the adsorption of bitumen droplets and therefore the bonding of the binder on the mineral surface. This is due to the double-layer electrostatic barrier, which prevents bitumen droplets from adsorption. However, this observation must be put into perspective, because if it seems to occur at equilibrium, the application of emulsions in road technique is in an area of non-equilibrium. Loss of part of the aqueous phase (e.g. by compaction or capillarity), which has a draining effect on residual surfactants, can accelerate the adsorption of bitumen globules on the mineral surface (Rodríguez-Valverde et al. 2002).

After the emulsion breaks, the cohesion build-up of the mixture increases (Deneuvillers and Poirier 2002; Poirier 2002). This step is crucial to assure the workability of the mix (Eckmann 2002), and its kinetics depends on many parameters, such as the CMA formulation or climatic conditions. Current studies dealing with cold mix design focused more on strength (Otieno et al. 2020), compactability or Marshall stability (Jain and Singh 2021; Thanaya 2007; Wang et al. 2018), with the aim of optimizing the total water content of the mixtures (Grilli et al. 2016; Latifi and Amini 2020). The cohesion build-up is sometimes informed and assessed via torque measurements (Odie et al. 2011a), cohesimeters (Yan et al. 2017), gyratory compaction tests (Casillas and Braham 2021) or workability tests (Serfass et al. 2012), although the existing research works have related the effect of curing conditions (Eckmann et al. 2002). The influence of surfactants on this property has not been addressed in the literature.

CMA has not yet been widely used as a surface course in pavement technology (Nassar et al. 2018). One of the causes that hinder its development (in comparison with hot mixes) is durability. Generally, a large part of the degradation process of asphalt layers is associated with a loss of performance under the influence of water, which affects the binder-mineral surface interface (Hefer et al. 2005). The durability of coated materials in the presence of water has always been a concern in road engineering and many studies have been undertaken in this field (Cui et al. 2014; Ling et al. 2014; Nassar et al. 2018), also in the case of recycled cold mixtures (Arimilli et al. 2016). The adhesion strength between the bituminous binder and aggregates determines the cohesion build-up and resistance of the mix to external mechanical forces and its moisture resistance, thus guaranteeing its long-term performance.

Numerous studies (Hefer 2005; Khan et al. 2016; Mercado and Fuentes Pumarejo 2016; Wu et al. 2022; Ziyani et al. 2016) have shown a direct relationship between the formulation of the emulsion (emulsifier nature and content, bitumen nature, bitumen grade and content, pH, etc.) and the phenomenon of binder-aggregate adhesion. Many research works have dealt with the water resistance of cold mix asphalt, but very often only at the level of the binder-aggregate interaction. Zhang *et al.* (Zhang et al. 2015) investigated the moisture sensitivity of the bitumen-aggregate interface, in particular the influence of the aggregate mineralogy, through three adhesion failure tests. Another study, based on the application of the stripping work theory, was conducted (Zhang et al. 2018) to assess the resistance of the binder to the effect of water in the bitumen-aggregate system, in relation with the aggregate mineralogical composition and the bitumen nature. Thanaya (Thanaya 2007) showed that when formulation and curing conditions were correctly performed, cold mixes presented a stiffness comparable to that of hot mixes for the same bitumen grade. Miljković (Miljković 2014) analyzed the effect of the emulsion formulation on the moisture resistance of cold mixes by varying the bitumen grade. Ling *et al.* (Ling et al. 2013) revealed by digital imaging analysis that the level of coating of the aggregates in the cold mixes improves the water resistance and workability. More recently, Chelelgo *et al.* (Chelelgo et al. 2018) considered the effect of varying the feed water and emulsion content on the moisture damage of virgin and recycled asphalt mixtures. Miljković *et al.* (Miljković et al. 2017) investigated the emulsifier content variation on the emulsion mortar water resistance and found an optimum, depending on the cement hydration process.

To our state of knowledge, very few studies have attempted to correlate both the nature and content of surfactant in the emulsion with the mechanical performance of virgin and recycled cold mixes at young age and after curing, and to establish a relationship between these two states of the mixtures. The purpose of this research is to assess the effect of the surfactant nature and content on the formulation of virgin (VCMA) and recycled cold mix asphalt (RCMA) and their properties, specifically in terms of cohesion build-up and resistance to moisture. These results would help to guarantee the workability and durability of virgin and recycled asphalt mixes with the bitumen emulsion.

3. Experimental methodology

3.1. Materials

0/4 and 4/10 grading granite aggregates extracted from a quarry in Côte d'Ivoire were supplied for the manufacture of CMA. 0/10 grading RAP (named RAP throughout the paper) milled from a wearing course in Côte d'Ivoire, were also used for the recycled formula. Limestone filler (particle size < 0.063 mm) was employed to obtain the desired gradation and because of its high reactivity with cationic emulsions. The binder content from RAP was 4.8 ± 0.1 wt%.

The chemical composition of the limestone filler, granite aggregates (0/4 fraction sieved to 0.063 mm sieve) and aggregates from RAP (after extraction) was determined using X-ray fluorescence spectrometry (S2 Ranger instrument, Bruker). The results showed a high proportion of SiO_2 in both granite and RAP (64.3 and 64.8 wt% respectively), and a low content (< 11 wt%) of alkaline or alkaline-earth elements (K_2O, MgO, Na_2O), whereas limestone contains a high CaO content (83.2 wt%). It is worth noting that the global composition of virgin aggregates and RAP is very similar.

The reactivity of the limestone filler, granite aggregates and RAP (both sieved at 2 mm) was determined using the rise in pH test, according to (Odie et al. 2011b). It consisted of monitoring the pH of an acid aqueous phase (initial pH = 2.0 ± 0.1) in contact with the mineral for 120 min. The results depicted in Fig. **1** reveal that limestone is very reactive because it is chemically rich in

CaO, unlike granite, which is an acid-type aggregate poor in alkaline elements, and RAP, which has a granitic origin and is covered with an aged non-reactive binder.

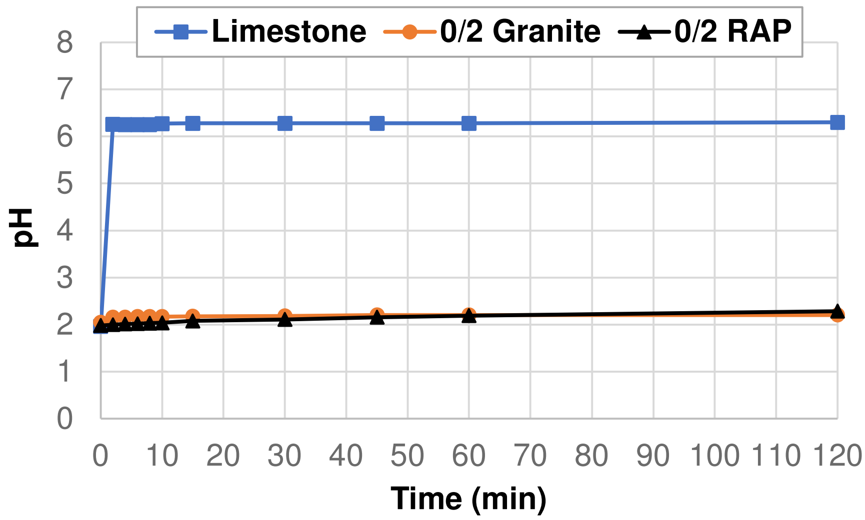


Fig. 1 Rise in pH of granite, limestone and RAP by acid attack (initial pH = 2.0 ± 0.1).

A 70/100 penetration grade pure bitumen (Aqualt®, Total) refined in France was used to fabricate all the emulsions. The penetration and Ring and Ball (R&B) softening point of this binder and the one extracted from RAP were determined according to EN 1426 (EN 1426 2018) and EN 1427 (EN 1427 2018), respectively. The results found for 70/100 bitumen (penetration: 76 ± 1 1/10 mm, R&B: 46.8 ± 0.1 °C) and RAP bitumen (penetration: 21 ± 1 1/10 mm, R&B: 74.6 ± 0.4 °C) are those expected for these types of binder.

Emulsions were manufactured in the laboratory using two cationic surfactant emulsifiers named A and B, by varying the emulsifier content at 0.9, 1.2, 1.5 wt% according to the mass of the bitumen emulsion. The surfactants were mixtures of amines and polyamines in different proportions in A and B. In accordance with the supplier's technical data sheet, B contains a higher proportion of molecules with long hydrocarbon chains than A. In addition, A includes lignin, whereas B is composed of fatty acids. These molecules were chosen according to their convenience in cold mix asphalt with the aggregates used. The bitumen content of the emulsions was 65 wt%. All the emulsions were produced in the laboratory using a colloid mill (Atomix®, Emulbitume), according to the same manufacturing protocol (phase temperatures: 50 and 140 °C for the aqueous phase and bitumen, respectively, colloid mill fractionation speed: 8900 rpm).

Tap water was employed to make emulsions and hydrochloric acid (32 %) was added to protonate the aminated bases and to obtain for each aqueous phase a pH of 2.0 ± 0.1. The emulsions were all slow-setting and were named A and B when they contained emulsifiers A and B, respectively. Their main characteristics are presented in Table 1. The binder content, Forshammer breaking index, pseudo-viscosity, sieve residue and pH were measured according to EN 16849 (EN 16849 2016), EN 13075-1 (EN 13075-1 2016), EN 12846-1 (EN 12846-1 2011), EN 1429 (EN 1429 2013) and EN 12850 (EN 12850 2009), respectively.

Table 1 Properties of the bitumen emulsions.

Emulsifier nature	**A**			**B**		
Emulsifier content (% by mass of emulsion)	0.9 %	1.2 %	1.5 %	0.9 %	1.2 %	1.5 %
Binder content (% by mass of emulsion)	63.7 ± 0.1	65.4 ± 0.0	64.1 ± 0.0	64.9 ± 0.2	64.8 ± 0.0	64.9 ± 0.2
Breaking index (Forshammer)	155.1 ± 3.1	157.1 ± 1.8	185.0 ± 0.7	213.6 ± 0.9	228.0 ± 2.9	250.5 ± 1.0
Pseudo-viscosity (s) (40 °C, 2 mm aperture)	37 ± 0	50 ± 1	36 ± 0	38 ± 0	38 ± 1	38 ± 0
Sieve residue (0.5 mm) (%)	0.02 ± 0.01	0.11 ± 0.05	0.01 ± 0.01	0.04 ± 0.01	0.01 ± 0.01	0.01 ± 0.01
pH	2.1 ± 0.1	2.1 ± 0.1	2.4 ± 0.2	2.6 ± 0.3	2.3 ± 0.2	2.8 ± 0.3

As shown in Table 1, at the same surfactant content, emulsion A breaks faster than emulsion B, according to the values of the conventional breaking index test.

3.2. Test methods

3.2.1. Emulsion-aggregate adhesivity test

The emulsion-aggregate couples were evaluated in terms of adhesion of the residual binder on aggregates according to the European standard EN 13614 (EN 13614 2014). The test consisted of mixing 200 g of aggregate (passing through a 10 mm sieve and retained in a 6.3 mm sieve) with the equivalent of 10 g of bituminous binder from the emulsion. After the complete coating of aggregates and 24 h of curing in an oven at 60 °C, these were subjected to the action of water at the same temperature for 20 h. Finally, their surface covered with the residual binder was assessed visually. As this test is not relevant for aggregates already recovered with a binder, it was not practiced on RAP.

3.2.2. Determination of the optimum total water content (WC)

Virgin and recycled asphalt mixtures were manufactured at a small scale from a total mass of dry aggregates of 500 g according to the particle size distribution curve shown in Fig. **2**. The recycling rate was 50 % in RCMA.

Three residual binder contents of 4.76, 5.21 and 5.66 wt% (to the total mass of mixture) were considered with a total mixing water content varying from 2.9 to 10.7 wt% (to the total mass of mixture) to determine the optimal total water contents, depending on the emulsifier content. The mass proportions of the various constituents are listed in Table 2. The formulation test protocol was based on the IFSTTAR test method No. 74 supplementing standard (NF P 98-257-1 2004) and is now recognized as the European standard EN 12697-55 (EN 12697-55 2019). It consisted of manual and visual assessments of the hydric state, consistency and coating of various mixtures after different curing times (0 h, 4 h and 24 h) to determine the optimal water content. Scores were assigned on a scale of 0-4 for each evaluation parameter. Finally, choices were made based on accepting suitability criteria for all parameters. The test revealed that the optimum binder contents were 5.21 wt% for virgin mixes, and 4.76 wt% for recycled ones.

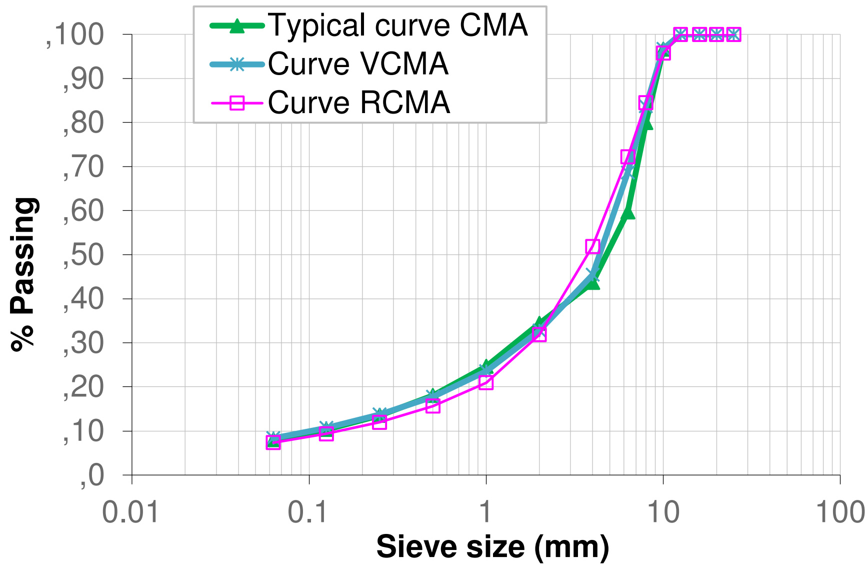


Fig. 2 Grading curves for virgin and recycled asphalt mixtures.

Table 2 Composition of virgin and recycled mixtures.

	VCMA			RCMA			
	Limestone filler	0/4	4/10	Limestone filler	0/4	4/10	RAP 0/10
Composition (% by mass of aggregates)	3	32	65	3	30	17	50
True density (g/cm^3)	2.76	2.75	2.68	2.76	2.75	2.68	2.54
Residual binder content (% by mass of mixture)	5.21			4.76*			

*As RAP was considered initially as a "black rock" (i.e. the bituminous binder of RAP was not remobilized), the binder content mentioned for recycled mixture is related to the binder from the emulsion only.

3.2.3. Assessment of the cohesion build-up and moisture resistance of cold mixtures

Several methods have been developed to measure the kinetics of cohesion build-up (Brion et al. 1999; Fabre des Essarts et al. 2016; Odie et al. 2006, 2011a). The cohesion build-up of virgin and recycled mixtures was evaluated using a spreadability-meter (cf. Fig. **3**), according to the standard EN 12697-53 (EN 12697-53 2019). This method was preferred to the gyratory compaction because this latter is not sensitive to workability changes at different temperatures and bitumen grades, in particular in the case of hot and warm mix asphalt (Bennert et al. 2010; Fabre des Essarts et al. 2016). The mold was filled with the material by dropping it from a height of 1 m through a filling shoot. The dimensions of the mold were 15 cm × 22 cm × 10 cm (length × width × height) and those of the stainless steel plate, linked to the force measurement, were 11.5 cm × 5 cm (length × height). The cohesion build-up of samples was assessed keeping the same mass at 6.0 ± 0.1 kg.

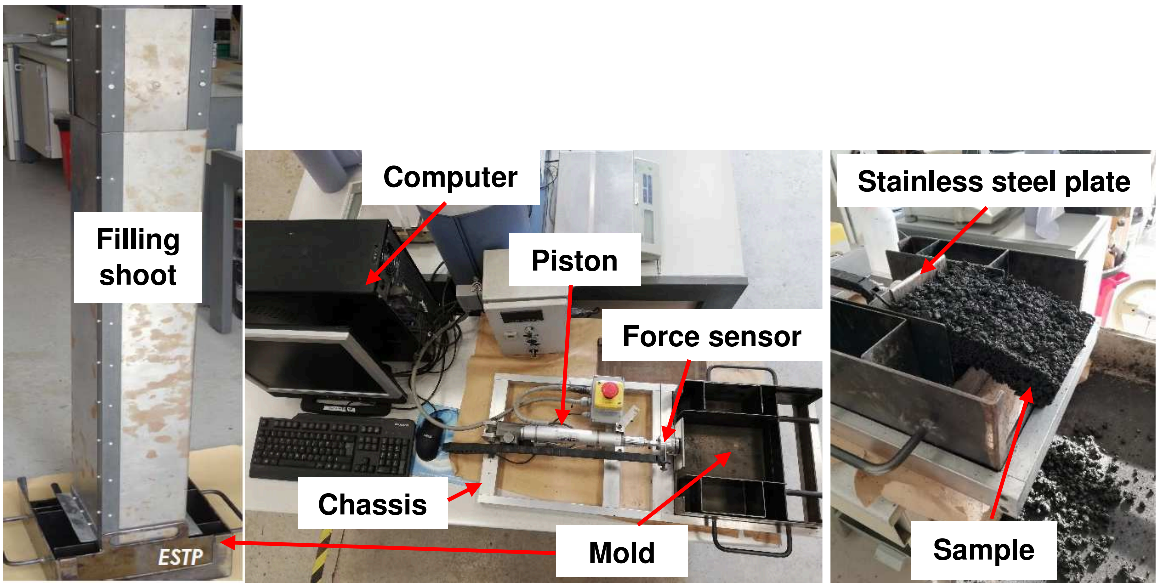


Fig. 3 Spreadability-meter device.

Each sample was previously positioned in the mold at t = 0 h. After a curing time under set conditions, it was pushed by the stainless steel plate using a piston at a constant speed of 1 cm/s. The shear force was recorded over time on the computer through a force sensor. The shear forces on the samples were measured immediately after manufacture (t_{0h}) and after storage in a climatic chamber at 35 °C and 20 % relative humidity, after curing for 4 and 24 h (t_{4h} and t_{24h}). The curing conditions were considered according to the results of (Serfass et al. 2011), and the curing times were adopted regarding those used to determine the optimum binder and total water contents at the small scale. Before the mixtures with the emulsion, the cohesion of virgin and recycled aggregates alone was measured at a dry state (as received) and after humidification to the optimum total water content in order to assess the internal friction in the aggregates. Each test was repeated at least in duplicate.

One of the sustainability criteria considered in this study was the moisture damage resistance of the virgin and recycled asphalt mixtures according to the emulsion formulation, in particular the nature and dosage of the emulsifier. Many methods have been developed to assess the water sensitivity of asphalt mixtures, as mentioned in the state-of-the-art (Mehrara and Khodaii 2013). In our study, the moisture damage resistance was evaluated using the test known as Duriez in accordance with the standard NF P 98-257-4 (NF P 98-257-4 2004).

Twelve test specimens were manufactured for each mixture at t_{0h} in 80 mm diameter cylindrical molds by applying a compaction force of 60 kN for 300 s with the optimal water contents retained and respective binder contents of 5.21 wt% for VCMA and 4.76 wt% for RCMA. The test pieces were removed from the mold the next day and cured for 7 days at 35 °C and 20 % relative humidity. After this curing time, the mass M_{J+8} of the specimens was weighed to the nearest 1 g, while the height h and the diameter φ were measured to the nearest 0.1 mm, on three different zones.

The apparent density *MVA* was calculated from the geometric measurements according to Eq. (1):

$$\mathrm{MVA} = \frac{(4 \times \mathrm{M_{J+8}})}{(\pi \varphi^2 \mathrm{h})} \tag{1}$$

From the measured geometric apparent densities, the specimens were divided into three batches. The average bulk density of each batch should be closest to the average bulk density of the whole. One batch of five was kept dry, the second batch of five was immersed and the remaining two samples were dedicated to hydrostatic bulk density weighing. The test pieces were stored for additional 7 days under the same conditions of temperature and humidity.

Finally, the compressive strengths of the dry (C) and immersed specimens (i) were measured, and the water resistance of the mixture was determined according the *i/C* ratio. This ratio was compared with the highest value of 0.80, which is required for the water resistance of hot mix asphalt for wearing courses.

4. Results and discussion

4.1. Emulsion-aggregate compatibility

The results of the binder adhesivity test are depicted in Fig. **4**. It appears that granite aggregates have a low binder covering with surfactant A, while the quality of adhesion seems very good with surfactant B. The good affinity of emulsions manufactured with B for aggregates is due to the strong lipophilic character of the surfactant linked to its hydrocarbon chain size, which is longer than that of surfactant A. A long carbon chain implies a higher affinity for oil than for water (Salager 1993). The adsorption of this surfactant on substrates leads to a better binder-aggregate adhesion. Therefore, the final adhesivity of the residual binder remains largely dependent on that of the emulsion, which is generally good for a "normally formulated cationic emulsion" (Syndicat des fabricants d'émulsions routières de bitume et de liants anhydres 2006). Meanwhile, it is strongly influenced by the emulsion-aggregate affinity, which is correlated with the presence of the emulsifier.

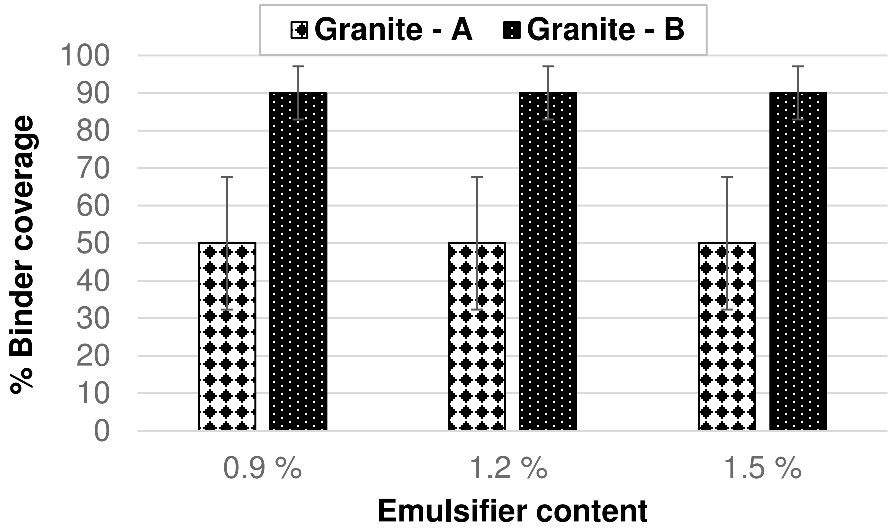


Fig. 4 Coverage levels of granite aggregates by the residual emulsion binder.

4.2. Optimal total water content of mixtures

According to the consistency tests on virgin and recycled asphalt mixes, the optimum total water contents for the respective residual binder contents of 5.2 and 4.7 wt% are shown in Fig. **5**. A decrease in the optimal total water contents is observed with the increase in surfactant content. This can be explained by the phenomenon of surfactant adsorption on minerals, which tends to make their surface more hydrophobic with the increase in surfactant concentration and thus favor their wetting by the bitumen droplets from the emulsion (Mercado et al. 2012).

Likewise, a difference in the optimum total water content can be noted, depending on the nature of the emulsifier used to manufacture the emulsion. This discrepancy can be explained by the relationship between each surfactant and water. The hydrophilic character of emulsifier A is favorable for the presence of water on the surface of the aggregate. Emulsifier B drives out water more effectively from the aggregate interface, which tends to rewet the mixture. Therefore, less water is required to achieve the optimum formulation conditions, consistency and cohesion.

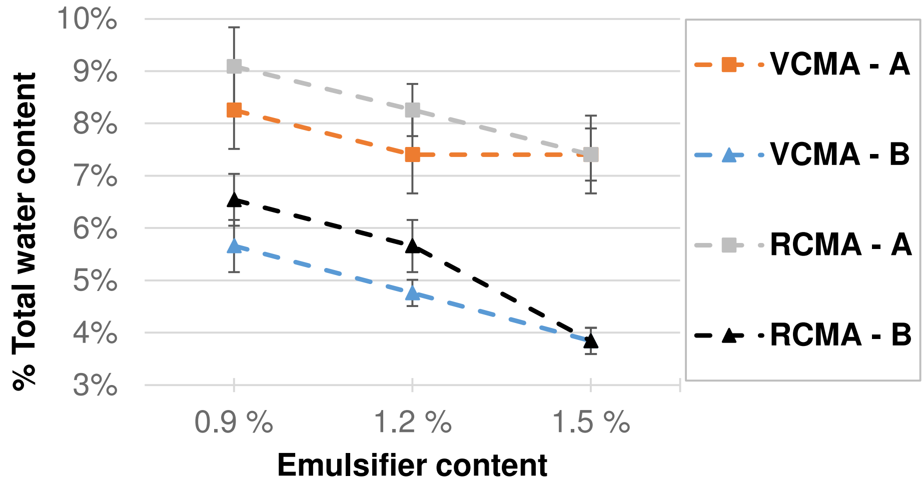


Fig. 5 Variation in optimal total water contents for virgin and recycled CMA at 5.21 and 4.76 wt% residual binder content, respectively.

At the same emulsifier content, the values of the optimal water content are lower for virgin aggregates than for recycled materials. Granite is a hydrophilic material, not very reactive and contains a large proportion of SiO_2 (cf. 3.1). Therefore, the adsorption of surfactants is greater in the virgin mixture than in the recycled mixture, because RAP is more hydrophobic. On the same scale of surfactant, this result shows that the quantity of water to be supplied for the new asphalt mix is lower than that for the recycled asphalt mix.

The trend in the variation of the optimal total water content observed in VCMA is the same as that for RCMA. This is because of the interactions of virgin aggregates with emulsion, which determine the quality of the coating and hydric state of the recycled mixtures. The relative increase in the optimal total water values of recycled mixtures compared to the virgin ones is explained both by the presence of RAP, which are hydrophobic, and by the decrease in residual binder content.

4.3. Cohesion build-up of virgin and recycled asphalt mixes

The variation in the shear forces of the mixtures during the duration of the test was monitored (cf. Fig. **6**). The curves differ according to the state of the mixture, the nature of the aggregates, the nature and content of the emulsifier. A previous work conducted on hot and warm asphalt mixtures has shown three types of shear curves: parabolic, plateau and peak shapes (Fabre des Essarts 2016).

The curve of the aggregate skeletons has a parabolic shape, indicating a resistance to the shear force due to the accumulation of aggregates in the mold. Compared to their dry state, wet virgin and recycled aggregates exhibit more cohesion, mainly under the effect of water, which binds the aggregates. VCMA and RCMA display a resistance peak at the start, reflecting the action of the bituminous binder between the aggregates. This shows that the adhesion process begins early with the manufacture of the mixture.

For VCMA, the curves have the appearance of a plateau with surfactant A, evolving towards the peak-plateau shape. With respect to surfactant B, the curves have a peak-plateau shape. The curves of RCMA have a peak-plateau shape, regardless of the nature of the surfactant. The adhesiveness of VCMA is influenced by the chemical composition of the emulsifier, in particular its hydrophobic nature. However, this effect does not appear in RCMA because of the aged binder of the RAP.

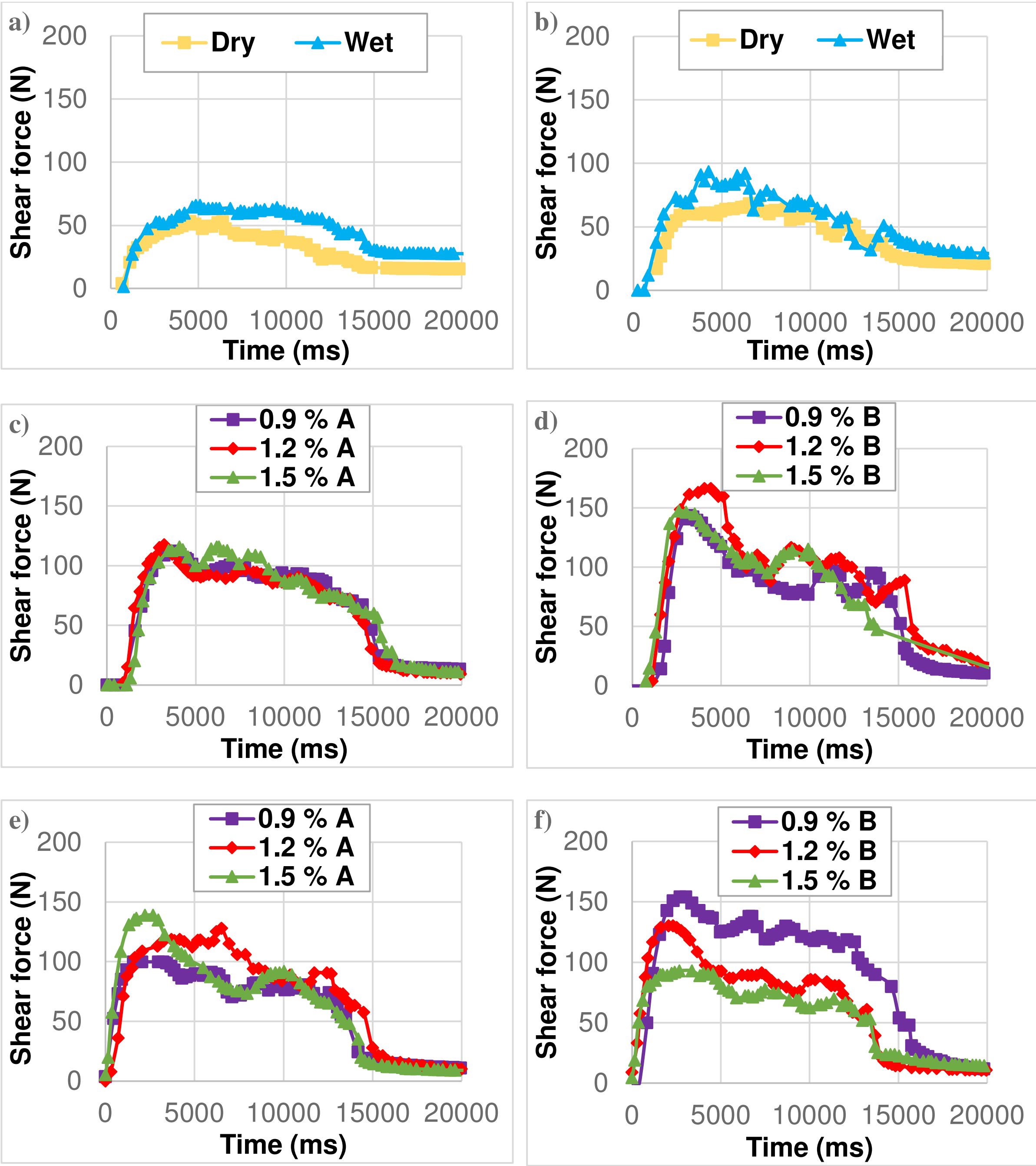


Fig. 6 Variation in the shear force vs time on virgin (a) and recycled (b) granular skeletons, on VCMA with emulsifier A (c) and emulsifier B (d), and on RCMA with emulsifier A (e) and emulsifier B (f) at t = 0 h.

The average maximum shear forces in the virgin and recycled aggregates alone, in dry and wet states, as well as in the virgin and recycled CMA, at t = 0 h, are indicated in Fig. **7**. Recycled aggregates have a stronger cohesion than virgin aggregates, and wet aggregates are more consistent than dry aggregates. Compared to virgin and recycled mixes, the cohesions remain lower.

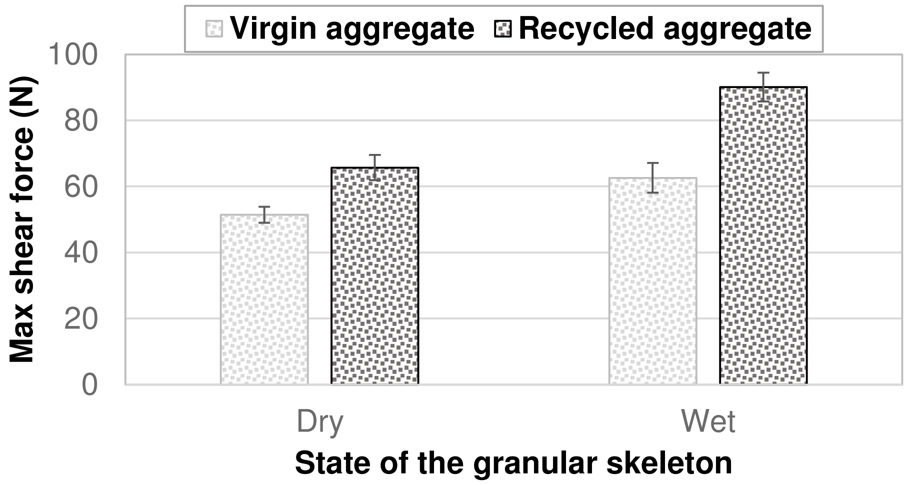
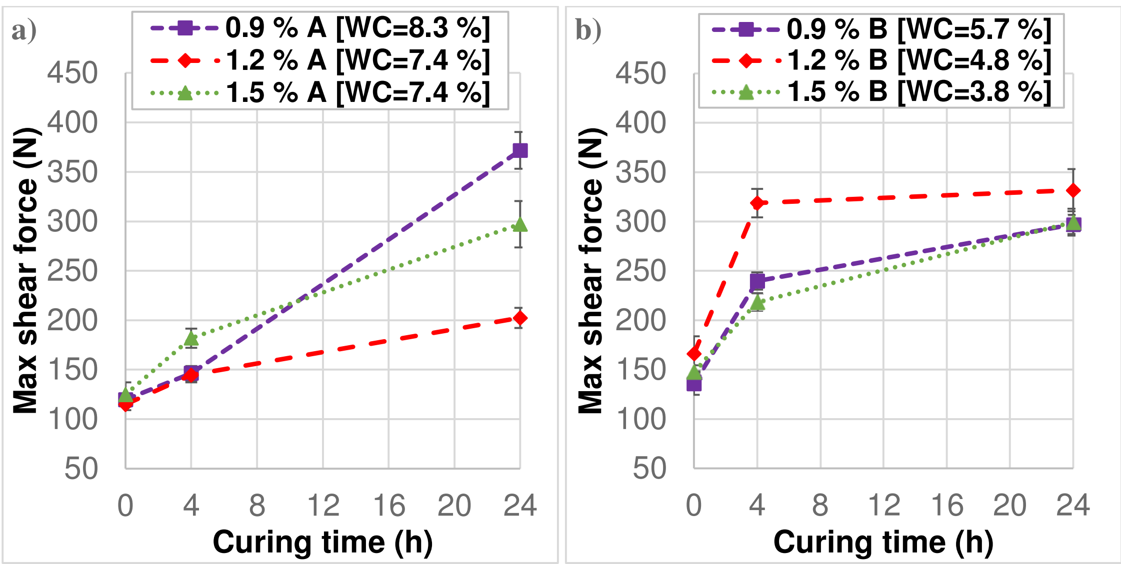


Fig. 7 Maximum shear force of virgin and recycled aggregates (at t = 0 h).

Fig. **8** shows the kinetics of the cohesion build-up of the mixtures at different curing times. The total water contents (WC) are those of the optima determined previously.



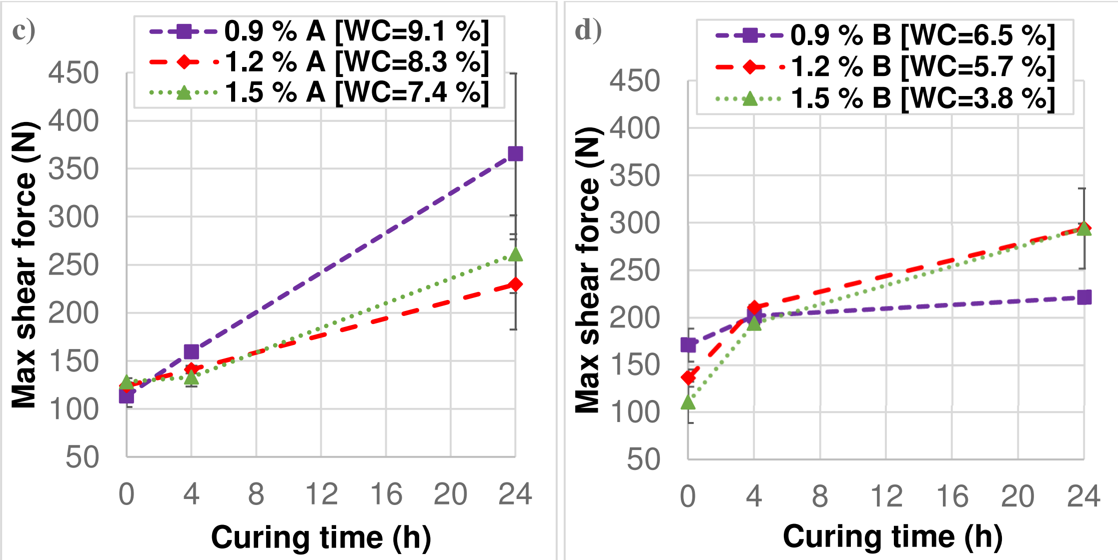


Fig. 8 Cohesion build-up kinetics of VCMA produced with surfactant A (a) and surfactant B (b) and RCMA manufactured with surfactant A (c) and surfactant B (d).
Curing conditions: 35 °C, 20 % relative humidity.

At t = 0 h, in comparison with surfactant A-based CMA, the mixes containing surfactant B exhibit higher cohesion build-up values and greater sensitivity to dosages. This trend can be attributed to the difference in the nature of both molecules. At 1.5 % content, the value for recycled CMA is slightly lower than for A, but comparable, according to the standard deviation. This results in optimum total water contents, which are different for the mixtures, as indicated above, and which are therefore liable to influence their cohesion. More water is retained at the binder-aggregate interface in mixtures with surfactant A than with surfactant B. The sooner the bond between the binder and the aggregate is created, the sooner the growth in cohesion occurs.

The cohesion build-up of recycled CMA increases slightly as the surfactant A content increases, whereas the mixtures fabricated with surfactant B show a significant decrease in cohesion with increasing surfactant content. These observations reflect the difference in the behavior of the mixes made from these two molecules, resulting from their chemical nature, as explained above. In particular, when the surfactant B content rises, the RAP surface becomes more hydrophilic, which is less favorable for cohesion build-up. This variation is opposite with A, which has a more hydrophilic character. The trend highlighted with recycled mixtures is less evident in the case of virgin CMA: the aggregates seem insensitive to surfactant content.

At the same surfactant content, the levels of cohesion for virgin and recycled CMA are equivalent with A, whereas a deviation exists with B. An optimum in force is depicted at 1.2 % for virgin mixtures and at 0.9 % for recycled mixtures.

The kinetics of cohesion build-up is almost linear for surfactant A-based virgin and recycled mixtures. In contrast, in the case of CMA with B, the cohesion kinetics slows down between 4 and 24 h. This can be ascribed to the variation in water content throughout curing, as mixtures manufactured with surfactant B contain less water at t = 0 h.

Moreover, the kinetics is faster after 4 h of curing with surfactant B than for emulsifier A, regardless of the content. It can be noted that the kinetics of the rise in cohesion is strongly dependent on the nature of the surfactant; this can be related to their chemical nature. The pronounced hydrophobic character of surfactant B has two consequences. First, its adsorption on the mineral surface effectively drives out water and ensures good adhesion in the presence of water. Then, the cohesion of the reconstituted bituminous binder after rupture of the emulsion will be stronger in the short term (0 and 4 h) owing to this good adhesion.

After 24 h, the mixtures lost a significant amount of water (25 to 30 wt%) compared to the state after 4 h (less than 5 wt%), and the adhesion of the binder to the aggregates is less affected by the presence of water during the test. Thus, the optimum for the increase in cohesion occurs at the same content for new and recycled mixtures: 0.9 % with surfactant A and 1.2 % with surfactant B.

Compared with VCMA, the increase in cohesion of RCMA is lower after 24 h, except for asphalt with 1.2 % surfactant A. This can be due to the presence of both hydrophilic (granite) and hydrophobic (RAP) aggregates. The adsorption configuration of the surfactants for this composite material is not the same as for a mixture composed of only virgin aggregates.

4.4. Moisture damage resistance of virgin and recycled asphalt mixes

Hydrostatic weighings were carried out on the specimens of virgin and recycled asphalt mixtures to determine the total voids, as shown in Fig. **9**. The graph reveals a slight increase in density with increasing surfactant content for both virgin and recycled asphalt mixtures, except at 1.5 % with surfactant A and virgin CMA. The higher the surfactant content, the more effective the wetting of the aggregates by the emulsion, which tightens the grains between them and reduces the number of voids. However, in the case of virgin mixtures, a high content of surfactant A is detrimental to compactness, due to the formation of a double layer of surfactant on the aggregates, which limits the effectiveness of wetting. This may also be due to the decrease in the optimal total water content, which reduces the pore pressures within the mixtures during compaction.

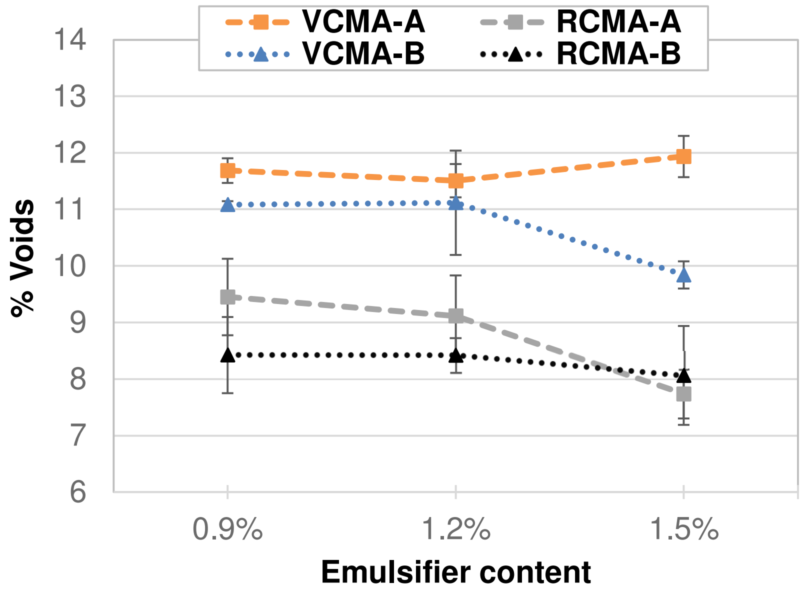


Fig. 9 Comparison of void content of virgin and recycled CMAs.

A higher void percentage is shown for the virgin mixtures than for the recycled ones. This is in agreement with a previous study (Ogundipe 2019). The performance of the recycled asphalt mix is in part due to the rolled shape of the RAP by the aged binder during the compaction processes and the occupation of voids by smaller aggregates. Compaction seems to be easier to implement with RAP than with virgin aggregates. Finally, the compactness of the samples appears better with surfactant B than with surfactant A, both for VCMA and RCMA.

Fig. **10** displays the compressive strength values in dry and wet conditions as well as the compressive strength ratio (*i/C*) determined with mixes manufactured with different emulsion formulations. The optimal total water contents were chosen according to the mixture optimization results (cf. Fig. **5**).

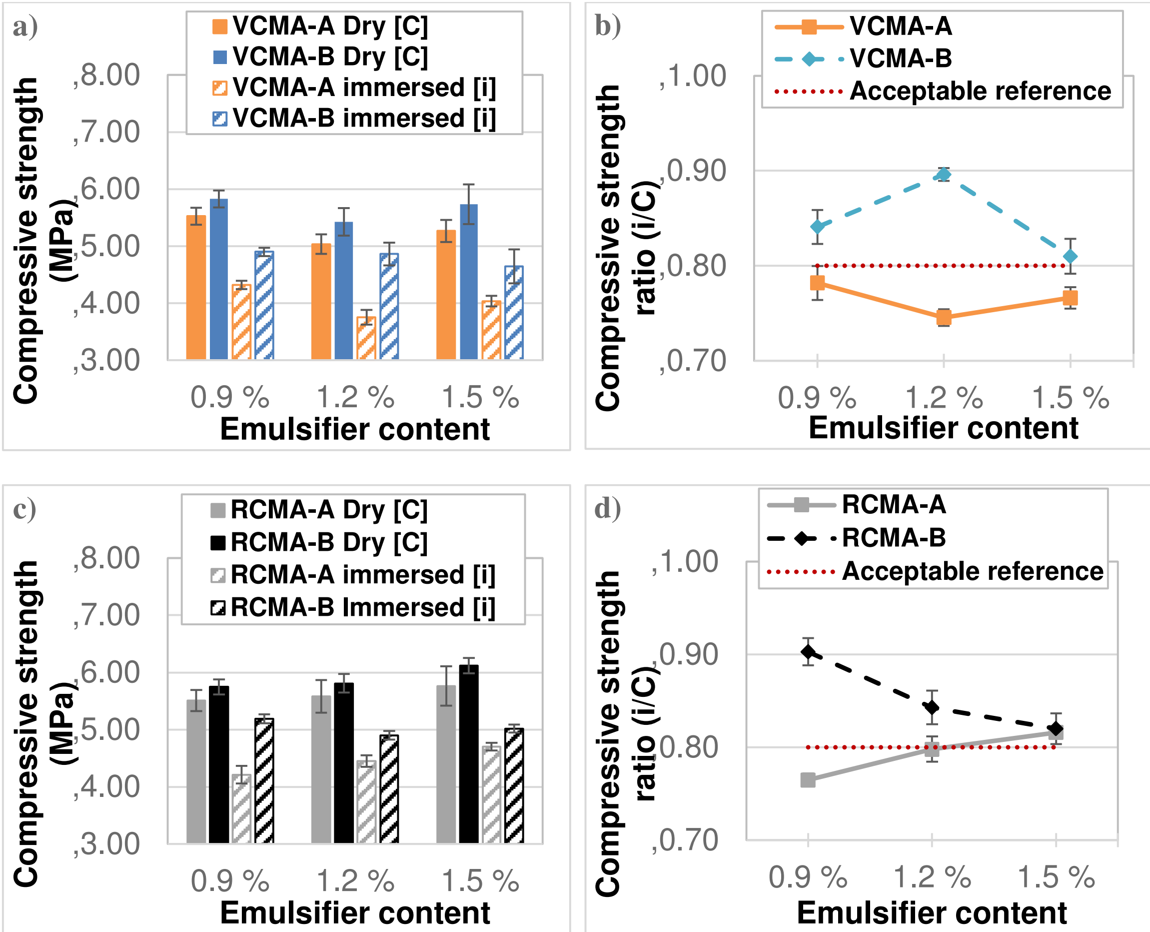


Fig. 10 Mechanical strengths (a, c) and moisture resistance (b, d) of VCMA and RCMA respectively, based on emulsifiers A and B.

The compressive strengths of the virgin and recycled asphalt mixes made with surfactant B are greater than those of mixtures with surfactant A at the same content. This is particularly true for the submerged specimens. The long hydrocarbon chain of B helps to strengthen the adhesion of bitumen, both with virgin aggregates and RAP. For the recycled CMA, the increase in the emulsifier content led to a different tendency in the wet specimen compressive strength, depending on the chemical nature. With A, the compressive strengths grow with increasing content, it is not the case with B.

The moisture resistance of virgin and recycled CMAs is better throughout the entire range of emulsifier contents for B than for A. This result is in accordance with the adhesivity test carried out, which indicates better adhesion of the residual binder with B (Fig. **4**). It should be noted that for surfactant B, the compressive strength ratios giving water resistance values are always greater than the reference value of 0.80. This is not the case with surfactant A, for which all the average values of the compressive strength ratio of VCMA and RCMA manufactured at 0.9 % content are lower than the reference value.

For virgin mixtures, it appears that a good binder-aggregate adhesivity and therefore a better water resistance can be conferred at optimum surfactant contents: 0.9 % for A and 1.2 % for B. Considering recycled mixtures, the water resistance improves with the increase in surfactant A content, and contrarily diminishes with B percentage. Optimum surfactant contents are observed at 1.5 % for A and 0.9 % for B. This is related to the molecular difference between the surfactants and mainly to their respective affinities with water.

A comparison of the mechanical properties of RCMA with those of VCMA depicts an increase in the compressive strengths of the test specimens. These findings could be due to the presence of RAP coated with the aged binder. This means that RAP, initially considered as a black rock, could contribute to the final properties of the mix. Actually, the adsorption of the free surfactants takes place both on the aged binder from the RAP via their lipophilic part and on the virgin aggregates via the polar part (cf. Fig. **11**). The position of the emulsifiers favors the participation of this binder in the mechanical performance of recycled mixture. The better long-term cohesion of recycled CMA compared to virgin CMA is due to the surfactant activities between RAP and virgin aggregates. The low percentage of voids can also explain the increase in the compressive strength of dry and wet specimens of recycled formulas compared to the virgin asphalt mix. However, the quality of water resistance of the recycled mixture compared to that of the virgin mixture depends on the surfactant chemistry. With A, the water resistance of the recycled CMA is better than that of the virgin ones. This is attributed to both the good performance of virgin granite aggregates with regard to water resistance and the presence of RAP. For B, recycled mixes hold as well and sometimes are better than virgin mixes for the same reason.

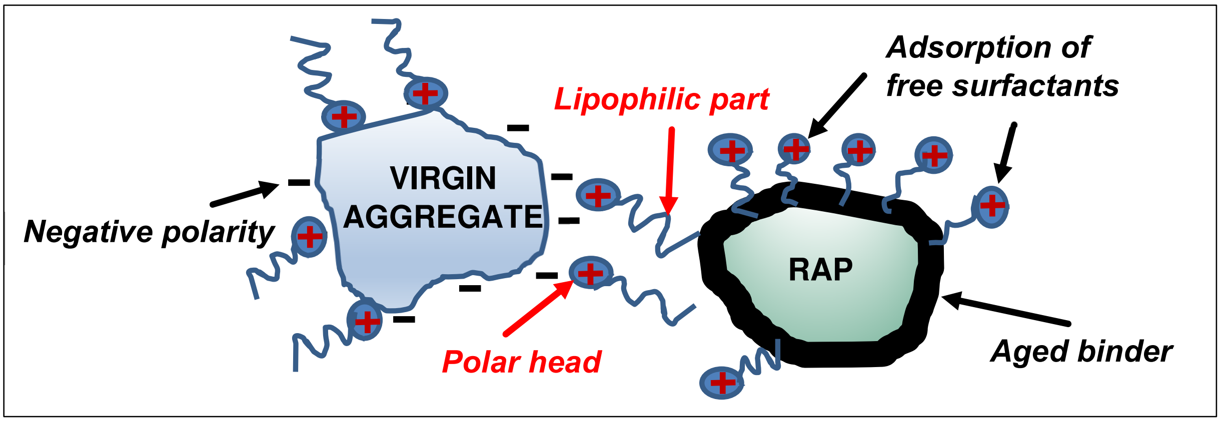


Fig. 11 Adsorption mechanism of surfactants on virgin aggregates and RAP in recycling.

On the scale of the mixtures, the surfaces of the virgin aggregates admit a determined quantity of free surfactants, which makes them completely hydrophobic and conducive to better adhesivity of the binder. Below or above this optimum amount, adhesivity is poor.

4.5. Relationship between breaking index, cohesion build-up (t_{0h}) and water resistance

Fig. **12** shows the variation in the water resistance and rise in cohesion of virgin and recycled CMA as a function of the emulsion breaking index.

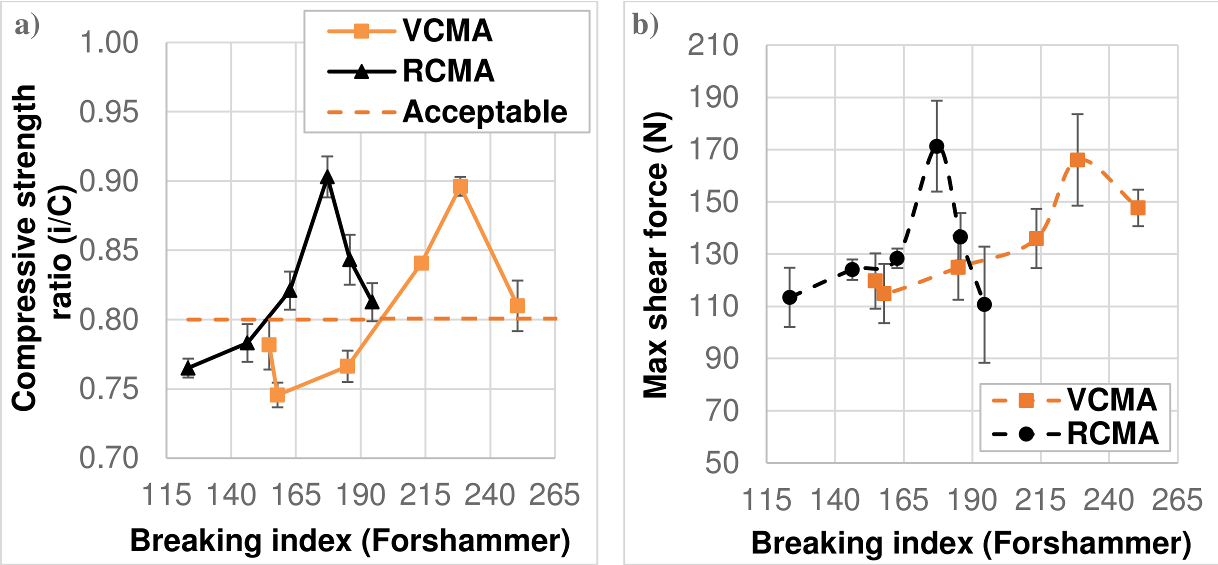


Fig. 12 Moisture resistance (a) and max shear force (t_{0h}) of VCMA and RCMA as a function of emulsion breaking index.

The moisture resistance of virgin and recycled CMAs varies with the emulsion breaking index. An accurate breaking index among the slow-breaking emulsions appears to be more favorable for moisture resistance than the others. There is an optimal breaking index of 228 and 177 for emulsions used to make virgin and recycled CMA, respectively. This is suitable for water resistance.

The breaking index represents the rate of emulsion rupture by the heteroflocculation of bitumen droplets on the substrate. This breakup mechanism operates in the case of non-reactive aggregates, such as granite and RAP. It is linked to the specific surface area of SiO_2 contained in the aggregates (Ziyani et al. 2014). A specific surface area of SiO_2 corresponds to a rupture "speed" to ensure an optimal heteroflocculation. Below this "speed", the mechanism is not effectively achieved due to poor coverage of the aggregates by surfactants (in nature or in quantity), and above, the heteroflocculation mechanism is delayed. In these two cases, it is to the detriment of the binder-aggregate adhesion.

4.6. Relationship between short term cohesion and moisture resistance of virgin and recycled granite cold mix asphalt

Fig. **13** illustrates the relationship between the short-term cohesion and moisture resistance of VCMA and RCMA from the results of 0 h, 4 h and 24 h cohesion build-up and compression tests on specimens with the same formula. According to the correlation coefficients, the relationship between the cohesion and water resistance of virgin asphalt mix is strong at 0 and 4 h and very weak at 24 h. As for the recycled asphalt, the correlation is strong at 0 h, medium at 4 h and poor at 24 h.

Very short-term cohesion and moisture resistance of virgin and recycled CMAs seem to be linked. Mixtures are likely to develop good resistance to moisture when they exhibit strong short-term cohesion. This correlation could be explained by the fact that at a young age, the cold asphalt mix presents a configuration in which there is a competition between water and bitumen droplets in the presence of surfactants. The same configuration occurs when the specimens are subjected to the water effect during the Duriez test. In the first case, adhesivity results in an increase in short-term cohesion and in the second case, it results in good moisture resistance.

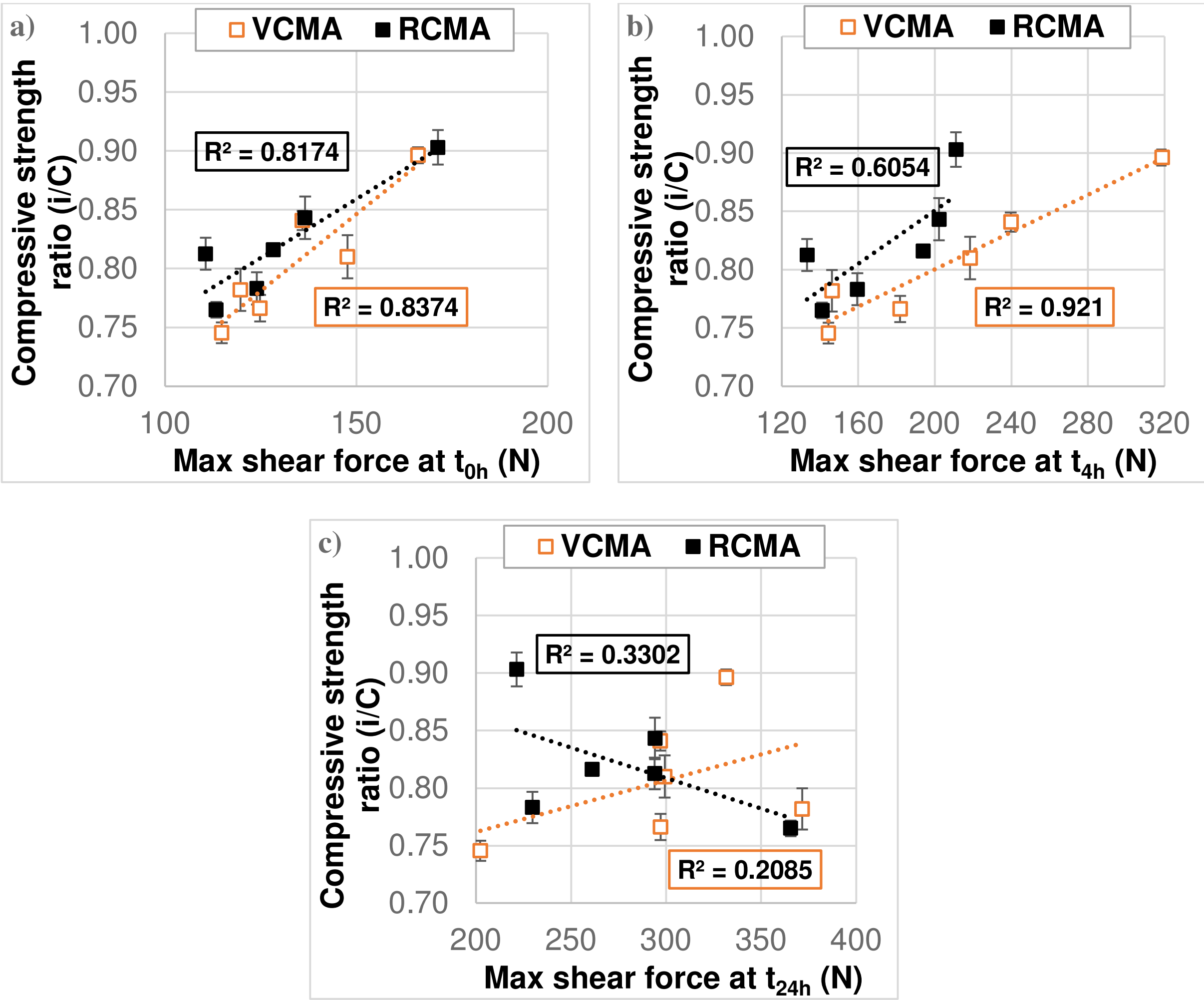


Fig. 13 Moisture resistance of VCMA and RCMA as a function of max shear force at t_{0h} (a), t_{4h} (b) and t_{24h} (c).

Conclusions and perspectives

It has been highlighted that the surfactant is an essential element in the formulation of an emulsion for cold mixes. Therefore, its use in road techniques should not be limited only to researching emulsification and stability properties without considering its contribution in the final properties of the mixture. The surfactant influences the formulation of the asphalt mixtures, in particular the content of additional water, which is all the less as the emulsion is very concentrated in emulsifier.

Depending on its nature and content, it ensures the emulsion-aggregate and emulsion-RAP compatibility with regard to the quality of the residual binder on the substrate at the end of the breaking process of the emulsion. Furthermore, it determines the durability of the binder-aggregate adhesion in the presence of a disturbing agent such as water. The surfactant activities also determine the cohesion build-up and its kinetics. This last property depends on the complex phenomenon of adsorption of ionic surfactants on substrates in the presence of water, which deserves to be elucidated.

In this study, the use of emulsion in the context of recycling showed that the water resistance of recycled CMA is related to that of VCMA, according to the virgin aggregates used. As the virgin CMA has good water resistance thanks to its SiO_2 content, this was the case with RCMA. However, by adjusting the emulsifier content, a recycled mixture is obtained, which performs better than a virgin mixture with incorporation of RAP, in terms of mechanical strength and water resistance. The reason is to be found in the interaction of the emulsified bitumen with both virgin aggregates and RAP.

From the point of view of moisture resistance, the durability of asphalt mixes is sought in terms of the surfactant chemistry and concentration. To obtain good performance with respect to water, a judicious choice of the nature of the surfactant must be made and the optimum content must be determined according to the nature of the aggregates. The study also showed that it is possible to predict the water resistance capacity from the behavior of the mixture in the very short term in the case of granite aggregates. Our findings suggest that the water resistance is as good as the mixture exhibits a strong cohesion during manufacture.

Future research should be carried out to highlight the influence of surfactants on other sustainability criteria, such as rutting and fatigue resistance and to verify the results with other types of aggregates. It would also be interesting to check whether the explanation of the behaviors observed at the level of asphalt mixes can be found at the scale of microscopic studies of the interaction between the emulsion and the road aggregates.

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