Cement recycling with help of biobased additives:

Report D3.1
Evaluation of reactivated cement stone and mortar

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Cement recycling with help of biobased additives
Report D3-1: Evaluation of reactivated cement stone and

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Contents

1 Introduction

1.1 Background of the research

The current most used material worldwide is concrete. Cement, one of the components of concrete, is responsible for about 7% of total CO_2 emissions in the planet. Half of this emissions is due to cement production. Therefore, alternative binders that can replace cement are of great contribution to reduce the environmental impact of concrete. At the same time, many concrete structures are reaching the end of their service life: they must be dismantled and in most cases demolished. The deposal of the demolished structures has become an issue since the concrete construction and demolition waste (CDW) must be disposed properly. An alternative that can help with the replacement of cement and the deposal of demolished concrete structures at the same time is recycling of the old cement paste. This is in line with the goals of the Dutch government which has as an aim by 2030 to reduce by 50% the CO_2 emissions of the construction industry.

In order to recycle the old cement paste to be used as new binder, this material must be finely grounded and then (preferably) reactivated. The current project focuses on the reactivation of the ground old cement paste by using biobased additives to enhance dissolution and precipitation.

1.2 Aim of the research

In this report, a new generation of biopolymers were used in combination with two CDW streams. The source of the first is mixed concrete from different sources, referred to as MX and used in previous research [1], [2]. The source of the second is from old concrete rich in blastfurnace slag, labeled SLG. In [1], [2], it was concluded that the addition of Na_2SO_4 and ground granulated blast-furnace slag (GGBS) generally enhances the mechanical properties of the mixtures. In this study, the new biopolymers are evaluated and compared to mixtures containing Na_2SO_4 and GGBS to determine whether these additives can be replaced by biopolymers without compromising the performance of the mixes.

1.3 Content of this report

Chapter 2 provides the experimental program, including materials, mix designs and experiments. In chapter 3, the results are presented, discussed and analyzed. Finally, chapter 4 provides the conclusions of the research.

2 Experimental program

2.1 Materials and set-up of the experimental program

The binders under investigation consisted of mixes with variations of GGBS content, CDW type and content and with different types of biopolymers with a fixed content as activator. CDW from concrete with slag, labeled as “SLG” and CDW from mixed concrete labeled “MX” were used. Six types of biopolymers were tested with differences in the length of their molecules and manufacturing process. In addition, two reference mixes were chosen for comparison with the mixes with biopolymers: i) CDW and GGBS and ii) CDW, GGBS and Na_2SO_4. The sodium sulfate is used as a set regulator. A summary of the materials used is given below.

- Precursors:
  - Concrete construction and Demolition Waste from concrete with slag provided by Urban Mine (SLG).
  - Concrete construction and Demolition Waste from mixed concrete provided by Urban Mine (MX).
  - ECO2CEM ground granulated blast-furnace slag (GGBS) supplied by Ecocem Benelux
- Additives:
  - Sodium sulphate (Na_2SO_4) provided by Sigma Aldrich.
  - Biopolymer provided by with WUR with the following IDs:

Table 2.1 Biopolymers used, ID used by WUR and ID used by TNO

ID WUR	ID TNO (Used in the report)
MD6 IH362 ox precipitated	MD6P
MD6 IH362 ox dialysed and freeze dried	MD6D
MD10 IH363 ox precipitated	MD10P
MD10 IH363 ox dialysed and freeze dried	MD10D
MD14 IH364 ox precipitated	MD14P
MD14 IH364 ox dialysed and freeze dried	MD14D

For the mix design, for both CDWs, two ratios by mass of the precursors (CDW and GGBS) were chosen: 100 wt-% CDW and 50 wt-% CDW + 50 wt-% GGBS. For each CDW stream and each ratio by mass, the additives were dosed by mass of the precursors. For the biopolymers, 0.1% was chosen, for Na_2SO_4 4%. The mixes were evaluated by measuring the Dynamic Modulus of Elasticity (DME) using an Ultrasonic Pulse Velocity (UPV) equipment, up to approximately 6 or 28 days. Afterwards, the compressive strength was determined. A total of 32 mixes were tested; an overview of the mixes and the test are given in Table 2.2 and Table 2.3 for SLG and MX, respectively.

Table 2.2 Test scheme of the SLG mixes.

<table>
<tr><th rowspan="2"></th><th colspan="2">100% SLG</th><th colspan="2">50% SLG + 50% GGBS</th></tr>
<tr><th>DME, length of the test (Days)</th><th>fc, age of testing (Days)</th><th>DME, length of the test (Days)</th><th>fc, age of testing (Days)</th></tr>
<tr><td>0</td><td rowspan="8">6</td><td rowspan="8">7</td><td rowspan="8">6</td><td rowspan="8">7</td></tr>
<tr><td>Na_2SO_4</td></tr>
<tr><td>MD6P</td></tr>
<tr><td>MD6D</td></tr>
<tr><td>MD10P</td></tr>
<tr><td>MD10D</td></tr>
<tr><td>MD14P</td></tr>
<tr><td>MD14D</td></tr>
</table>

Table 2.3 Test scheme of the MX mixes.

<table>
<tr><th rowspan="2"></th><th colspan="2">100% MX</th><th colspan="2">50% MX + 50% GGBS</th></tr>
<tr><th>DME, length of the test (Days)</th><th>fc, age of testing (Days)</th><th>DME, length of the test (Days)</th><th>fc, age of testing (Days)</th></tr>
<tr><td>0</td><td rowspan="8">6</td><td rowspan="8">7</td><td rowspan="3">6</td><td rowspan="3">7</td></tr>
<tr><td>Na2SO4</td></tr>
<tr><td>MD6P</td></tr>
<tr><td>MD6D</td><td rowspan="3">28</td><td rowspan="3">28</td></tr>
<tr><td>MD10P</td></tr>
<tr><td>MD10D</td></tr>
<tr><td>MD14P</td><td>6</td><td>7</td></tr>
<tr><td>MD14D</td><td>28</td><td>28</td></tr>
</table>

2.2 Mortar mix compositions and mixing procedures

The mortar mixes were designed with a similar earth-dry consistency based on the water demand of the precursors and with similar ratios between the paste and the aggregate content. The water demand of the GGBS and the MX is reported in [1]. Using the same methodology, the water demand of the SLG was obtained with a value of 0.32 g/g. Table 2.4 to Table 2.6 present the mass in kg per m^3, volume in m^3 per m^3 and relevant data of the mixes with SLP. The same information for the mixes with MX is presented in Table 2.7 to Table 2.9 The mixes with the biopolymers share the same mix design except for the type of biopolymer used.

Table 2.4 SLG Mortars mix design by mass.

Mix design in mass per m³ (kg)						
	100 SLG	100 SLG + 4Na	100 SLG + Bio*	50 SLG + 50 GGBS	50 SLG + 50GGBS + 4Na	50 SLG + 50GGBS + Bio*
SLG	416	397	412	219	210	218
GGBS	0	0	0	219	210	218
Na_2SO_4	0	16	0	0	17	0
Biopolymer*	0.00	0.00	0.41	0.00	0.00	0.44
Water	162	161	161	166	166	166
Sand - EN 196	1553	1560	1560	1560	1560	1560
Water in Agg	47	47	47	47	47	47
Total Water	209	208	208	213	213	213
Total	2178	2181	2180	2210	2211	2210

*Refers to: MD6P, MD6D, MD10P, MD10D, MD14P and MD14D

Table 2.5 SLG Mortars mix design by volume.

Mix design in mass per m³ (m³)						
	100 SLG	100 SLG + 4Na	100 SLG + Bio*	50 SLG + 50 GGBS	50 SLG + 50GGBS + 4Na	50 SLG + 50GGBS + Bio*
SLG	0.17	0.17	0.17	0.17	0.09	0.09
GGBS	0.00	0.00	0.00	0.00	0.08	0.07
Na_2SO_4	0.00	0.006	0.00	0.00	0.00	0.006
Biopolymer*	0.00	0.00	0.00041	0.00041	0.00	0.00
Water	0.16	0.16	0.16	0.16	0.17	0.17
Air	0.02	0.02	0.02	0.02	0.02	0.02
Sand - EN 196	0.60	0.60	0.60	0.60	0.60	0.60
Water in Agg	0.05	0.05	0.05	0.05	0.05	0.05
Total Water	0.21	0.21	0.21	0.21	0.21	0.21
Total	1.00	1.00	1.00	1.00	1.00	1.00

*Refers to: MD6P, MD6D, MD10P, MD10D, MD14P and MD14D

Table 2.6 SLG Mortars mix design relevant properties.

	100 SLG	100 SLG + 4Na	100 SLG + Bio*	50 SLG + 50 GGBS	50 SLG + 50GGBS + 4Na	50 SLG + 50GGBS + Bio*
Theoretical density (kg/m³)	2180	2180	2180	2210	2210	2210
Paste/Agg (kg/kg)	0.40	0.40	0.40	0.42	0.42	0.42
Paste/Agg (m³/m³)	0.64	0.63	0.63	0.63	0.63	0.63
w/b (kg/kg)	0.39	0.39	0.39	0.38	0.38	0.38
w/b (m³/m³)	0.94	0.94	0.93	0.93	1.00	1.00

*Refers to: MD6P, MD6D, MD10P, MD10D, MD14P and MD14D

Table 2.7 MX Mortars mix design by mass.

Mix design in mass per m³ (kg)						
	100 MX	100 MX + 4Na	100 MX + Bio*	50 MX + 50 GGBS	50 MX + 50GGBS + 4Na	50 MX + 50GGBS + Bio*
MX	403	387	402	221	213	221
GGBS	0	0	0	221	213	221
Na_2SO_4	0	15	0	0	17	0
Biopolymer*	0.00	0.00	0.40	0.00	0.00	0.44
Water	165	165	165	164	164	164
Sand - EN 196	1560	1560	1559	1562	1560	1561
Water in Agg	47	47	47	47	47	47
Total Water	212	212	212	210	211	210
Total	2174	2175	2173	2215	2214	2214

*Refers to: MD6P, MD6D, MD10P, MD10D, MD14P and MD14D

Table 2.8 MX Mortars mix design by volume.

Mix design in mass per m³ (m³)						
	100 MX	100 MX + 4Na	100 MX + Bio*	50 MX + 50 GGBS	50 MX + 50 GGBS + 4Na	50 MX + 50 GGBS + Bio*
MX	0.17	0.16	0.17	0.09	0.09	0.09
GGBS	0.00	0.00	0.00	0.08	0.07	0.08
Na_2SO_4	0.000	0.006	0.000	0.000	0.006	0.000
Biopolymer*	0.00	0.00	0.00041	0.00	0.00	0.00041
Water	0.17	0.17	0.17	0.16	0.16	0.16
Air	0.02	0.02	0.02	0.02	0.02	0.02
Sand - EN 196	0.60	0.60	0.60	0.60	0.60	0.60
Water in Agg	0.05	0.05	0.05	0.05	0.05	0.05
Total Water	0.21	0.21	0.21	0.21	0.21	0.21
Total	1.00	1.00	1.00	1.00	1.00	1.00

*Refers to: MD6P, MD6D, MD10P, MD10D, MD14P and MD14D

Table 2.9 MX Mortars mix design relevant properties.

	100 MX	100 MX + 4Na	100 MX + Bio*	50 MX + 50 GGBS	50 MX + 50GGBS + 4Na	50 MX + 50GGBS + Bio*
Theoretical density (kg/m³)	2174	2175	2173	2215	2214	2214
Paste/Agg (kg/kg)	0.39	0.39	0.39	0.42	0.42	0.42
Paste/Agg (m³/m³)	0.63	0.63	0.63	0.63	0.63	0.63
w/b (kg/kg)	0.41	0.41	0.41	0.37	0.37	0.37
w/b (m³/m³)	0.98	0.98	0.98	0.97	0.97	0.97

*Refers to: MD6P, MD6D, MD10P, MD10D, MD14P and MD14D

2.3 Dynamic E-modulus and compressive strength on mortar cylinders

The measurements were executed using an Ultrasonic Measuring Test System IP 8 from Ultra Test. The setup of the equipment is shown in Figure 2.1.

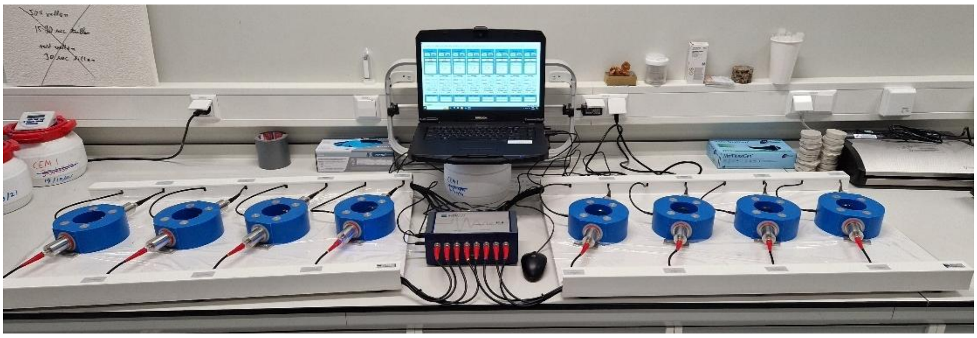


Figure 2.1 Experimental set up for the development of the dynamic E-modulus of elasticity by means of UPV.

The experiments were performed at the mortar lab of Bouwinnovatie Lab Delft (BLD) of TNO in a 20 °C control environment with a maximum RH of 65%. The general procedure of the experiments is as follows:

1. UPV and temperature sensors are placed into the moulds and connected to the datalogger. The moulds and the sensors are coated with Vaseline spray to ease the demoulding after the measurements are finalized.
2. In the software, the name and properties for each mix are input. The length between the UPV sensors is also input. It is important that the value input corresponds with the actual length between the sensors. This can be double check by doing measurements in air and verifying if the speed of the P-wave (343 m/s) is obtained.
3. The fresh mixtures are casted in the moulds following the guidelines of the NEN-EN-196-1:2016 [3]. The moulds are placed on the vibration table where they are filled and compacted. The excess of the mix is removed and the top layer is flattened. Figure 2.2 gives an example of the sample after compaction. Afterwards, the mass of the fresh sample in the moulds is recorded, to use later as an input to compute the DME.

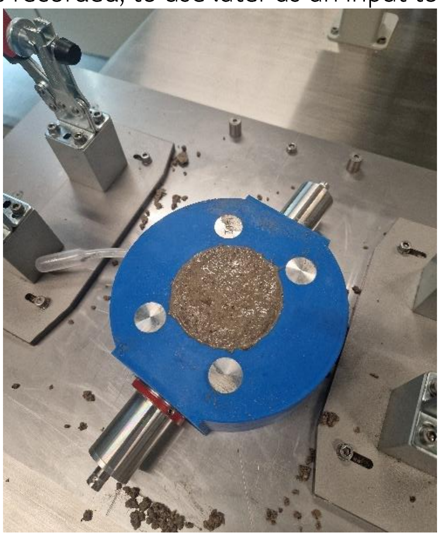


Figure 2.2 Mould filled and flattened on the compaction table.

4. Once the mixes are in the moulds, they are covered with a lid and a dead weight on top of it, as shown in Figure 2.3. Next, the monitoring is started and run for a predefined time during which the ultrasonic waves are send through the specimens and the travel times are recorded. The ultrasonic wave travel times and temperature are recorded every minute.

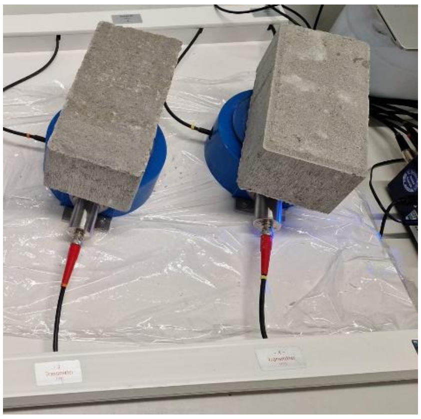


Figure 2.3 Covering of the moulds with plastic lid and weight on top.

5. Once the test is finalized, the data is retrieved and using equation (1), the development of the DME of the samples is obtained. For this, a fix mould volume of 186 cm^3 is used.

$$E_{dyn} = v^2 \cdot \left(\frac{m}{V}\right) \cdot \frac{(1+\mu)\cdot(1-2\mu)}{1-\mu} \qquad (1)$$

Where:
- E_{dyn}: Dynamic E-modulus (Pa)
- v: Ultrasonic pulse velocity (m/s)
- m: Mass casted
- V: (fixed) volume
- μ: Poisson ratio assumed as 0.20.

6. Finally, the samples are demoulded, wrapped and tested in compression at 7 or 28 days following the guidelines in the NEN–EN 196-1:2016 [3]. Figure 2.4 gives a schematic overview of the process.

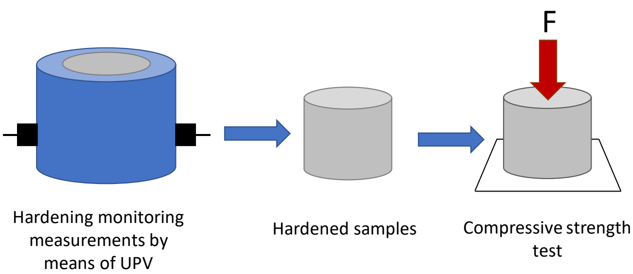


Figure 2.4 Compaction process for UPV measurements

2.3.1 Dynamic E-modulus projections

As shown in Table 2.3r, some of the DME experiments were run for 6 days and others for 28 days. To compare the results of both measurements, the data of the experiments at 6 days were fitted and then projected to 28 days. Using equation (2), the 3 free parameters A, s and t_x were fitted to the measured data using the least squares technique. A and s are parameters used to fit the shape of the curve. Given that the equation is an exponential function, the shape of the curve might in some cases never fit properly with the data, especially when a delay effect is present. In this case, the parameter t_x is used to shift the graph horizontally helping to find the best fit.

$$Q = A \cdot \left(1 - e^{-s \cdot (t - t_x}\right) \qquad (2)$$

3 Results

3.1 DME results for reference mixes without biopolymers

The DME results for the mixes without GGBS and with GGBS are shown in Figure 3.1 a and b. In both figures, the results for the SLP (CDW stream from sleepers) reported in [2] are shown for comparison and discussion. For the mixes without GGBS, the use of Na_2SO_4 improves the DME. Compared to the mixes with 50% GGBS, the DME is significantly lower, showing that the use of GGBS is needed to improve the mechanical properties of the mixes.

For the mixes with GGBS, the use of Na_2SO_4 also improves and accelerates the development of the DME. The mix with SLP, GGBS and sodium sulfate initially develops the DME faster, after which it stabilizes. The DEM of the equivalent mixes with SLG and MX develops at a lower and constant ratio, the mix with MX obtaining higher values. The results obtained are in line with the ones presented in [2], where the mixes with higher GGBS and Na_2SO_4 contents obtained the best mechanical properties regardless of the source of CDW.

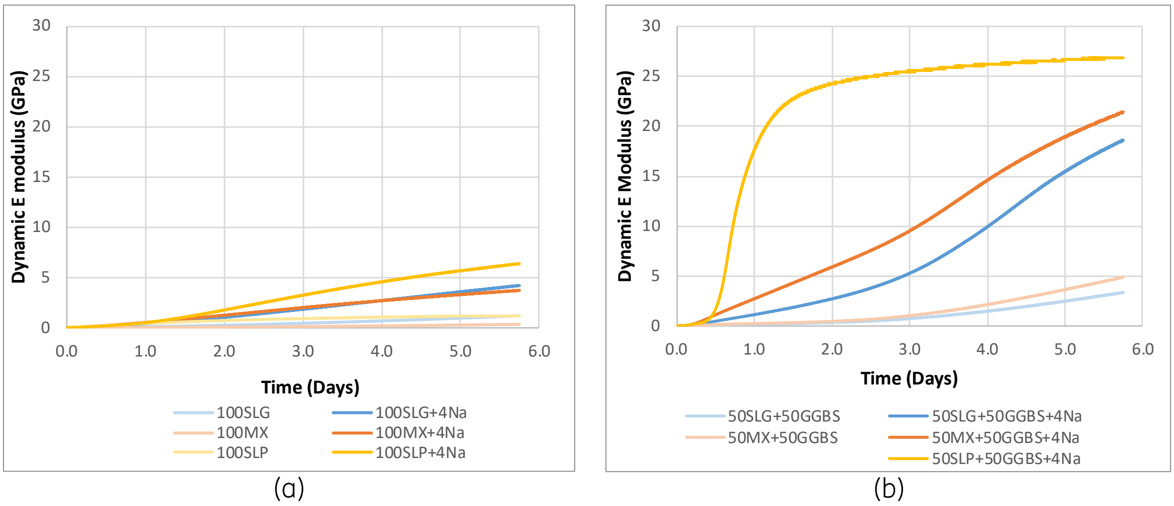
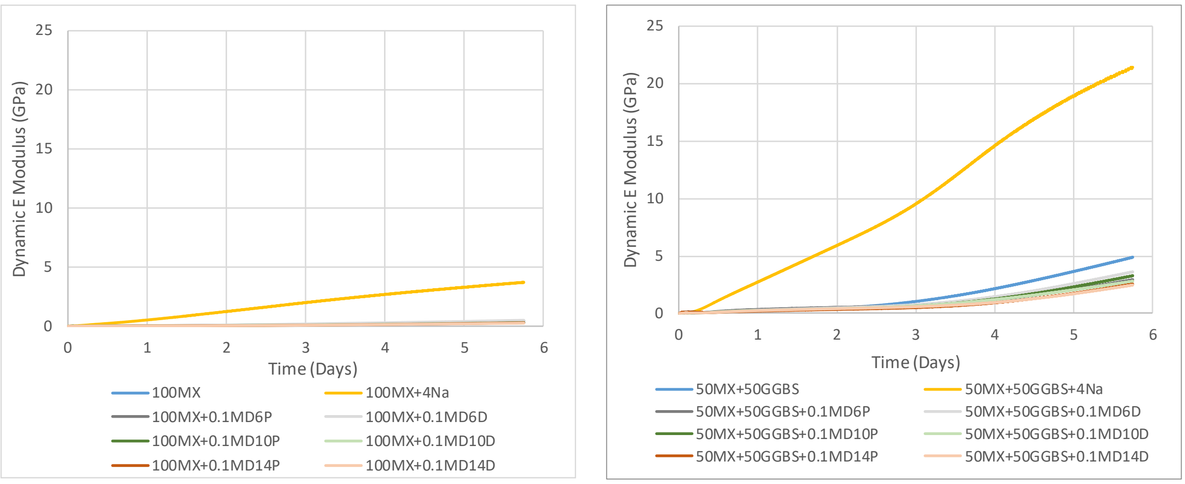


Figure 3.1 Mixes without biopolymers, DME results: a) Mixes without GGBS, b) Mixes with 50% GGBS.

3.2 DME Results until 6 days for mixes with biopolymers

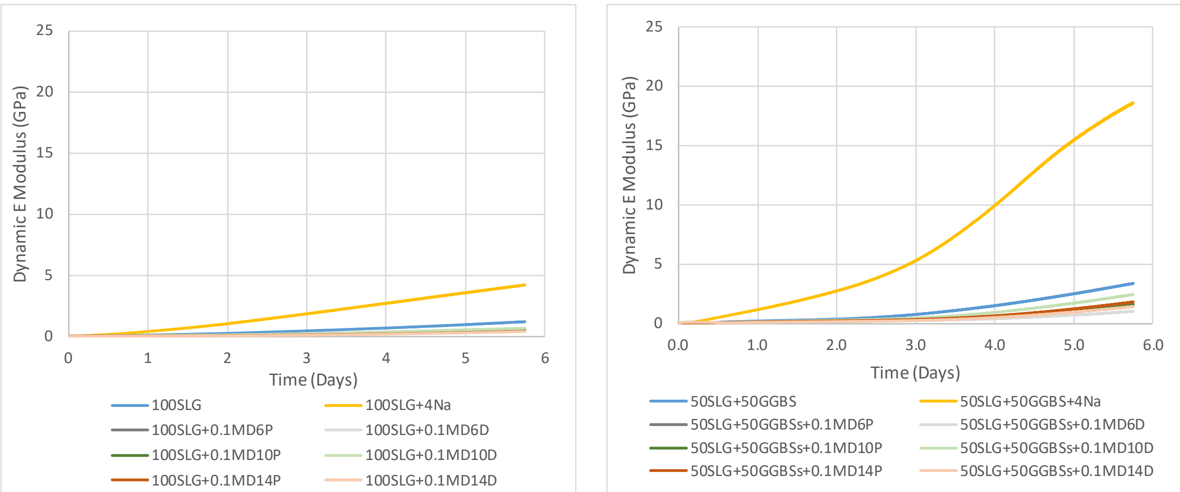
Figure 3.2 presents the results for the mixes with 100% MX and 50% MX + 50% GGBS. Figure 3.3 presents the same information for the mixes with SLG. For both the MX mixes with and without GGBS with biopolymers 0.1MD6D, MD10D, MD10P and MD14S, the measurements continued until 28 days. They are reported in the following section.
For the SLP and MX mixes without GGBS, the mixes with Na_2SO_4 had the best performance, although the DME values are still very low compared to the mixes with GGBS. For the mixes

with 50% GGBS, taking as a reference the mixes without any additive (50% MX or SLG + 50% GGBS), two observations are made. First, the mixes with Na_2SO_4 perform better than the reference, as observed before. Second, regardless of the type of biopolymers, their use hampers the development of the DME and results in lower final values.



(a) (b)

Figure 3.2 MX mixes with biopolymers, DME results at 6 days: a) Mixes without GGBS, b) Mixes with 50% GGBS.



(a) (b)

Figure 3.3 SLG mixes with biopolymers, DME results at 6 days: a) Mixes without GGBS, b) Mixes with 50% GGBS.

3.3 DME results until 28 days for mixes with MX and biopolymers

Figure 3.4 presents the experimental and projected results of the DME until 28 days. For mixes 50%MX + 50%GGBS and 50%MX + 50%GGBS + 4% Na_2SO_4, the results presented are experimental until 6 days and then projected until 28 days. For the other mixes, the results are all experimental. For the mix 100%MX + 4% Na_2SO_4, given the low development of the

DME, the results could not be fitted using equation (1); only the experimental results until 6 days are shown.

For the mix with 100% MX and Na_2SO_4 the measurement at 6 days is very similar to the ones at 28 days with biopolymers. Compared to the results of the mixes with 50% GGBS, the results with 100% MX are very low. For the mixes with 50% GGBS, the projected data of mixes 50% MX + 50% GGBS and 50% MX + 50% GGBS + 4% Na_2SO_4 indicate that at all ages these mixes have higher DME values than the mixes with biopolymers. Moreover, the final DME values of the mixes with biopolymers at 28 days are very similar to the experimental results of the mix with Na_2SO_4 at 6 days. Therefore, it can be said that compared to the mix with Na_2SO_4, the delay in the development of the DME due to the use of the biopolymers does not compensate on the longer term by for examples reaching a higher values.

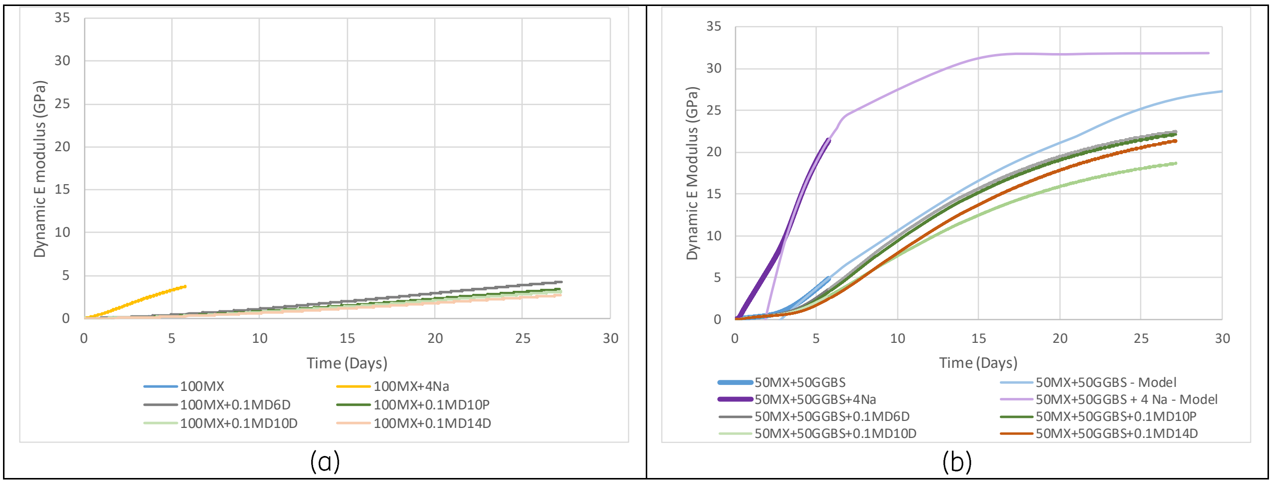
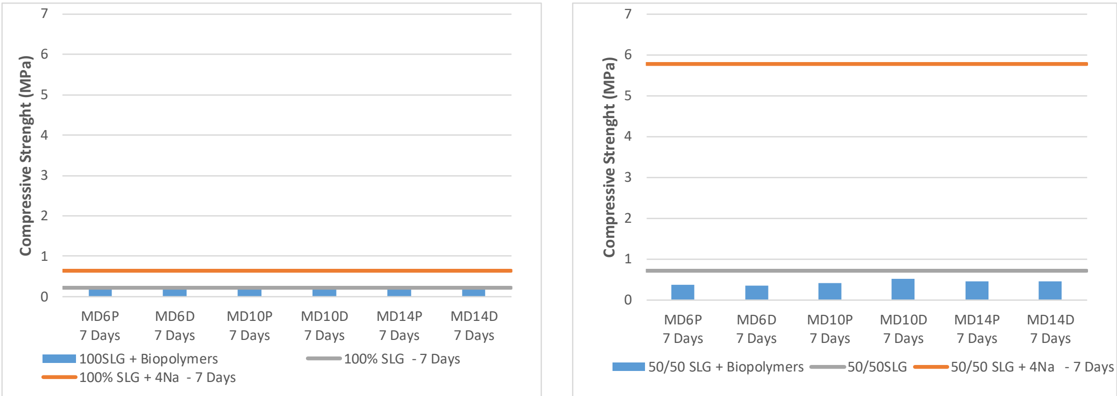


Figure 3.4 MX mixes with biopolymers, DME results at 28 days: a) Mixes without GGBS, b) Mixes with 50% GGBS.

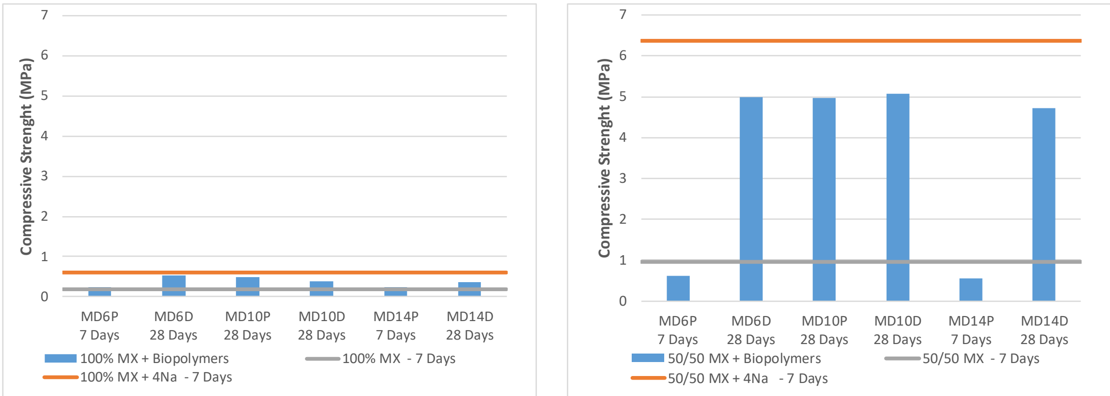
3.4 Compressive strength of DME cylinders

Figure 3.5 and Figure 3.6 show the results of the compressive strength at 6 or 28 days for the mixes with SLG and MX, respectively. The results are in line with ones of the DME. For both types of CDW (SLG and MX), the mixes without GGBS have a very low performance compared to the ones with GGBS. For the mixes with SLG and GGBS, the mix with Na_2SO_4 has a much higher compressive strength while the ones with biopolymers have lower strengths. For the mixes with MX, the strength at 6 days of the mix with GGBS and Na_2SO_4 is higher than that of the mixes with biopolymers at 28 days. This is comparable to the DME results. The use of the biopolymers does not result in higher mechanical properties, not even at higher ages.



(a) (b)

Figure 3.5 SLG mixes compressive at 7 days: a) Mixes without GGBS, b) Mixes with 50% GGBS.



(a) (b)

Figure 3.6 MX mixes compressive at 7 and 28 days: a) Mixes without GGBS, b) Mixes with 50% GGBS.

3.5 Compressive strength prediction of mortar bars

As mentioned earlier, part of the current work aims to do a feasibility study about the activation of the SLG and MX with the different biopolymers. The feasibility is evaluated using the relation stablished in [2] between the DME and the compressive strength of the mortar bars, both at 7 days (See Figure 3.7). The predictions indicate that the mixes without GGBS and the mixes with biopolymers (irrespective of the GGBS content) will have a very low compressive strength. For the mixes without biopolymers, the mix with the highest strength would be 50%SLP + 50% GGBS+ 4% Na_2SO_4, shown as a reference and presented in [2], followed by mix 50% MX + 50% GGBS + 4% Na_2SO_4 and finally 50% SLG + 50% GGBS + 4% Na_2SO_4.

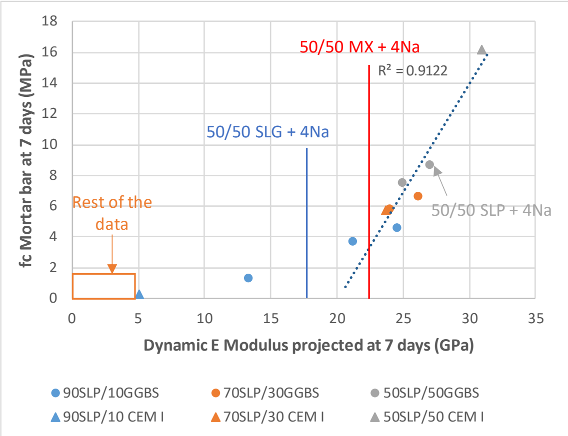


Figure 3.7 Relation between DME and mortar bar compressive strength at 7 days.

4 Conclusions

The results obtained in the current work are in line with those obtained in [2]. Regardless the type of CDW, higher contents of GGBS and Na_2SO_4 improve the performance of the mixes in terms of DME and compressive strength. Compared to the reference mixes, the use of the biopolymers, regardless of their composition, delays the hardening process of the mixes, hampering the development and final values of DME and compressive strength regardless age. At 28 days, mixes containing biopolymers have similar or lower mechanical properties than mixes with Na_2SO_4 tested at 7 days.
The predicted compressive strength indicates that the best mixes are those with GGBS and Na_2SO_4. At 28 days, the predicted strength of the mixes with biopolymers is lower than that of the mixes without biopolymers. Therefore, it is not advised to continue research on the mixes in the current report that include biopolymers.

5 References

[1] J. F. Garzón Amórtegui and J. H. M. Visser, “Cement recycling with help of biobased additives. Report D2.2a Performance of ultrafine CDW as binder component: effect of the first generation biobased additives,” *TNO, Delft*, vol. In preparation, 2024.

[2] J. F. Garzón Amórtegui and J. H. M. Visser, “Cement recycling with help of biobased additives: Report D2.2b Performance of ultrafine CDW as binder component: effect of the second and third generation biobased additives,” *TNO, Delft*, vol. In prepration, 2024.

[3] “NEN-EN 196-1: Methods of testing cement - Part 1: Determination of strength,” 2016.

6 Signature

TNO ⟩ Mobility & Built Environment ⟩ Delft, 6 January 2025

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