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An application of the Michaelis–Menten model to analyze the curing process of cold recycled bituminous mixtures

Andrea Graziani [a], Carlotta Godenzoni [a,*], Fabrizio Cardone [a], Edoardo Bocci [b], Maurizio Bocci [a]

[a] Università Politecnica delle Marche, Dipartimento di Ingegneria Civile Edile e Architettura via Brecce Bianche, 60131 Ancona, Italy
[b] Università degli Studi eCampus, Via Isimbardi 10, 22060 Novedrate (CO), Italy

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Abstract

In this paper the laboratory curing process of two types of cold recycled mixtures manufactured during the construction of an experimental pavement section along an Italian motorway was investigated. Specifically, a cement–bitumen treated material (CBTM) mixture and a cement treated material (CTM) mixture, produced both on site and in laboratory, were tested. Moisture loss by evaporation (*DW*), indirect tensile stiffness modulus (*ITSM*) and indirect tensile strength (*ITS*) were measured in order to evaluate the curing process. The measured data were analyzed using the nonlinear Michaelis–Menten (MM) model with the aim to characterize the rate at which the mixture properties evolve over time and their values at the long-term cured state. The results showed that the adopted curing variables (*DW*, *ITSM* and *ITS*) gave a comparable description of the curing process, when evaporation was allowed and that the MM model gave an appropriate description of the evolutive behavior of CBTMs and CTMs. Finally, the results showed that in the initial curing stage the effect of cement hydration prevailed on that of emulsion breaking.

1. Introduction

1.1. Background

Nowadays, savings in energy and non-renewable natural resources as well as cost-effectiveness, make the application of cold recycling technologies a strategic solution for the rehabilitation of bituminous pavements [2,13,24]. In particular, full-depth reclamation (FDR) obtained worldwide success due to the performance quality achieved at lower costs, shorter construction periods and lower environmental impact as compared to in-plant recycling solutions [1,22]. The FDR process basically consists in milling the entire thickness of the asphalt layers together with a predetermined amount of the underlying granular or cement-stabilized layer and stabilizing the milled material, i.e. a blend of reclaimed asphalt pavement (RA) and reclaimed aggregates (RAg), with specific binding agents. Thus, FDR potentially allows the production of a 100% recycled pavement layer, without any transportation or reheating of aggregates [4,24]. Virgin aggregates and water can also be added in order to improve aggregate gradation and enhance laydown and compaction.

A combination of bituminous binder (plain or modified bitumen, either as emulsion or foam) and hydraulic binder (Portland cement, lime and fly ash) is commonly adopted in order to obtain the required mechanical and durability properties of the cold recycled layers [3,7,15,16,22,27].

* Corresponding author.
E-mail addresses: a.graziani@univpm.it (A. Graziani), c.godenzoni@pm.univpm.it (C. Godenzoni), f.cardone@univpm.it (F. Cardone), edoardo.bocci@uniecampus.it (E. Bocci), m.boccii@univpm.it (M. Bocci).
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Depending on the type and dosage of the binders, the FDR technology allows the production of cold recycled mixtures (CRMs), with different mechanical behaviors. In particular, when a combination of bitumen and cement is used, the mixture can be considered a cement–bitumen treated material (CBTM). Generally, CBTMs are characterized by a cement content higher than 1% and a bitumen/cement ratio equal to or less than one ($B/C \leqslant 1$). Differently, when only cement is used as binder, the mixture can be regarded as a cement treated material (CTM) [12].

As compared to hot or warm asphalt mixtures either recycled or not, CRMs can be considered as evolutive materials, where a certain *curing* period is necessary for them to achieve the long-term mechanical properties, e.g. strength and stiffness. Because of the simultaneous presence of both bituminous and hydraulic binders, curing of CBTMs is the result of different time-dependent mechanisms [5,6]. When CBTMs are produced using bitumen emulsion, curing of the bituminous phase is characterized by two phenomena that are strictly interrelated: emulsion breaking and water expulsion. Indeed, flocculation and coalescence of bitumen droplets, that lead to the formation of continuous bituminous films, are generally due to the increase in the crowding pressure induced by moisture loss [14]. In particular, this happens when over-stabilized bitumen emulsion is used, because this type of emulsion is characterized by a high stability and does not break when mixed with cement. The curing process of CBTMs also involves cement hydration since it confers enhanced stiffness and strength to the mixture [4,8].

Moreover, the time-dependent physical phenomena leading to curing influence each other. In the early curing stage, cement promotes emulsion breaking and contributes to the bitumen coalescence by reducing the free water within the mixture [8,23,25]. In the meantime, the presence of bitumen emulsion could reduce the rate of hydration of cement and hinder the formation of well-structured cementitious bonds [20,26]. Finally, it is important to highlight that while the curing process of the bituminous phase is strictly related to moisture loss, the cement hydration process requires a moist environment and does not entail any mass loss.

Several research studies [4,8,9,19] showed that monitoring the evolution over time of both physical (i.e. moisture content) and mechanical (i.e. strength and stiffness) properties of CRMs is a valid procedure in order to get a *quantitative measure* of curing. In this context, an original approach to the characterization of the curing process of CRMs based on the evaluation of the rate at which mixture properties evolve over time (*curing rate*) and of their *long-term value* was proposed in [10]. The approach was based on the application of a mathematical model, the Michaelis–Menten model [17] that proved to be effective when applied to laboratory produced mixtures.

However, it should be recognized that laboratory curing procedures can hardly simulate actual field curing conditions, mostly because the factors that influence field curing are extremely variable. Among these factors, one can list mixture composition (aggregate gradation, binder type and dosage), environmental conditions (temperature and relative humidity) as well as construction features (degree of compaction, layer thickness, drainage conditions, construction phases). For this reason, comparing the effects of laboratory and field curing is challenging task that requires the same experimental conditions and modeling approach to be applied.

1.2. Project description

Starting from 2011, the Polytechnic University of Marche was involved in a Publicly-founded research project aimed at the characterization of the mechanical performance of cold recycled mixtures. Within this project, a full scale experimental pavement section was constructed with the aim of: (a) characterizing the performance of different CRMs, produced by FDR, in terms of evolution of mixture properties over time (i.e. characterization of the curing effects) and (b) monitoring the mechanical response of CRMs under real traffic and environmental conditions.

The experimental pavement section was constructed in April 2015 near to the city of Ancona (Italy), during the widening of the A14 motorway, which runs along the Adriatic coast of Italy. The standard pavement cross section of the motorway was designed in order to withstand a traffic of 10 Million ESAL/year and consisted of a 300 mm asphalt concrete course (200 mm base course, 60 mm binder course and 40 mm porous wearing course), a 300 mm cement treated subbase course and a 200 mm granular foundation.

The experimental section was 80 m long and 6.75 m wide, interesting the width of both the emergency and the slow lane (Fig. 1a). Along this section, divided in two contiguous subsections of identical length (40 m + 40 m), the standard 300 mm cement treated layer was replaced with two different CRMs layers realized on site with a FDR technique (Fig. 1b):

1. Cement-treated material, CTM (from 0.0 to +40.0 m);
2. Cement–bitumen treated material, CBTM (from +40.0 to +80.0 m).

Moreover, the experimental section (Fig. 1) was instrumented with four time domain reflectometer probes, coupled with four temperature sensors that allow moisture content and temperature data to be recorded over time, three earth pressure cells EPC with different measuring ranges and two H-shaped asphalt strain gauges.

2. Objective and methodology

The objective of this paper is to analyze the laboratory curing process of the CRMs manufactured during the construction of the experimental pavement section. To this aim, experimental tests were carried out on both mixtures

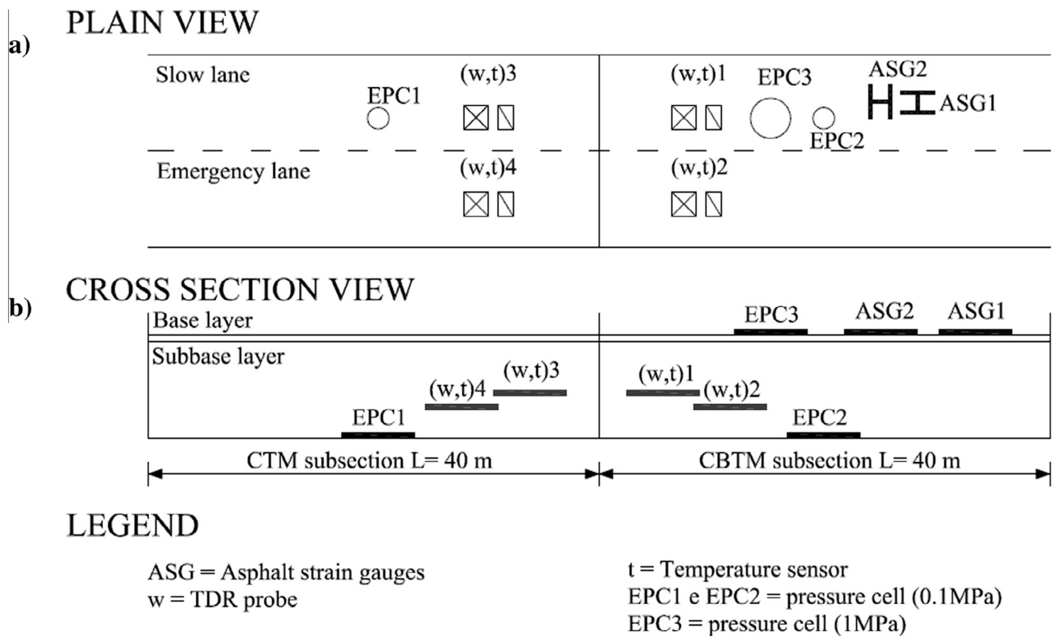

Fig. 1. Experimental pavement section: (a) plain and (b) cross section view.

directly produced at the jobsite and sampled during the construction operations (CBTM-SITE, CTM-SITE) and mixtures produced in the laboratory (CBTM-LABO, CTM-LABO) using the same aggregates and binders.

The curing process was analyzed by measuring the evolution of moisture loss by evaporation (DW), indirect tensile stiffness modulus ($ITSM$) and indirect tensile strength (ITS), then the experimental results were modeled using the Michaelis–Menten model [10,17]. This allowed to characterize the curing process of the investigated mixtures by estimating the rate of evolution and the long-term value of the selected properties. The effects of mixture type (CBTM vs. CTM), mixing procedure (SITE vs. LABO) and curing condition (sealed vs. unsealed) were evaluated.

Within the framework of the project described in Section 1.2, the curing parameters obtained in this paper will be compared with those estimated from the sensors installed inside the pavement in order to compare, on a parametric basis, the effects of laboratory and the site curing.

3. Experimental program

3.1. Materials

The same reclaimed aggregates were used for the CBTM and CTM mixtures. The granular blend was composed of 50% of RA and 50% of RAg; RA was obtained from the milling of the binder and base courses of the existing pavement, whereas the RAg was obtained from the milling of the existing cement-treated subbase.

The aggregates were sampled from the field section, during the construction operations, and characterized in terms of gradation, particle density, water absorption and bitumen content. Results are summarized in Table 1 and Fig. 2.

A pozzolanic cement type IV/A (P) with strength class 42.5R (EN 197-1) was used in this project. The dosages were equal to 3% and 2% (by dry aggregate mass) for CTM and CBTM mixtures, respectively.

A cationic slow setting bituminous emulsion C60B10 (EN 13808) was selected to produce the CBTM mixtures. This emulsion is specifically formulated for cold in-place recycling, guaranteeing high mixing stability with cement (over-stabilized emulsion) and good workability during the compaction phase [10,11]. The employed emulsion content was 3% (by dry aggregate mass), corresponding to 1.8% of fresh bitumen.

3.2. Mixtures

The mixtures tested in the present study were produced:

- directly on site during FDR operations (CBTM-SITE, CTM-SITE);
- in laboratory (CBTM-LABO, CTM-LABO).

A total water content w_{tot} equal to 6% and 5% (by dry aggregate mass), was adopted for mixtures produced on site and for those fabricated in the laboratory, respectively. After field mixing operations, wet mixtures (CBTM-SITE and CTM-SITE) were sampled, transported and compacted in the laboratory.

3.2.1. On site production

Before the construction of the instrumented pavement section, the asphalt concrete and CTM layers were milled without altering the foundation layer.

Table 1
Physical properties of granular materials.

Material	Water absorption (%) (EN 1097-6)	Particle density (Mg/m^3) (EN 1097-6)	Bitumen content (%) (EN 12697-1)
RA	1.00	2.443	3.59
RAg	0.90	2.596	–
50%RA + 50%RAg	0.95	2.519	–

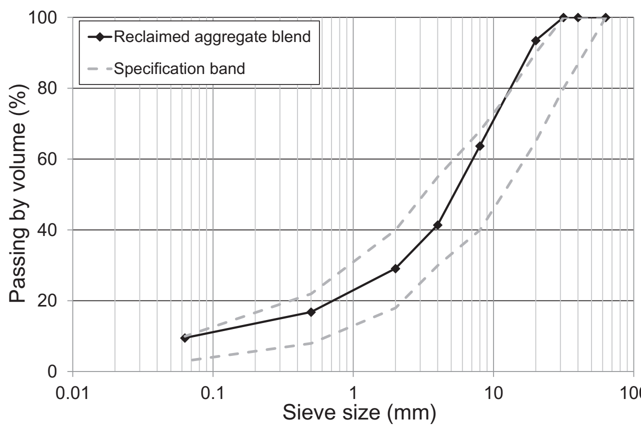

Fig. 2. Gradation of aggregate blend (EN 933-2) and specification limits for A14 motorway construction.

First, the RA was spread on the prepared foundation and leveled to reach an uncompacted thickness of approximately 200 mm (Fig. 3a). Subsequently, the RAg was spread on the loose RA material and leveled to the final uncompacted thickness of about 400 mm (Fig. 3b). Finally, RA and RAg were blended with a recycler and levelled (Fig. 3c). At this moment, the aggregate blend (50% RA +50% RAg) without binders, was sampled to evaluate the moisture content which resulted $w_{site} = 4.82\%$ (by dry aggregate mass).

The subbase was lightly compacted using a vibrating smooth-drum roller in order to obtain a levelled and stable support for the following operations. On CTM section, around 1% (by dry aggregate mass) of water was added in order to enhance the compactability of the material. On site, w_{tot} was composed of the site moisture content ($w_{site} = 4.82\%$ by dry aggregate mass) and the water obtained from emulsion w_{em} (CBTM-SITE) or added during construction operations (CTM-SITE).

Different cement dosages (2% and 3% by dry aggregate mass for CBTM and CTM respectively) were spread using a proper vehicle, equipped with volumetric batchers (Fig. 3d). Then, the recycler coupled to a tank was used to stabilize a thickness of 400 mm with bitumen emulsion for a length of 40 m (Fig. 3e). For the remaining 40 m, the recycler mixed the CTM layer for the same thickness of 400 mm with no emulsion addition.

The second sampling was carried out, from the stabilized cold recycled layers (CTM and CBTM) before compacting. Sampled materials, sealed in plastic bags, were immediately transported to the laboratory to start the experimental activities reported in the following sections (Compaction and Curing). The treated layers were finally compacted by a 14 ton vibrating smooth drum roller and a 25 ton pneumatic tire roller (Fig. 3f).

3.2.2. Laboratory production

Concerning to laboratory procedure, the total water content w_{tot} was composed of the water from the emulsion (w_{em}) and additional water (w_{add}), which is added in two parts. The first part, related to the water absorption ($w_{add\_1} = w_{abs}$) of the constituent aggregates, was added to the dry aggregate blend the day before mixing. Then, the wet mixture (aggregate containing w_{add_1}) was stored in a sealed plastic bag for 12 h at room temperature, in order to ensure a homogeneous moisture condition and to allow absorption by the aggregates. Subsequently, the aggregate blend was thoroughly mixed, gradually adding the remaining part of the mixing water (w_{add_2}), cement and emulsion in sequence. Samples were mixed using a mechanical mixer at room temperature for at least two minutes, time required to guarantee a good particle coating [9,11].

3.3. Compaction

The specimens employed for mechanical testing were compacted in a 150 mm diameter mold by means of a gyratory compactor adopting the following protocol: constant pressure of 600 kPa, gyration rate of 30 rpm and angle of inclination of 1.25° (EN 12697-31).

For the mixtures produced on site (CBTM-SITE and CTM-SITE), 4500 g of loose mixture were compacted at 180 gyrations obtaining a specimen height of about 110 mm. For the mixtures produced in the laboratory (CBTM-LABO and CTM-LABO), 2800 g of loose material were compacted at 100 gyrations obtaining a specimen height of about 70 mm.

3.4. Curing

Specimens were cured in a climatic chamber at the temperature of 20 ± 2 °C, with a constant relative humidity of 50 ± 5%. In addition, part of the CBTM-LABO specimens were also cured in sealed conditions to avoid free water evaporation. The first procedure was identified as DRY curing, whereas the second procedure was identified as WET curing (Table 2).

Fig. 3. Construction of CBTM and CTM layers: (a) RAP material restoring; (b) placing of RAg layer; (c) mixing of the milled material; (d) spreading of cement; (e) stabilization with bitumen emulsion; (f) final compaction.

3.5. Testing methods

The curing process was analyzed by measuring moisture loss by evaporation (*DW*), indirect tensile stiffness modulus (*ITSM*) and indirect tensile strength (*ITS*) of compacted specimens at different curing times and conditions. The testing program is summarized in Table 2.

DW was measured by carefully weighting each specimen before mechanical testing. *ITSM* was measured by applying repeated load pulses with a rise time of 124 ms and a pulse repetition period of 1.0 s. For each specimen the load was adjusted using a closed loop control system in order to achieve a target diametral deformation of 2 μm (EN 12697-26, Annex C). *ITSM* test was performed on only CBTM-LABO-DRY and CBTM-LABO-WET specimens because preliminary observations showed that the other mixtures were too brittle and failed during the test. Immediately after *ITSM* tests, cured specimens were

Table 2
Summary of testing program.

Mixture		Curing		Testing (number of specimens)		
Type	Production	Condition (50% RH, 20 °C)	Times [days]	DW	ITSM	ITS
CBTM	LABO	DRY	1, 3, 7, 28, 90	14	10	14
CBTM	LABO	WET	1, 3, 7, 28, 90	13	10	13
CBTM	SITE	DRY	7, 14, 28, 90	9	0	9
CTM	LABO	DRY	1, 3, 7, 28, 90	9	0	9
CTM	SITE	DRY	7, 14, 28, 90	7	0	5

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tested by means of a mechanical testing machine for the assessment of the *ITS*. The equipment applied a compression force along the two generatrices until the specimen reached a splitting failure. The load was applied with constant rate of deformation of 50 ± 2 mm/min (EN 12697-23). Both *ITSM* and *ITS* tests were carried out at 20 °C.

3.6. Michaelis–Menten model

The curing effect on physical (*DW*) and mechanical (*ITSM* and *ITS*) properties of the studied materials, is evaluated using a procedure based on the Michaelis–Menten (MM) model [17]. The MM model is a nonlinear model that describes an asymptotic evolution of the measured response as a function of time (predictor variable), through the evaluation of two parameters:

$$f(t,(y_A,K_c)) = \frac{y_A \cdot t}{K_c + t} \tag{1}$$

where $y_A > 0$ is the asymptotic value of the response (when $t \to \infty$, i.e. *long-term* condition) and $K_c > 0$, also known as the Michaelis constant, represents the curing time when the response is equal to $y_A/2$ (Fig. 4) [21]. It is underlined that, because of their physical meaning, both y_A and K_c are restricted to positive values and thus Eq. (1) defines a concave rectangular hyperbola through the origin.

At the beginning of curing ($t = 0$), the MM model predicts a zero value for the considered curing variables *DW*, *ITSM* and *ITS*. As curing time increases, the response asymptotically approaches the long-term value y_A. The Michaelis constant K_c is used as a measure of the *initial curing rate*: a lower K_c value means a faster increase in *DW*, *ITSM* and *ITS*.

In addition, the curing rate can be also estimated using the slope of the MM curve, in particular the larger the slope the faster the evolution of the response. The slope is calculated as:

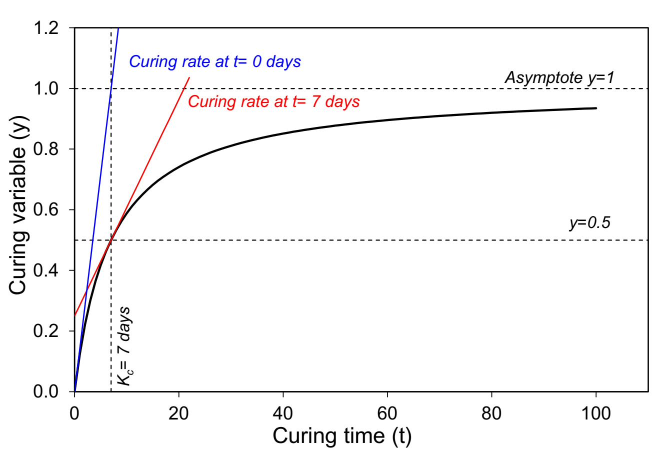

Fig. 4. Michaelis–Menten model: an example with $y_A = 1$ and $K_c = 7$ days.

$$f'(t,(y_A,K_c)) = \frac{y_A \cdot K_c}{(K_c + t)^2} \tag{2}$$

In this paper, the slope at the curing time $t = K_c$ ($f'(K_c,(y_A,K_c)) = \frac{y_A}{4 \cdot K_c}$) was evaluated (Fig. 4, red line).

It is interesting to note that the function described by Eq. (1) can also be used to model the relationship between mechanical properties and moisture loss, thus eliminating the explicit influence of curing time. For example, considering *ITS* and *DW*, we have

$$DW = \frac{y_{A,DW} \cdot t}{K_{c,DW} + t} \tag{3}$$

and

$$ITS = \frac{y_{A,ITS} \cdot t}{K_{c,ITS} + t} \tag{4}$$

Obtaining t from Eq. (3), substituting it into Eq. (4) and rearranging the terms, we get

$$ITS = \frac{a_{ITS} \cdot DW}{b_{ITS} + DW} \tag{5}$$

where

$$a_{ITS} = \frac{y_{A,ITS} \cdot K_{c,DW}}{K_{c,DW} - K_{c,ITS}} \tag{6}$$

$$b_{ITS} = \frac{y_{A,DW} \cdot K_{c,ITS}}{K_{c,DW} - K_{c,ITS}} \tag{7}$$

Thus, again, *DW* and *ITS* (or *ITSM*) are linked through a MM-type equation, although in this case the regression parameters of a_{ITS} and are not required to be both positive as in the original MM-model. Indeed, since the parameters y_A and K_c are both positive, the sign of a_{ITS} and b_{ITS} depend on the relative magnitude of $K_{c,DW}$ and $K_{c,ITS}$.

Specifically, if $K_{c,DW} > K_{c,ITS}$, i.e. if the increase in *ITS* up to one half the asymptotic value is faster than the analogous increase in *DW*, both a_{ITS} and b_{ITS} are positive. On the other hand, if $K_{c,DW} < K_{c,ITS}$ the initial moisture loss is faster than the strength increase, and both a_{ITS} and b_{ITS} are negative. As an example, the latter situation was observed in [10].

If we consider the curvature of Eq. (5)

$$c_{ITS} = \frac{d^2 ITS}{dDW^2} = \frac{-2 \cdot a_{ITS} \cdot b_{ITS}}{(b_{ITS} + DW)^3} \tag{8}$$

we can also observe that, if $K_{c,DW} > K_{c,ITS}$, i.e. if both a_{ITS} and b_{ITS} are positive, c_{ITS} is negative and thus the curve is concave. On the other hand, if $K_{c,DW} < K_{c,ITS}$, i.e. if both a_{ITS} and b_{ITS} are negative, c_{ITS} is positive and thus the curve is convex, as long as $|b_{ITS}| > DW$ (such a condition was always fulfilled by the results reported in [10]). Finally, if $K_{c,DW} \approx K_{c,ITS}$, the curvature is very small and Eq. (5) degenerates into a straight line.

Those mathematical considerations lead to an interesting physical interpretation of the curing process of CBTM mixtures. If the curve $ITS = ITS(DW)$ is concave

(Fig. 5, line "a"), is possible to conclude that the initial development of strength is faster than the initial development of moisture loss. From this it can be inferred that the kinetics of cement hydration is faster with respect to the kinetics of emulsion breaking/setting and hence the initial curing rate is regulated by the cement hydration.

On the other hand, if the curve $ITS = ITS(DW)$ is convex (Fig. 5, line "b"), is possible to conclude that the initial development of strength is delayed with respect to the initial development of moisture loss. From this it can be inferred that the initial curing process is controlled by the breaking/setting process of the bitumen emulsion: water evaporation leads to an increase in bitumen concentration, which subsequently leads to coalescence of the droplets, emulsion breaking, formation of continuous bitumen films and, ultimately, to an increase in mechanical properties (*ITS* and *ITSM*).

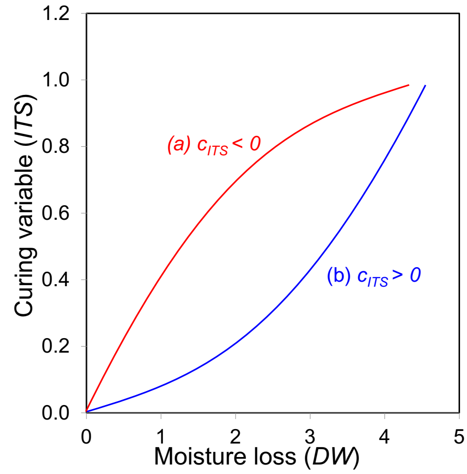

Fig. 5. Relationship between curing rates of DW and ITS and curvature of $ITS = ITS(DW)$

4. Results and analysis

4.1. Volumetric properties

The volumetric properties of the 52 specimens (36 CBTM specimens and 16 CTM specimens) were first analyzed in order to evaluate their homogeneity and verify the reliability of the compaction procedure.

The mass of each compacted specimen was recorded and compared with the mass of the loose mixture placed in the mold. In Fig. 6a, the empirical probability density function of the mass loss for CBTM and CTM specimens are compared. The density curves show that the mass loss during compaction was very small (less than 0.5%) and almost identical for CBTM and CTM specimens. Moreover, visual observations performed during extrusion, confirmed that all specimens were homogeneous and stable and that the mass loss was due to emulsion and fine aggregate particles remaining on the inner surface of the mold.

The results of volumetric analysis, in terms of average value and standard deviation of voids in the mixture V_m and voids filled with liquids *VFL* are summarized in Table 3. Moreover, in Fig. 6b, the empirical probability density functions of V_m for the four materials are compared.

It can be observed that CBTM mixtures, fabricated both on site and in laboratory, were characterized by a lower V_m with respect to CTM mixtures. This can be explained by the presence of the bitumen droplets. In fact, inside the CBTM mixture, 1.8% of bitumen (by dry aggregate mass) corresponds to about 3.75% by mixture volume, which is not present inside CTM mixture. A further contribution to the lower V_m values of CBTM with respect to CTM, may also derive from an improvement of compactability due to the lubricating effect of the bitumen droplets [11].

As far as *VFL* is concerned, it can be noted that all specimens were characterized by values lower than 90%. This means that no specimen approached saturation ($VFL = 100\%$) and hence, no drainage was likely to occur during the compaction phase (this was also confirmed by the mass loss measurements). In Table 3, a significant difference between the average *VFL* values of CBTM and CTM can also be observed. This confirms that in CBTM mixtures a large fraction of V_m is occupied by the bitumen droplets.

Overall, the analysis of mass loss during compaction, V_m and *VFL*, allowed to verify the reliability and the homogeneity of the specimen production procedure.

4.2. Evolution of material properties and model fitting

The evolution of *DW*, *ITSM* and *ITS* as a function of curing time, is shown from Figs. 7–9. The MM model was fitted to the experimental data using R [https://www.r-project.org], a free software environment for statistical computing. The parameters estimates were calculated using the nonlinear fitting function `nls()`, which runs a least-squares estimation [18,21]. The regression curves are superposed to the experimental data, whereas the estimated values of the regression parameters, their standard errors and the standard error of the residuals are summarized in Table 4.

The adequacy of the regression model was checked performing an analysis of residuals [18,21]. In Figs. 10a and 11a, the QQ plots for the standardized residuals of *DW* and *ITS*, are reported for both materials properties. The points plotted along the equality line confirming that the regression errors may be considered normally distributed. In Figs. 10b and 11b the plots of the standardized residuals versus fitted values of *DW* and *ITS*, are reported. As it can be observed the standardized residuals were in the range from −2 to 2 and no particular pattern can be observed in the plots. Thus the adequacy of the model and the absence of outliers are confirmed.

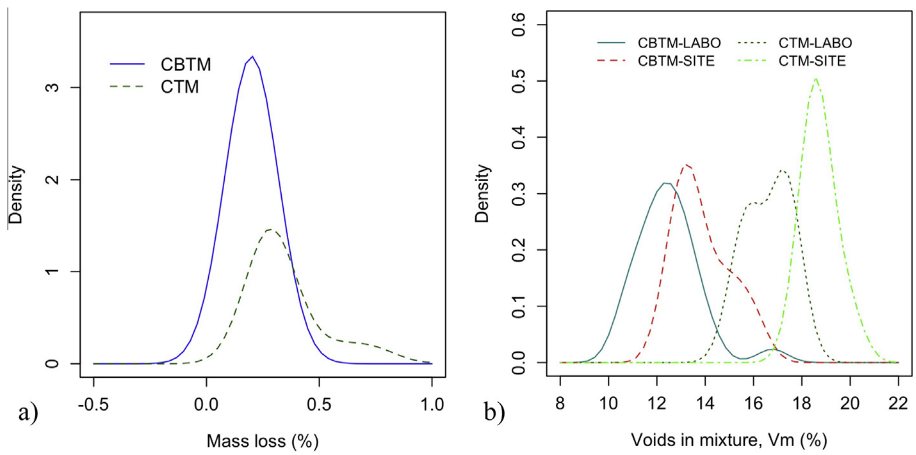

Fig. 6. Empirical probability density function of: (a) mass loss and (b) voids in the mixture

Table 3
Volumetric properties of the compacted specimens.

Materials	*V*m		*VFL*	
	Avg. value [%]	Std. Dev. [%]	Avg. value [%]	Std. Dev. [%]
CBTM-LABO	12.47	1.283	87.28	8.397
CBTM-SITE	13.87	1.165	78.04	6.524
CTM-LABO	16.60	0.907	58.29	4.266
CTM-SITE	18.74	0.599	48.60	1.632

4.2.1. Moisture loss

From Fig. 7 it can be observed that, for mixtures CBTM-LABO-DRY and CBTM-SITE-DRY, *DW* after 7 days of curing was 1.97% and 1.93%, respectively. A small difference can also be noticed between the considered mixtures at longer curing times (90 days), when *DW* of about 3.8% and 3.5% was measured for mixtures CBTM-LABO-DRY and CBTM-SITE-DRY, respectively. Analogously, for mixtures CTM-LABO-DRY and CTM-SITE-DRY, *DW* after 7 days was 2.35% and 1.4%, respectively. This difference progressively increased and at 90 days *DW* of 3.7% and 2.3% were measured. The results obtained with mixture CBTM-LABO-WET showed a completely different trend since, in this case, the specimen was sealed and therefore evaporation was virtually impossible.

A parametric evaluation of the *DW* evolution was obtained considering the MM model for all mixtures subjected to DRY curing conditions. Specifically, the estimated value of K_c was used to evaluate the initial curing rate (i.e. the time required to reach one half of the asymptotic value), whereas the estimated value of y_A was used to evaluate the long-term (asymptotic) behavior.

For mixtures CBTM-LABO-DRY and CBTM-SITE-DRY, K_c was 2.4 days and 6.5 days, respectively (Table 4). Analogously for mixtures CTM-LABO-DRY and CTM-SITE-DRY, K_c was 1.9 days and 5.5 days, respectively. This trend of the initial curing rate, is also confirmed by analyzing the values of the slope $y'(K_c)$ summarized in Table 4. In fact, it can be observed that higher $y'(K_c)$ corresponds to lower K_c and consequently faster initial curing rate. Overall, the result highlighted that initial moisture loss by evaporation for mixtures produced on site, was more than 2 times slower with respect to that registered for mixtures produced in the laboratory.

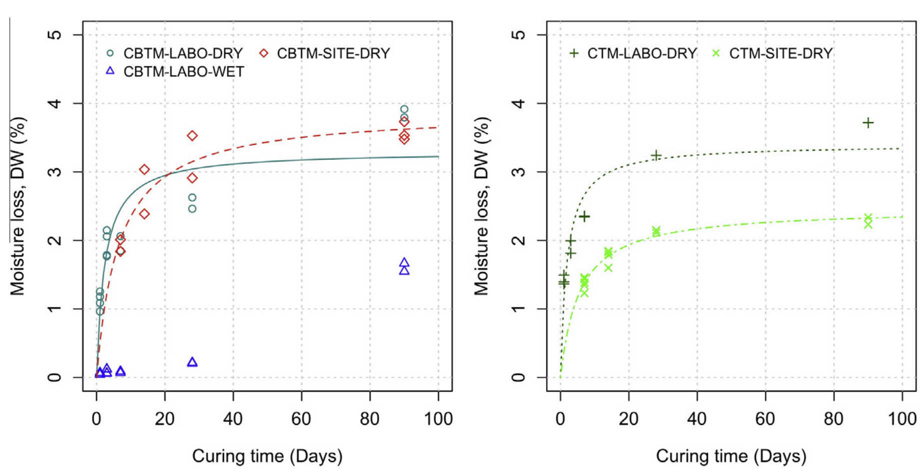

Fig. 7. Evolution of moisture loss (*DW*) versus curing time.

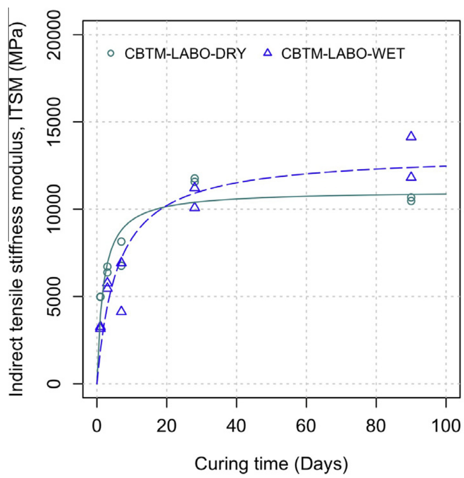

Fig. 8. Evolution of indirect tensile stiffness modulus (*ITSM*) versus curing time

Considering the long-term behavior, it can be observed that for mixtures CBTM-LABO-DRY and CBTM-SITE-DRY the asymptotic value y_A was 3.3% and 3.9%, respectively, whereas, for mixtures CTM-LABO-DRY and CTM-SITE-DRY the value of y_A was 3.4% and 2.5%, respectively. Hence, it can be concluded that the production procedure adopted for the studied mixtures (LABO-DRY or SITE-DRY), influenced the moisture loss of CTM mixture at both short and long curing times. These findings can be related to the different volumetric properties of the mixtures (Table 3).

4.2.2. Indirect tensile stiffness modulus

Fig. 8 reports the *ITSM* results obtained on mixtures CBTM-LABO-DRY and CBTM-LABO-WET at different curing times. The plot highlights the effect of the curing condition (DRY or WET) on *ITSM* evolution. Similar to

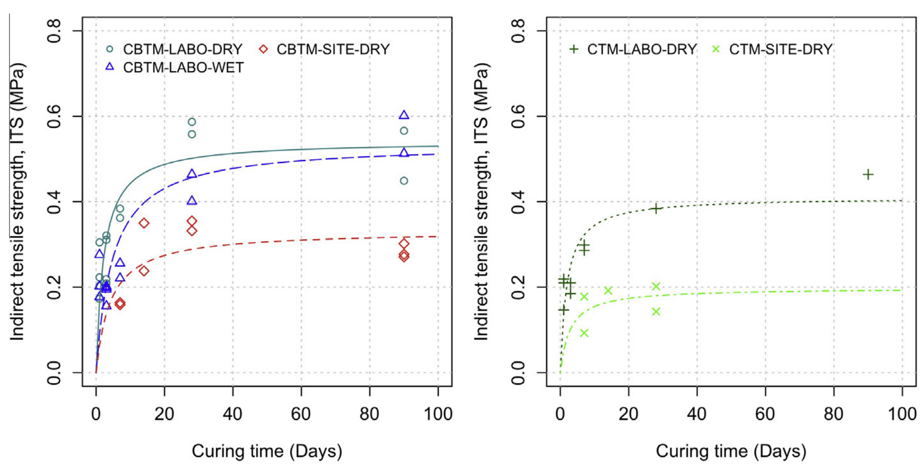

Fig. 9. Evolution of indirect tensile strength (*ITS*) versus curing time.

Table 4
Regression parameters of Michaelis–Menten model for the time evolution of *DW*, *ITSM* and *ITS*.

Mixture	y_A		K_c		$y'(K_c)$	Residual std. error
	Estimate	Std. error	Estimate	Std. error	Estimate	
Moisture loss vs. *time*	[%]	[%]	[days]	[days]	[%/day]	[%]
CBTM-LABO-DRY	3.30	0.24	2.40	0.62	0.34	0.4234
CBTM-LABO-WET						
CBTM-SITE-DRY	3.88	0.19	6.54	1.41	0.15	0.2642
CTM-LABO-DRY	3.40	0.22	1.94	0.45	0.44	0.3006
CTM-SITE-DRY	2.47	0.07	5.51	0.56	0.11	0.0911
ITSM vs. *time*	[MPa]	[MPa]	[days]	[days]	[MPa/day]	[MPa]
CBTM-LABO-DRY	11060	630	1.80	0.48	1536	1145
CBTM-LABO-WET	13201	1146	5.86	1.85	536	1564
ITS vs. *time*	[MPa]	[MPa]	[days]	[days]	[MPa/day]	[MPa]
CBTM-LABO-DRY	0.54	0.04	2.23	0.60	0.06	0.0726
CBTM-LABO-WET	0.54	0.06	4.89	1.71	0.03	0.0856
CBTM-SITE-DRY	0.33	0.04	4.17	2.63	0.02	0.0583
CTM-LABO-DRY	0.41	0.04	1.90	0.69	0.05	0.0568
CTM-SITE-DRY	0.20	0.05	2.77	4.16	0.02	0.0457

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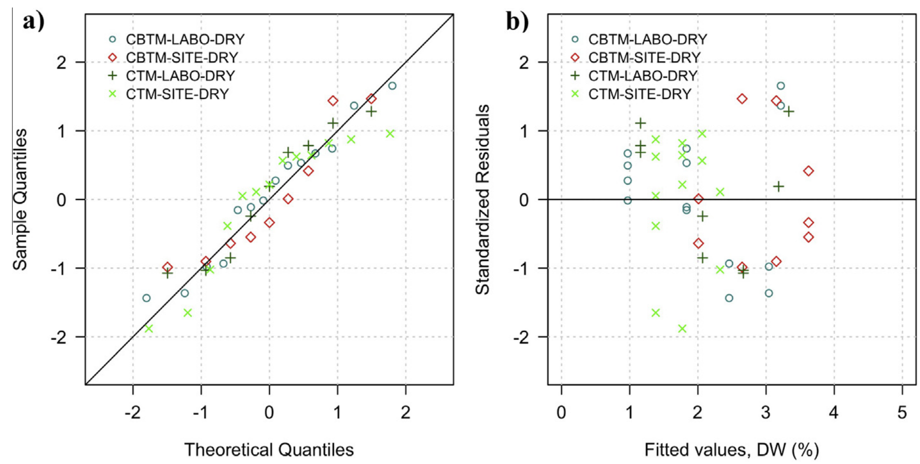

Fig. 10. Residual plots for *DW*: (a) normal QQ plot, (b) standardized residuals versus fitted values.

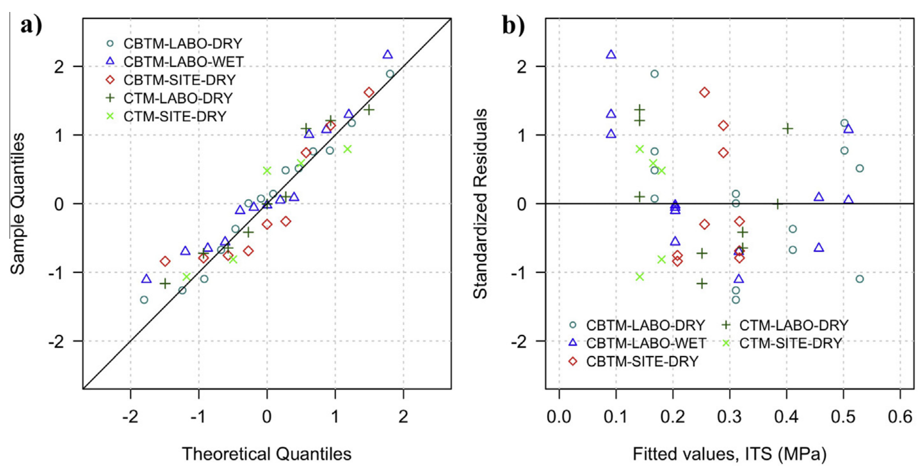

Fig. 11. Residual plots for *ITS*: (a) normal QQ plot, (b) standardized residuals versus fitted values.

DW, this effect was evaluated by analyzing the parameters of MM model.

As far as the initial curing rate is concerned, the MM model indicates that mixture CBTM-LABO-DRY required 1.8 days to reach one half of the asymptotic *ITSM* value. Differently for mixture CBTM-LABO-WET, K_c increased up to 5.9 days. Hence, dry curing condition resulted in a higher initial curing rate (Table 4). This result is an effect of emulsion breaking due to moisture loss by evaporation in DRY-cured specimens and it is also confirmed by the higher slope $y'(K_c)$ measured on mixture CBTM-LABO-DRY with respect to mixture CBTM-LABO-WET (Table 4).

As far as the long-term curing is concerned, the asymptotic *ITSM* value estimated by the MM model for mixtures CBTM-LABO-DRY and CBTM-LABO-WET was 11060 MPa and 13201 MPa, respectively. This highlights the importance of water available inside the specimen, in order to promote the cement hydration process.

4.2.3. Indirect tensile strength

The *ITS* evolution (Fig. 9) showed a trend similar to that observed with *ITSM* (Fig. 8).

As far as the initial curing is concerned, the MM model indicates that mixtures CBTM-LABO-DRY and CBTM-SITE-DRY reached one half of the asymptotic *ITS* value after 2.2 days and 4.2 days, respectively, whereas, mixture CBTM-LABO-WET required 4.9 days. Analogously, for CTM-DRY specimens the laboratory or site production procedure resulted in a K_c increase from 1.9 days to 2.8 days, respectively.

It is worth noting that K_c values obtained for *ITS* were always lower with respect to those estimated for *DW*, i.e. in the first part of curing, strength development was faster than the moisture loss. The observations carried out analyzing K_c values, are also confirmed by the values of the slope $y'(K_c)$ reported in Table 4. Since moisture loss can be directly associated with the curing of bituminous emulsion, this also suggests that the effect of cement hydration was more important at shorter curing times.

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As far as the long-term curing performance is analyzed, the asymptotic values of *ITS* for mixtures CBTM-LABO-DRY and CBTM-SITE-DRY was 0.54 MPa and 0.32 MPa, respectively. In addition, mixture CBTM-LABO-WET was characterized by an asymptotic value of 0.53 MPa. This suggests that the curing condition (DRY or WET) did not affect the *ITS* development of CBTM mixtures (produced in laboratory). Regarding CTM specimens, the estimated asymptotic *ITS* for CTM-LABO-DRY and CTM-SITE-DRY was 0.41 MPa and 0.19 MPa, respectively.

4.3. Relation between moisture loss and mechanical properties

In Fig. 12 the measured values of *ITS* are reported as a function of the corresponding measured values of *DW*. Eq. (5) was fitted to the experimental data using the least-squares criterion, then the fitted regression curves are superposed to the experimental data. The values of the fitted parameters a_{ITS} and b_{ITS} are summarized in Table 5.

For CBTM mixtures, a_{ITS} and b_{ITS} are both positive and thus, as predicted by Eq. (8), the curvature is negative (concave curve). As explained in Section 3.6, the physical interpretation of the concavity is that the initial curing process of the tested CBTM mixtures was characterized by a faster increase in *ITS* with respect to *DW* and thus in this phase the effect of cement hydration prevailed on the effect of evaporation and emulsion breaking. For mixtures CBTM-LABO-DRY and CBTM-SITE-DRY, the same conclusion could be drawn by comparing the fitted values of the Michaelis constant K_c for both *DW* and *ITS* (Table 4). Indeed, the same physical interpretation is clearly valid also for mixture CBTM-LABO-WET (where evaporation is negligible), even though it was not possible to fit the MM model to the *DW* evolution.

For CTM mixtures, the relationship between *DW* and *ITS* was plotted only for the CTM-LABO-DRY (Fig. 12b) because in the case of CTM-SITE-DRY, the number of *ITS* measurements (5) did not allow to obtain a reliable fitting (only two degrees of freedom).

4.4. Relation between mechanical properties

In Fig. 13, the measured values of *ITS* are reported as a function of the corresponding measured values of *ITSM*, for the mixtures CBTM-LABO-DRY and CBTM-LABO-WET.

Following the same procedure described in Section 3.6, it can be shown that the relation $ITSM = ITSM(DW)$ is described by an equation equal to Eq. (5) and, consequently, the same nonlinear function can also be used to describe the relationship between *ITS* and *ITSM*:

$$ITS = \frac{a_{ITSM} \cdot ITSM}{b_{ITSM} + ITSM} \tag{9}$$

where α_{ITSM} and β_{ITSM} can be obtained by a nonlinear regression procedure.

First, fitting of the Eq. (9) was performed separately for mixtures CBTM-LABO-DRY and CBTM-LABO-WET. The fitted regression curves are superposed to the experimental data in

Fig. 13 (dashed lines), whereas the values of the fitted parameters α_{ITSM} and β_{ITSM} are summarized in Table 6. As it can be observed, the fitting appears to be dependent on the curing procedure: DRY vs. WET. Specifically, for the mixture CBTM-LABO-DRY the regression parameters are both negative (convex curve) indicating that *ITSM* increased at a faster rate with respect to *ITS*. The same conclusion could be drawn by comparing the fitted values of the Michaelis constant K_c for *ITSM* and *ITS*: 1.80 days and 2.23 days, respectively (Table 4). On the other hand, for the mixture CBTM-LABO-WET the regression parameters are both positive (concave curve) indicating that *ITS*

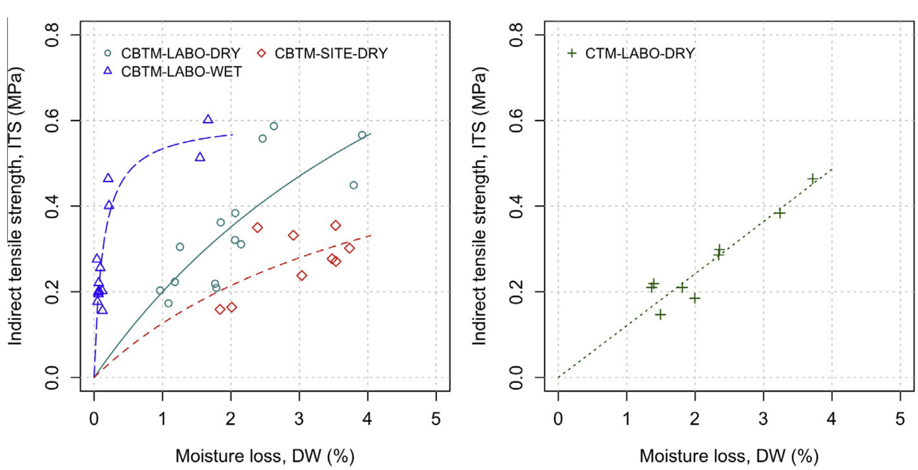

Fig. 12. Relationship between moisture loss (*DW*) and indirect tensile strength (*ITS*).

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Table 5
Regression parameters of the relationship between *DW* and *ITS*.

Mixture	a_{ITS}	b_{ITS}	c_{ITS}	Residual std. error
ITS vs. *DW*	[MPa]	[%]	[–]	[MPa]
CBTM-LABO-DRY	1.45	6.26	−0.074	0.087
CBTM-LABO-WET	0.60	0.13	−71.00	0.072
CBTM-SITE-DRY	0.71	4.58	−0.068	0.061
CTM-LABO-DRY	−65.07	−539.06	+4.479	0.036

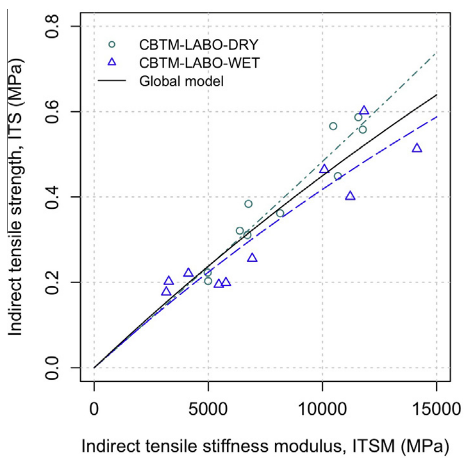

Fig. 13. Relation between indirect tensile stiffness modulus (*ITSM*) and indirect tensile strength (*ITS*).

increased at a faster rate with respect to *ITSM*, in the initial curing stage.

However, since actually the data points of the two mixtures are superposed, a third model was fitted to all the available measurements of *ITSM* and *ITS*, regardless of the curing procedure. The fitted parameters of the "global" model (CBTM-LABO) are summarized in Table 6, whereas the fitted regression curve is superposed to the experimental data in Fig. 13 (continuous line). A statistical comparison between the two regression approaches (separate regressions vs. global regression) was performed using the *F*-test, according to the procedure described in [21]. As a result, the value of the *F* statistic was 2.655, corresponding to a *p*-value of 0.101 which suggests that the difference between the two separate fits for WET and DRY conditions is not statistically significant, and therefore the use of the global model is appropriate.

5. Conclusions

In this paper, the laboratory curing process of two types of cold recycled mixtures manufactured during the construction of an experimental pavement section was investigated. Moisture loss by evaporation (*DW*), indirect tensile stiffness modulus (*ITSM*) and indirect tensile strength (*ITS*) were measured and the Michaelis–Menten (MM) model was fitted to the experimental data.

Based on the experimental results and analysis, the following conclusions can be drawn:

- The adopted curing variables (*DW*, *ITSM* and *ITS*) gave a comparable description of the curing process, when evaporation was allowed.
- The evolutive behavior of cement–bitumen treated materials (CBTMs) and cement treated materials (CTMs) was also similar, in that both mixture types exhibited an asymptotic trend and comparable curing rates.
- The MM model gave an appropriate description of the curing process in terms of evolution of material properties and allowed to identify and estimate specific parameters to measure both the initial curing rate and the long-term performance.
- CBTM mixtures cured in sealed conditions exhibited a slower curing rate and a higher long-term performance, in terms of ITSM, with respect to CBTM mixtures cured in unsealed conditions. This highlighted the importance of water available inside the specimen in order to promote the cement hydration process.
- For CBTM mixtures, the ITS development in the first part of curing was faster than the *DW*, hence, since *DW* can be directly associated with the curing of bituminous emulsion, this suggests that, in the initial curing stage, the effect of cement hydration prevailed on that of emulsion breaking.

Table 6
Regression parameters of the relationship between *ITS* and *ITSM*.

Mixture	a_{ITSM}	b_{ITSM}	c_{ITSM}	Residual std. error
ITS vs. *ITSM*	[MPa]	[MPa]	[MPa]	[MPa]
CBTM-LABO-DRY	−12.7	−2.7E+5	0.000	0.043
CBTM-LABO-WET	3.11	6.45E+4	−1.495	0.065
CBTM-LABO	4.06	8.03E+4	0.000	0.060

- The relation between *ITS* (or *ITSM*) and *DW* can be described using the same nonlinear equation of the MM model, but without the same constraints on the values of the fitted parameters. Moreover, the curvature of the regression curves shown to have a physical interpretation when CBTM mixtures are analyzed. When applied to the CBTM mixtures tested in this study, the model gave a coherent description of the experimental data and confirmed that their initial curing process was characterized by a faster increase in *ITS* with respect to *DW*.
- The relationship between *ITS* and *ITSM* can also be described by the same nonlinear equation of the MM model. When applied to the CBTM mixtures tested in this study, the MM model showed that the effect of the curing condition on the relationship between *ITS* and *ITSM* was not statistically significant.

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