Low-carbon cementitious composite incorporated with biochar and recycled fines suitable for 3D printing applications: hydration, shrinkage and early-age performance

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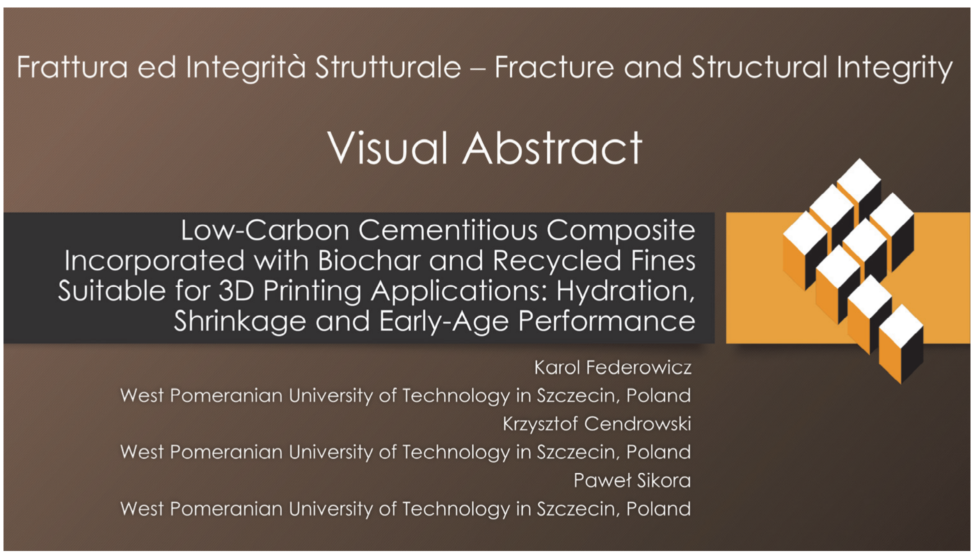

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INTRODUCTION

In recent years, we have observed significant advancements in concrete technology coupled with the automation of production processes. One of the most extensively studied innovations is the integration of 3D printing with cement-based materials. The printing technology is already being utilized on an industrial scale [1]. Known as additive manufacturing, 3D printing technology enables the creation of complex geometric structures without traditional formwork [2]. The application of 3D concrete printing (3DPC) in construction necessitates the adaptation of conventional concrete mixes to meet new technological requirements. Critical parameters include rheological properties, which affect the pumpability and extrudability of the material, setting time (which allows for rapid construction), and the fluidity and consistency of the mix (the material must be sufficiently plastic for pumping while maintaining enough rigidity to hold its shape without formwork) [3,4]. Adapting concrete mixes to the specific demands of 3DPC technology presents a complex and more challenging problem than modifying traditional concrete formulations.

The construction sector is currently focusing not only on the advancement of technology itself but also on reducing its environmental impact. 3D printing mixes are characterized by a high binder and fine particle content, leading to a significant carbon footprint [5]. Despite the reduced material usage, structures produced through additive manufacturing are far from achieving carbon neutrality. To lower the carbon footprint of these materials, the most commonly employed strategies involve substituting portions of the binder or aggregate with waste materials. Research in this area, primarily focused on traditional concretes, has been conducted by Restuccia et al. [6], who employed biochar; Roa et al. [7], who incorporated demolition waste; Khushnood et al. [8], who utilized nanomaterials derived from peanut and hazelnut shells, and Beibei Xiong et al. [9], who used recycled PET aggregate. The impact of mineral additives on concrete properties has been the subject of scientific analysis for many years, but in the context of 3D printing technology, not all established relationships for traditional concretes are confirmed by current research, highlighting the need for further studies and optimization of these solutions [10].

Incorporating biochar as a component in concrete enables the production of low or even zero-emission materials, representing a significant step towards achieving carbon neutrality in construction. This is particularly important given that over 4 billion tons of concrete are produced annually [11], with concrete components producing up to 7% of global CO2 emissions [12]. Current studies suggest that adding 2% by weight of biochar accelerates the cement hydration process due to the internal curing effect [13]. Additionally, Gupta et al. [14] have reported using biochar to reduce the overall shrinkage of the concrete mix. However, with higher biochar content, a significant reduction in mechanical strength is observed, which is attributed to the increased porosity of the material [13].

Another approach to achieving more sustainable concrete involves using construction and demolition waste (CDW) to replace aggregate or cement. Currently, comprehensive studies in this area are lacking. The use of CDW fines in 3D printing has been analyzed by Zhang et al. [15], who demonstrated that incorporating CDW dust can delay the onset of drying shrinkage in 3D printed concrete (3DPC). When using recycled aggregate, it is crucial to consider its high water absorption, which can reach up to 18%, potentially affecting the consistency of the printed mix [16]. De Vlieger et al. [17] found that using recycled fine aggregate (RFA) can enhance buildability and increase yield stress, which are significant advantages of 3D printing technology.

This article compares the effects of two promising methods for reducing the carbon footprint of 3D printing concrete mixes on their properties. The study analyzes the partial replacement of cement with biochar and recycled fines. It examines the impact of both materials on the rheological properties and the hydration process during the early age of the 3D printing mix.

MATERIALS AND METHODS

Mix design

The reference mix designed and tested in this study consisted of Portland cement CEM I 42.5R, fly ash, microsilica, natural fine aggregate, SIKA VC111P superplasticizer, and tap water. The chemical composition and basic parameters of Portland cement CEM I 42.5R, supplied by CEMEX, Rudniki, Poland, are presented in Tab. 1. ImmerBau, Poznań, Poland, supplied fly ash, while the microsilica was provided by Mikrosilika Trade, Stalowa Wola, Poland. Natural aggregate in river sand (sieved to 2 mm) was sourced locally from SKSM S.A. Szczecin, Poland. Biochar (BC), derived from sawmill wood waste and plants, was supplied by Fluid S.A., Poland. The recycled fines (RF) were obtained by crushing, grinding, and sieving waste from C30/37 structural concrete, with both BC and RF being less than 0.125 mm. The specific density of all materials, determined using a helium pycnometer ULTRAPYC1200e, is presented in Tab. 2.

Chemical composition							
	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	Cl
Vol.%	62.5	20.3	5.0	3.3	1.8	3.0	<0.1
Setting time [min]							
Initial				128			
Final				163			
Specific Surface Area (Blaine)				4604 cm^2/g			

Table 1: The cement CEM I 42.5R characteristics [18].

Specific density [g/cm³]						
CEM I 42.5R	Fly ash	Silica Fume	River sand	VC111-P	Biochar	Recycled fines
3.07	2.28	2.22	2.64	1.07	1.44	2.80

Table 2: Specific density of used materials.

Thermogravimetric analysis of the biochar and recycled fines was performed using a TG5500 TA instrument with a heating rate of 10 °C min^{-1}. The materials were analyzed in air and inert atmosphere (nitrogen), with gas flow set at 25 ml/min. The TGA plots are presented in Fig. 1. Plots of the biochar and recycled fines in both atmospheres are presented in Fig. 1a and Fig. 1b, respectively.

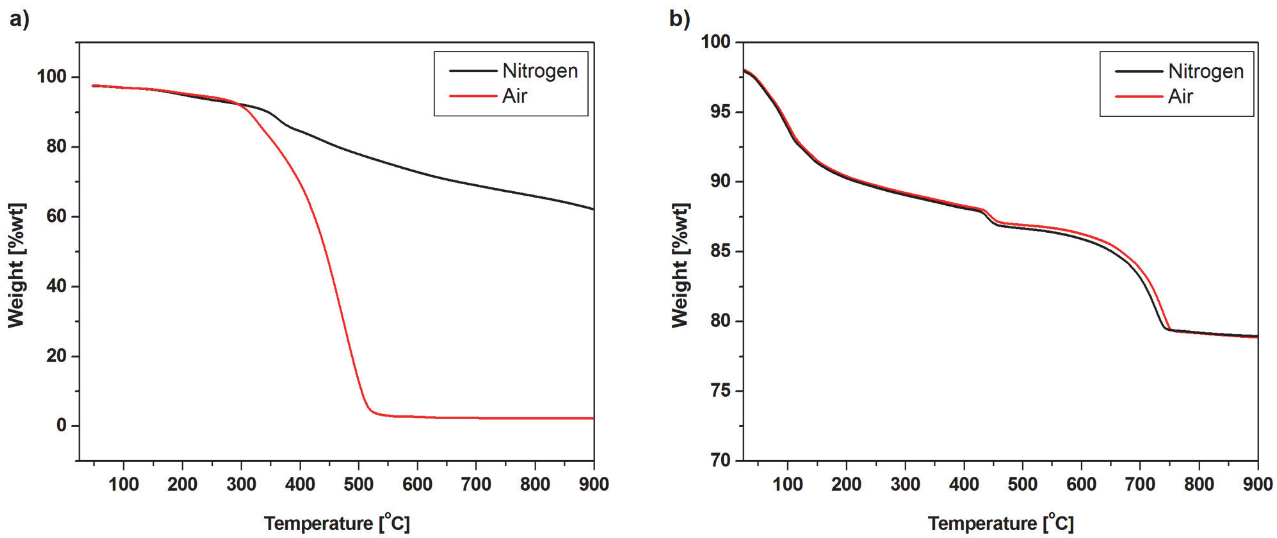

Figure 1: Thermogravimetric analysis of the biochar (a) and recycled fines (b), in air and nitrogen flow.

The TGA plot of biochar (in nitrogen) can be divided into three segments: 25-150 °C, 322-384 °C, and 385-900 °C. The first segment corresponds to water evaporation, around 4 %wt. The second segment clearly shows a decrease in weight – 5 %wt. This segment corresponds to the carbonization of remaining organic residues. The last stage corresponds to the thermal decomposition and carbonization of organic residues. The decrease was measured at 23 %wt. The TGA analysis performed in the air can be divided into two main segments: water evaporation and burning carbon/organic materials. The first stage shows a similar weight decrease to the analysis performed in an inert atmosphere. On the other hand, the second stage starts earlier at 281 °C and ends at 533 °C, during which material loses 89 %wt. After TGA in the air, the combustion residue remains, making up to 3 %wt.

As presented in Fig. 1b, using air or inert gas does not influence the weight of the recycled fines during heating. In the plot, three segments can be distinguished corresponding to the water evaporation (25-150 °C), decomposition of the CSH phase (413-466 °C), and decomposition of calcium carbonate (553-750 °C). During this segment, material lost around 8 %wt, 2 %wt, and 7 %wt, respectively.

The analysis of material weight decrease during temperature changes shows that recycled fines are more stable regarding atmosphere changes. The second conclusion is that biochar can burn entirely after exposure to higher temperatures, leaving additional air bubbles.

Based on the recommendations from the literature [19] and previous studies [5], a reference 3D printed concrete (3DPC), designated as REF, was designed. Subsequently, four mixes with biochar and four with recycled fines were developed, replacing 1.25%, 2.5%, 5%, and 10% of the cement volume, respectively. The mixes were designated BCx and RFx for the biochar and recycling fines mixes, respectively, where x indicated the replacement level. The exact compositions of all mixes are presented in Tab. 3.

	REF [kg/m³]	BC125 [kg/m³]	BC250 [kg/m³]	BC500 [kg/m³]	BC1000 [kg/m³]	RF125 [kg/m³]	RF250 [kg/m³]	RF500 [kg/m³]	RF1000 [kg/m³]
Cement	600.0	592.5	585.0	570.0	540.0	592.5	585.0	570.0	540.0
Fly ash	180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0
Silica Fume	90.0	90.0	90.0	90.0	90.0	90.0	90.0	90.0	90.0
Sand	1225.0	1225.0	1225.0	1225.0	1225.0	1225.0	1225.0	1225.0	1225.0
Water	210.0	210.0	210.0	210.0	210.0	210.0	210.0	210.0	210.0
SP	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6
Biochar	0.0	3.5	7.0	14.1	28.1	-	-	-	-
Recycled fines	-	-	-	-	-	6.9	13.7	27.4	54.8

Table 3: Mixture design.

Since the designed mixes differed only in the binder composition—replacing cement with biochar or recycling dust—the water, aggregate, and superplasticizer amounts remained fixed. The quantities of fly ash and silica fume were also constant, allowing for a precise investigation of the additives' impact on the printed concrete's hydration process, rheology, and early properties. The reference mix contained 870 kg of binder per 1 m³, with a water-to-cement ratio (w/c) of 0.35 and a water-to-binder ratio (w/b) of 0.24. The water-to-binder ratio remained unchanged across all tested mixes, while the w/c ratio varied between 0.35 and 0.39, which falls within the range recommended in the literature for 3D-printed concrete.

Rheology

A preliminary rheological test used to assess the suitability of a mixture for 3D printing is the determination of the spread flow diameter following EN 1015-3. Based on literature recommendations [20] and authors' previous works [5,21], it can be assumed that the spread flow should be 130mm to 180mm. The mixture exhibits higher green strength with lower spread flow values, but its pumpability and extrudability parameters deteriorate. Conversely, with higher spread flow values, the situation is reversed, and each printing setup (printer and pump) requires individual adjustment of these parameters. The presented studies tested the spread flow 15 minutes after adding water to the binder.

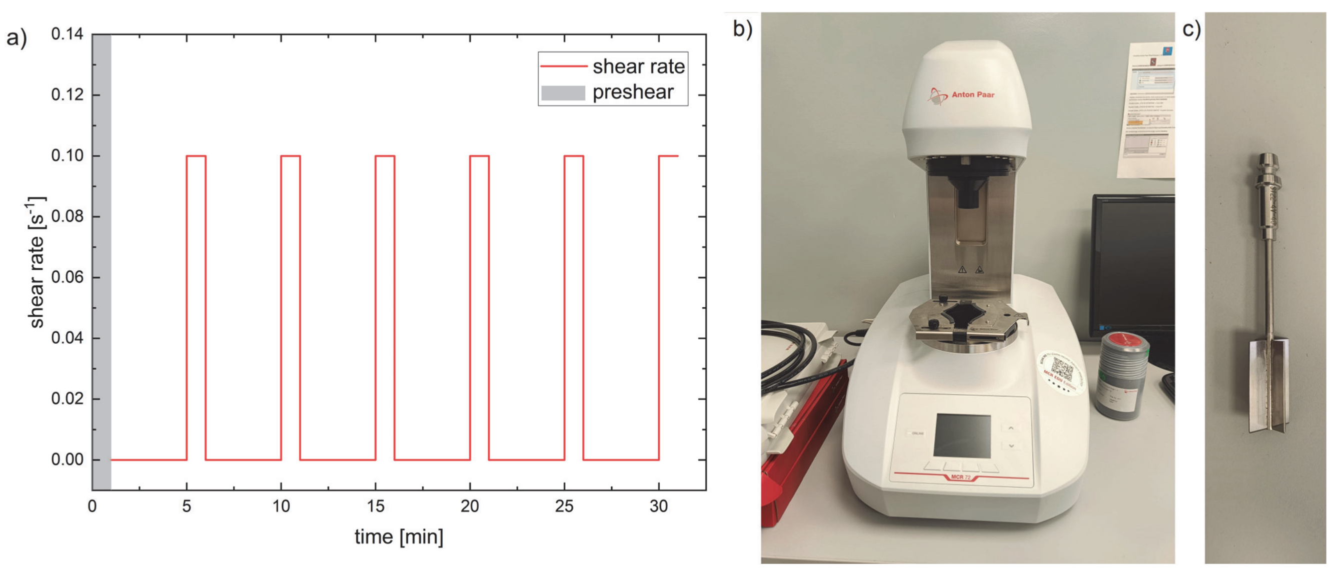

Figure 2: Measurement of static yield stress of 3DPC mixture: (a) graphical protocol of test, (b) rheometer Anton Paar MCR72, (c) vane geometry used.

After initially qualifying the mixtures as suitable for 3D printing, the static yield stress (SYS) measurement was conducted using an Anton Paar MCR72 rheometer with a vane-type measuring spindle and a specially designed measurement cell that eliminates the "wall slip" phenomenon. The test was initiated immediately after the mixing process was completed, with the first measurement taken 5 minutes after the start of the test. The test was performed at fixed time intervals. A constant shear rate of 0.1 s^{-1} was applied during the tests. The testing procedure and the measuring spindle are presented in Fig. 2 and can be found also in [21].

Isothermal calorimetry

Isothermal calorimetry was used to study the hydration process. In this method, samples weighing approximately 12.4 grams in plastic vials were placed in a measurement chamber equipped with heat flow sensors to measure the heat released. An inert reference sample with the same heat capacity was prepared to minimize measurement inaccuracies. The difference in heat flow measurement between the test and the reference samples represents the heat released during the hydration process. The studies utilized an 8-channel TAM Air isothermal calorimeter from TA Instruments. Before each measurement, the calorimeter was calibrated according to the manufacturer's recommendations, using the same type of plastic vials filled with sand. Calibration lasted up to 7 days. The baseline measurement was performed at least 24 hours before the test until signal stabilization was achieved. The experiments were conducted at a temperature of 20±0.2 °C.
The test samples were placed in the calorimeter immediately after mixing and recording the exact actual mass with an accuracy of 0.001 g. Due to the sample volume and the manufacturer's recommendations, the tests were conducted on pastes rather than 3D printed concrete mixture. The binder phase was solely evaluated since the water and aggregate content were constant across all mixtures. The measurements were conducted for a minimum of 7 days.

Total shrinkage deformation

The impact of biochar and recycled fine additives on the development of total shrinkage during the first 24 hours was studied for all mixtures. Previous studies [22] have shown that this period is crucial for developing deformations in 3D-printed concrete due to increased water evaporation and the absence of traditional formwork. Shrinkage testing was conducted using the Shrinkage-Cone apparatus produced by Schleibinger, Germany. The concept of the test and the measurement setup are illustrated in Fig. 3.

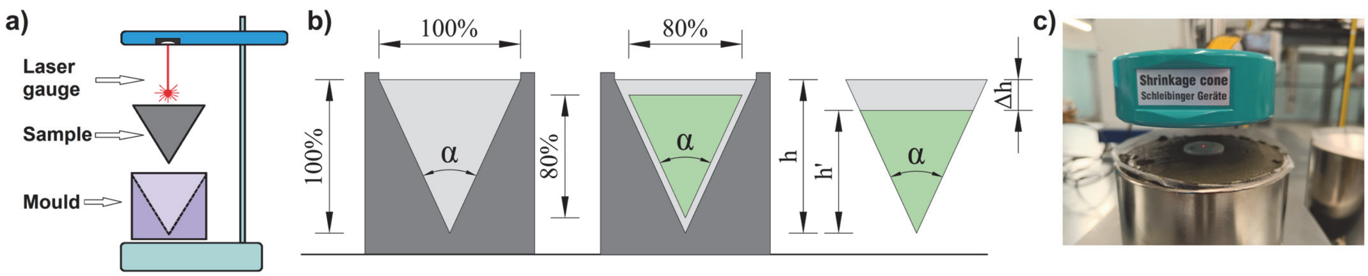

Figure 3: Total shrinkage measuring device: setup configuration (a), geometry of sample (b) and sample during test (c).

A steel mold lined with friction-reducing foil was filled with the mixture, compacted, and a flat reflective measurement point was placed on the upper surface. The change in the distance to the reference point was measured with an accuracy of 2 μm at 5-minute intervals. Due to the sample's appropriate geometry, the cone's measured height change corresponds to the volume change. It is important to note that the shrinkage determined this way does not represent the actual deformation of the printed element due to the different surface-to-volume ratios of the sample. However, it allows for comparing the binder composition's effect on total shrinkage.

Early-Age performance

A critical mechanical parameter for 3D printable concrete mixtures is the material's ability to bear loads (primarily the self-weight of successive printed layers) in a plastic state. This parameter is referred to as buildability or green strength. This study determined green strength using cylindrical samples with a height-to-diameter ratio of 2 (diameter d=60mm, height h=120mm). Green strength was assessed through a uniaxial unconfined compression test (UUCT), also known as a squeezing test.
A specially designed testing set-up was used, as illustrated in Fig. 4a. The setup included a force gauge with a reading range of up to 500N, two inductive displacement sensors with a gauge length of 200mm, and a QuantumX strain gauge bridge that recorded measurements at a frequency of 5Hz. During the test, a constant displacement rate of 0.25mm/s was applied. Samples were tested 30 and 60 minutes after the initial water contact with the binder. Until the time of testing, the samples were stored in plastic molds.

Additionally, the early development of the dynamic modulus of elasticity was studied using ultrasound testing with a Vikasonic device produced by Schleibinger, Germany. The test sample was shaped like a truncated cone with diameters of 70mm and 80mm and a height of 40mm. Measurement probes with a frequency of 54kHz were used, with a transmitter excitation voltage of 1500V, and measurements were taken every 60 seconds.
The study was supplemented by determining the compressive strength at one day, three days, and seven days. These tests were conducted based on the EN 1015-11 standard using cubical samples with dimensions of 40×40×40mm. For the first 24 hours, the samples were stored in sealed molds and then stored in water at a temperature of 20±2 °C until testing.

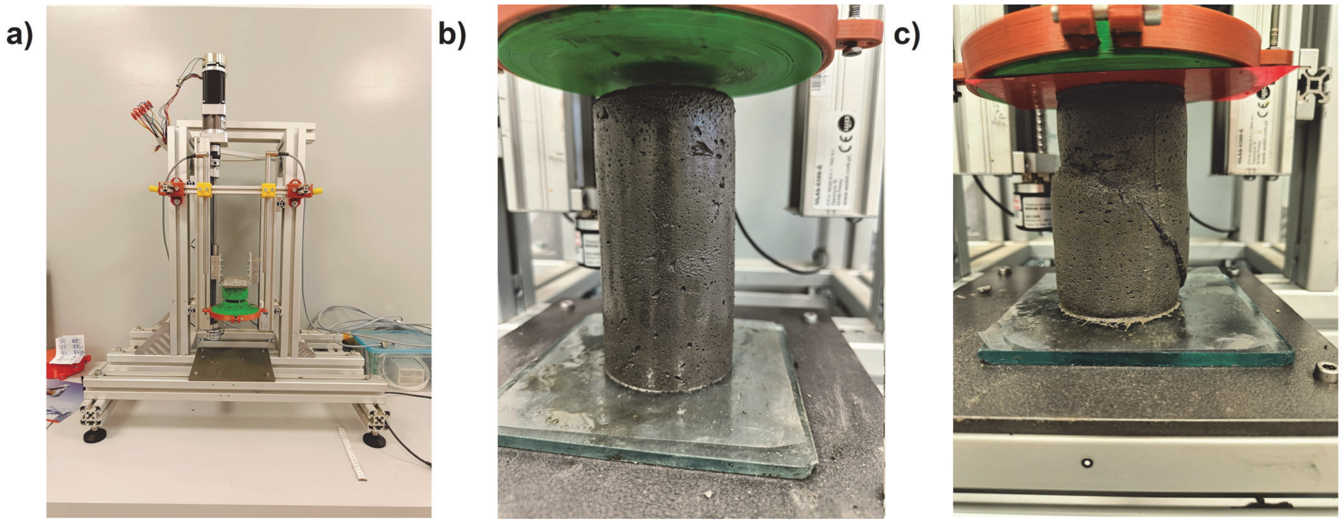

Figure 4: Squeezing test: a) set-up, b) sample before testing c) sample during after testing.

Microstructure

Open porosity and water absorption tests were conducted to assess changes in the microstructure of the cement matrix. For this purpose, three cubic samples with dimensions of 40x40x40mm were prepared for each mixture. After 24 hours of curing in molds, the samples were immersed in water at a temperature of 20±2 °C and stored until the 28th day of curing. Subsequently, using a hydrostatic balance, the saturated samples were weighed in air and under water, allowing for the determination of the sample cement matrix volume. The samples were then placed in an oven and dried for at least seven days until a constant mass was achieved. The mass of the dry sample was then recorded. Open porosity was calculated using Eqn. 1, and the water absorption of the samples was calculated using Eqn. 2.

$$OP = \frac{m_{wet} - m_{dry}}{V} \quad (1)$$

$$WA = \frac{m_{wet} - m_{dry}}{m_{dry}} \quad (2)$$

where:
OP – open porosity [%],
WA – water absorption [%],
m_{wet} – mass of saturated sample,
m_{dry} – mass of dried sample,
$V = \frac{m_{wet} - m_{dry}}{\rho}$ – volume of sample [cm³],
ρ – water density equals $1\frac{g}{cm^3}$.

Additionally, all mixtures were analyzed using optical microscopy. This analysis focused on the distribution of biochar within the cement matrix and changes in pore structure across the sample cross-section. The biochar and recycled fines images were taken using a Delta Optical microscope (Delta Optical, SZ-430B, Mississauga, ON, Canada) equipped with a 20 MP camera (DLT-Cam PRO).

RESULTS

Rheology

Fig. 5 presents the combined mean results (two perpendicular measurements for each mix) for all nine tested mixtures. The reference mixture exhibited an average spread flow of 155mm at 15 minutes after adding water. This mean value is often accepted as a reference level in the available literature [21]. When the cement was replaced with recycled fines, no significant differences were observed in the consistency and fluidity of the mixture, with the spread flow ranging from 154mm to 158mm, depending on the replacement level. This could be attributed to recycled fines' relatively low water absorption (<0.125 mm) compared to cement particles.

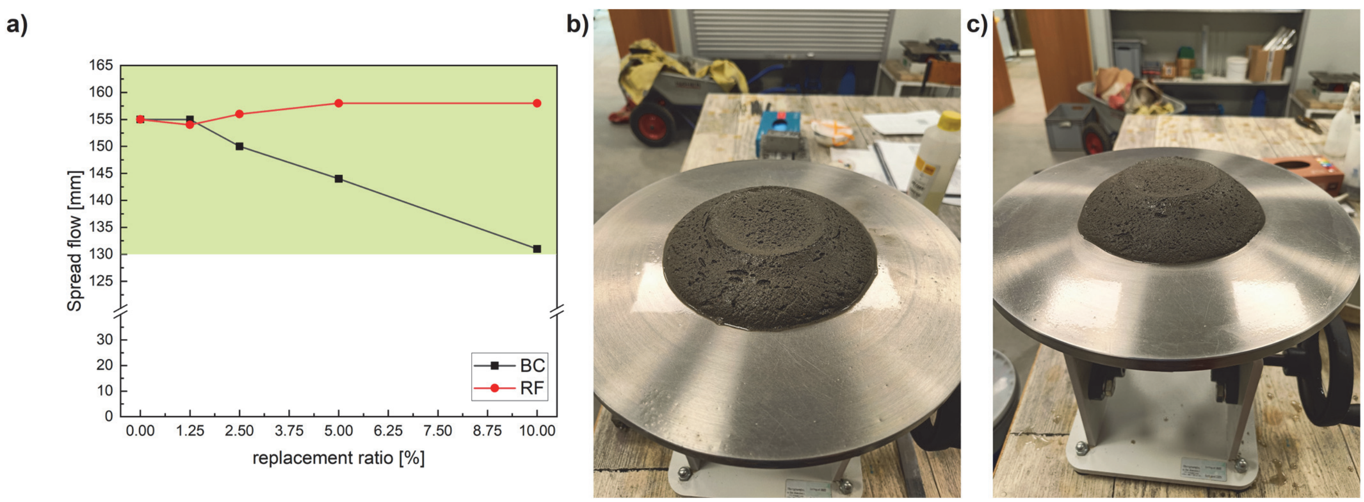

Figure 5: Spread flow of: a) all tested mixtures, b) REF, c) BC1000.

In the case of biochar, its high water absorption and impact on early rheological properties were visible. Replacing cement with biochar at a 1.25 vol.% did not affect the results noticeably. However, a rapid deterioration in the mixture's consistency was observed with further increases in the replacement ratio. BC1000 mixture exhibited a 15% lower spread flow (131 mm) when compared to REF, which is essentially at the limit of the material's suitability for 3D printing using a screw extruder or a rotor-stator pump.

More detailed information on the impact of biochar and recycled fines was obtained from SYS testing using a rotational rheometer. For the reference mixture, a near-linear development of SYS can be observed during the first 15 minutes of testing, followed by a continued but less intense increase in mixture stiffness, reaching shear stress levels of 543 Pa after 35 minutes of testing.

With the gradual replacement of cement with recycled fines, maximum shear stresses can be reduced, reaching as low as 339 Pa for RF1000. Notably, some measurements are very similar for the analyzed mixtures; however, the overall trend is clearly visible and is presented in Fig. 6a.

The situation is reversed in the case of mixtures with the addition of biochar. Increasing the biochar content leads to a rapid increase in shear stresses within the mixture, resulting in a rise in SYS. At replacement levels up to 5%, a stress increase can be observed from 458 Pa for the reference mixture after 15 minutes to 779 Pa for BC125 and 888 Pa for BC500. For BC1000, shear stresses reached 1313 Pa after 15 minutes of testing. After 25 minutes, the mixture with 10% biochar content became too stiff to continue testing, leading to material shearing in the measurement cell and a wall slip effect, which is why a stress drop is visible in Fig. 6b.

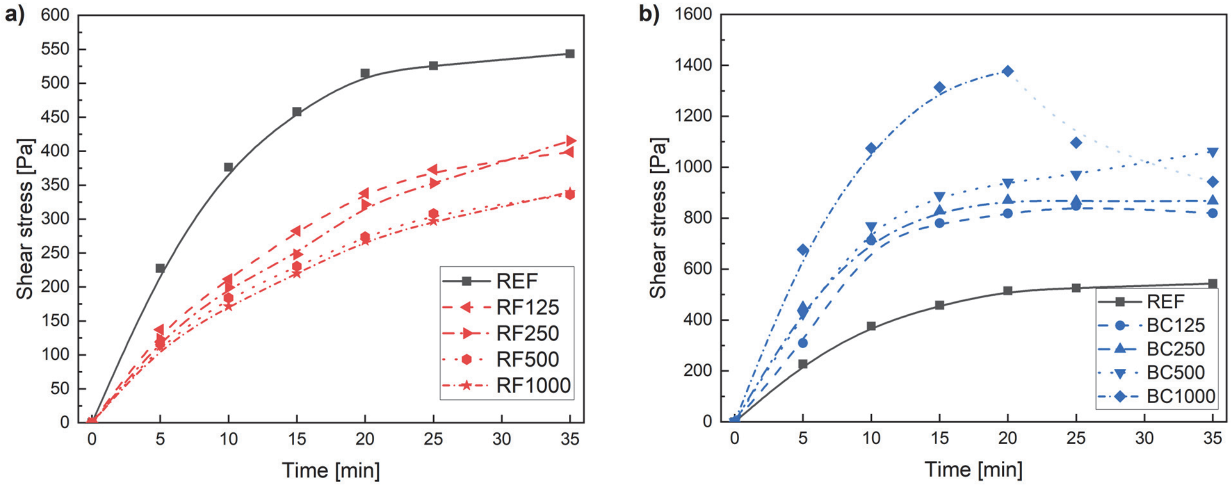

Figure 6: Static yield stress results for: a) recycled fines, b)biochar.

Isothermal calorimetry

Fig. 7 shows the normalized heat flow for mixtures with the addition of recycled fines and biochar due to isothermal calorimetry testing for the first 72 hours at 20°C. It is worth highlighting that the hydration process is delayed because only the binder phase was evaluated with superplasticizer dosage equivalent to the entire mix (with aggregate). However, noticeable trends between specimens can be distinguished. After an initial stabilization period, the heat release rate during hydration started to increase from 4 hours, reaching a maximum value after approximately 16 hours of testing. For recycled fines, no significant shift (acceleration or delay) in the occurrence of the normalized heat flow peaks during hydration was observed. At low cement replacement levels up to 2.5 vol.%, a slight increase in the maximum heat flow can be observed, which is also reported by other studies [23,24]. It is stated in the literature that at small replacement ratios, inert fillers can enhance cement hydration in the first hours due to the increased availability of water, especially in low w/c mixes. Increasing the RF content above 5 vol.% noticeably reduces the heat released, as the previously mentioned additional water effect increases the effective w/c ratio.

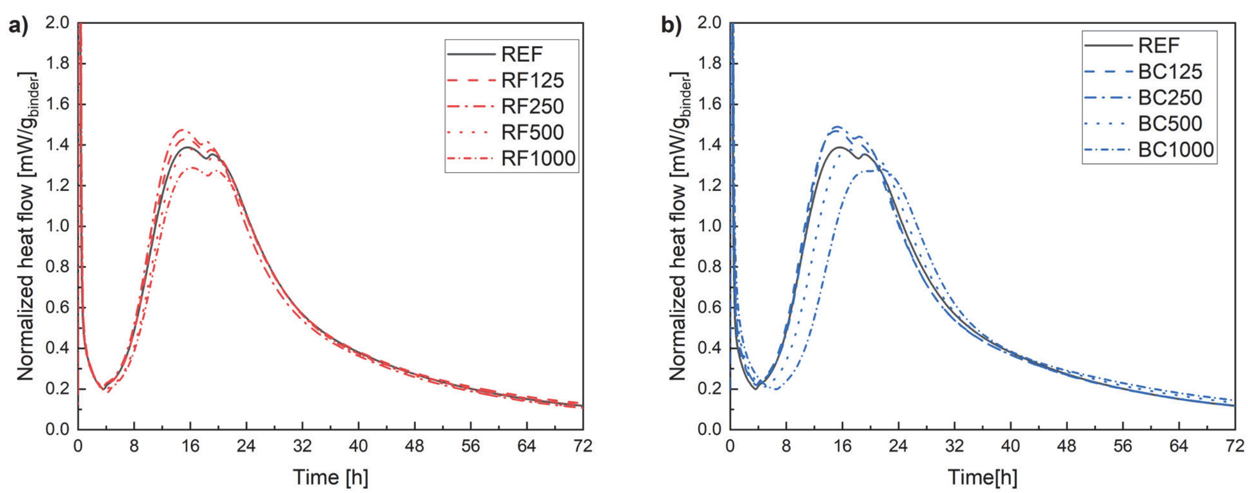

Figure 7: Normalized heat flow for paste with: a) recycled fines, b) biochar.

A similar trend can be observed for mixtures with biochar. Low cement replacement levels allow for an increase in the amount of heat released without noticeable hydration delay. A similar conclusion can be found in the literature [23,24]. Further replacing cement with biochar reduces the amount of heat released during hydration and significantly delays it, as clearly observed for mixtures BC500 and BC1000.

Total shrinkage deformation

Fig. 8 presents the total shrinkage measurements for mixtures with recycled fines (RF) and biochar (BC) during the first 12 hours. Although measurements were taken over 24 hours, readings stabilized after 12 hours. Thus, the presented data range was adjusted to improve the clarity of the observed changes. Analyzing the shrinkage behavior of the reference mixture, an initial phase of rapid deformation can be identified, mainly due to free water transport from the mixture to the surrounding environment. A change followed in the deformation rate due to the reduced amount of available water and ongoing hydration processes. After 6 hours of measurements, deformation stabilization occurred, resulting from the initial setting of the cement matrix, which, due to its high binder content, was very dense and rigid, minimizing volumetric changes in the sample under conditions of limited drying.

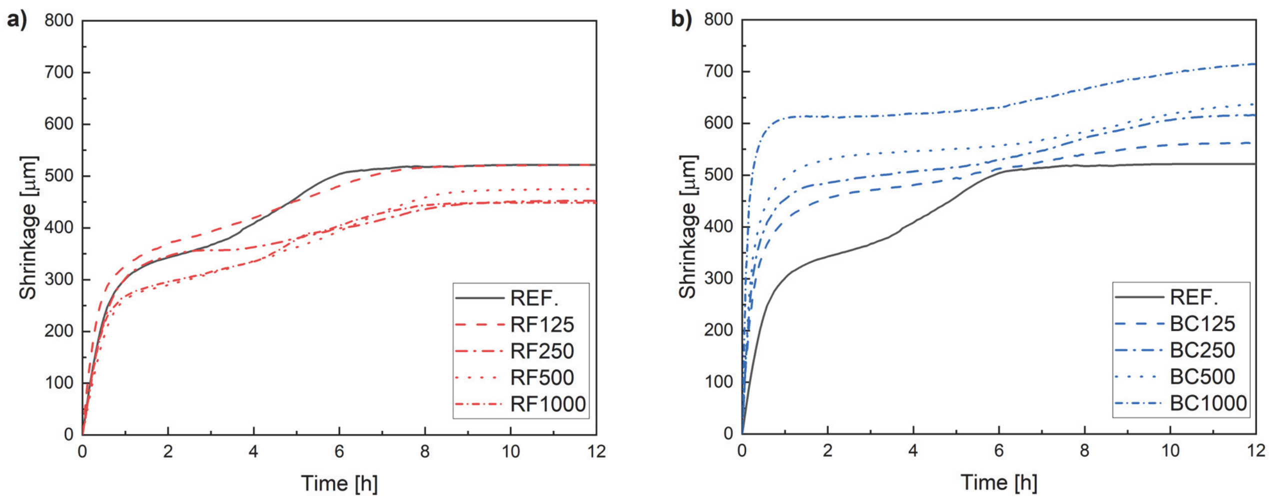

Figure 8: Total shrinkage in first 24h of curing: a) recycled fines, b) biochar.

Replacing cement with RF at 1.25 vol.% neutrally impacted shrinkage development. A slight extension of the deformation period after 6 hours of testing can be observed, which does not significantly affect the total measurement after 12 hours. Increasing the amount of non-reactive RF in the mixture reduces total shrinkage and extends the period of deformation increase. Slower deformation rates reduce the risk of cracking at an early age.

Using BC as a cement replacement negatively affects the total shrinkage of the mixture. BC, as a material with high water absorption capacity, increases shrinkage, especially in the early stages, by absorbing moisture from the mixture. This effect becomes more pronounced with higher replacement levels. The rapid drying of the mix within the first hour, increasing its stiffness, results in a milder deformation progression compared to the reference mixture. For the BC1000 mixture, stabilization of deformations can be observed between 1 hour and 6 hours, which may be related to the biochar's release of previously absorbed water.

Early-Age performance

Fig. 9 presents the results of green strength measurements 30 and 60 minutes after water addition for mixtures containing recycled fines. Due to the lack of standardized procedures for testing and analyzing green strength, a strain level of ε=0.05 was adopted for samples tested after 30 minutes and ε=0.07 for samples tested after 60 minutes, based on previous studies [5,21]. Within these adopted strain ranges, the stress-strain relationship for all tested mixtures exhibited a linear character.

In the case of mixtures containing recycled fines (RF) at 30 minutes, it was observed that replacing cement increased the self-settlement of the samples due to their weight. The reference mixture (REF) showed virtually no initial deformations. For mixtures with a low RF content, in addition to increased initial settlements, the compressive stresses at a strain of ε=0.05 were observed compared to REF. This increase in the load-bearing capacity of the fresh mixture is confirmed by calorimetric studies, where the RF125 and RF250 mixtures also released more heat during hydration. Additionally, the increase in load-bearing capacity may also result from the change in the contact surface due to the initial deformations of the test sample. Further increasing the RF content at the expense of cement led to a decrease in green strength, which for the RF1000 mixture meant initial deformations at a level of ε=0.03 and a reduction in strength from 3.40 kPa to 2.30 kPa.

No initial deformations were observed for samples maturing for 60 minutes before testing. Interestingly, all mixtures with RF showed higher green strength than the reference mixture at both ε=0.05 and ε=0.07 strains. The increase in the effectively available mixing water in the initial hydration period may have caused the RF125, RF250, and RF500 mixtures to increase plastic state strength significantly. Although the RF100 mixture had a higher load-bearing capacity than REF, it significantly lagged behind the other RF mixtures.

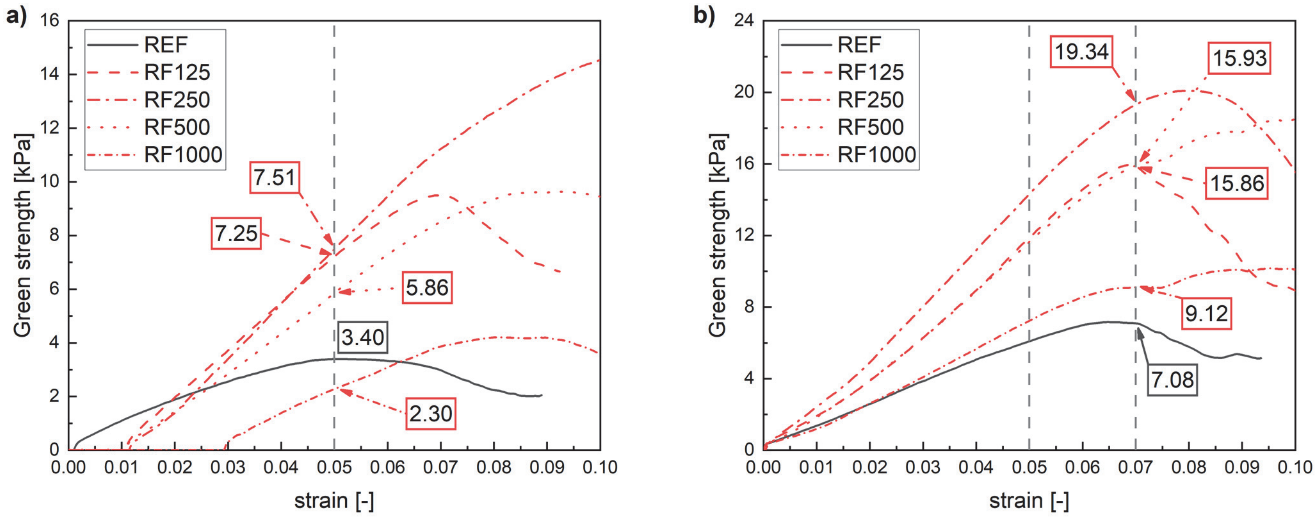

Figure 9: Green strength results of RF mixes after: a) 30 min, b) 60 min.

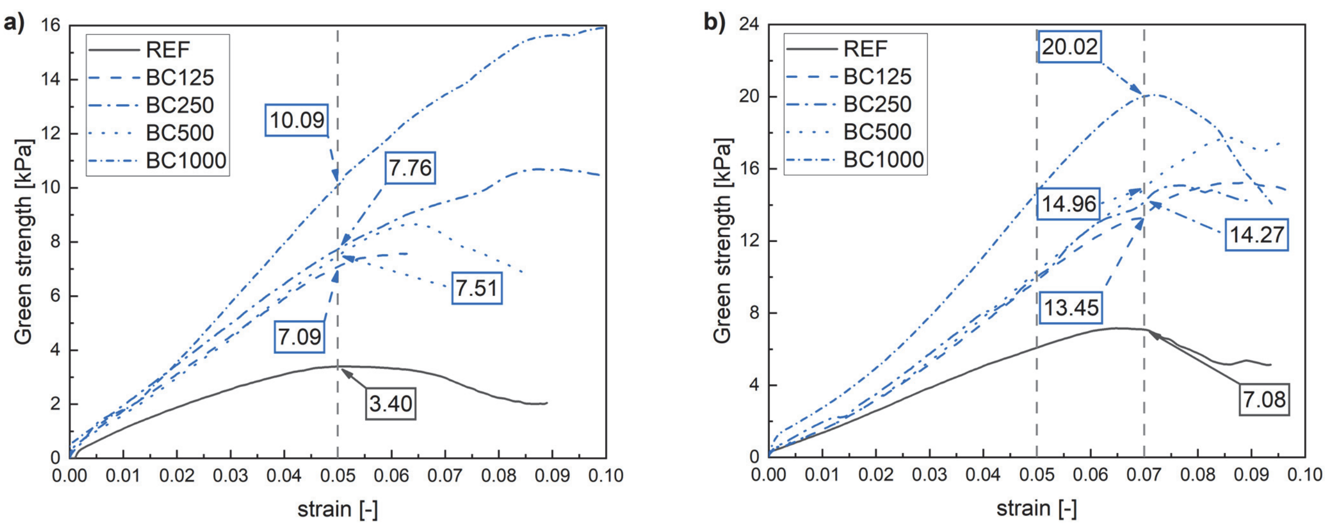

Figure 10: Green strength results of BC mixes after: a) 30 min, b) 60 min.

Fig. 10 presents similar results for mixtures with biochar. Unlike with recycled fines, adding biochar did not increase initial deformations at 30 or 60 minutes into the testing. In the first testing interval, a noticeable increase in compressive strength was observed. The BC125, BC250, and BC500 mixtures exhibited similar results, which were more than twice as high as the REF mixture. The best results were achieved with a 10 vol.% replacement of cement. The increase in plastic state strength can be attributed to the rapid drying of the mixture due to the absorption of water by the biochar. After 60 minutes, the same trends were observed, with mixtures containing biochar having green strength 90% to even 185% higher than the reference mixture.

Fig. 11 presents the results of the dynamic modulus of elasticity (DME) development measurements for mixtures with recycled fines (RF) during the first 24 hours of curing. Partial cement replacement with recycled fines did not affect the overall trend of modulus development. The final DME results for the RF125 and RF250 mixtures were 30.3 GPa and 29.0 GPa, respectively, representing an increase of 7% and 12% compared to the reference mixture, which reached 27.1 GPa after 24 hours of curing. The increase in the stiffness of the cement matrix is supported by calorimetric studies, which also confirmed higher activity in mixtures with up to 2.5 vol.% recycled fines.

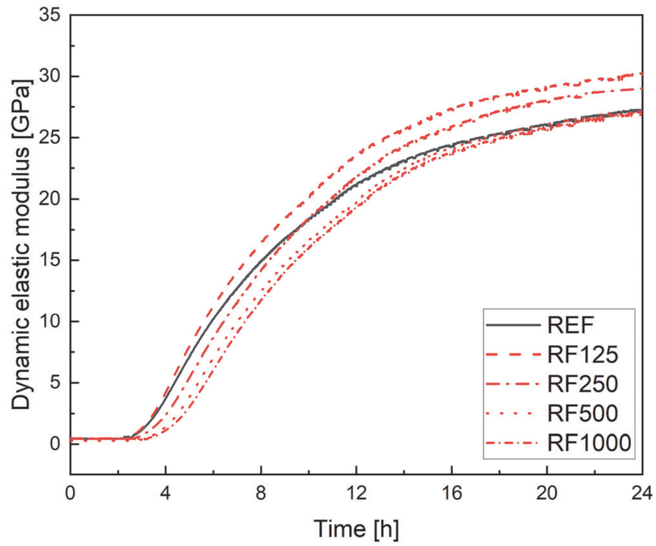

Figure 11: Dynamic modulus of elasticity development of mixtures with recycled fines.

For the RF500 and RF1000 mixtures, a delay in stiffness development was observed in the initial hours, which was ultimately mitigated after 20 hours of curing. These mixtures eventually achieved a DME of 26.8 GPa and 27.1 GPa, respectively.

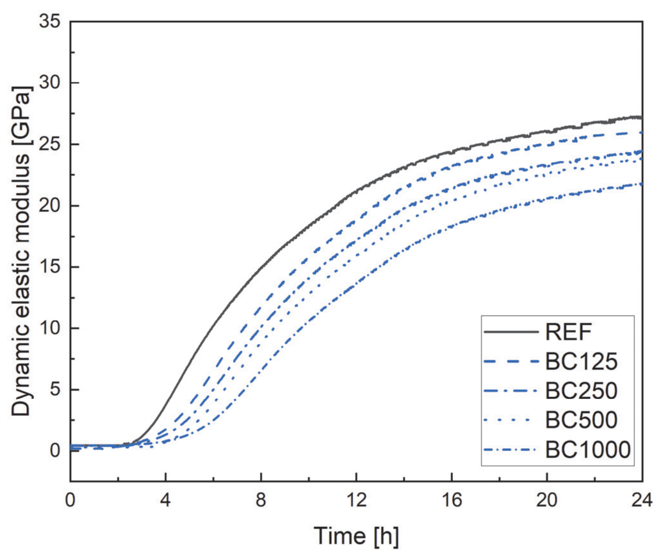

Figure 12: Dynamic modulus of elasticity development of mixtures with biochar.

Fig. 12 presents analogous results for mixtures with biochar additives. Interestingly, all modified mixtures with biochar exhibited a delayed increase in the dynamic modulus of elasticity (DME) over time. The delay was more pronounced with higher levels of cement replacement by biochar. The mixtures with biochar achieved DME values of 26.0 GPa, 24.5 GPa, 23.9 GPa, and 21.8 GPa, respectively. The mixture with 10 vol.% biochar represented a reduction in DME of nearly 20%, which contrasts sharply with the increase in green strength for this mixture.
The explanation for this can be found in the drying effect of the mixture, where biochar absorbs water. This absorption increased the strength in the initial minutes of setting but ultimately reduced the degree and rate of hydration due to the limited amount of free water.

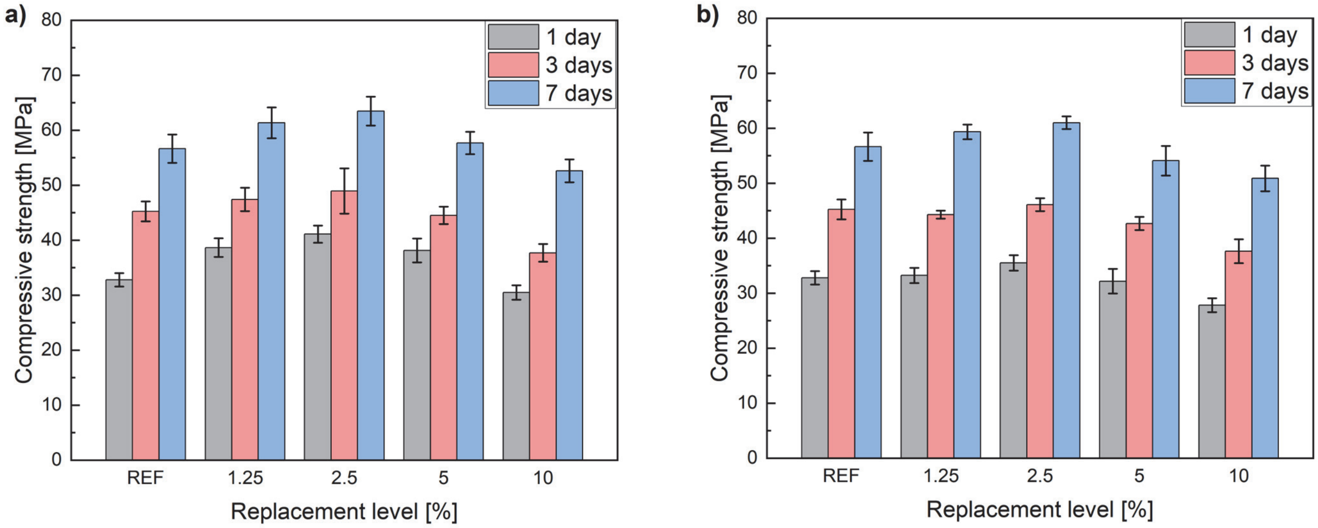

Figure 13: Compressive strength results of: a) recycled fines mixtures, b) biochar mixtures.

Fig. 13 presents the mean compressive strength results (3 specimens for each test) of the mortars. The data are also presented in Tab. 4, along with the standard deviation and coefficient of variation. The compressive strength results correlate with the calorimetric studies. At low levels of cement replacement with recycled fines, an increase in performance was observed in all test periods. Beyond a critical level, further cement replacement with RF led to a deterioration in strength. Replacing 1.25 vol.% and 2.5 vol.% accelerated the strength gain, especially within the first 24 hours, with the differences being significantly smaller after seven days.
In the case of using biochar, the effect of cement replacement was less pronounced, especially in the first 24 hours, where no significant differences were observed. The most considerable decrease in compressive strength was noted for the BC1000 mixture, which was 15%. In later periods, the differences were even more minor, although BC125 and BC250 showed a slight increase in strength compared to the REF. After seven days, BC250 gained just under 8%, while BC1000 lost 10% of compressive strength.

	1 day			3 days			7 days		
	f_{cm} [MPa]	StD [MPa]	CoV [%]	f_{cm} [MPa]	StD [MPa]	CoV [%]	f_{cm} [MPa]	StD [MPa]	CoV [%]
Ref.	31.81	1.22	3.7	45.25	1.80	4.0	56.65	2.59	4.6
RF125	38.64	1.69	4.4	47.40	2.13	4.5	61.35	2.80	4.6
RF250	41.10	1.55	3.8	48.95	4.13	8.4	63.47	2.63	4.1
RF500	38.12	2.17	5.7	44.52	1.59	3.6	57.68	2.04	3.5
RF1000	30.49	1.31	4.3	37.70	1.12	3.0	52.61	2.09	4.0
BC125	33.24	1.38	4.2	44.29	0.73	1.7	59.33	1.35	2.3
BC250	35.53	1.41	4.0	46.11	1.17	2.5	60.99	1.15	1.9
BC500	32.17	2.24	7.0	42.67	1.20	2.8	54.10	2.69	5.0
BC1000	27.82	1.27	4.6	37.63	2.17	5.8	50.88	2.33	4.6

Table 4: Mean compressive strength with standard deviation and coefficient of variation.

Microstructure

Microscopic images of 3D-printed concrete samples and pristine aggregates are presented in Fig. 14. In the reference 3D printed concrete samples (images a and d), empty cavities formed by the air bubbles or from the loose aggregate can be noticed. Similar cavities were seen in the 3D-printed concrete supplemented with recycled fine aggregates. Compared to the reference sample, the amount of cavities in recycled fine slightly increased. The image of recycled fine aggregates is presented in Fig. 14c. Since recycled fine aggregates have a size below 125 mm and a color similar to river sand used in samples, it is difficult to identify recycled aggregates in the 3D-printed concrete.

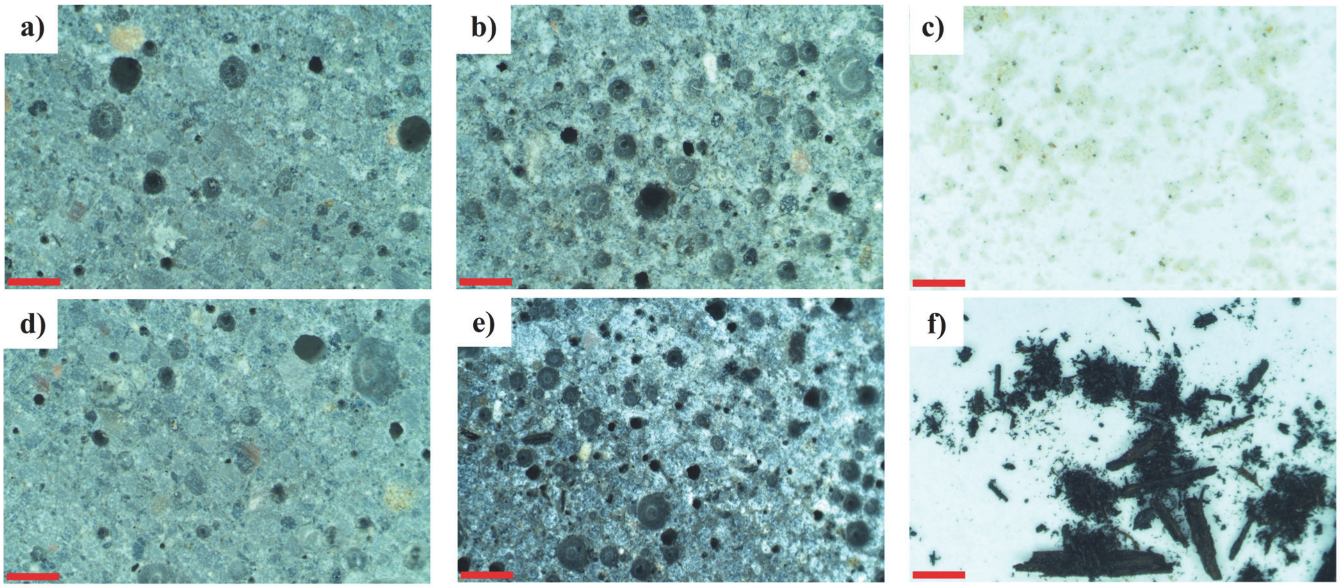

Figure 14: The optical microscope images of reference 3D printed concrete(a and d), 3D printed concrete with recycled fines (b) and biochar (d). Images (c) and (f) shows pictures of recycled fines and biochar, respectively. The length of the red bar corresponds to the 1 mm.

Compared to the reference sample, image (e) of 3D printed concrete supplemented with biochar shows black, rod-like structures. The black elements were identified as biochar, presented in the image (f). Also, the porosity of samples with biochar (e) significantly increased.

The microstructure of the cement composite was also indirectly studied by determining the impact of biochar and recycled fines on the materials' open porosity and water absorption (with 3 specimens for each mix and a coefficient of variation between 1.20% and 7.27%). The aggregate results are presented in Fig. 15. Analyzing the effect of biochar on the material's porosity, a clear relationship between the increase in void spaces within the cement matrix and the amount of cement replaced by BC can be observed. The previously mentioned microscopic studies also confirm this. The formation of air voids in the material is associated with the volumetric change of biochar as it absorbs mixing water (the material swells), and as the cement matrix hardens and forms, the biochar releases the absorbed moisture, contracts, and creates voids. Additionally, since biochar reduces the workability of the mixture, it negatively impacts the ability to vibrate and de-air the sample properly. Such properties were not observed when replacing cement with recycled fines. Although there was a change in open porosity between the reference sample and the RF125 sample, further increases in recycled fines content did not affect this parameter.

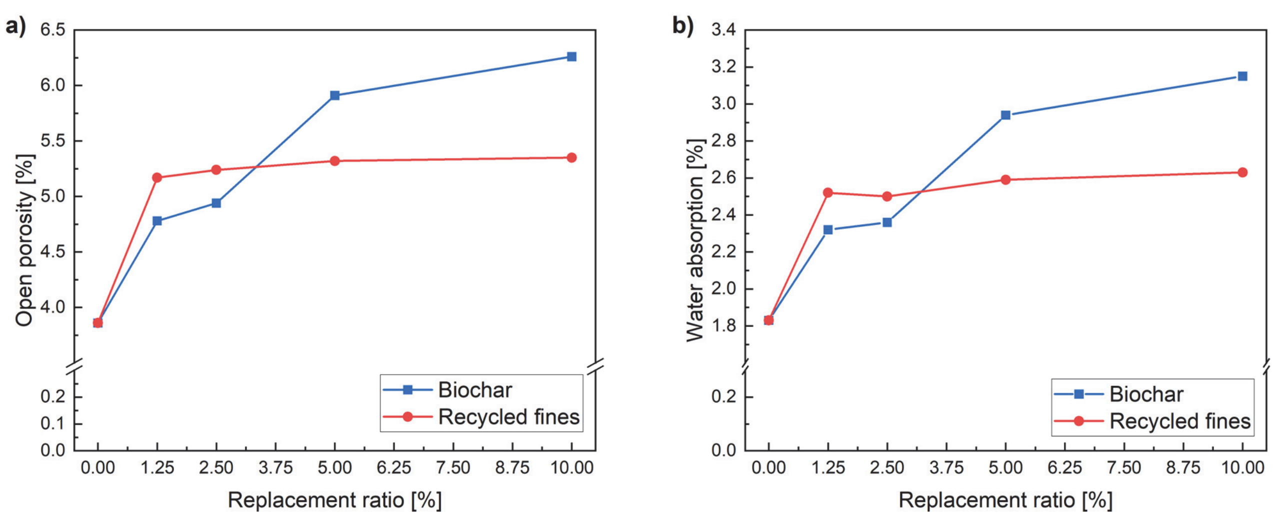

Figure 15: Influence of cement replacement on: a) open porosity, b) water absorption.

The water absorption test also confirms this. Mixtures with biochar, which showed high porosity, also had significantly higher water absorption than the reference mixture (REF). The water absorption did not depend on the degree of replacement when using recycled fines as a cement replacement, similar to open porosity. It is also worth noting that all mixtures exhibited generally very low water absorption, not exceeding 3.2%, which suggests high durability and resistance to atmospheric conditions, such as freeze-thaw cycles.

Discussion

Analyzing the rheological properties of mixtures with the addition of recycled fines, it can be observed that the spread flow diameter measurements correspond with the rheometric testing results. During the initial testing period for SYS (after 5 minutes), the results for the RF125-RF1000 mixtures are very similar. The static yield stress ranges from 137.1 Pa to 112.8 Pa and decreases with increasing RF content. The trend in spread flow diameter is less pronounced, but this test also indicated an increase in the fluidity of the mixture. Using biochar with high water absorption capacity reduced spread flow diameter by up to 15%, while the SYS increased by 197%. Similar findings were presented by Gupta et al. [14], where the replacement of cement with biochar up to 5% by weight led to a significant increase in the viscosity of the paste. These findings are also in line with those of Vergara et al. [1], who demonstrated that the incorporation of biochar decreases the fluidity of 3D printed concrete. At first glance, it may seem that the differences between these two parameters are disproportionate. Still, it should be noted that the spread flow diameter test is a straightforward testing method with low sensitivity to changes occurring in the material. Despite literature recommendations regarding the required spread flow diameter for a mixture to be considered printable, this condition is insufficient. Many cementitious mixtures with a spread flow diameter of 160 mm will not be printable.

Calorimetric studies revealed changes in the dynamics and quantity of heat released by the various mixtures, depending on the type of cement substitute used. The REF mixture achieved a maximum normalized heat flow (NHF) of 1.39 mW/g. Replacing 2.5 vol.% of cement with recycled fines increased by 5.8%. Other researchers, such as Ali et al. [24] and Gupta and Kua [23], reported similar results. When 10 vol.% of the cement volume was replaced with RF, the normalized heat flow decreased by 7.2%, comparable to the reduced binder content. Interestingly, in the case of DEM development, the RF250 mixture achieved a modulus 6.8% higher than REF while simultaneously generating a higher normalized heat flow of 6.2%. RF1000, despite having a final DEM nearly identical to REF, exhibited a slower increase in stiffness, which aligns with the reduced NHF of 7.2%. In the case of biochar, an explicit dependency was not observed, which may be related to the bidirectional moisture transport mechanism. During the early stage of hydration, moisture is absorbed from the mixture. Subsequently, as the relative humidity of the cement matrix decreases, the biochar releases the stored moisture.

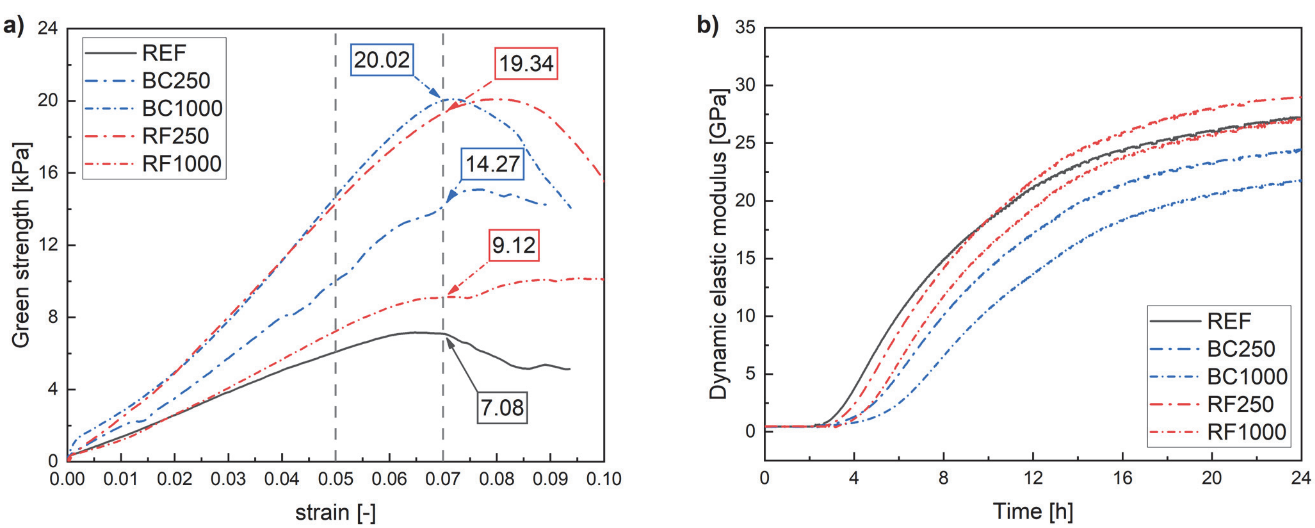

Figure 16: Comparison of influence of 2.5 vol.% and 10 vol.% cement replacement on: a) green strength after 60 min, b) dynamic elastic modulus.

This is well illustrated by comparing DEM and green strength after 60 minutes, as shown in Fig. 16. Despite BC250 and BC1000 achieving higher plastic strength (due to the water absorption by biochar), they had lower DEM after 24 hours because the water was released back into the matrix, forming air voids. In contrast, recycled fines, which have low water absorption capacity in the initial period, facilitated the acceleration of the hydration reaction (increased NHF), translating into an increase in DEM at the optimal cement replacement level.

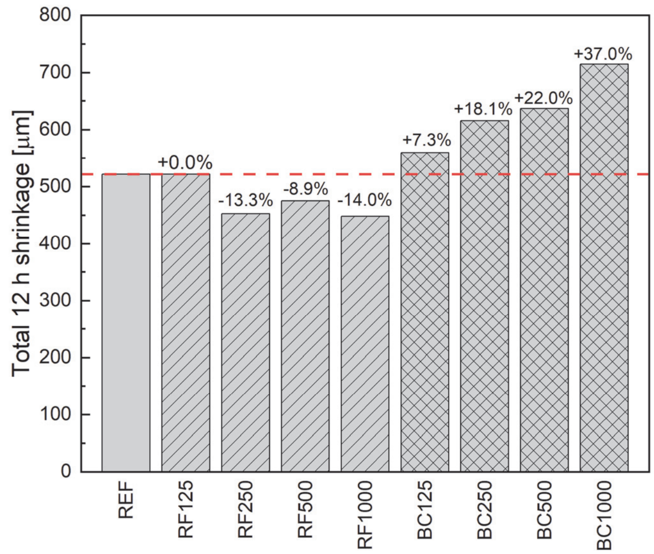

Figure 17: Total 12h shrinkage of all tested mixes.

Fig. 17 presents the total shrinkage of all mixtures after 12 hours. It can be observed that recycled fines as a cement substitute reduce total shrinkage, whereas biochar increases it. Similar influence of BC was previously pointed out by Gupta et. al. [14]. The reduction in shrinkage with RF should primarily be attributed to the increased amount of free mixing water in the initial period, which decreases plastic shrinkage [25]. Zhang et. al. [15] also proved that replacing up to 20% of cement with BC in 3DPC can lead to reduction in long-time total shrinkage. As previously demonstrated, biochar initially absorbs mixing water, increasing the deformation of the mixture. When the biochar releases moisture, the cement matrix is sufficiently rigid that it cannot compensate for the shrinkage deformations.
The replacement of cement up to 10 vol.% has a negligible impact on the early compressive strength of the tested elements. Those findings are in line with available in literature [14] and can be consider as negligible. This is primarily due to the overall amount of binder in the mixture. Regardless of the cement replacement level, the material had a compressive strength of over 50 MPa after seven days, which is adequate for structural applications. The results obtained are summarized and presented in Tab. 5.

	Recycled fines				Biochar			
	1.25%	2.50%	5.00%	10.0%	1.25%	2.50%	5.00%	10.0%
Spread flow	↔	↔	↔	↔	↔	↘	↘	↘
SYS	↘	↘	↘	↘	↗	↗	↗	↗
Normalized heat flow	↗	↗	↔	↘	↗	↗	↔	↘
Shrinkage	↔	↘	↘	↘	↗	↗	↗	↗
Green strength (after 30 min)	↗	↗	↗	↘	↗	↗	↗	↗
Dynamic elastic modulus	↗	↗	↔	↔	↘	↘	↘	↘
Strength	↔	↗	↘	↘	↔	↗	↘	↘
Porosity	↔	↔	↔	↔	↗	↗	↗	↗

↗ - increases; ↘ - decreases; ↔ - no difference.

Table 5: Summarized influence of recycled fines and biochar on 3DPC performance.

Conclusions

After conducted analyses, several key conclusions can be formulated:

- Replacing up to 10 vol.% of cement with eco-friendly waste material to produce a 3D printable concrete (3DPC) mixture is possible.
- The addition of recycled fines has a neutral impact on the mixture's spread flow diameter but increases the printed elements' initial deformations.
- Due to its water absorption capacity, biochar reduces the mixture's fluidity, allowing for faster printing of structures without initial deformations (increasing buildability).
- Replacing up to 2.5 vol.% of cement increases the normalized heat flow, translating into a faster gain in mechanical properties.
- Adding biochar without increasing the mixing water content increases shrinkage deformations in the first 12 hours, whereas recycled fines help to reduce them.
- Replacing up to 10 vol.% of cement with recycled fines and biochar does not significantly affect early compressive strength.
- Biochar increases the material's porosity by creating air voids due to the absorption and release of water into the cement matrix during hydration.

In summary, recycled concrete fines and biochar are eco-friendly materials that can partially replace cement in mixtures intended for 3D printing. Both materials affect specific parameters, but applying appropriate technological treatments makes it possible to create a more sustainable 3D printable mixture. Further research is essential to analyze the possibility of simultaneously using concrete waste and pre-wetted biochar.

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References

[1] Vergara, L.A., Perez, J.F., Colorado, H.A. (2023). 3D printing of ordinary Portland cement with waste wood derived biochar obtained from gasification. Case Studies in Construction Materials. 18, e02117. DOI: 10.1016/j.cscm.2023.e02117.

[2] Lloret, E., Shahab, A.R., Linus, M., Flatt, R.J., Gramazio, F., Kohler, M., Langenberg, S. (2015). Complex concrete structures. Computer-Aided Design. 60, pp. 40-49. DOI: 10.1016/j.cad.2014.02.011.

[3] Gosselin, C., Duballet, R., Roux, Ph., Gaudillière, N., Dirrenberger, J., Morel, Ph. (2016). Large-scale 3D printing of ultra-high performance concrete – a new processing route for architects and builders. Materials & Design. 100, pp. 102-109. DOI: 10.1016/j.matdes.2016.03.097.

[4] Tay, Y.W.D., Panda, B., Paul, S.C., Noor Mohamed, N.A., Tan, M..J, Leong, K.F. (2017). 3D printing trends in building and construction industry: a review. Virtual and Physical Prototyping. 12(3), pp. 261-276. DOI: 10.1080/17452759.2017.1326724.

[5] Federowicz, K., Techman, M., Skibicki, S., Chougan, M., El-Khayatt, A.M., Saudi, H.A., Błyszko, J., Abd Elrahman, M., Chung, S.Y., Sikora, P. (2023). Development of 3D printed heavyweight concrete (3DPHWC) containing magnetite aggregate. Materials & Design. 233, pp. 112246. DOI: 10.1016/j.matdes.2023.112246.

[6] Restuccia, L., Ferro, G.A. (2016). Promising low cost carbon-based materials to improve strength and toughness in cement composites. Construction and Building Materials. 126, pp. 1034-1043. DOI: 10.1016/j.conbuildmat.2016.09.101.

[7] Rao, A., Jha, K.N., Misra, S. (2007). Use of aggregates from recycled construction and demolition waste in concrete. Resources, Conservation and Recycling. 50(1), pp. 71-81. DOI: 10.1016/j.resconrec.2006.05.010.

[8] Khushnood, R.A., Ahmad, S., Restuccia, L., Spoto, C., Jagdale, P., Tulliani, J.M., Ferro, G.A. (2016). Carbonized nano/microparticles for enhanced mechanical properties and electromagnetic interference shielding of cementitious materials. Frontiers of Structural and Civil Engineering. 10(2), pp. 209-213. DOI: 10.1007/s11709-016-0330-5.

[9] Xiong, B., Falliano, D., Marano, G.C., Restuccia, L., Di Trapani, F., Ferro, G.A. (2021). Experimental Characterization of Mortar with Recycled PET Aggregate: Preliminary Results. Procedia Structural Integrity. 33, pp. 1027-1034. DOI: 10.1016/j.prostr.2021.10.114.

[10] Vergara, L.A., Colorado, H.A. (2020). Additive manufacturing of Portland cement pastes with additions of kaolin, superplastificant and calcium carbonate. Construction and Building Materials. 248, 118669. DOI: 10.1016/j.conbuildmat.2020.118669.

[11] Chen, L., Zhang, Y., Wang, L., Ruan, S., Chen, J., Li, H., Yang, J., Mechtcherine, V., Tsang, D.C.W. (2022). Biochar-augmented carbon-negative concrete. Chemical Engineering Journal. 431, 133946. DOI: 10.1016/j.cej.2021.133946.

[12] Miller, S.A., Moore, F.C. (2020). Climate and health damages from global concrete production. Nature Climate Change. 10(5), pp. 439-443. DOI: 10.1038/s41558-020-0733-0.

[13] Chen, L., Wang, L., Zhang, Y., Ruan, S., Mechtcherine, V., Tsang, D.C.W. (2022). Roles of biochar in cement-based stabilization/solidification of municipal solid waste incineration fly ash. Chemical Engineering Journal. 430, 132972. DOI: 10.1016/j.cej.2021.132972.

[14] Gupta, S., Krishnan, P., Kashani, A., Kua, H.W. (2020). Application of biochar from coconut and wood waste to reduce shrinkage and improve physical properties of silica fume-cement mortar. Construction and Building Materials. 262, 120688. DOI: 10.1016/j.conbuildmat.2020.120688.

[15] Zhang, H., Xiao, J., Duan, Z., Zou, S., Xia, B. (2022). Effects of printing paths and recycled fines on drying shrinkage of 3D printed mortar. Construction and Building Materials. 342, 128007. DOI: 10.1016/j.conbuildmat.2022.128007.

[16] Robayo–Salazar, R.,Vargas, A., Martínez, F., Mejía de Gutiérrez, R. (2024). Utilization of powders and fine aggregates from the recycling of construction and demolition waste in the 3D printing of Portland-based cementitious materials. Cleaner Materials. 11, 100234. DOI: 10.1016/j.clema.2024.100234.

[17] De Vlieger, J., Boehme, L., Blaakmeer, J., Li, J. (2023). Buildability assessment of mortar with fine recycled aggregates for 3D printing. Construction and Building Materials. 367, 130313. DOI: 10.1016/j.conbuildmat.2023.130313.

[18] Katzer, J., Halbiniak, J., Langier, B., Major, M., Major, I. (2021). Influence of Varied Waste Ceramic Fillers on the Resistance of Concrete to Freeze–Thaw Cycles. Materials. 14(3), 624. DOI: 10.3390/ma14030624.

[19] Pacheco, J., Santos, K., Sikora, P., Skibicki, S., Techman, M., Federowicz, K., Reales, O., Vieira, M., Leporace-Guimil, B., Tošić, N., Pepe, M. Recycled Aggregates and 3D printing technology: production requirements, printability and way forward (Recycl3D project report D.1.1.). DOI: 10.5281/zenodo.7866197.

[20] Jayathilakage, R., Rajeev, P., Sanjayan, J. (2022). Rheometry for Concrete 3D Printing: A Review and an Experimental Comparison. Buildings. 12(8), 1190. DOI: 10.3390/buildings12081190.

[21] Skibicki, S., Federowicz, K., Hoffmann, M., Chougan, M., Sibera, D., Cendrowski, K., Techman, M., Pacheco, J.N., Liard, M., Sikora, P. (2024). Potential of Reusing 3D Printed Concrete (3DPC) Fine Recycled Aggregates as a Strategy towards Decreasing Cement Content in 3DPC. Materials. 17(11), 2580. DOI: 10.3390/ma17112580.

[22] Federowicz, K., Kaszyńska, M., Zieliński, A., Hoffmann, M. (2020) Effect of Curing Methods on Shrinkage Development in 3D-Printed Concrete. Materials. 13(11), 2590. DOI: 10.3390/ma13112590.

[23] Gupta, S., Kua, H.W. (2019). Carbonaceous micro-filler for cement: Effect of particle size and dosage of biochar on fresh and hardened properties of cement mortar. Science of The Total Environment. 662, pp. 952-962. DOI: 10.1016/j.scitotenv.2019.01.269.

[24] Ali, D., Agarwal, R., Hanifa, M., Rawat, P., Paswan, R., Rai, D., Tyagi, I., Srinivasarao Naik, B., Pippal, A. (2023). Thermo-physical properties and microstructural behaviour of biochar-incorporated cementitious material. Journal of Building Engineering. 64, 105695. DOI: 10.1016/j.jobe.2022.105695.

[25] Deysel, R.C., Boshoff, W.P., Smit, M.S. (2023). Implementing capillary pressure control measures to prevent plastic shrinkage cracking in concrete. Construction and Building Materials. 397, 132407. DOI: 10.1016/j.conbuildmat.2023.132407.