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Substituted N-Phenyl-5-(2-(phenylamino)thianol-4-yl)isoxanole-3-carboxamides Are Valuable Antitubercular Candidates that Evade Innate Efflux Machinery

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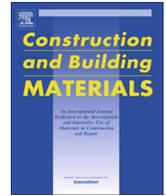
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Use of bending beam rheometer test for rheological analysis of asphalt emulsion-cement mastics in cold in-place recycling

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HIGHLIGHTS

- The lack of standardized procedures for analyzing thin semisolid films of AEC mastics was assessed.
- The introduction of glass microspheres, acting as “inert solid skeleton”, in the production of beam specimens was suggested.
- A consistent unconventional BBR testing protocol for AEC mastics was proposed.
- A feasibility study for validating the new BBR modified experimental setup was presented.

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ABSTRACT

This paper focused on the possibility of exploiting the potential of the bending beam rheometer (BBR) test for analyzing asphalt emulsion-cement (AEC) mastics tailored for cold in-place recycling applications in the first weeks of curing, i.e. phase which implies the coexistence of viscoelastic and materials. A consistent modified BBR testing protocol, which includes the experimental solutions devised for the practical execution of these unconventional rheometric measurements (sample preparation and test procedure), was proposed. The authors suggested to introduce glass microspheres, acting as “inert solid skeleton”, in the production of AEC mastics for BBR prismatic beams, to study the interaction between asphalt emulsion and cement in thin film and to limit the specimens’ shrinkage and warpage during the curing period. Finally, a feasibility study for validating the new modified experimental setup was presented, highlighting, with an explanatory overview of the types of results that can be expected, the macroscopic behaviors of some AEC mastics as a function of different parameter (asphalt binder to cement ratio, curing time and temperature).

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1. Introduction

Asphalt emulsion-cement (AEC) composites represent well-established solutions in many road construction and pavement engineering applications: cement-asphalt emulsion treated base, cold-in-place recycling technology and slab track system represent only some main examples [1–3]. With the widespread use of these composites, also called CAEC (cement-asphalt emulsion composite), CBEM (cold bituminous emulsion mixture), C-ETM (cement-emulsion treated mixture), CBTM (cement-bitumen treated material), (CBEA) (cement bitumen emulsion asphalt), a number of studies received extensive attention since the 1970s [4]. Today, in a sustainable development framework, the use of AEC composites in cold-in-place recycling (CIR) is gaining world-wide recogni-

tion and popularity. Specifically, CIR is a rehabilitation treatment consisting of milling and pulverizing a portion of the existing asphalt pavement surface, remixing it at ambient temperature with emulsion, water and cement to produce a restored recycled layer [3,5]. This technique offers economic savings and environmental benefits: reusing the existing materials, i.e. the reclaimed asphalt pavement (RAP), it reduces the consumption of virgin aggregates and asphalt binder, while the cold nature of the process decreases the negative impacts on the environment (reduction of fumes and odor) and preserves energy [6,7]. In this application, the primary binder is the asphalt emulsion (4–6% by mass) whereas cement is used as an admixture (1–3% by mass) to significantly improve the early performances of the mix. Although the simultaneous presence of so different binders does not produce a new one [8], the physical and mechanical properties over time of the AEC mixtures (e.g. workability, strength and stiffness) depend on the dosages and the relative proportions between the asphalt

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binder contained in the emulsion and the cement, i.e. on the asphalt to cement ratio (A/C) [1,7]. The combined use of these binders makes it possible to obtain mixtures having on the one hand lower temperature susceptibility and higher stiffness, load-bearing capacity and resistance to permanent deformation than asphalt mixture and on the other higher flexibility, deforming ability and fatigue resistance than cement treated materials [3,9–14]. Over the years the optimum blending ratios of these component materials have derived from the observation of the in-situ results, especially those related to the laying of road pavements (base or sub-base layers), and from economic and operational considerations.

Some authors propose to consider the asphalt concrete as a multiscale material having at least four characteristic elements [15]: a) binder, b) mastic, which results from a combination of binder and filler-sized aggregates (particle size smaller than 75 μm), c) fine aggregate mixture (FAM), which is obtained mixing binder, filler, air and fine aggregate (particle size generally smaller than 2 mm) and d) mixture which is composed of binder, filler, air, fine aggregate and coarse aggregates having generally a particle size smaller than 37.5 mm. As far as AEC composites are concerned, the same representation can be adopted, but another element which plays a key role, i.e. water, must be included. Water is contained in the asphalt emulsion, but generally a supplementary quantity is added to increase the mixture workability, to avoid the premature breaking of the emulsion and to give the necessary contribution to the cement hydration. Even though cement hydration consumes water, a relatively large amount of water can still remain entrapped in these composites. At the same time, when using a high quantity of cement, a non-hydrated part can persist as solid powder. In the first case there is an evolution delay of the internal structure, strength and stiffness [7,9,13,16,17], while in the second case non-hydrated cement does not contribute to the development of these performances [18]. Studies on AEC mastic (also called AEC paste) are mainly focused on the early-age evolution of rheological proprieties, which is an indicator of the workability as well as of the stability and demulsifying behavior of asphalt emulsion [19–21]. The scientific research on AEC-FAM (also defined AEC mortar) and AEC mixture instead examined the changes in the mechanical properties over time: asphalt emulsion breaking and setting, water evaporation, hydration and hardening of cement are time dependent processes [5,22–24].

The performances of AEC mortars and mixtures mainly depend on the rheological properties of their corresponding mastics. Thus, experiments at the scale of AEC mastic are extremely significant because they allow the physicochemical interactions that occur between emulsified asphalt, water, filler sized aggregates and cement to be emphasized [25]. The investigation of the mastics viscoelastic properties represents a fundamental step to understand how the dosage of the components and the A/C ratio can affect the overall behavior of the corresponding mortars and mixtures and to determine whether asphaltic or cementitious behavior prevails. Some studies based on the use of the dynamic shear rheometer (DSR) have been conducted for analyzing the AEC mastic response to permanent deformation, the rheological and recovery behavior, the interfacial adhesion with aggregate, as a function of some parameter like A/C ratio and temperature [26–29]. But, rheological studies conducted to date on AEC mastics have necessarily been limited to the mere aspect of the viscosity evolution of the fresh mix in the first hours after the contact between asphalt emulsion and cement, especially to understand the timing of mixing, paving and compaction of the mixtures in road construction site. From a strictly rheometric point of view, the evolution over time of the mechanical behavior of AEC mastics in thin film has not been studied, due to the lack of instruments able to measure the viscosity of mixtures that tend progressively to assume a solid-like

behavior at ordinary temperatures as a result of the progressive growth of the resistant cement bonds.

In the light of the above the authors suggest to study the behavior of the AEC mastics tailored for CIR applications in the first weeks of curing, i.e. phase which implies the coexistence of viscoelastic materials (asphalt binder) and brittle materials (cementitious bonds), exploiting the potential of the bending beam rheometer (BBR). The flexural creep stiffness or flexural creep compliance, determined from this test, would represent a very interesting parameter to describe the stress-strain-time response of AEC mastics at the test temperature within the linear viscoelastic response range. Moreover, using the BBR to test these mastics has several advantages, such as equipment availability, reduced specimen size and theoretically valid assumptions (beam theory and elastic-viscoelastic correspondence principle) [30,31]. But, although the BBR is a recognized solution to give responses about the low-temperature behavior of asphalt binders, the use of this instrument for AEC mastic is far from obvious. Thus, the main objective of this paper was to establish a consistent testing protocol, that outlined in detail all the practical steps for the sample preparation and the test procedure, to analyze AEC mastics characterized by a wide range of consistency (fluid, semi-solid, solid) using the BBR approach. All the critical operational issues emerged following the BBR standard procedure were also highlighted. Finally, a feasibility study for validating the new modified BBR experimental setup was presented, highlighting, with an explanatory overview of the types of results that can be expected, the macroscopic behaviors of some test mixtures characterized by different A/C ratios.

2. Bending beam rheometer (BBR) test

The BBR, which was introduced since the 1990s [32], is used to measure the low-temperature response of asphalt paving binders according to several specifications [33–35]. Specifically, flexural creep stiffness (S) and stress relaxation capacity (m-value), i.e. the slope of the stiffness versus time curve in a log-log scale, are measured in three-point bending on a beam of asphalt binder (6.4 ± 0.1 mm thick, 12.7 ± 0.1 mm wide and 127 ± 5 mm long) [36]. A load of 980 ± 50 mN is applied for 240 s at the mid-point of the sample, which is immersed in a cold liquid bath (temperatures lower than 0 °C, generally between -30 °C and -10 °C). The beam deflection (δ) is measured with respect to loading time using a linear variable differential transducer (LVDT). According to the elementary Bernoulli-Euler theory of bending for prismatic beam the mid-point deflection at time t (δ(t)) can be calculated by using Eq. (1)

$$\delta(t) = \frac{P \cdot L^3}{48 \cdot E \cdot I} \quad (1)$$

where P is the applied load, L is the span length, E is the elastic modulus and I is the moment of inertia of the section. For a viscoelastic material the displacement depends on the loading time, so the elastic modulus can be replaced by the time-dependent flexural creep stiffness (S(t)) which is determined by Eq. (2)

$$S(t) = \frac{P \cdot L^3}{4 \cdot b \cdot h^3 \cdot \delta(t)} \quad (2)$$

where b and h are the beam width and thickness, respectively [32].

The m-value (Eq. (3)), which ranges from 0 to 1, expresses the material response type: 0 corresponds to the limit conditions of elastic solid and 1 to the limit conditions of viscous fluid.

$$m(t) = \left| \frac{d \log[S(t)]}{d \log(t)} \right| \quad (3)$$

3. Approach to the use of BBR for the analysis of AEC mastics

The development of a BBR testing protocol for analyzing AEC mastics required numerous preliminary tests for optimizing the sample preparation and the test procedure.

3.1. Sample preparation

Since a standardized procedure for the production of AEC mastics is not available, the first attempt was conducted according to a previous study [21] adding in the following order cement, water and lastly cationic asphalt emulsion. Cement ($\rho = 3.15 \text{ g/cm}^3$), water ($\rho = 1.00 \text{ g/cm}^3$) and asphalt emulsion ($\rho_{\text{asphalt}} = 1.02 \text{ g/cm}^3$) were dosed by volume, considering the volumetric A/C ratio ranging between 0 and 5 ($0.00 \div 1.62$ by mass) and the water to cement ratio (W/C) ranging between 1 and 3 ($0.32 \div 0.96$ by mass). These mixtures were then poured into the aluminum molds supplied with the BBR (metal bars were preliminary covered with the plastic strips). After trimming the filled molds, specimens were cured in laboratory ($T = 22 \pm 1 \text{ }^\circ\text{C}$, $\text{RH} = 50\%$) and wet conditions ($T = 22 \pm 1 \text{ }^\circ\text{C}$, $\text{RH} = 90\%$) before demolding. After trimming the filled molds, specimens were stored in laboratory ($T = 22 \pm 1 \text{ }^\circ\text{C}$, $\text{RH} = 50\%$) and high humidity conditions ($T = 22 \pm 1 \text{ }^\circ\text{C}$, $\text{RH} = 90\%$) before demolding, according to curing strategies used for AEC mixtures [37].

Following this procedure, several critical issues and drawbacks emerged already during the beam preparation phase. Many mixtures resulted to be fluid and could be poured into the molds in one pass, whereas others ($A/C \geq 2.3$ with $W/C \leq 2.3$) required an external mechanical action to evenly spread the mixture inside, compromising the uniqueness of the sample preparation procedure. In the curing phase, two different aspects caused problems with the dimensional stability of the AEC samples. Firstly, the swelling of some specimens with the formation of tiny bubbles (white foam) coming to the surface of the beams were observed. In parallel, a significant corrosion of the aluminum elements which constitute the molds occurred. This phenomenon was principally due to the reaction between the aluminum mold and the alkalis (OH) contained in the cement that produces hydrogen gas: the presence of the cationic asphalt emulsion accelerated and increased these effects [38]. Thus, a protective paint coating was applied on a new set of BBR aluminum bars.

Secondly, the samples with high W/C ratio showed a volume reduction (shrinkage) with consequent shape change (warping) after few hours of curing, both in dry and wet condition, due to the evaporation of the water contained in the mixtures. This behavior compromises the geometric hypotheses about the application of the analytical functions derived from the de Saint-Venant beam model (elementary Bernoulli-Euler theory of bending). To overcome this problem and to study the interaction between asphalt emulsion and cement in thin film, as actually occurs, the authors proposed to introduce a solid fraction, acting as "solid skeleton", in the production of AEC mastics for BBR prismatic beams. The selection of the optimal solid component was dictated by different chemical and physical requirements. Firstly, a chemically stable and non-porous material which does not absorb asphalt emulsion and water and does not affect the asphalt emulsion breaking and the cement setting process is needed. Besides, regularly-shaped particles would ensure several advantages: isotropic properties, low stress concentration around the particles, uniform shrinkage in all directions (no warpage) and high workability. The final decision felt on glass microspheres, which represent ideal aggregates: the glass composition, the very low oil and water absorption, the high chemical resistance and the near perfect spherical shape make them excellent for this application

[39]. Soda-lime silica glass microspheres (72% SiO_2 , 15% Na_2O , 6% CaO , and 4% MgO) available on the market with a nominal diameter of 400–600 μm have been selected. This grain size was chosen to maintain the ratio between the microspheres diameter and the specimen thickness (6.4 mm) less than 1/10 so as to reasonably neglect the wall or boundary effect [40]. From the data declared by the manufacturer (Table 1), the actual particle size and the shape of the glass microspheres were evaluated using a laser diffractometer Mastersizer 3000 (Malvern) in a wet dispersion configuration and an optical microscope (Fig. 1).

After a preliminary study useful to determine the best quantities to control, three parameters were considered:

- A/C: volumetric asphalt (asphalt content in the emulsion) to cement ratio;
- ϕ_{gm} : glass microspheres volume concentration, i.e. ratio of the volume of the glass microspheres to the sample total volume;
- ϕ_{w} : water volume concentration, i.e. ratio of the volume of water (emulsion water + added water) to the sample total volume.

Low ϕ_{gm} and high ϕ_{w} ratios led to the production of specimens with a compromised geometry due to water evaporation. On the other hand, high ϕ_{gm} ratios made mixtures with poor workability and specimens potentially characterized by irregular cavities in the middle. A good compromise between a suitable mixture workability and the BBR beam dimensional stability was found considering $\phi_{\text{gm}} = 0.5$ and $\phi_{\text{w}} = 0.3$; this means that each specimen was composed in volume of 50% glass microspheres and 30% water; the remaining 20% was divided between asphalt and cement, according to the considered A/C ratio.

Details of mixing procedure and sample preparation are graphically shown in Fig. 2. Specifically, a fixed amount of pre-wetting water was initially added to glass microspheres (Fig. 2a) and stirred until a homogeneous mixture was obtained. Then, the cement was put, and the mixture mixed for one minute, to enhance the workability and avoid the emulsion breaking. Afterwards, asphalt emulsion was added (Fig. 2b) and stirred for one minute. Once a homogeneous mixture was obtained, it was poured into the test molds starting at one end and moving slowly toward the other (Fig. 2c). Each mold was manually vibrated through 10 S from a height of about 2 cm in order to allow the mixture to evenly spread inside. Then, the overfilling on the upper face of the specimen was trimmed using a spatula (Fig. 2d). The filled molds were stored at lab condition prior to demolding; it is recommended to demold the specimens after at least 48 h of curing time, the first 12 of which in a box covered with a polyethylene film (higher RH) to improve the hydration reaction of cement [23,37]. Before demolding, the molds were cooled in a cold chamber ($T = -10 \text{ }^\circ\text{C}$) for three minutes to stiffen the test specimens so they can be readily demolded without distortions (Fig. 2e).

3.2. Test procedures

As already pointed out, the original BBR test provides a measure of low temperature flexural-creep stiffness and relaxation proper-

Table 1

Main properties of glass microsphere used in this study, as declared by the manufacturer.

Parameter	Nominal value
Particle size [μm]	400–600
Particle density [g/cm^3]	2.46
Apparent density [g/cm^3]	1.5–1.6
Hardness	Rockwell 46, Vickers 645, Mohs 6–7
Melting point [$^\circ\text{C}$]	730

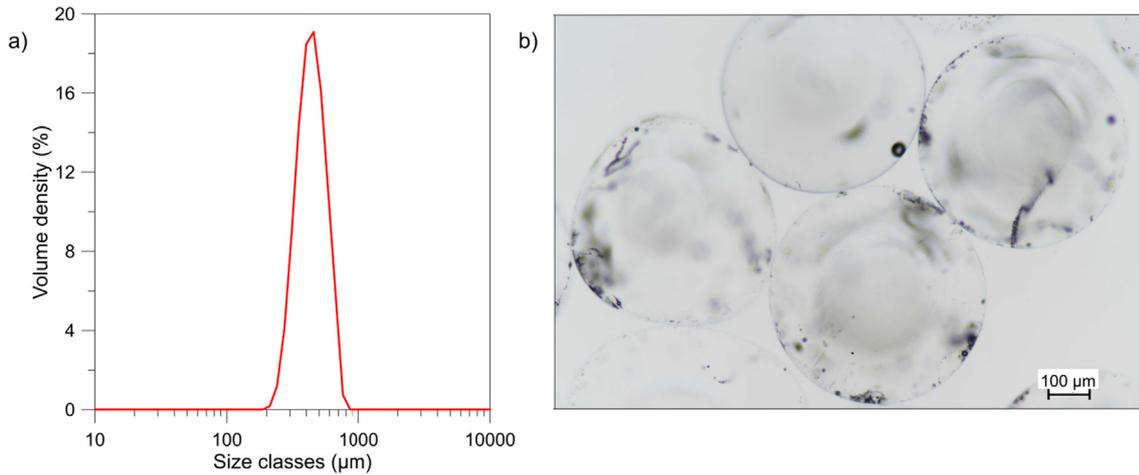


Fig. 1. Particle size distribution (a) and microscope image (b) of glass microspheres.

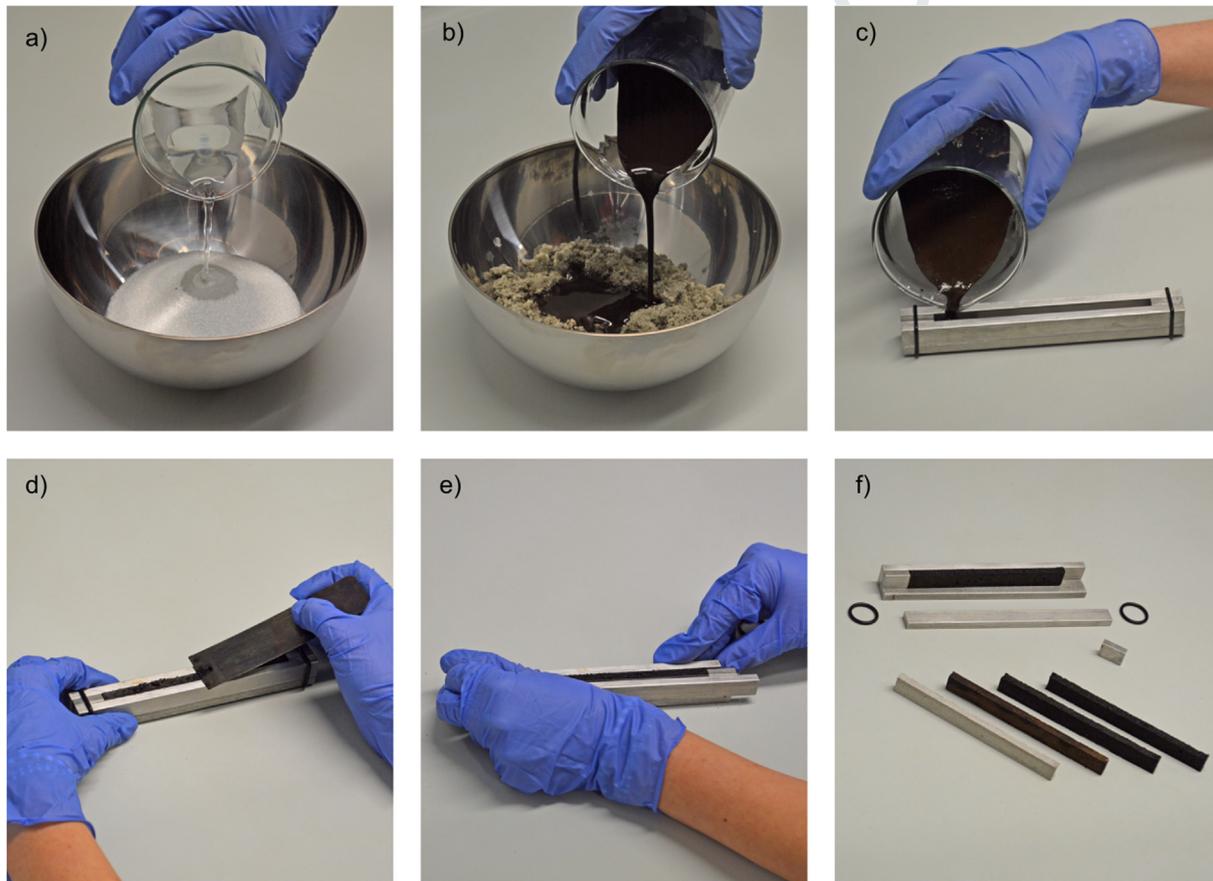


Fig. 2. Mixing procedures and sampling preparation: addition of pre-wetting water to glass microspheres (a); addition of asphalt emulsion to glass microspheres, water and cement (b); pouring of the mixture into the test specimen mold (c); trimming of the upper face of the specimen (d); specimen demolding (e); samples suitable to be tested with the BBR (f).

ties of asphalt binder. In this case, the materials to be tested are AEC mastics in which cement and glass microspheres guarantee a stiffer behavior of the samples also at higher temperatures. Thus, tests were performed at above-zero temperatures to analyze the mastics behavior closer to the ordinary conditions and to ignore the contribution of possible residual frozen water entrapped in the samples. Initially, the standard procedure used for the binder testing (load of 980 ± 50 mN for 240 s) was followed. But, under these loading conditions, most of the tested specimens showed a highly thermo-dependent behavior and deflections greater than

the limits for the small strain theory where the elementary bending theory is valid. A reduced load of 490 ± 20 mN was applied for 240 s to maintain the deflection within the linear elasticity limits.

4. Feasibility study

4.1. Material and methods

An experimental study was planned to evaluate the feasibility of using the BBR approach to test AEC mastics following the pro-

posed procedure. A slow setting (over-stabilized) cationic asphalt emulsion (emulsifier: polyamines), classified as C60B4 according to EN 13808 [41], was selected. The main properties of the asphalt emulsion are listed in Table 2. A Portland limestone cement CEM II/B-LI 32, 5R was used: setting time higher than 75 min and a content of sulphates and chloride lower than 3.5% and 0.1%, respectively. The solid component consisted of the above defined glass microspheres.

Glass microspheres, water, cement and asphalt emulsion were dosed by volume. Values of ϕ_{gm} and ϕ_w ratios equal to 0.5 and 0.3 were used. On the basis of the CIR construction practice, A/C ratios equal to 0, 1, 3 and 5 were considered, in which A/C = 0 represented a cement paste without asphalt emulsion (Table 3). The analyzed mastics were identified by the acronym AC followed by a number representing the volumetric A/C ratio.

Modified BBR tests were carried out at different curing times: 3, 7, 14 and 28 days. After demolding, test specimens were cured at $22 \text{ }^\circ\text{C} \pm 2 \text{ }^\circ\text{C}$ and $55\% \pm 5\%$ of RH. Once the curing time was reached, the tests were carried out at the temperature of $10 \text{ }^\circ\text{C}$ after 60 min of conditioning. On the 28-day cured specimens, the tests were also carried out at temperatures of 5 and $15 \text{ }^\circ\text{C}$. The whole data set was constituted by 120 measurements: five specimens for each of the four mixtures at four curing times (3, 7, 14 and 28 days) at $10 \text{ }^\circ\text{C}$ and 40 (20 for each temperature) for the 28-day cured specimens at 5 and $15 \text{ }^\circ\text{C}$.

4.2. Results and discussions

4.2.1. Influence of loading time

The deflection vs loading time plot for different A/C ratios at 28 days of curing time is reported in Fig. 3. An instantaneous deformation, which increased with increasing the A/C ratio, occurred immediately after load application. Then, the deflection rate (change in deformation with respect to loading time) of the AEC mastics, which reflects the materials' rheological properties, resulted to be function of the A/C ratio. Specifically, the deflection rate increased by decreasing the amount of cement (higher A/C

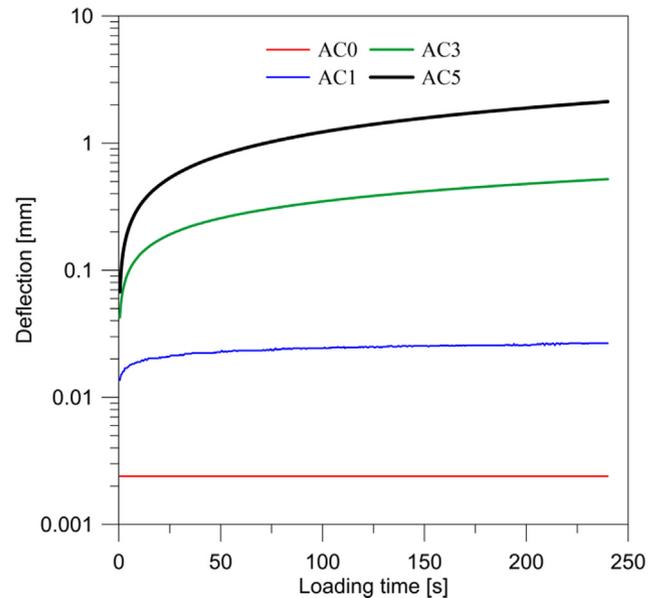


Fig. 3. Deflection vs Loading Time for different mastics at 28 days of curing time and at the temperature of $10 \text{ }^\circ\text{C}$.

ratio). The deflection of the beams made exclusively with cement (AC0) remained constant throughout the test, showing an expectable elastic solid behavior. This behavior was reflected also for the flexural creep stiffness (S) and stress relaxation capacity (m-value) in all the analyzed curing times (Fig. 4). AC3 and AC5 mixtures showed a significant stiffness reduction over time, highlighting a viscoelastic nature (delayed deformation response with respect to the load application). The AC1 mastic showed instead an intermediate behavior, presenting high stiffness values which slightly declined with the loading time: the maximum m-value was approximately 0.12 and remained almost constant during the test. For the 3-day curing tests, the deflection of the AC5 samples reached the equipment's limit after about 40 s of loading, so only values up to 30 s were registered.

As mentioned, the m-value can give information about the AEC mastics response type: 0 corresponds to the limit conditions of elastic solid, i.e. typical of cement, and 1 to the limit conditions of viscous fluid, i.e. typical of a pure asphalt binder.

4.2.2. Influence of curing time

Curing time plays an active role in the development on the flexural stiffness. By way of example, the stiffness vs curing time graph for different A/C ratios, considering the S values measured at 30 s of loading (S(30)), is reported in Fig. 5. All the analyzed mastics showed a progressive increase in flexural creep stiffness over curing time as a function of asphalt binder and cement contents. The AC0 and AC1 mastics showed an almost linear stiffness growth with the curing time: they registered stiffness values at 28 days

Table 2

Main properties of the asphalt emulsion, as declared by the manufacturer.

Parameter	Reference standard	Nominal value
Particle polarity	EN 1430	+
Residual binder content [%] (m/m)	EN 1428	58–62
Breaking behavior: mineral filler method [%]	EN 13075-1	110–195
Mixing stability with cement [%]	EN 12848	≤ 2
Residue on sieving – 0.5 mm sieve [%]	EN 1428	≤ 0.2
Viscosity at $40 \text{ }^\circ\text{C}$ – efflux time [s]	EN 12846-1	15–70
Adhesivity of asphalt emulsions by water immersion test [%]	EN 13614	≥ 75
Settling tendency	EN 12,847	≤ 10
<i>Tests on residue from distillation test</i>		
Needle penetration at $25 \text{ }^\circ\text{C}$ [dmm]	EN 1426	≤ 100
Softening point [$^\circ\text{C}$]	EN 1427	$\geq 43^\circ$

Table 3

Composition and volumetric properties of tested AEC mastics.

	A/C		W/C		ϕ_{gm}	ϕ_w	ϕ_a	ϕ_c
	[v/v]	[m/m]	[v/v]	[m/m]				
AC0	0.0	0.000	1.5	0.476	0.500	0.300	0.000	0.200
AC1	1.0	0.324	3.0	0.952	0.500	0.300	0.100	0.100
AC3	3.0	0.971	6.0	1.905	0.500	0.300	0.150	0.050
AC5	5.0	1.619	9.0	2.857	0.500	0.300	0.167	0.033

v/v = volume ratio; m/m = mass ratio.

ϕ_a = Asphalt volume concentration; ϕ_c = Cement volume concentration.

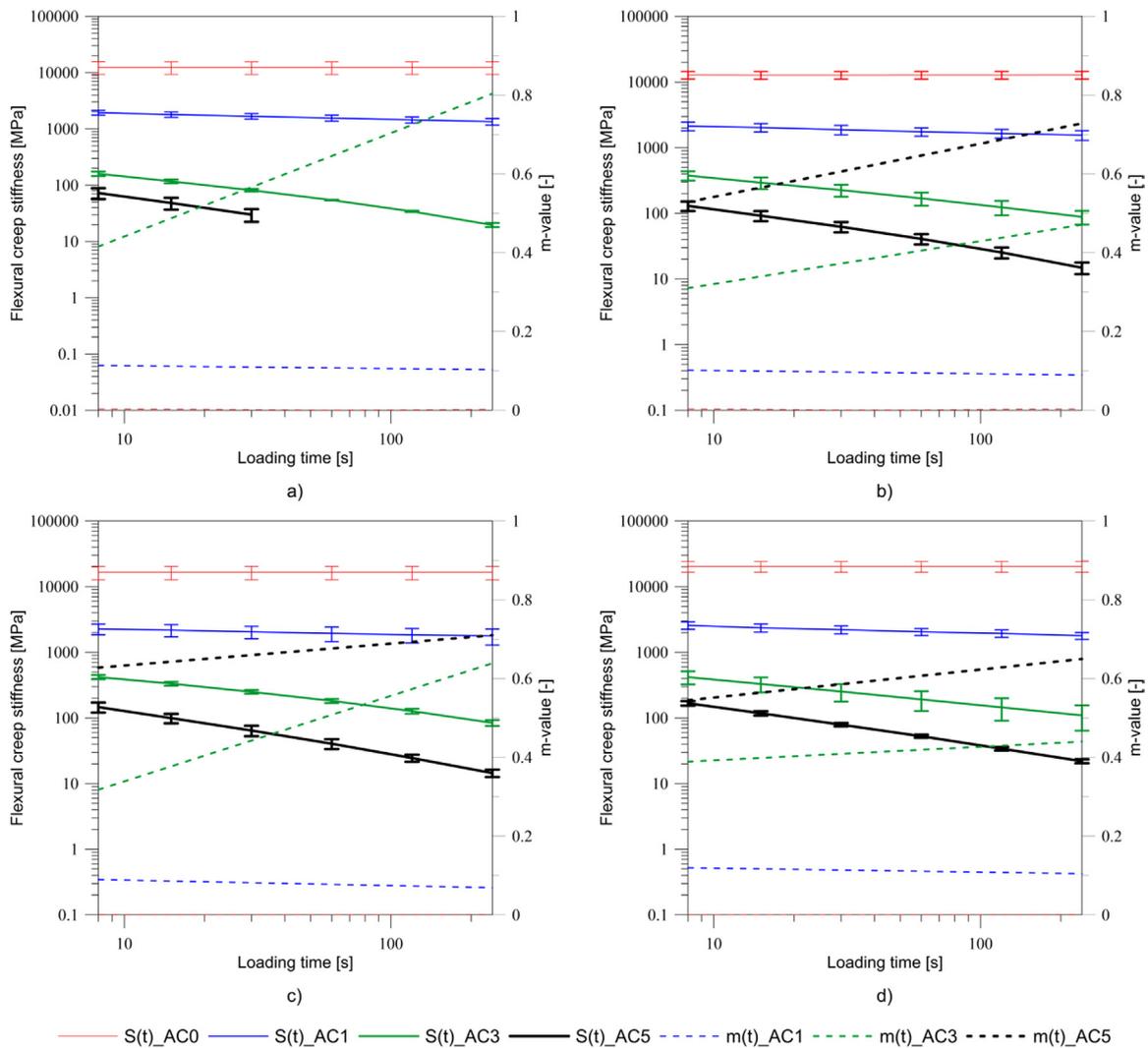


Fig. 4. Flexural creep stiffness and m-value vs loading time for different A/C ratio and at the temperature of 10 °C for 3 (a), 7 (b), 14 (c) and 28 (d) days of curing.

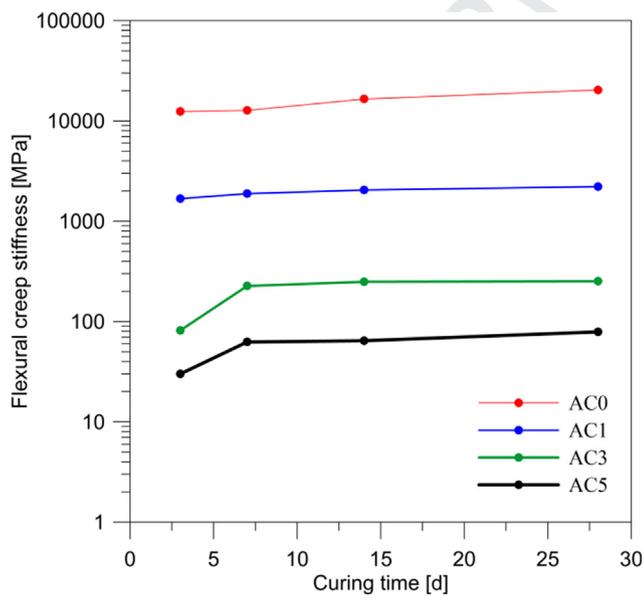


Fig. 5. Flexural creep stiffness $S(30)$ vs curing time for different A/C ratio.

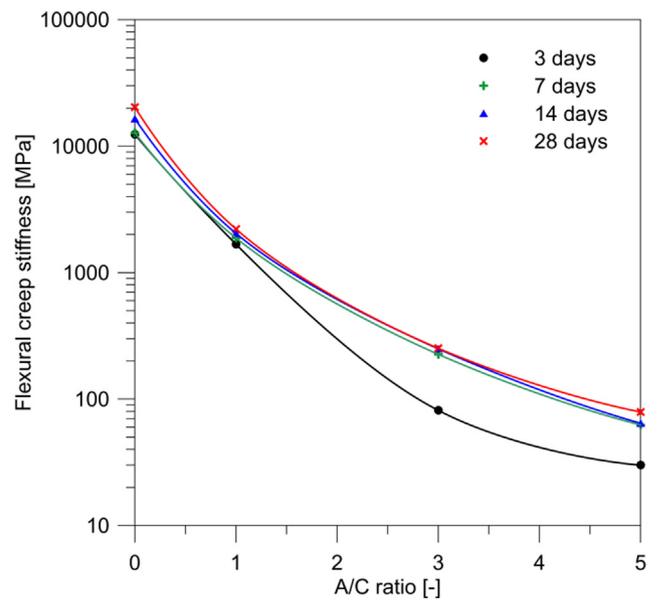


Fig. 6. Flexural creep stiffness $S(30)$ vs A/C ratio for different curing time.

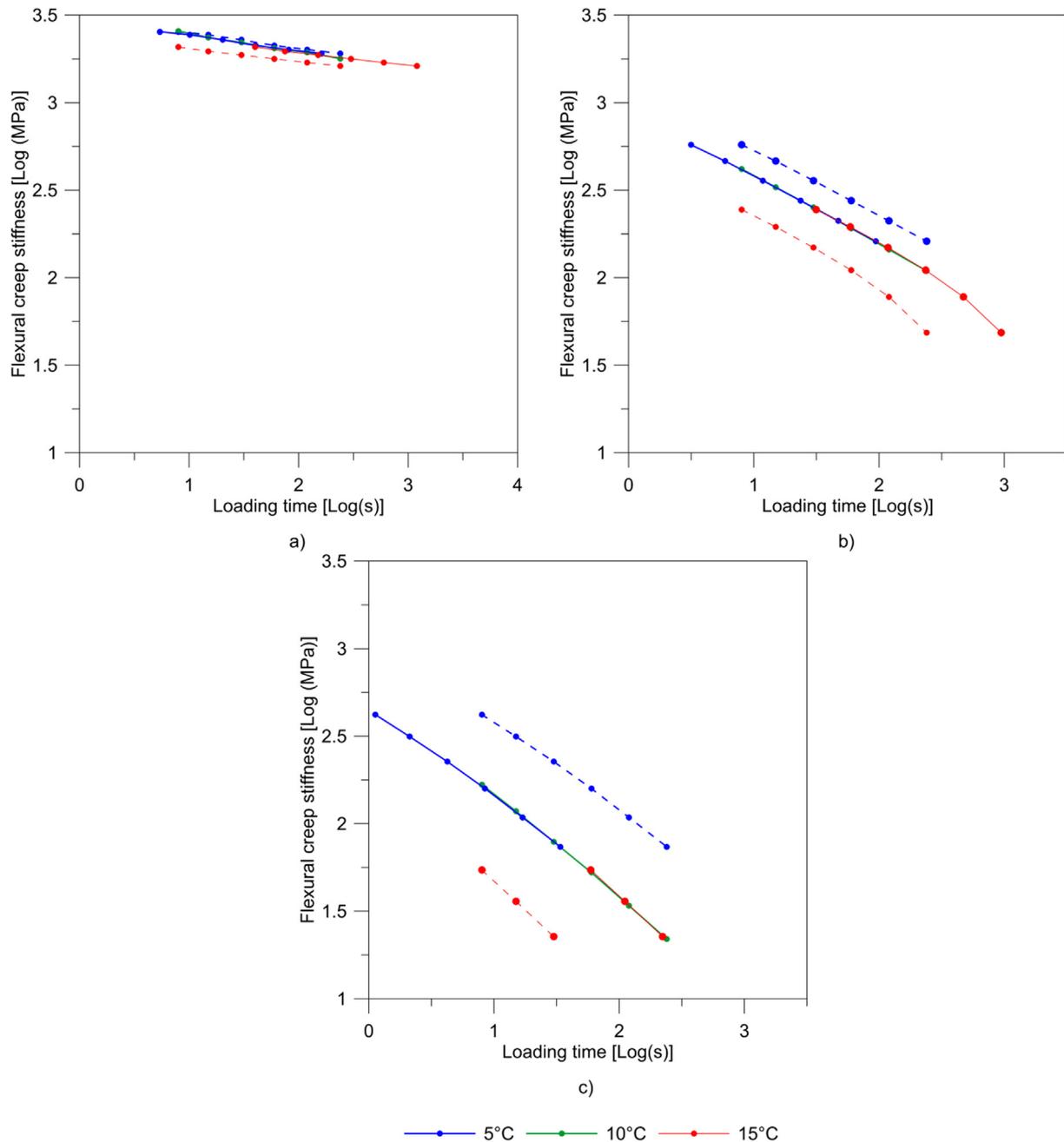


Fig. 7. Time-temperature superposition principle applied to AC1 (a), AC3 (b) and AC5 (c).

402 ($S(30)_{28d}$) equal to 1.6 and 1.3 times higher than those recorded at
 403 3 days ($S(30)_{3d}$). A sharp rise in stiffness during the first week of
 404 curing was instead observed for the AC3 ($S(30)_{7d}/S(30)_{3d} = 2.8$)
 405 and AC5 ($S(30)_{7d}/S(30)_{3d} = 2.1$), while after 7 days of curing, the
 406 trend was comparable with those of AC1. For the same curing time,
 407 a considerable drop in stiffness, more evident at the earlier stage of
 408 curing, was measured by increasing the asphalt binder content, or
 409 reducing the cement content (Fig. 6). Both these trends confirm that
 410 the rheological properties of AEC mastics vary considerably
 411 over time as a function of the A/C ratio. In practice, unbalanced
 412 amounts of cement are often used, during the construction of
 413 sub-base layers (with the risk of reducing the fatigue life), to
 414 quickly reach high stiffness values which are generally post-
 415 monitored with in-situ sampling (coring) or with deflectometric
 416 tests on already completed pavements. Using the BBR test, the time

required for the development of suitable mechanical properties, as
 a function of the binders' dosage, can be now properly calculated
 and verified.

4.2.3. Influence of temperature and time-temperature superposition

As already pointed out, AEC mastics are time-dependent products. Asphalt is a thermo-rheologically simple material for which the time-temperature superposition (TTS) principle can be applied to determine temperature-dependent mechanical properties from known data measured at a reference temperature. But, this principle is valid for the viscoelastic materials: it is not applicable for cement. Thus, the analysis of the flexural creep stiffness curves at different temperatures (5 °C, 10 °C and 15 °C) was useful to verify the applicability of TTS to AEC by varying the A/C ratio. TTS overlays of temperature sweep data are shown in Fig. 7, while the shift

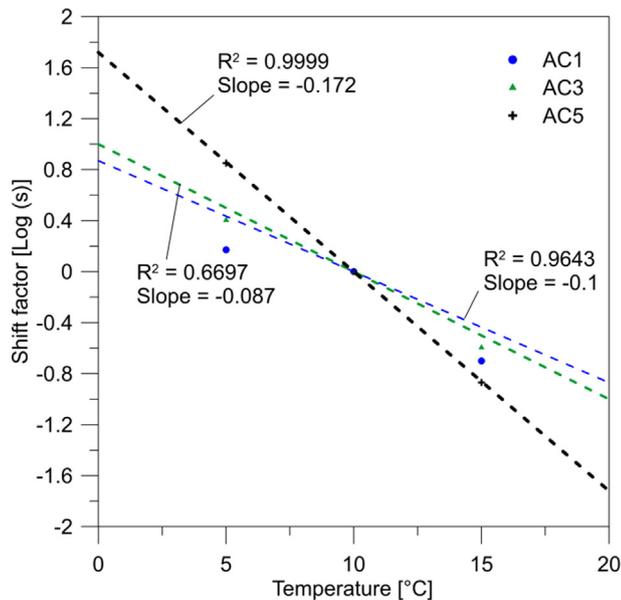


Fig. 8. Shift factor of mastics.

the warpage of the specimens during the curing phase and to study the interaction between asphalt emulsion and cement in thin film. Soda-lime silica glass microspheres with a nominal diameter of 400–600 μm were selected. They represent chemically stable and non-porous materials which do not absorb asphalt emulsion and water and do not affect the asphalt emulsion breaking and the cement setting process. Besides, regularly-shaped particles would ensure several advantages: isotropic properties, low stress concentration around the particles, uniform shrinkage in all directions and high workability. The grain size was chosen to maintain the ratio between the microspheres diameter and the specimen thickness less than 1/10, so as to reasonably neglect the wall effect. As far as the mix design is concerned, a good compromise between a suitable mixture workability and the BBR beam dimensional stability was found considering ϕ_{gm} and ϕ_w equal to 0.5 and 0.3: this means that each specimen was composed in volume of 50% glass microspheres and 30% water; the remaining 20% was divided between asphalt and cement, according to the considered A/C ratio. Tests were performed at above-zero temperatures to analyze the mastics behavior closer to the ordinary conditions and to ignore the contribution of possible residual frozen water entrapped in the samples, applying a reduced load (490 ± 20 mN for 240 s) to maintain the deflection within the linear elasticity domain. Finally, detailed mixing procedure and sample preparation were identified.

The results of the feasibility study, performed on a set of mixtures characterized by different A/C volumetric ratios on the basis those generally used in CIR applications, offered possible interpretation keys about these mixtures. The trend of the flexural creep stiffness and of the m-value by varying the A/C ratio can give significant information about the mastics behavior, in terms of prevalence of asphalt (viscous fluid) or cement (elastic solid) contribution. These rheometric measurements resulted to be ideal to highlight the time and temperature dependency of several related phenomena which affect these mixtures, such as asphalt emulsion breaking and the setting, water evaporation, cement hydration and hardening, also verifying the applicability of the time-temperature superposition principle. In summary, the modified BBR test represents a good approach to analyze the behavior of AEC mastics as a function of different parameter (A/C ratio, curing time and temperature), providing a rigorous and controllable theoretical assumption in the laboratory for optimizing the mix-design in full-scale or to evaluate, in back analysis, the reasons for successes and failures.

Declaration of Competing Interest

None.

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factor curves are plotted in Fig. 8 considering the temperature of 10 °C as the reference temperature. The horizontal shift factors were graphically calculated: the shift factor can not be modelled with the William-Landel-Ferry equation due to the limited available data. In the first approximation, the data were fitted with a linear interpolation (Fig. 8) in order to highlight the difference between mastics in terms of temperature dependency. AC5 mastic was characterized by the greater slope, i.e. it was the most temperature-dependent mixture. In addition, AC5 also showed the highest coefficient of determination (R^2), indicating that the shift factors can actually be fitted by a linear interpolation. On the contrary, AC1 mastic showed the lowest slope. The use of higher cement content, gives more cement hydration products as well as greater/strongest cementitious bonds: a growing stiffness is related to a drop in the temperature susceptibility because cement presents a lesser deformability, which remains constant in the ordinary temperature range, than asphalt binder. Increasing the asphalt binder amount, it partly covers the cement grains and interrupts the continuity of the cementitious bonds, reducing the stiffness and consequently increasing the temperature susceptibility. Thus, BBR test represents a suitable approach to analyze the behavior of AEC mastics as a function of temperature, also for above-zero temperatures, for a wide range of A/C ratios. By performing tests at several temperatures, the possibility of rigorously applying the TTS principle to these mixtures is verifiable.

5. Conclusions

The possibility of using the BBR test for analyzing AEC mastics tailored for the CIR application was investigated. A consistent testing protocol, which includes all the practical steps for the sample preparation and the test procedure, was proposed and validated with a feasibility study. Several modifications to the BBR standard procedure have been proposed.

Firstly, test specimen molds were protected with a paint coating to avoid the corrosion of the aluminum elements due to the reaction with the alkalis contained in the cement and the cationic emulsifier present in the asphalt emulsion. A solid fraction, acting as “solid skeleton”, was introduced in the production of AEC mastics for BBR prismatic beams to limit and control the shrinkage and

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