

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

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Report D2.2b

Performance of ultrafine CDW as binder component

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1 Introduction

1.1 Background of the research

This research is part of the project “Cement recycling met behulp van biobased chemicaliën” (cement recycling with help of biobased chemicals) which has as aim to use recycled hardened cement paste as binder / cement replacement in the new concrete. It aims at recycling old hardened cement paste via chemical routes by using biobased additives, at room temperature and in an alkaline environment. If successful, the results will contribute considerable to the goals of the Dutch government to reduce by 50% the CO₂ emissions of the construction industry by 2030, since new cement contribute considerably to the CO₂ emissions (with 1 tons of (Portland)cement producing ca. 1 tons of CO₂). In addition, it will contribute to the disposal of recycled concrete (fines) and thus contribute also to the aims of increasing circularity and reducing the use of primary materials.

In the previous report concerning the effectivity of a first set of biobased polymers in activating ultrafine Construction and Demolition Waste (CDW), it was found that the ‘first generation’ biopolymers worked at most as plasticizer, which lead to a decrease in water-binder ratio and in this way improved the strength [1]. Also, to obtain some strength, the binder required both slag and sodium sulfate (Na₂SO₄) to enhance the development of the mechanical properties. Quick scan experiments (so-called Vicat tests) for a wide range of biopolymers are mostly run at the Wageningen Food & Biobased Research (WUR) where the biobased materials are developed. The most promising biopolymers are next evaluated at TNO in additional tests like the microcalorimetry tests in which the heat development of the chemical reactions can be monitored. Next, mortar bars are cast and tested for mechanical strength. It was concluded from the first series of experiments that correlating the Vicat and the calorimetry test on the one hand with the mechanical properties was not straightforward and that another tests was required to make the connection between the quick scan test and the mechanical properties. Instead of the microcalorimetry set up in which the heat development during hardening can be monitored, in this study, the development of the dynamic modulus of elasticity (DME) of the mortar or paste during the hardening process is monitored using ultrasonic pulse velocity. As the DME is itself a mechanical property, it can be connected directly to other ones such the compressive strength.

1.2 Aim of the research

In this project, a single stream of CDW from railway sleepers labeled as “CDW_SLP” was used. Similarly, a single biopolymer (ND IH304 ox DO 1) with very high Degree of Oxidation (of 1.00 as compared to a max. of 0.22 in the previous research [2]) was tested. As in previous works, the main goal of the research is to test the performance of CDW_SLP when combined in different ratios with slag, Na₂SO₄ and biopolymer (further BIO) in order to obtain an optimum binder that can (fully or partially) replace traditional cements in concrete applications. In addition, mixes with different ratios of only CEM I and CDW_SLP were made and used as reference. The performance of CDW_SLP was determined as follows:

- Using the Ultrasonic Measuring Test System, the speed of development of the DME and its maximum value as a function of the contents of GGBS, Na₂SO₄ and BIO were investigated.
- Based on the results obtained from the DME, mortar bars have been cast for the most promising mixes with biopolymers and bending and compressive strength have been determined.

- Using the results of the DME and the compressive strength of the mortar bars, establish a relationship between these properties. This will allow in the future to predict or estimate the strength of the mortar bars using only the Ultrasonic Measuring Test System, improving the efficiency to assess the performance of a CDW and obtain the best binders.

1.3 Content of this report

Chapter two presents the experimental program, including materials. Chapter three focuses on the mix design. The results of all tests are presented in chapter four and analyzed in chapter five. Finally, conclusions from the current study are given in chapter six.

2 Experimental programme

2.1 Set-up of the program

Two types of experiments are conducted: ultrasonic pulse velocity (UPV) monitoring of the development of the dynamic modulus of elasticity (DME) during hardening up to ca. 7 days and compressive / bending strength at 7, 14 and 28 days. The two types of experiments are set up in such a way to investigate if a relationship between both properties (DME and compressive strength) can be established. This is expected to be linear for linear elastic materials. Therefore, during the first, plastic, phase of hardening of the mortars, a different, possibly non-linear relationship may be found. Since the binders under investigation (ultrafine CDW_SLP + GGBS) are reacting very slowly, mixes with CEM I 42.5 N and ultrafine CDW_SLP (SLP) were designed as reference. These mixes did not include any additives. Three ratios were chosen: 50 wt.% SLP + 50 wt.% CEM I, 70 wt.% SLP + 30 wt.% CEM I and 90 wt.% SLP + 10 wt.% CEM I. The test scheme is shown in Table 2.1.

Table 2.1 Test scheme of the reference mortar mixes.

Mix design by mass (%)	Test	
	DME	Strength
SLP/CEM I		
90/10	X	x
70/30	x	x
50/50	x	x

Mixes with ground granulated blastfurnace slag (GGBS or slag) and CDW_SLP (SLP) were designed for the same ratios as for the reference mixes: 50 wt.% SLP + 50 wt.% GGBS, 70 wt.% SLP + 30 wt.% GGBS and 90 wt.% SLP + 10 wt.% GGBS. Sodium sulphate (Na_2SO_4) was incorporated using 0 %, 2 % and 4 % by mass of the sum of the precursors. Since slag is not a very rapid reacting material, the sodium sulfate is used as set regulator, but the optimum dosage still has to be established. For the biopolymer, BIO, 0.1 wt.% and 0.5 wt.% of the sum of the precursors was chosen. The mixes for the UPV and strength tests are shown in Table 2.2.

Table 2.2 Test scheme of the SLP/GGBS mortar mixes

Mix design by mass (%)			Test	
SLP/GGBS	Na ₂ SO ₄	BIO	DME	Strength
100/0	0	0	x	
		0.1	x	
		0.5	x	
	4	0	x	
90/10	0	0	x	x
		0.5	x	x
	2	0	x	x
		0.5	x	x
	4	0	x	x
		0.1	x	
		0.5	x	
70/30	0	0		x
	2	0	x	x
	4	0	x	x
		0.1	x	
		0.5	x	
50/50	0	0		x
	2	0	x	x
	4	0	x	x
		0.1	x	
		0.5	x	

Mixes with CDW_SLP, GGBS, Na₂SO₄ and BIO had been tested by UPV first. Only after the results were available, the most promising mixes have been casted as mortar bars for the strength development.

2.2 Materials

The following materials were used in this study:

- Precursors:
 - Concrete construction and demolition waste from railway sleepers (CDW_SLP) provided by Urban Mine, in this report named SLP for brevity.
 - ECO2CEM ground granulated blast-furnace slag (GGBS) supplied by Ecocem Benelux.
- Additives:
 - Sodium sulphate (Na₂SO₄) provided by Sigma Aldrich.
 - Biopolymer with WUR-id “ND IH304 ox DO 1” labelled as “BIO” in the current report.

Some specifications of the precursors are given in Table 2.3, a full analysis of the characteristics is given in Visser et al. [1].

Table 2.3: Characterization of the precursors SLP and GGBS.

	Solid density (kg/m ³)	D50 (um)	Surface area (m ² /g)	In demi-water:		
				pH (-)	Conductivity (S/m)	Zetapotential (mV)
SLP	2410	51.2	3.4	12.9	0.53	1.7
GGBS	2600	11.6	1.4	9.9	0.02	1.4

For the SLP, XRD analysis showed that the stream consists of quartz, portlandite, calcite, albite and ettringite as mineral phases. The quartz is likely from milled sand and gravel, while the calcite may come from either carbonated cement products (portlandite or CSH), aggregates or fillers. Ettringite is most likely a cement hydrate or alteration product. Most of the cement hydrates, however, will be amorphous, and cannot be analyzed in the XRD. The presence of the portlandite implies that not all cement paste of the sleepers is carbonated.

The SLP ultrafine is basic: when mixed with water it lead to a solution that has a pH of 12.9, indicative of an equilibrium with the calcium phases ($\text{Ca}(\text{OH})_2$ or calcium-poor CSH phases) and some alkali which leads to reasonably high conductivity of 0.53 S/m.

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.

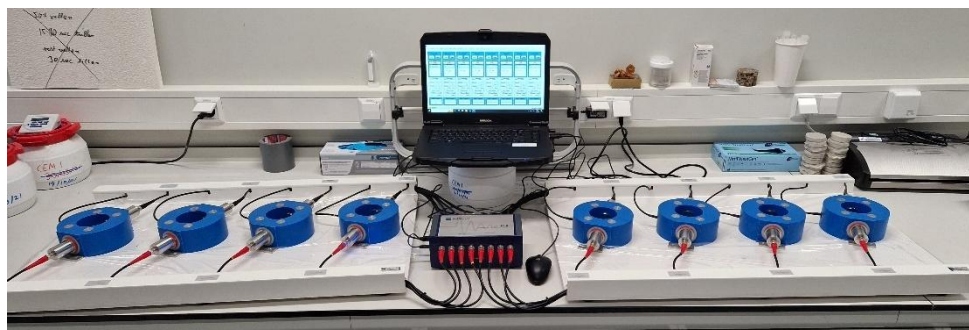


Figure 2.1 Experimental set up for the development of the dynamic E-modulus of elasticity by means of UPV.

The experiments were performed at the mortar lab of TNO in a controlled environment of 20 °C and 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.

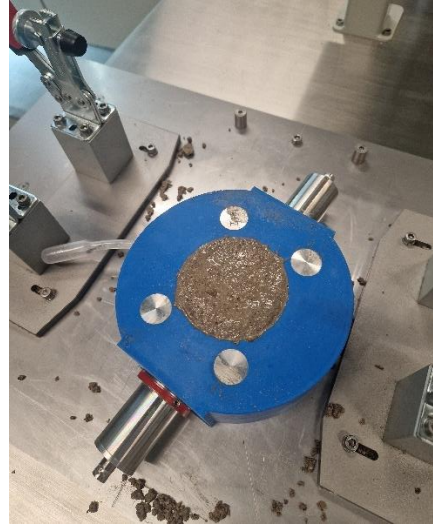


Figure 2.2 Mould filled and flattened on the compaction table.

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.

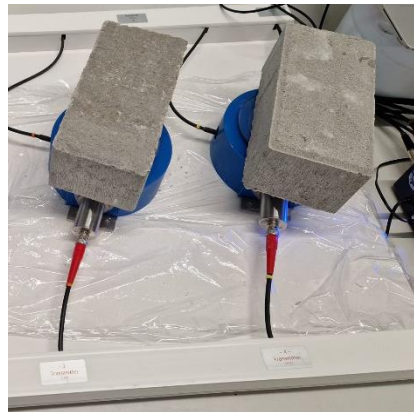


Figure 2.3 Covering of the moulds with plastic lid and dead weight on top.

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 cm³ is used.

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

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 days following the same procedure of section 2.4. Figure 2.4 gives a schematic overview of the process.

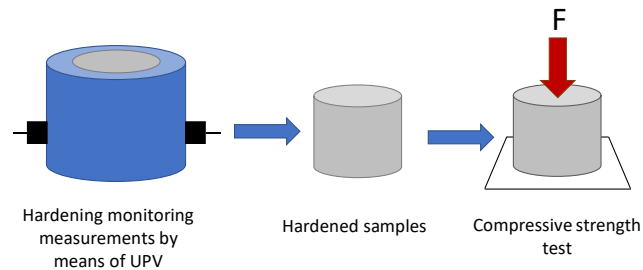


Figure 2.4 Compaction process for UPV measurements.

2.4 Mechanical properties on mortar bars

3-point bending strength and compressive strength have been determined on mortar bars. The samples are tested in two-fold at 7, 14 and 28 days. Figure 2.5 shows the set-up used for them mortar bars. The test followed the guidelines of NEN-EN 196-1:2016 [3].

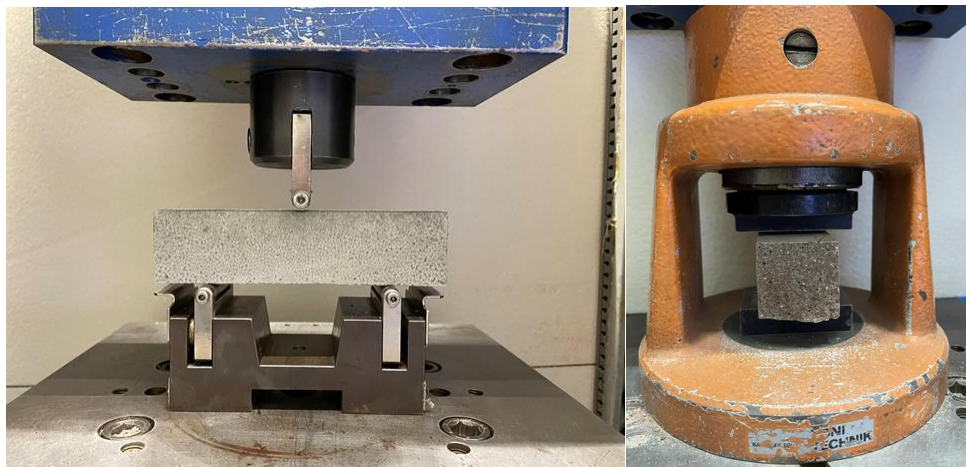


Figure 2.5 Experimental setup for 3 point bending strength and compressive strength.

2.5 Mix compositions

The mortar mixes were design with a similar earth-dry consistency using the results from the water demand presented in Visser et al [1] and with similar ratios between the paste and the aggregate content. Table 2.4 to Table 2.15 present the mass in kg per m³, volume in m³ per m³ and relevant data of the mixes with SLP and GGBS. The same information for the mixes with CEM I is presented in Table 2.16 to Table 2.18.

Table 2.4 Mortars mix design in mass 100% SLP + 0% GGBS.

Mix design in mass per m ³ (kg)				
	100SLP+ 0GGBS+ 0Na+0B	100SLP+ 0GGBS+ 4Na+0B	100SLP +0GGBS +0Na +0.1B	100SLP +0GGBS +0Na +0.5B
SLP_SLP	437	419	437	436
GGBS	0.0	0.0	0.0	0.0
Na2SO4	0.0	16.8	0.0	0.0
BIO	0.0	0.0	0.4	2.2
Water	154	153	153	154
Sand - EN 196	1553	1557	1552	1548
Water in Agg	47	47	47	46
Total Water	200	200	200	200
Total	2190	2193	2189	2186

Table 2.5 Mortars mix design in mass 90% SLP + 10% GGBS.

Mix design in mass per m ³ (kg)							
	90SLP+ 10GGBS+ 0Na+0B	90SLP+ 10GGBS+ 2Na+0B	90SLP+ 10GGBS+ 4Na+0B	90SLP+ 10GGBS+ 0Na+0.5B	90SLP+ 10GGBS+ 2Na+0.5B	90SLP +10GGBS +4Na +0.1B	90SLP +10GGBS +4Na +0.5B
SLP	383	379	373	386	379	379	378
GGBS	43	42	41	43	42	42	42
Na2SO4	0.0	8.4	16.6	0.0	8.4	16.9	16.8
BIO	0.0	0.0	0.0	2.1	2.1	0.4	2.1
Water	159	160	160	157	158	157	157
Sand - EN 196	1559	1552	1550	1555	1552	1552	1548
Water in Agg	47	47	47	47	47	47	46
Total Water	205	207	207	204	204	203	203
Total	2191	2189	2189	2190	2189	2194	2190

Table 2.6 Mortars mix design in mass 70% SLP + 30% GGBS.

Mix design in mass per m ³ (kg)				
	70SLP+ 30GGBS+ 2Na+0B	70SLP+ 30GGBS+ 4Na+0B	70SLP +30GGBS +4Na +0.1B	70SLP +30GGBS +4Na +0.5B
SLP	291.9	287.0	290.0	289.3
GGBS	125.1	123.0	124.3	124.0
Na2SO4	8.34	16.4	16.57	16.53
BIO	0	0	0.41	2.07

Mix design in mass per m ³ (kg)				
	70SLP+ 30GGBS+ 2Na+0B	70SLP+ 30GGBS+ 4Na+0B	70SLP +30GGBS +4Na +0.1B	70SLP +30GGBS +4Na +0.5B
Water	165.9	166.2	162.6	162.8
Sand - EN 196	1557.4	1555.9	1559.6	1555.8
Water in Agg	46.7	46.7	46.8	46.7
Total Water	212.6	212.9	209.4	209.5
Total	2195.3	2195.1	2200.2	2197.1

Table 2.7 Mortars mix design in mass 50% SLP + 50% GGBS.

Mix design in mass per m ³ (kg)				
	50SLP+ 50GGBS+ 2Na+0B	50SLP+ 50GGBS+ 4Na+0B	50SLP +50GGBS +4Na +0.1B	50SLP +50GGBS +4Na +0.5B
SLP	209.2	205.3	207.8	207.3
GGBS	209.2	205.3	207.8	207.3
Na ₂ SO ₄	8.37	16.42	16.62	16.58
BIO	0	0	0.42	2.07
Water	170.2	171.6	168.3	168.6
Sand - EN 196	1560.2	1556.7	1558.4	1554.4
Water in Agg	46.8	46.7	46.8	46.6
Total Water	217.0	218.3	215.1	215.3
Total	2203.9	2201.9	2206.0	2202.9

Table 2.8 Mortars mix design in volume 100% SLP + 0% GGBS.

Mix design in volume per m ³ (m ³)				
	100SLP+ 0GGBS+ 0Na+0B	100SLP+ 0GGBS+ 4Na+0B	100SLP +0GGBS +0Na +0.1B	100SLP +0GGBS +0Na +0.5B
SLP	0.18	0.17	0.18	0.18
GGBS	0.00	0.00	0.00	0.00
Na ₂ SO ₄	0.00	0.01	0.00	0.00
BIO	0.00	0.00	0.00044	0.0021
Water	0.15	0.15	0.15	0.15
Air	0.02	0.02	0.02	0.02
Sand - EN 196	0.60	0.60	0.60	0.60

Mix design in volume per m ³ (m ³)				
	100SLP+ 0GGBS+ 0Na+0B	100SLP+ 0GGBS+ 4Na+0B	100SLP +0GGBS +0Na +0.1B	100SLP +0GGBS +0Na +0.5B
Water in Agg	0.05	0.05	0.05	0.05
Total Water	0.20	0.20	0.20	0.20
Total	1	1	1	1

Table 2.9 Mortars mix design in volume 90% SLP + 10% GGBS.

Mix design in volume per m ³ (m ³)							
	90SLP+ 10GGBS +0Na+ 0 BIO	90SLP+ 10GGBS +2Na+ 0BIO	90SLP+ 10GGBS +4Na+ 0BIO	90SLP+ 10GGBS +0Na+ 0.5BIO	90SLP+ 10GGBS +2Na +0.5B	90SLP+ 10GGBS +4Na + 0.1BIO	90SLP+ 10GGBS +4Na + 0.5Bio
SLP	0.16	0.16	0.16	0.16	0.16	0.16	0.16
GGBS	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Na ₂ SO ₄	0.00	0.00	0.01	0.00	0.00	0.01	0.01
BIO	0.00	0.00	0.00	0.0021	0.0021	0.00042	0.0021
Water	0.16	0.16	0.16	0.16	0.16	0.16	0.16
Air	0.02	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	0.60
Water in Agg	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Total Water	0.21	0.21	0.21	0.20	0.20	0.20	0.20
Total	1	1	1	1	1	1	1

Table 2.10 Mortars mix design in volume 70% SLP + 30% GGBS.

Mix design in volume per m ³ (m ³)				
	70SLP+ 30GGBS+ 2Na+0B	70SLP+ 30GGBS+ 4Na+0B	70SLP +30GGBS +4Na +0.1B	70SLP +30GGBS +4Na +0.5B
SLP	0.12	0.12	0.12	0.12
GGBS	0.04	0.04	0.04	0.04
Na ₂ SO ₄	0.00	0.01	0.01	0.01
BIO	0.00	0.00	0.00042	0.0021
Water	0.17	0.17	0.16	0.17
Sand - EN 196	0.02	0.02	0.02	0.02
Water in Agg	0.60	0.60	0.60	0.59
Total Water	0.05	0.05	0.05	0.05
Total	0.21	0.21	0.21	0.21

Table 2.11 Mortars mix design in volume 50% SLP + 50% GGBS.

Mix design in volume per m ³ (m ³)				
	50SLP+ 50GGBS+ 2Na+0B	50SLP+ 50GGBS+ 4Na+0B	50SLP +50GGBS +4Na +0.1B	50SLP +50GGBS +4Na +0.5B
SLP	0.09	0.09	0.09	0.09
GGBS	0.07	0.07	0.07	0.07
Na₂SO₄	0.00	0.01	0.01	0.01
BIO	0.00	0.00	0.00042	0.0021
Water	0.17	0.17	0.17	0.17
Air	0.02	0.02	0.02	0.02
Sand - EN 196	0.60	0.60	0.60	0.60
Water in Agg	0.05	0.05	0.05	0.05
Total Water	0.22	0.22	0.22	0.22
Total	1	1	1	1

Table 2.12 Mortars mix design relevant properties 100% SLP + 0% GGBS.

	100SLP+ 0GGBS+ 0Na+0B	100SLP+ 0GGBS+ 4Na+0B	100SLP +0GGBS +4Na +0.1B	100SLP+ 0GGBS+ 0Na+0B
Theoretical Density (kg/m³)	2190	2190	2190	2190
Paste/Agg (kg/kg)	0.41	0.41	0.41	0.41
Paste/Agg (m³/m³)	0.67	0.67	0.68	0.68
w/b (kg/kg)	0.35	0.35	0.35	0.35
w/b (m³/m³)	0.84	0.85	0.84	0.84

Table 2.13 Mortars mix design relevant properties 90% SLP + 10% GGBS.

	90SLP+ 10GGBS+ 0Na+0B	90SLP+ 10GGBS+ 2Na+0B	90SLP+ 10GGBS+ 4Na+0B	90SLP+ 10GGBS+ 0Na+0.5B	90SLP+ 10GGBS+ 2Na+0.5B	90SLP +10GGBS +4Na +0.1B	90SLP +10GGBS +4Na +0.5B
Theoretical Density (kg/m³)	2190	2190	2190	2190	2190	2190	2190
Paste/Agg (kg/kg)	0.40	0.41	0.41	0.41	0.41	0.41	0.42

	90SLP+ 10GGBS+ 0Na+0B	90SLP+ 10GGBS+ 2Na+0B	90SLP+ 10GGBS+ 4Na+0B	90SLP+ 10GGBS+ 0Na+0.5B	90SLP+ 10GGBS+ 2Na+0.5B	90SLP +10GGBS +4Na +0.1B	90SLP +10GGBS +4Na +0.5B
Paste/Agg (m ³ /m ³)	0.67	0.67	0.68	0.67	0.67	0.68	0.68
w/b (kg/kg)	0.37	0.37	0.37	0.36	0.36	0.36	0.36
w/b (m ³ /m ³)	0.91	0.91	0.91	0.88	0.89	0.87	0.87

Table 2.14 Mortars mix design relevant properties 70% SLP + 30% GGBS.

	70SLP+ 30GGBS+ 2Na+0B	70SLP+ 30GGBS+ 4Na+0B	70SLP +30GGBS +4Na +0.1B	70SLP +30GGBS +4Na +0.5B
Theoretical Density (kg/m ³)	2200	2200	2200	2200
Paste/Agg (kg/kg)	0.41	0.41	0.41	0.41
Paste/Agg (m ³ /m ³)	0.67	0.67	0.67	0.68
w/b (kg/kg)	0.39	0.39	0.38	0.38
w/b (m ³ /m ³)	0.99	0.99	0.95	0.98

Table 2.15 Mortars mix design relevant properties 50% SLP + 50% GGBS.

	50SLP+ 50GGBS+ 2Na+0B	50SLP+ 50GGBS+ 4Na+0B	50SLP +50GGBS +4Na +0.1B	50SLP +50GGBS +4Na +0.5B
Theoretical Density (kg/m ³)	2200	2200	2200	2200
Paste/Agg (kg/kg)	0.41	0.41	0.42	0.42
Paste/Agg (m ³ /m ³)	0.67	0.67	0.67	0.67
w/b (kg/kg)	0.40	0.40	0.39	0.39
w/b (m ³ /m ³)	1.05	1.06	1.02	1.01

Table 2.16 Mortars mix design in mass - mixes with CEM I.

Mix design in mass per m ³ (kg)			
	50SLP + 50 CEMI	70SLP + 30 CEMI	90SLP + 10 CEMI
SLP	241	320	398

CEM I 42.5N	241	137	44
Water	162	156	154
Sand - EN 196	1548	1560	1558
Water in Agg	46	47	47
Total Water	208	203	201
Total	2238	2221	2201

Table 2.17 Mortars mix design in volume – mixes with CEM I.

Mix design in volume per m³ (m³)			
	50SLP + 50 CEMI	70SLP + 30 CEMI	90SLP + 10 CEMI
SLP	0.10	0.13	0.17
CEM I 42.5N	0.08	0.04	0.01
Water	0.16	0.16	0.15
Air	0.02	0.02	0.02
Sand - EN 196	0.60	0.60	0.60
Water in Agg	0.05	0.05	0.05
Total Water	0.21	0.20	0.20
Total	1.00	1.00	1.00

Table 2.18 Mortars mix design relevant properties – mixes with CEM I.

	50SLP+ 50GGBS+ 2Na+0B	50SLP+ 50GGBS+ 4Na+0B	50SLP +50GGBS +4Na +0.1B
Theoretical Density (kg/m³)	2240	2220	2220
Paste/Agg (kg/kg)	0.45	0.42	0.41
Paste/Agg (m³/m³)	0.64	0.63	0.63
w/b (kg/kg)	0.34	0.34	0.35
w/b (m³/m³)	0.89	0.94	0.83

3 Results

3.1 SLP / CEM I blends

Figure 3.1 presents the development of DME versus time for the mixes with CEM I and SLP. Two mixes with 100% CEM I with $w/b = 0.36$ and $w/b = 0.41$ have been measured in another project [4]. They are shown as reference. The results show that the 100 % SLP mix hardly hardens. The mix with only 10% CEM I has a minor improvement in comparison to the 100% SLP mix. After ca 6 days, it reaches a DME of 5 GPa. The mixes with 30% CEM I / 70% SLP and 50% CEM I / 50% SLP have a considerably higher DME at all ages, with 24 GPa and 30 GPa respectively at the end of the test. The mixes with only CEM I (regardless of the w/b ratio) have, however, a considerable higher.

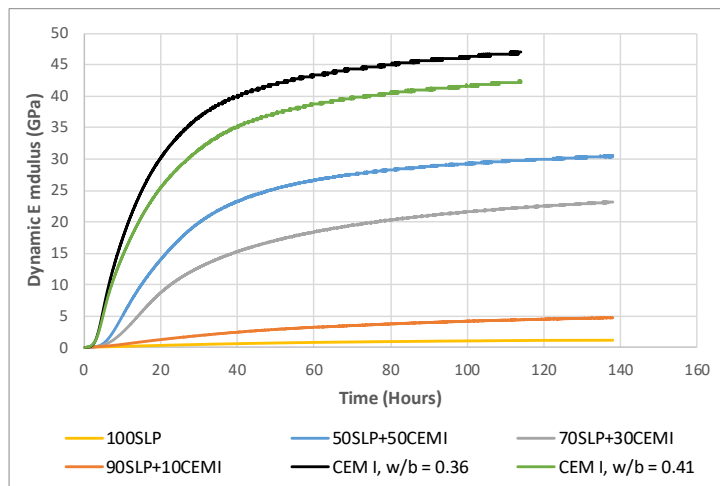


Figure 3.1 Development of DME vs. time for mixes with CEM I, the w/b of the mixes with SLP are 0.34-0.35 excluding the water in the SLP (see also Section 2.5).

Figure 3.2 presents the results of the compressive strengths on the cylinders after demoulding and storing until an age of 7 days. The sample with 100 % SLP and with 90 % SLP / 10% CEM I crumbled during the demoulding procedure, so the strength results are indicative only. The results indicate an inverse relationship between the compressive strength and the SLP content.

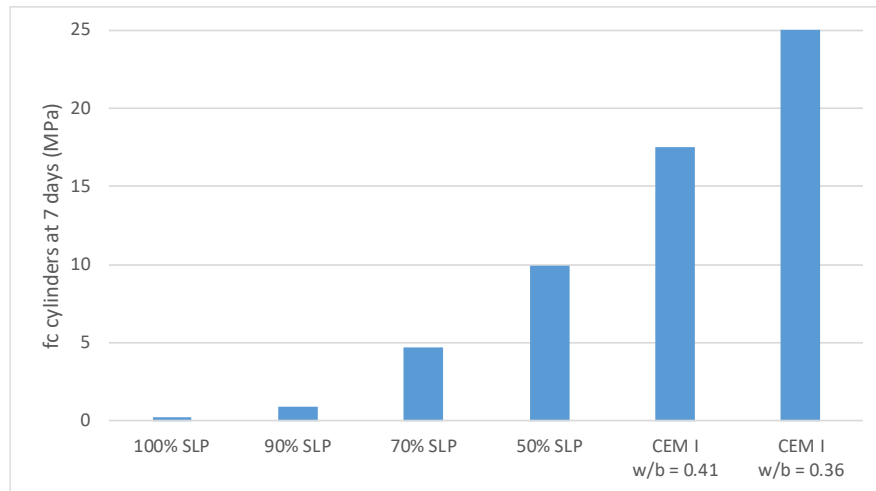


Figure 3.2 Compressive strength at 7 days for DEM cylinders with CEM I.

Figure 3.3 and Figure 3.4 show the results for the compressive and bending strength of the mortar bars with SLP/CEM I. The results at 28 days of the mixes with only CEM I are shown as reference. The results are comparable to the results obtained on the cylinders: the mixes with higher contents of CEM I reach higher strengths. The compressive strength difference between the 0 SLP / 100 % CEM I and the 50 % CEM I / 50 % SLP is considerable: the strength loss is more than 60 %. For the bending strength, the difference is lower, ca. 40-45 %.

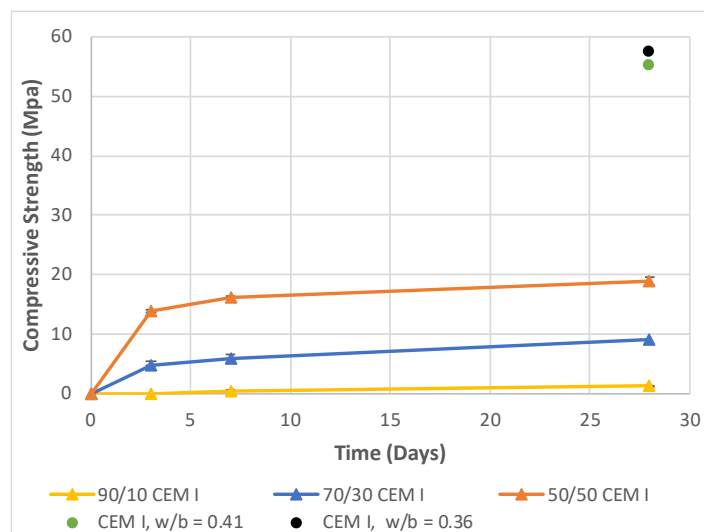


Figure 3.3 Compressive strength of mortar bars up to 28 days with SLP/CEM I.

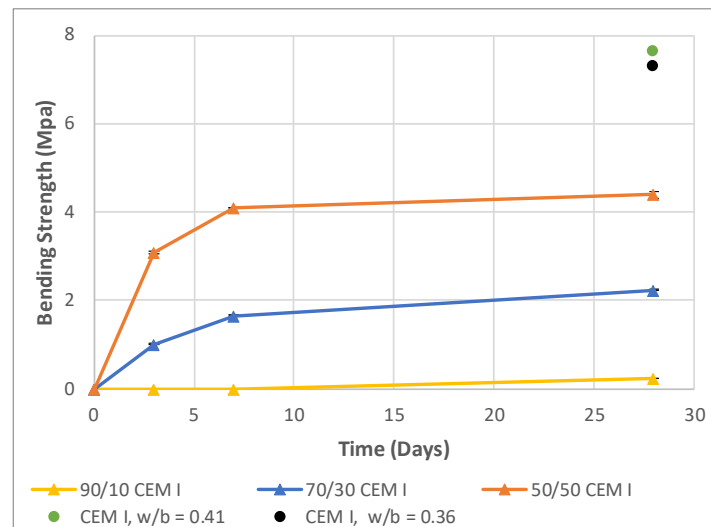


Figure 3.4 Bending strength of mortar bars up to 28 days with SLP/CEM I.

3.2 SLP / GGBS mixes

3.2.1 SLP / GGBS mixes without biopolymer

Figure 3.5 presents the results for the mixes with SLP and GGBS with variations in the sulfate content. The results have two main outcomes. First, for both 2 and 4% sulphate, an increase in GGBS increases the speed of the development of the DME and its final value. For example, for a sulphate content of 2%, in Figure 3.5(a) the mix reached a value of 20 GPa at 105 hours, in Figure 3.5(b) it took 45 hours and in Figure 3.5(c) only 30 hours. The second outcome is that for the same GGBS content, the mixes with higher sulphate content reach higher DME values. Based on this, it is not surprising that the mix with the highest DME is the mix with the largest amount of reactive components, 50% SLP + 50% GGBS + 4% Na_2SO_4 .

Looking at Figure 3.5(a), it is noted that the increment in DME from 0% Na_2SO_4 to 2% Na_2SO_4 is much larger than from 2 to 4 % Na_2SO_4 . When Na_2SO_4 , there is always an optimum value that gives the best performance of the binder. In this case, it is noted that the higher the amount of Na_2SO_4 , the smaller the improvement of the system. Thus it is likely that for 6% and larger Na_2SO_4 contents, the effect will be smaller or even negative. The optimum amount of Na_2SO_4 is also influenced by the GGBS content and the quality of the CDW.

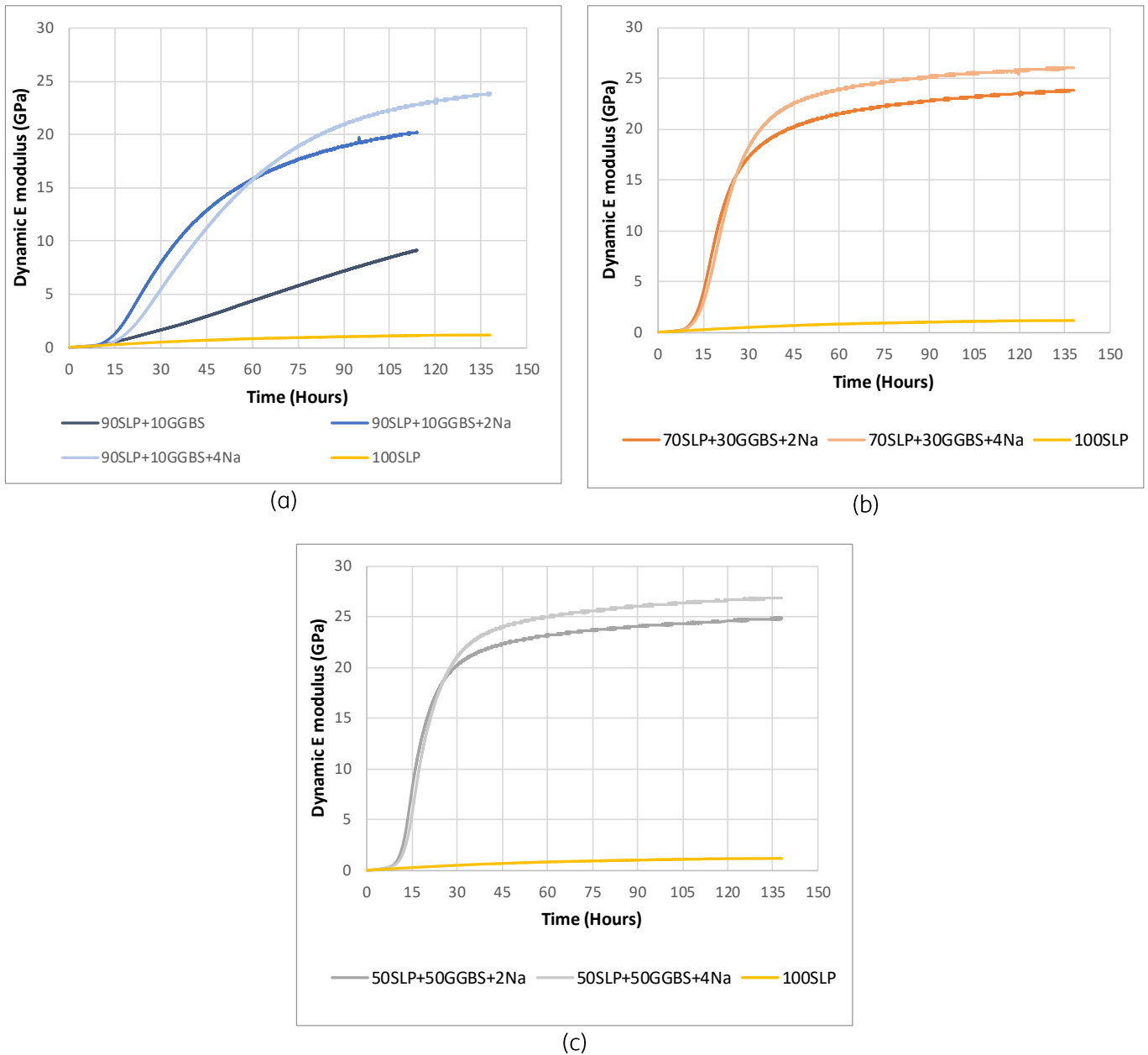


Figure 3.5 Development of DME vs. time for mixes with GGBS and Sodium sulphate. (a) 90% SLP, (b) 70% SLP and (c) 50% SLP.

3.2.1.1 SLP + GGBS + Na_2SO_4 + biopolymer mixes

Figure 3.6 presents the results for the mixes with SLP + GGBS + Na_2SO_4 + biopolymer in the following order: (a) mixes with only SLP, (b) with 90% SLP + 10% GGBS, (c) with 70% SLP + 30% GGBS and (d) with 50% SLP + 50% GGBS. In all the figures, the mix with only 100% SLP is presented as a reference. In general terms, it is observed that dynamic E-modulus of mixes with higher contents of GGBS develop faster; in most cases they also reach higher final values. The results for the mixes with only SLP show that the use of Na_2SO_4 improves the development of the DME (as shown in the previous section) while the biopolymer does not seem to have any positive effect. Contrary, it seems to slightly reduce the final value of the DME.

For the mixes with GGBS, it is observed that the use of the biopolymer delays the hardening. This effect is in general more pronounced as the GGBS content increases. For example, taking as a reference a value of 10 GPa for the DME, a comparison between the difference in time that takes for the mixes with only sodium sulphate and the mixes with 0.1% and 0.5 % biopolymer is as follows: For figure 3.6(b) the difference between the mix without biopolymer and the one with 0.1% is approximately 10 hours. Meanwhile, the mix 0.5% biopolymer did not reach this value within the length of the experiment. In figure 3.6(c), the difference between the mix with 0.1% is around 11.4 hours, with 0.5% is 101 hours. For figure 3.6(d), the values are 23.5 hours and 120 hours, respectively.

Despite of the delaying effect, it is noticed in figures 3.6(c) and 3.6(d) that the mixes with 0.1% biopolymer finally reach the same values. It is likely that if the experiment would have run longer also the mixes with 0.5% biopolymer would have reach the same values as the mixes with sulphates only.

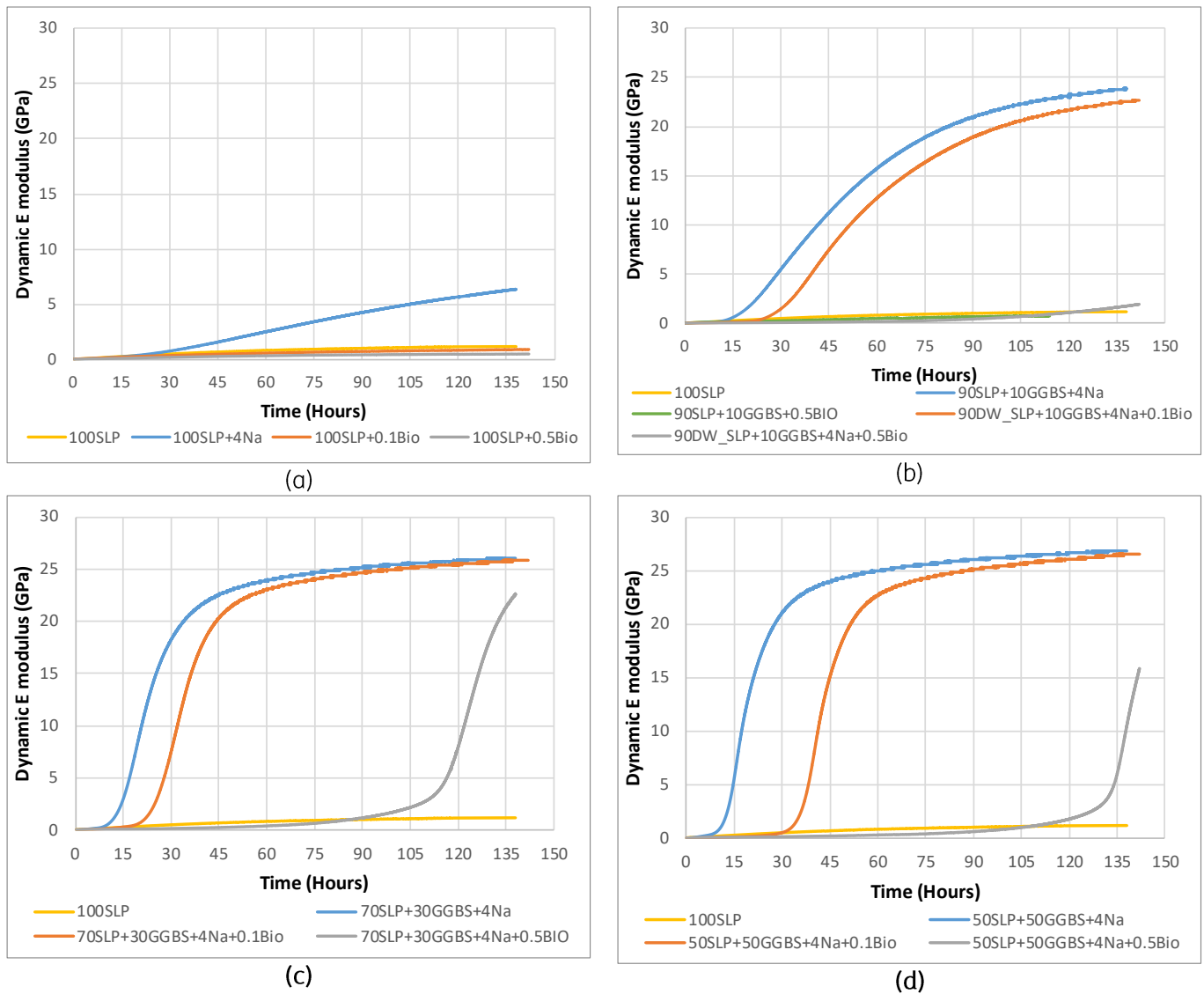


Figure 3.6 Development of DME vs. time for mixes with GGBS, Sodium sulphate and biopolymer. (a) 100% SLP, (b) 90% SLP, (c) 70% SLP and (d) 50% SLP.

3.2.2 Compressive strength of cylinders

Figure 3.7 presents the results for the mixes with SLP + GGBS + Na₂SO₄ + biopolymer in the following order: (a) mixes with only SLP, (b) with 90% SLP + 10% GGBS, (c) with 70% SLP + 30% GGBS and (d) with 50% SLP + 50% GGBS. The results are in line with those for the DME, where the mixes with higher content of GGBS and without biopolymer have the highest strengths. The mixes with only SLP show very low strengths. In most cases, they partially crumble upon demoulding. In terms of the sodium sulphate content, 3.7(b), (c) and (d) show that for the mixes without biopolymers, the mixes with 4% Na₂SO₄ have a higher strength than the mixes with 2%. Similarly, for the mixes with 4% Na₂SO₄, in almost all the cases an increase in the biopolymer content caused a reduction in the compressive strength of the samples. This is most clear for the mix 90% SLP + 10% GGBS + 4% Na₂SO₄ and 0.5% Bio, which partially crumbles upon demoulding like the mixes with only SLP. The mix with the highest compressive strength was the one with 70% SLP content and 4% Na₂SO₄ followed by the mix with 50% SLP and 4% Na₂SO₄.

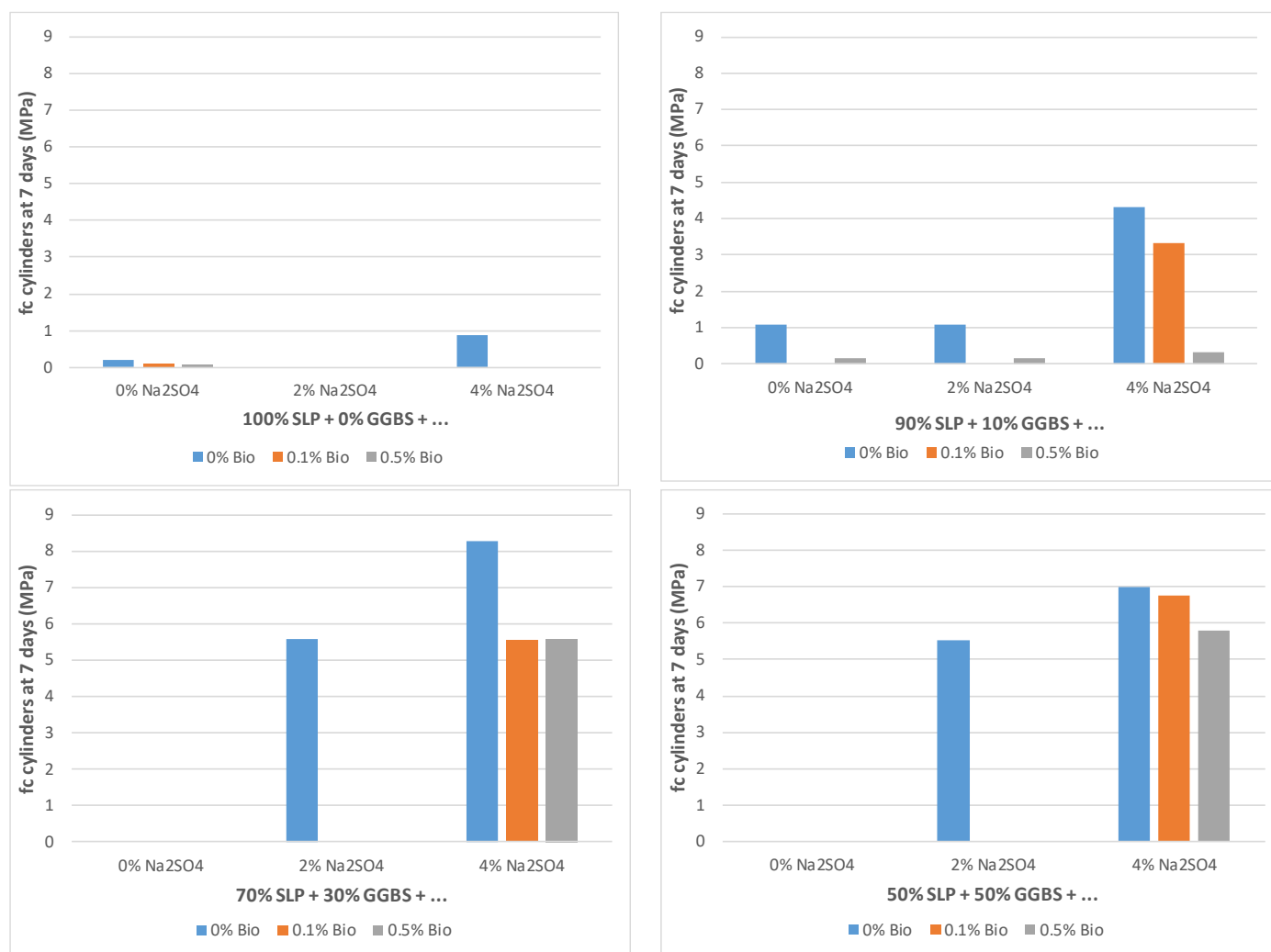


Figure 3.7 Compressive strength at 7 days for DME cylinders with variations of GGBS, sodium sulfate and biopolymer content. (a) 100% SLP, (b) 90% SLP, (c) 70% SLP and (d) 50% SLP.

3.2.3 Compressive strength of the mortar bars

Figure 3.8 presents the results for the mixes with SLP and GGBS with variations in the sulfate. Only in figure 3.8(a) mixes with biopolymer are presented. In the other 2 figures, only variations in the sodium sulphate content are shown. For figure 3.8(a), the mixes with sodium sulfate reach the highest strength at all ages, while the mixes with biopolymers do not harden even after 28 days. In figures 3.8(b) and (c), a similar behaviour was observed despite of the GGBS content. At early ages, in both cases, the mixes with sodium sulphate reached higher strengths, but at 28 days the mixes without this set regulator reached a higher compressive strength. The mixes with 4% sodium sulfate content have at all ages a higher strength than the mixes with 2% regardless of the GGBS content.

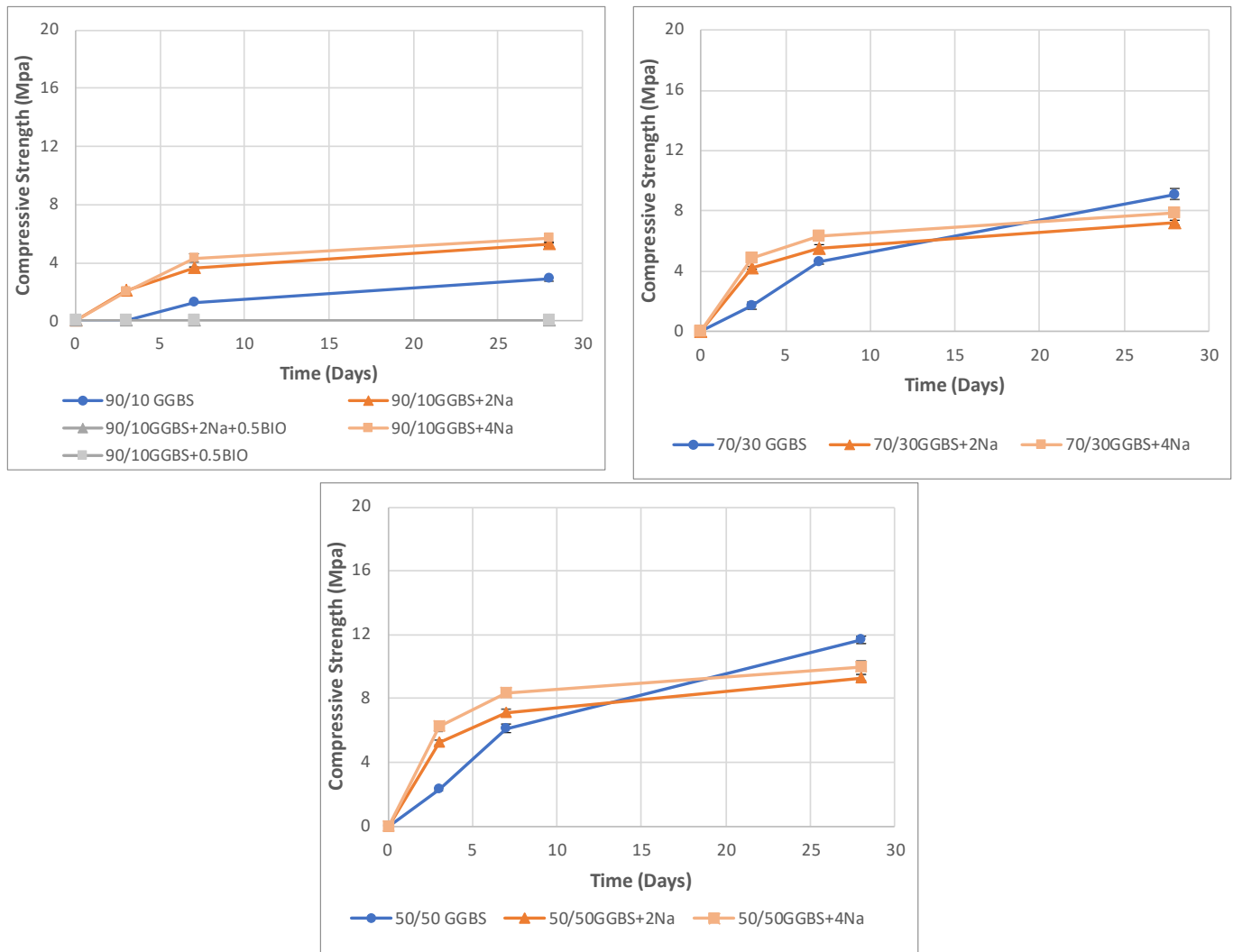


Figure 3.8 Compressive strength mortar bars up to 28 days with variations of GGBS and sodium sulfate. (a) 90% SLP, (b) 70% SLP and (c) 50% SLP.

3.2.4 Bending strength of the mortar bars

Figure 3.9 presents the results for the mixes with SLP and GGBS with variations in the sulfate using the same order as shown for the compressive strength. In general, the results obtained show the same trend as for the compressive strength. First, the mixes with biopolymers did

not reach any strength after 28 days (Figure 3.9(a)). Second, for the mixes with sodium sulphate, higher sulfate content resulted in higher strengths at all ages, regardless of the GGBS content. Third, in figures 3.9(b) and (c), the mixes with sulphate developed higher mechanical properties at early ages, but at 28 days the mixes without sodium sulphate reach similar or higher values.

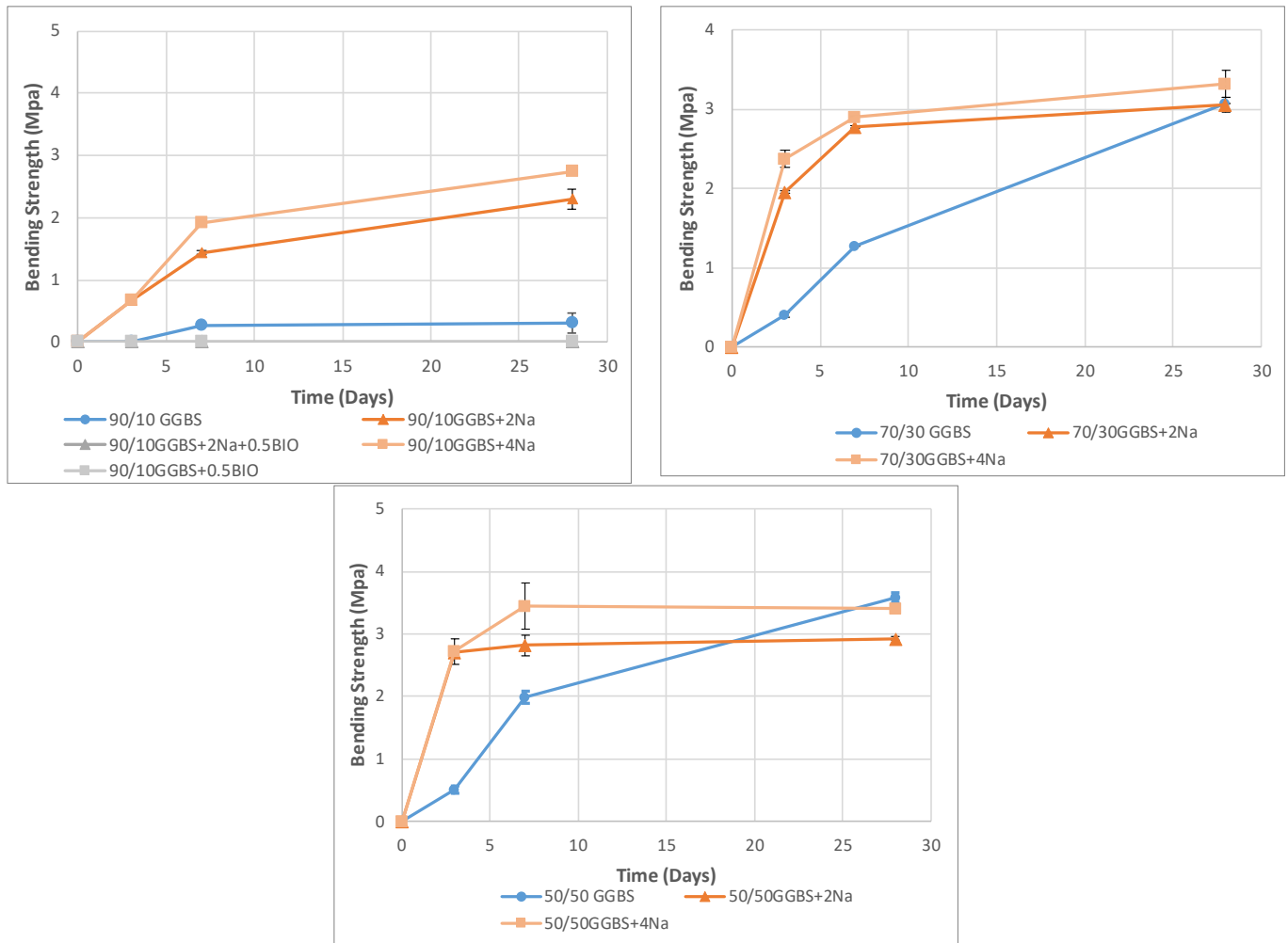


Figure 3.9 Bending strength mortar bars up to 28 days with variations of GGBS and sodium sulfate. (a) 90% SLP, (b) 70% SLP and (c) 50% SLP.

4 Analysis and discussion

4.1 Relation between SLP content vs. DME and compressive strength for DME cylinders

4.1.1 SLP content vs DME

Figure 4.1 presents the comparison between the SLP content and the DME value at the end of the test. The subfigures are divided as follows: 4.1(a) Mixes with variations in the GGBS and sodium sulphate content, 4.1(b) Mixes with variations of GGBS and biopolymer content and a fix amount of sodium sulfate (4%) and 4.1 (c) mixes with a variable amount of CEM I. In subfigures (a) and (b), there are dotted lines between 90% and 100% SLP content, indicating that the latter was not measured and the value shown is an estimated based on the results of the other mixes.

In 4.1(a), the mixes with 4% Na_2SO_4 always have a higher DME value regardless the SLP content. By increasing the GGBS content with only 10%, the DME value has a large increment from 6 GPa to 20 and 24.5 GPa for the mixes with 2% and 4% sodium sulfate, respectively. However, as the concentration rises from 10% to 30%, the increase in the DME is smaller, and reduces further from 70% to 50%. This indicates that the influence of the GGBS in the DME decreases as larger amounts are added. It is unlikely that mixes with higher values of GGBS would result in a DME significantly higher than the ones obtained. In 4.1(b), in comparison to the mix without biopolymer, the impact of adding 0.1% biopolymer is minimal, while adding 0.5% significantly reduces the final DME value. Based on the results of 4.1(a) and (b), the best results are obtained with 50% GGBS, 4% sodium sulfate and without biopolymers.

For the mixes with CEM I, the highest DME was obtained for the mix with 50% CEM I and 50% SLP, which was also higher than the mixes with GGBS. The DME decreased as the CEM I content was reduced. However, the mix 90% SLP + 10% CEM I had a lower DME than the mix with 100% SLP. It is likely that since CEM I dissolves at a much higher rate than the SLP, the dissolution of the small amount of CEM I in the mix 90% SLP + 10% CEM I resulted in saturation of the solution with (mainly) calcium ions, hampering the dissolution of the SLP. When combined with CEM I, SLP acts as a filler. It is likely that a mix with 70% CEM I and 100% CEM I would result in a DME higher than the ones obtained. Comparison between the systems with GGBS and with CEM I show that they perform very similar around 70% SLP content. If this value is increased to 90%, the mixes with GGBS performed better. If this value is reduced to 50% (or lower), the mixes with CEM I will perform better.

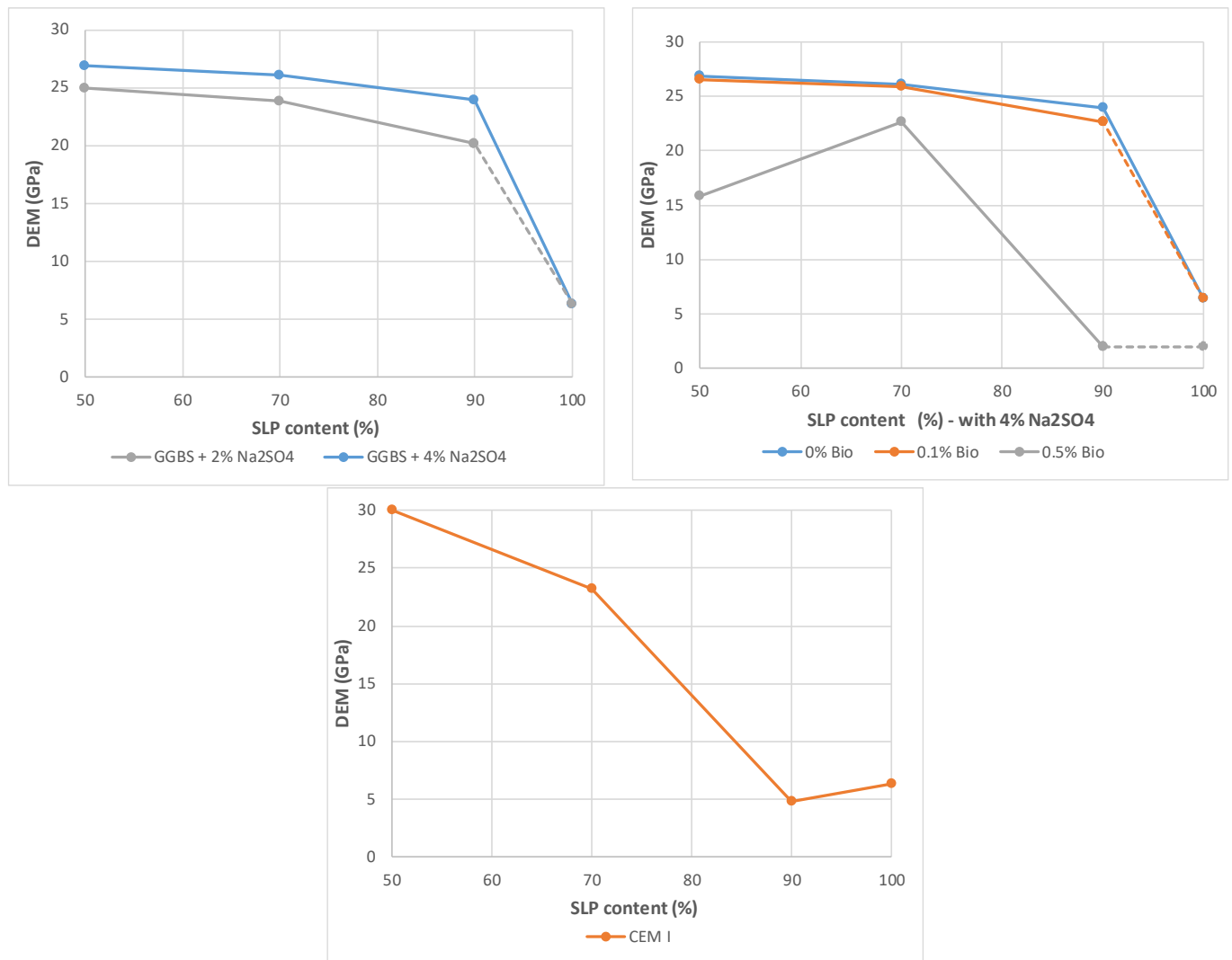


Figure 4.1 DME measurements vs. CDW content for different set of mixes. (a) 2% and 4% sodium sulfate, (b) 4% sodium sulfate with biopolymer and (c) CEM I.

4.1.2 SLP content vs f_c at 7 days

Figure 4.2 presents the comparison between the SLP content and compressive strength (f_c) of the cylinders at 7 days. The figure is subdivided in the same way as in Figure 4.1. Dotted lines are also included to indicate theoretical values that could be obtained for some mixes with 100% SLP content. The results show similar trends with those presented in Figure 4.1. In 4.2(a), the mixes with higher sodium sulphate show a higher strength regardless the SLP content. Compared to the DME, the difference in compressive strength was larger between the mixes with 2% and 4% sodium sulfate. In 4.2(b), the mixes without biopolymer performed better than the ones with it. The mixes with 50% and 90% SLP and 0.1% biopolymer have a similar performance as the ones without biopolymer, but there is a large difference in strength for the mix with 70% SLP. The SLP mixes with 0.5% biopolymer had the lowest strengths, especially with 90% SLP, the strength was considerably lower. The mixes with CEM I in 4.2(c)s show the same trend as for the DME. As the SLP act as a filler, the higher the amount of SLP, the lower the strength.

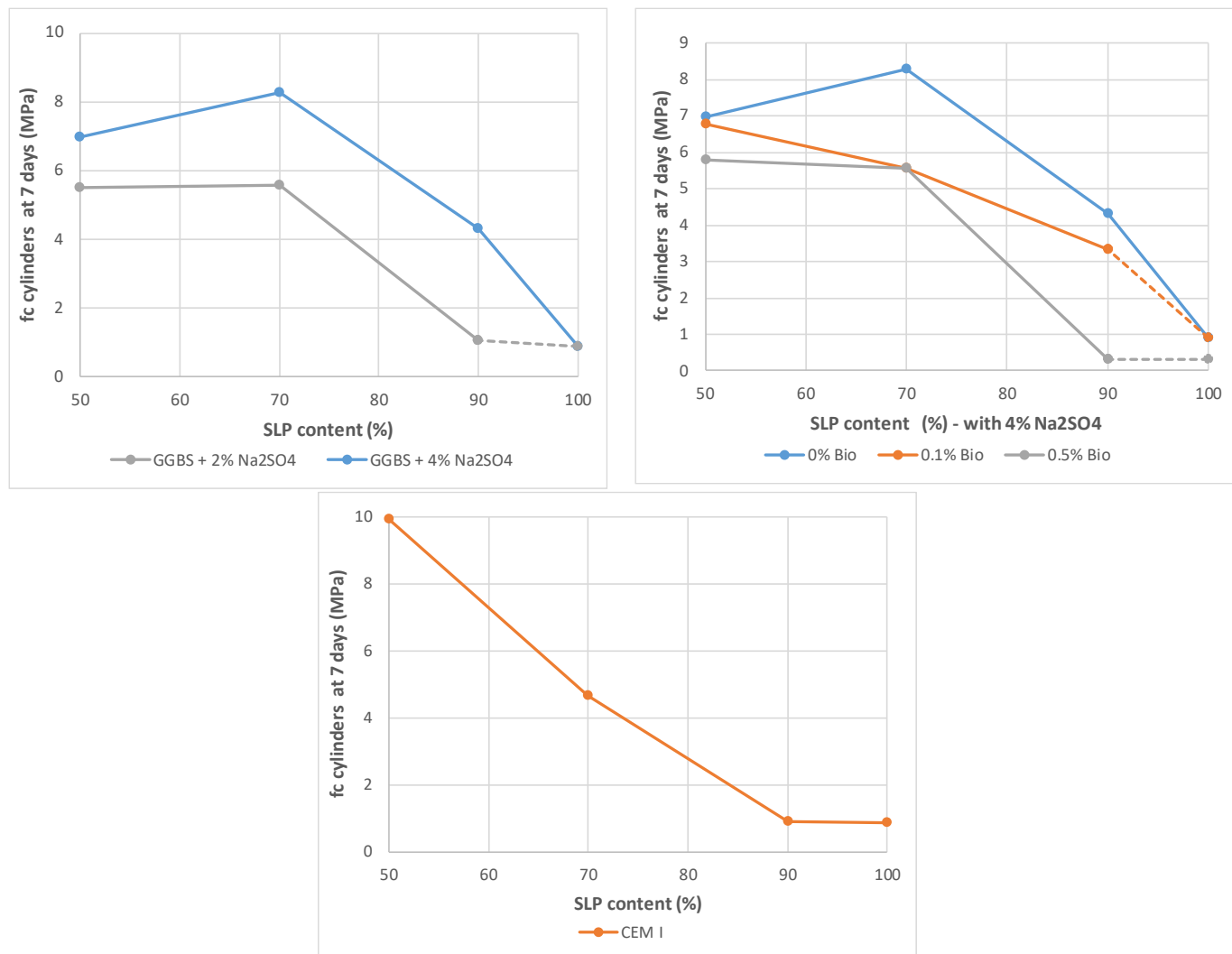


Figure 4.2 f_c at 7 days vs. CDW content for different set of mixes. (a) 2% and 4% sodium sulfate, (b) 4% sodium sulfate with biopolymer and (c) CEM I.

4.2 Relation between SLP content vs. compressive strength at 28 days for mortar bars

Figure 4.3 shows the relation between the SLP content and the strength at 28 days for the mortar bars. The results for 100% SLP and 100% SLP + 2% Na₂SO₄ were taken from [2]. The results show a similar trend as the one obtained for the DME samples. For the mixes with GGBS, the mixes with 50% and 70% SLP without sodium sulfate show the highest compressive strength. For the same SLP content, the mixes with 2 and 4 % sodium sulfate had similar strengths. The mixes with 90% SLP showed a reduction in strength regardless of the sodium sulfate content, with only 3.5 MPa for the mix without sodium sulfate. The mix with only SLP did not harden after 28 days, the one with 2% sodium sulfate reached a very low compressive strength.

For the mixes with CEM I, the blend with 50% SLP had the highest strength, while the mix with 70% SLP had a similar strength as the mixes with GGBS. The mix with 90% SLP had a strength lower than the mixes with GGBS.

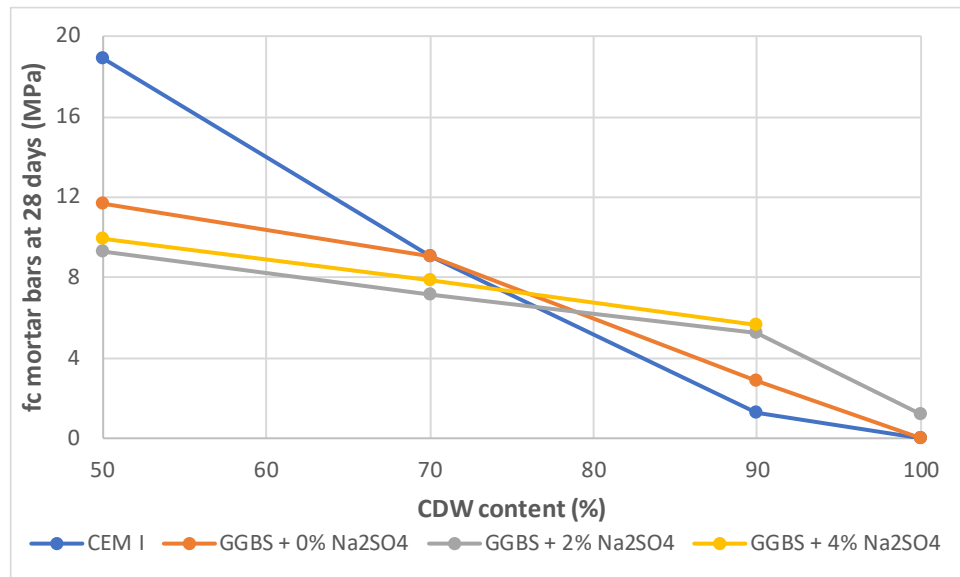


Figure 4.3 f_c at 28 days vs. CDW content for mixes with GGBS + Na₂SO₄ and CEM I.

4.3 Relation between DME values vs compressive strength of mortar bars at 7 days

The DME was measured up to different ages, mostly between 4 and 6 days. Therefore, the DME was projected to 7 days and then compared with the compressive strength of the mortar bars. Based on the experience of the authors, the development of the DME can be described using an exponential function as the one presented in equation (2). For this case, the 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 the data properly, especially when a delay effect is present (See

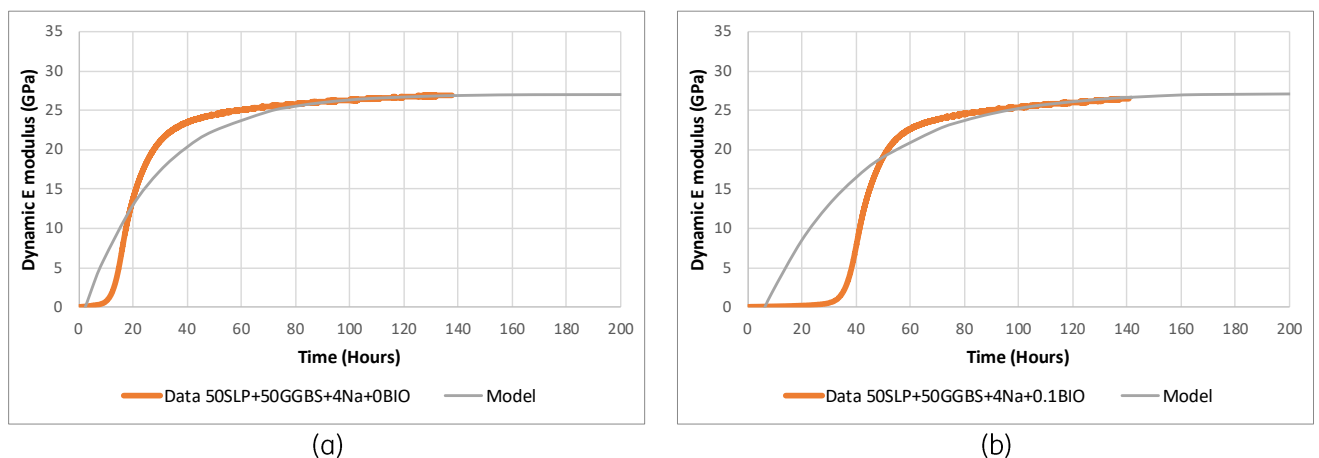


Figure 4.4). In this case, the parameter t_x is used to shift the graph horizontally helping to find the best fit.

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

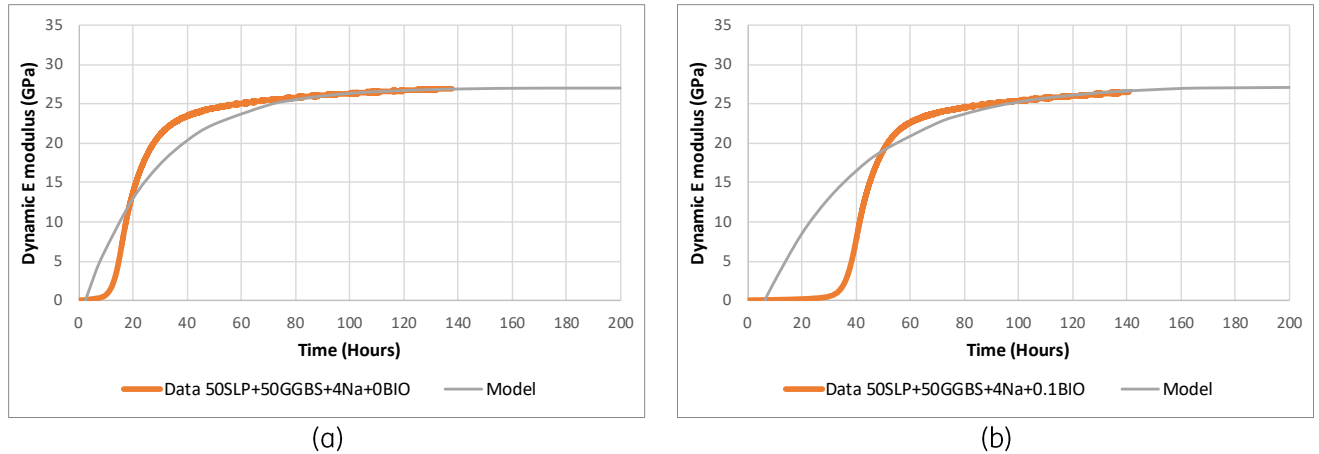


Figure 4.4 Data fitted for DME using experimental data from the IP 8 UPV.

Once all the DME data are projected to 7 days, they are plotted against the compressive strength of the mortar bars at the same age (Figure 4.5). However, Equation (1) in section 2.3, assumes that the specimens must have sufficient strength, otherwise, the DME values obtained are not valid. For this reason the samples that had compressive strengths lower than 5 MPa were discarded, leaving only the mixes with 70% and 50% SLP content for the correlation. In Figure 4.5, the mixes with 90% SLP content are shown for visualization purposes only. A good coefficient of determination was obtained with a value of 0.91, indicating that the results of the DME can be used to estimate the compressive strength of the mortar bars at 7 days.

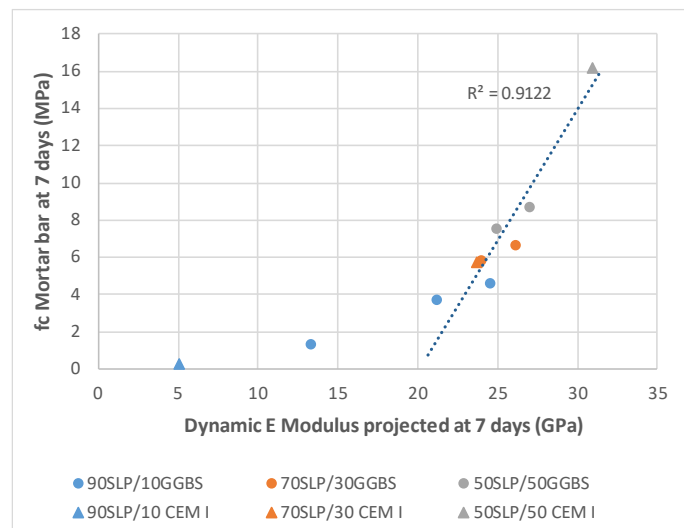


Figure 4.5 Relationship between DME of the cylinders and compressive strength (f_c) of the mortar bars at 7 days.

5 Conclusions

Two series of mixes with SLP were tested. The first using GGBS, Na_2SO_4 and a biopolymer to enhance the mechanical properties and the second using CEM I instead of GGBS. The first series show that a higher content of GGBS increases the mechanical properties of the mixes. Higher sodium sulfate contents increase the mechanical properties up to 7 days. However, at 28 days, the mixes with SLP contents of 50% and 70% reach higher strengths without sodium sulfate. The use of the biopolymer hampered the hydration process of all mixes regardless of their SLP or sodium sulfate content.

In the mixes with CEM I, SLP works as filler. Therefore, lower concentrations of CEM I will always result in lower mechanical properties at all ages. The mixes with 30% SLP performed similar using either CEM I or GGBS with sodium sulfate. At 50% SLP, the mix with CEM I performed better than the ones with GGBS, being the mixes with the highest mechanical properties. At 90% SLP content, the mixes with GGBS performed better than the one with CEM I.

The DME measurements using IP8 UPV proofed to be a good technique to assess the compressive strength of the mixes at 7 days. It is important to realize that any reactions other than those that took place during measurement of the DME will affect the relationship between DME and compressive strength at later ages, possibly resulting in wrong predictions.

6 References

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7 Signature

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