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NON-DESTRUCTIVE EVALUATION OF ECO-FRIENDLY CEMENTITUOUS MATERIALS BY ULTRASOUND

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Abstract

Ultrasonic methods have been developed in the past to study properties of cement based materials in the fresh and hardening state. However, most of the methods only consider a certain type of ultrasonic waves. To derive elastic parameters of fresh concrete like the Poisson's ratio and elastic modules it is required to obtain shear waves as well as compressional waves. It is certainly much more difficult to establish a setup to transmit and record shear waves in a way that the onset of these slower waves (compared to compressional waves) can be detected as clear as necessary to calculate shear wave velocity values with the required accuracy. A test setup for testing cement paste with different ultrasonic waves is presented. Tests have been conducted that show reasonable ultrasonic compressional and shear wave transmission right after mixing. Thus ultrasound is found to be suited for the characterisation of paste mixtures and the determination of changes in the rheological properties already before setting. Test results from different cementitious mixes with a special focus on eco-pastes are presented. These eco-pastes show optimized packing density (using micro and eco fillers as replacement of Portland cement clinker).

Key words: Ultrasound, compressional waves, shear waves, eco filler, packing density, setting, hardening

1. Introduction

The properties of cement based materials in the fresh and hardening state are currently measured with rather conventional methods. Ultrasonic methods have been developed in the past using through-transmission techniques and analysing the whole waveform. Material properties as for example the workability are investigated based on parameters like the compressional wave velocity, the energy and the frequency content or even the derivative of the signals [1, 2 and 3]. Ultrasound is already accepted to be a very useful tool to investigate the setting and hardening process of cementitious materials. However, many investigations and signal interpretation strategies are more or less empirical and is applicable only on certain type of mixes of similar composition. Especially new binder developments in the concrete sector and its investigation by ultrasound shows that the interpretation with empirical methods are sometimes insufficient.

It is for example not feasible to derive the Poisson's ratio of fresh concrete or to get information even on the elastic modules data based on compressional waves only if the mix to be investigated cannot be classified into a group of "standard" mixture proportions. This is for example the case for new mixes with reduced binder contend and optimized packing density using micro-filler made of inert materials that are more "eco-friendly". To study the setting and hardening process of such new binder compositions it useful to obtain also shear waves beneath compressional waves [4]. But it is certainly much more difficult to establish a setup to transmit and record shear waves in a way that the onset of these slower waves (compared to compressional waves) can be detected as clear as necessary to calculate shear velocity values with the required accuracy.

2. Materials

The main materials, used for this paper are CEM I 52.5 N-SR3, limestone filler of different grain size classes (so-called eco-filler 3 µm ≤ d50 ≤ 30 µm and micro-filler d50 < 3µm) [5]. Material properties of basic materials are presented in Table 1 and particle size distribution of the materials and the corresponding mixes is shown in Figure 1.

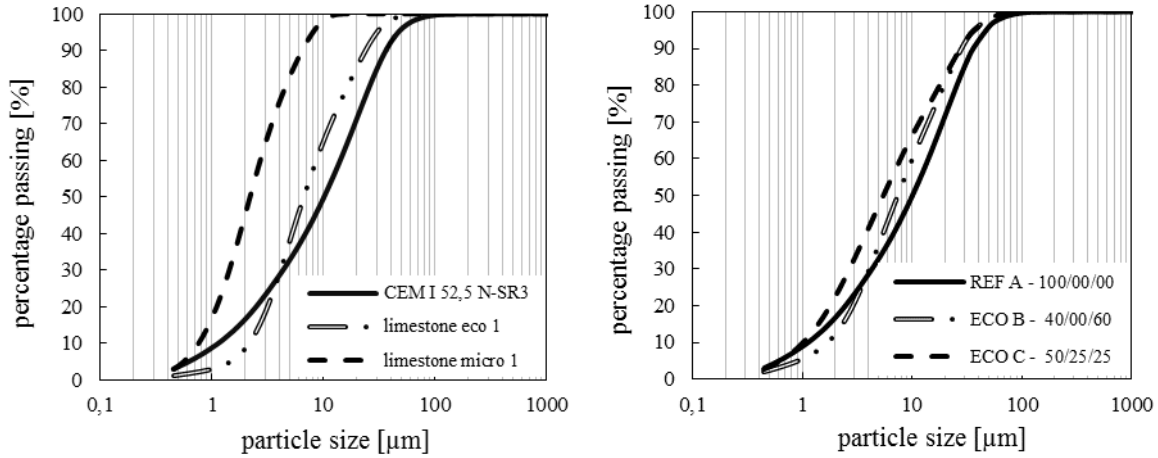

Figure 1: particle size distribution of materials (left) and mixtures (right).

The grain size distribution analysis were performed by laser diffraction (HELOS) and automatically generated with the device software WINDOX 5.6.0.0 from the detected laser diffraction pattern as a result report with average diameter, standard deviation and output. As complex indices of refraction of the different materials, the proposed values from the ISO 13320:2009 were used. The results of the average diameter are shown in Table 1.

Table 1: Properties of investigated materials

	type	true density ρ_0	mean diameter d_{50}	Blaine-value	water demand (at saturation) V_{ws}/V_p	water demand (for flowability f=170 mm) $V_{wf,\,170}/V_p$	GWP	PEI
		g/cm³	µm	cm²/g	-	-	$kgCO_2/t$	MJ/t
OPC 1	CEM I 52,5 N-SR3 PMCP2	3.17	10.5		0.71	1.13	831	4030
LE1	limestone eco 1	2.70	6.9	4032	0.65	0.68	25	717
LM1	limestone micro 1	2.73	2.2	9314	0.61	0.65	36	1006

Additionally, the amount of water to reach a certain workability of a water/powder-mix plays a major role. Table 1 shows properties of source materials covered in this paper. The values for water demand V_{ws}/V_p, which is the volume of water at saturation point and $V_{w,f,i}/V_p$, which is the volume of water for a certain flowability and V_p which is the volume of powder water-powder mixes, were determined by a new method presented by Juhart [5]. This new approach combines the so-called "mixing energy method (MEM)", cp. Marquardt [6] to determine the void content of a powder by its water demand at saturation point with the spread flow test (ST) according to the procedure of Okamura [7] for determining the flowability of pastes, therefore we call it MEM-ST. It can be used for a single material as well as a mix of granular materials. In the first step a certain volume of dry powder (V_p) is introduced into a mixer that is able to record changes in mixing energy input and power consumption Additionally the amount of water added is measured continuously with the help of a flow-meter. In the next step - while mixing with constant speed and continuously adding water - the saturation point of a granular material or mix is determined as the peak of the power consumption. At this point, immediately before saturation, capillary bridges between particles cause a maximum of shear resistance [8]. There the water demand (V_{ws}/V_p) corresponds to a minimum void content resulting in a maximum packing density; the mix appears to be "earth-moist". In the following phase additional water is added stepwise. At each step the spread flow (f,i) is determined on a dry glass plate with a Hägermann cone (according to EN 1015-3 [9] but without any shocks) - and the corresponding water demand ($V_{wf,i}/V_p$) is recorded [5].
For the following tests three different basic mixes were investigated with three different consistencies each. The consistency was adjusted by just modifying the added water (see table 2). While the reference mixes (REF) are based on CEM I cement only the ECO B mixes are modified in a way that 60% of CEM I was replaced by the ECO Filler (LE1), but without using the package density optimisation method. The ECO C mixes are mixture compositions with optimized packing density as described above.

Table 2: Composition and properties of the investigated mixtures.

		REF A1	**ECO B1**	**ECO C1**	**REF A2**	**ECO B2**	**ECO C2**	**REF A3**	**ECO B3**	**ECO C3**
flowability		standard consistency EN 196-3			ø = 190 mm			ø = 275 mm		
Cem I 52.5		100	40	50	100	40	50	100	40	50
$LIME_{ECO}$	[V-%]	0	60	25	0	60	25	0	60	25
$LIME_{MICRO}$		0	0	25	0	0	25	0	0	25
w/c [/]		0.28	0.59	0.38	0.40	0.85	0.42	0.48	1.03	0.43
V_w/V_p		0.90	0.74	0.61	1.27	1.09	0.66	1.53	1.31	0.68
V_w/V_c	[-]	0.90	1.86	1.21	1.27	2.72	1.32	1.53	3.27	1.35
$V_{w,s}/V_p$ (Vicat)		0.9**	0.74**	0.61	-	-	-	-	-	-
$V_{w,s}/V_p$ (MEM-ST)		0.72	0.69	0.61	0.72	0.69	0.61	0.72	0.72	0.61
$f_{cm,1d}$		47.9	19.5	42.8	30	7.7	42.7	19.7	4	37.1
$f_{cm,7d}$	[N/mm²]	91.3	46.1	80.5	57.3	21.9	74.6	37.5	12.7	73.8
$f_{cm,28d}$		107	58.1	100.1	82.9	29.1	84.8	53.2	19.7	
density	[kg/m³]	2114	2023	2111	1949	1916	2136	1860	1841	2110
Vicat initial set	[h]	5:21	3:41	3:03	7:58	6:26	03:28	10:15	09:19	03:54
Vicat final set	[h]	6:52	4:31	4:13	8:58	8:04	04:25	10:55	10:17	05:32

3. Ultrasound experimental setup for simultaneous p- and s-wave measurements

Figure 2 shows the experimental test setup that is used for a combined p- and s-wave measurement. This test setup is similar to that proposed by a RILEM recommendation worked out by RILEM TC 218-SFC [11]. However, besides the usage of a container equipped with p-wave transducers with a center frequency of 500 kHz an additional container with two broadband s-wave transducers with a center frequency of 250 kHz are used. A sensor distance of 50 mm was found to be sufficient for both containers. The sensors are coupled by a thin polyimide film (d=25µm) directly through the mix to allow for best signal transmission. A detailed system description is given in Krüger [12].

One of the most crucial parts is to extract as accurate as possible the onset time (i.e. the arrival time) of the signal in relation to the trigger time. Therefore, onset of the signals has to be discriminated from noise. There are various possibilities to do this since there are threshold and energy based methods and auto-regressive processes [10, 12]. For the following tests a picking algorithm called AIC-Picker is used to detect the p-wave onset time. This picker is based on the Akaike Information Criterion (AIC) [13] and was adapted to ultrasonic signals by Kurz, Grosse and Reinhardt [10].

To determine the onset time of the shear wave, the time signal is transformed into a time-frequency domain by means of a continuous wavelet transform (for details see [14]).

To study the setting and hardening time at very early age in the following a test time of 24 hours was considered with a test interval of 5 minutes. In a post processing procedure the measurements were analysed and further elastic parameters were calculated. If it is assumed that the material to be tested is homogeneous and isotropic the dynamic elastic properties can be calculated from the shear wave velocity v_s, the compressional wave velocity v_p and the materials density ρ_c by using the following equations:

$$\sigma_{dyn} = \frac{\frac{1}{2} \cdot v_p^2 - v_s^2}{v_p^2 - v_s^2} \tag{1}$$

$$E_{dyn} = \frac{(1 + \sigma_{dyn}) \cdot (1 - 2\sigma_{dyn})}{(1 - \sigma_{dyn})} \cdot v_p^2 \cdot \rho_c = (2 + 2\sigma_{dyn}) \cdot v_s^2 \cdot \rho_c \tag{2}$$

$$G_{dyn} = \frac{E_{dyn}}{2 + 2\sigma_{dyn}} = v_s^2 \cdot \rho_c \tag{3}$$

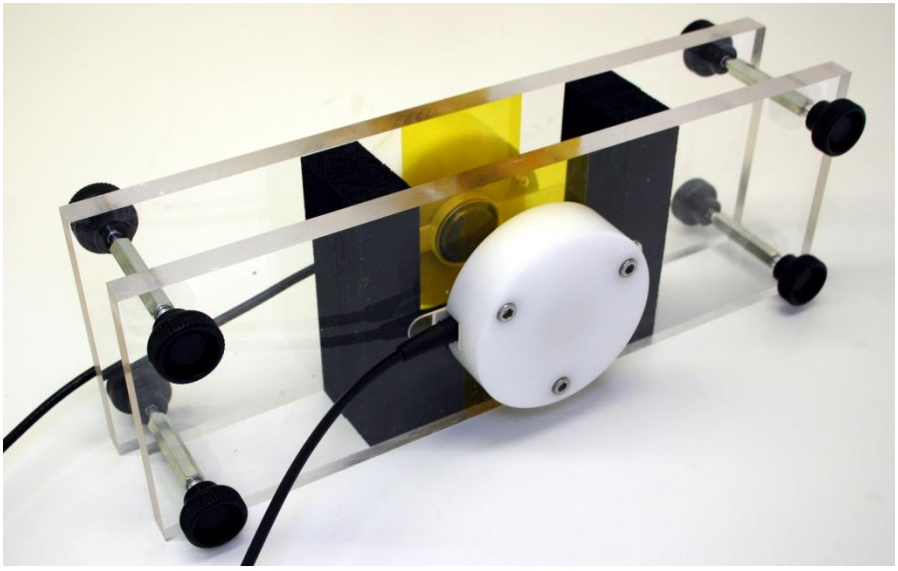

Figure 2. Test container for combined compressional and shear wave testing.

4. Test results and evaluation of the mixes

To study the setting and hardening process at very early age especially investigations were conducted within the first 24 hours of hydration at room temperature 20±2°C and relative humidity of 65%. One of the benefits of ultrasound is that within that time hydration processed can be studied permanently and non-destructive. An example of the change in compressional and shear wave velocity during hydration is given in Figure 3 (left). It can be seen that at very early age in the dormant period of the mix no significant change in wave velocity is obviously measureable and that during further hydration the wave velocities increase from very low velocities up to values of several thousand m/s after one day. From that determined wave

velocities dynamic elastic properties can be calculated like it is described in equations (1) to (3) and plotted in Figure 3 (right).

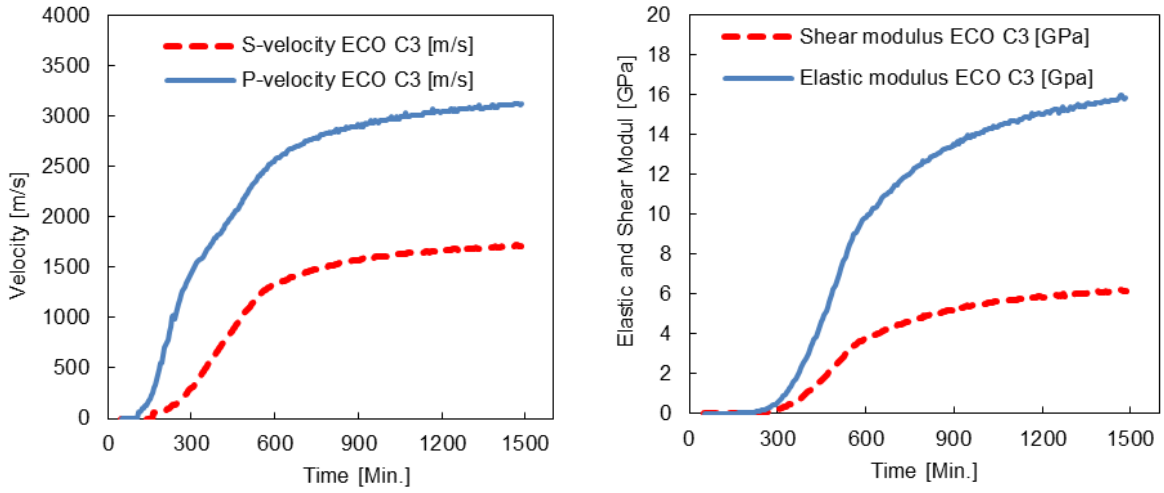

Figure 3. Evolution of compressional and shear velocity (left) and compressional and shear modulus (right) of ECO C3 mix.

One of the main advantages of analysing the dynamic elastic properties instead of the wave velocities only is that it is more feasible to correlate elastic properties with other mechanical values like strength or initial or final setting time according to Vicat, which is a penetration test that is itself strongly correlated with the shear strength and shear modulus. An additional advantage is that the calculated elastic properties also take into account the density of the material so it includes an additional and variable material parameter relevant to mechanical characteristics of the investigated materials.

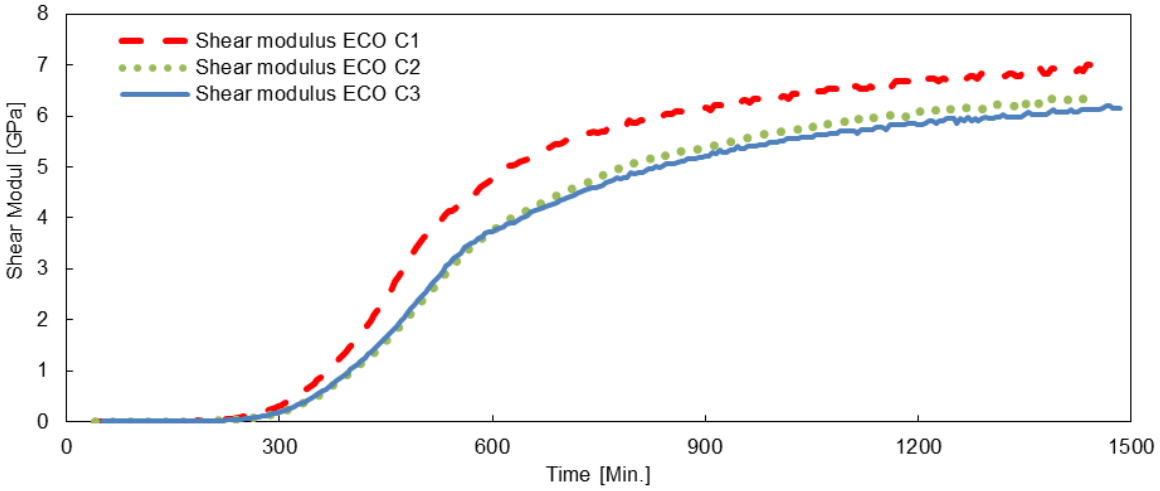

Figure 4. Evolution of compressional and shear modulus of the three ECO C3 mixes

To compare the results of the different tests conducted some values were extracted from the continuous ultrasound measurements, i.e. wave velocities and calculated elastic properties at

the initial and final setting time according to the Vicat needle test for each mix and also values after 24 hours of hydration where also strength was determined (see table 3).

Table 3: Characteristic material properties of the tested mixtures.

		REF A1	**ECO B1**	**ECO C1**	**REF A2**	**ECO B2**	**ECO C2**	**REF A3**	**ECO B3**	**ECO C3**
vp, initial vicat	[m/s]	1177	614	667	1437	1353	1169	1483	1469	1023
vs, initial vicat	[m/s]	156	110	74	254	195	126	292	326	128
vp, final vicat	[m/s]	1519	1017	1291	1545	1516	1625	1520	1513	1579
vs, final vicat	[m/s]	373	207	220	406	335	406	362	383	418
E, initial vicat	[GPa]	0.15	0.07	0.03	0.37	0.22	0.10	0.47	0.58	0.10
G, Initial vicat	[GPa]	0.05	0.02	0.01	0.13	0.07	0.03	0.16	0.20	0.03
E, final vicat	[GPa]	0.86	0.26	0.30	0.94	0.63	1.03	0.72	0.79	1.08
G, final Vicat	[GPa]	0.29	0.09	0.10	0.32	0.22	0.35	0.24	0.27	0.37
vp, 24h	[m/s]	3167	2861	3262	2804	2317	3125	2540	1996	3105
vs, 24h	[m/s]	1750	1522	1820	1487	1163	1721	1294	896	1703
E, 24h	[GPa]	16.58	12.22	17.82	11.24	6.91	16.23	8.26	4.06	15.72
G, 24h	[GPa]	6.48	4.69	6.99	4.31	2.59	6.33	3.12	1.48	6.12

It has to be noted that the Vicat needle test is designed to be conducted with a standard consistency that guarantees a comparable plasticity at the beginning of the test. This means that Vicat setting times obtained from mixes with other consistency than the standard consistency might not be interpreted correctly to represent the initial setting time of the material. Especially if the water/binder ratio is changed and thus the particle density shows variation, the percolation process during hydration is expected to behave different. Finally, an increased capillary porosity can be expected during further hydration if the total water added to the mix is not needed for the hydration of the used binder. As can be seen from table 2 the mixes show different densities – mainly due to i) more or less optimisation of particle size distribution and thus the packing density and ii) adding additional water to vary the consistency – right after mixing and also very different strength after one day of hydration. It is clear that strength is not only dominated by the used binder but also strongly by the density of the matrix (see Fig. 7). The optimization of the packing density by the use of micro fillers is one of the concepts of developing eco-friendly cementitious matrices with reduced cement clinker content like it is presented here. It can be assumed that due to the higher packing density the mean distance between each particle is lower compared to that of mixes with lower packing density, either given by a non-optimized particle size distribution (see mixes REF A and ECO B) or even be adding additional water. This lower mean particle distance has also effect on the strength development dominated by the hydration of the cement. The different reactions during the hydration process are itself complex with its time dependent formation of hydration products, which is also influenced by the available pore space respectively particle distance. It can be assumed that the evolution of the viscoelastic properties of the matrix during hydration will depend on the mean particle distance and that also the viscous and the elastic properties will be altered in the same manner. This might be the reason why the dynamic elastic shear modulus

determined by the ultrasound shear wave velocities do not correlate at a constant value with the initial setting time given by the Vicat test, which is a destructive test providing a value that depends on the viscoelastic properties of the material, i.e. shear modulus and shear strength. Moreover, Fig. 6 (right) shows that higher shear moduli are to be expected at the individual initial setting time according to Vicat needle test if packing density is less. Having that assumptions in mind it is obviously not feasible to obtain an initial setting time just by analysing ultrasound values like the compressional or shear wave velocity without a former calibration on reference mixes (see Fig. 6 (left)). This is especially true for the analysis of the compressional wave velocity only, because this velocity is at early stage strongly influenced by the presence of air within the mix as well as the total water content [1, 15]. However, it is on the other hand not feasible to use the Vicat needle test on every mix composition to get an idea of initial setting because the test is not designed for variable initial consistencies, nor you will get an idea of the full hydration process and the evolution of mechanical material properties.

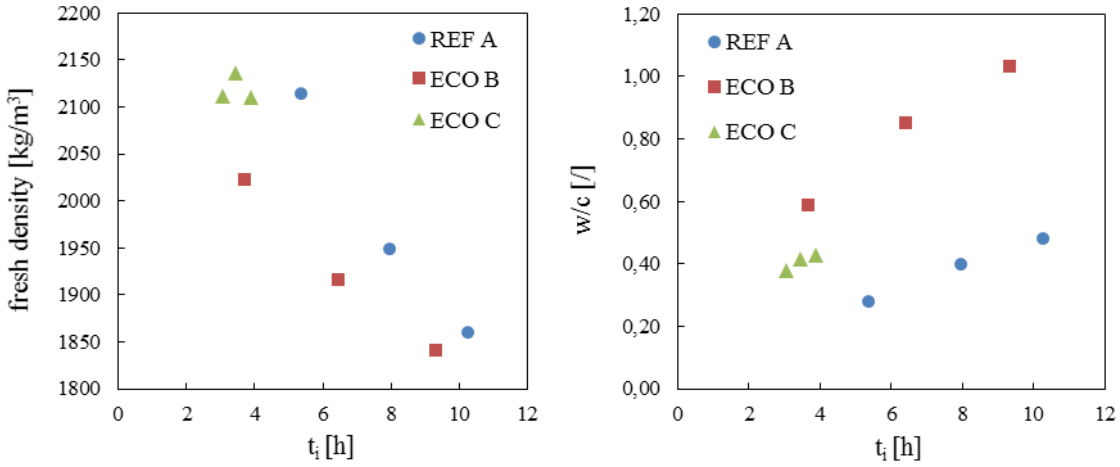

Figure 5. Density at fresh state (left) and water/cement ratio (right) versus setting time according to Vicat needle test.

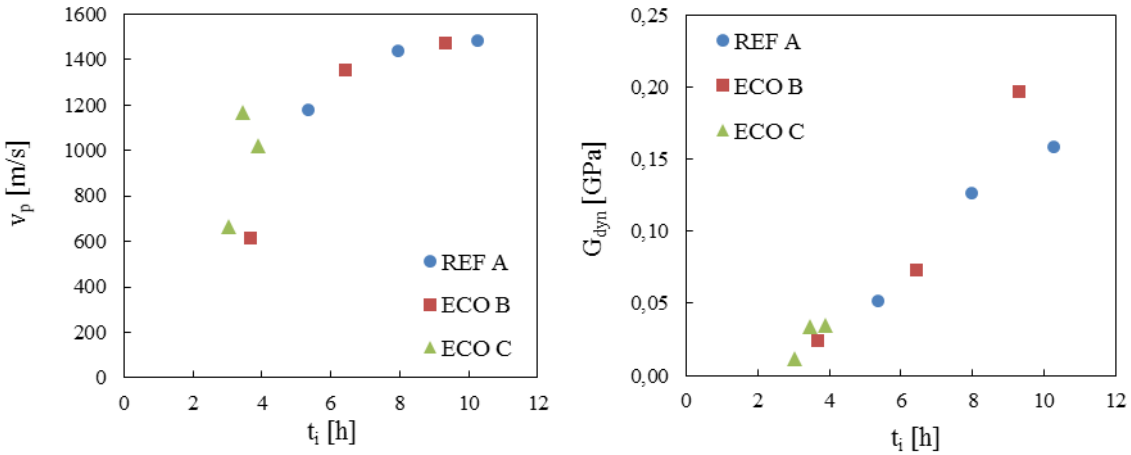

Figure 6. Compressional wave speed versus setting time (left) and shear modulus versus setting time according to Vicat needle test (right).

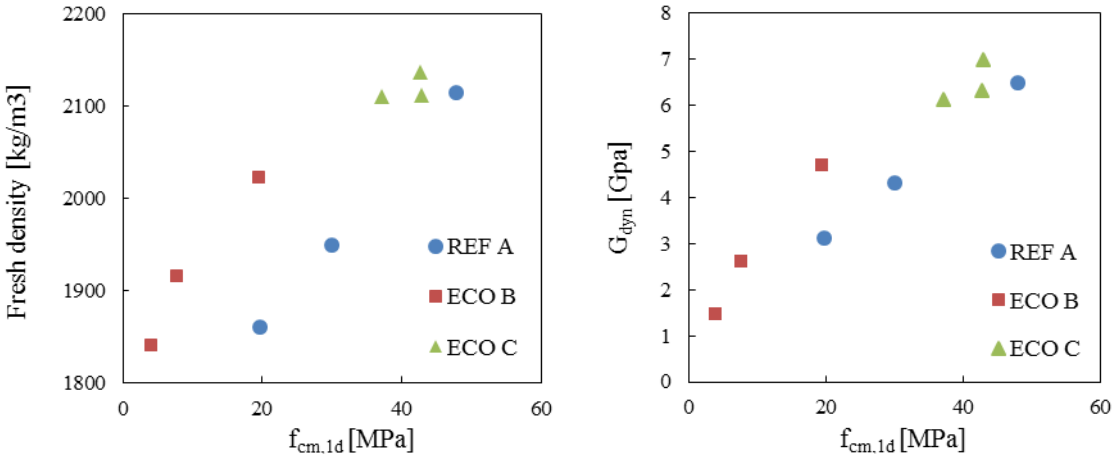

Figure 7. Density at fresh state versus strength (left) and shear modulus versus strength (right); 1 day values.

5. Conclusions

From the test series and the results presented in this paper several conclusions can be drawn:

- Ultrasound measurements are found to be very useful to characterize the setting and hardening behaviour of cement pastes as well as eco-friendly cementitious pastes with reduced cement clinker but optimized packing density.
- However, the use of compressional wave velocities only might result in misleading interpretation of the setting and hardening process especially if it will be correlated with initial and/or final setting times (according to Vicat) without former calibration. This is because the compressional wave speed at early stage is strongly influenced by the presence of air within the mix as well as the total water content resp. density of the mix.
- The dynamic elastic properties (dynamic elastic modulus and dynamic shear modulus) derived from the ultrasound compressional and shear wave velocities show good correlation with the strength development independently from the mixture composition. In addition to that, the dynamic elastic modules show also higher sensitivity on mechanical properties evolution compared to the wave velocities.
- Although Vicat needle test can be conducted with consistencies different from the standard consistency, the interpretation of such mixes with respect to the initial setting time is questionable as Vicat needle penetration is influenced by the total water amount and variable air presence within the mix. For this reason it is assumed that the evolution of shear modulus derived from the ultrasound measurements is a more reliable indicator for initial setting time of any mixture composition.

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