

Mechanical Properties of Hybrid Cement Based Mortars Containing Two Biopolymers

Z. Abdollahnejad, M. Kheradmand, F. Pacheco-Torgal

Abstract—The use of bio-based admixtures on construction materials is a recent trend that is gaining momentum. However, to our knowledge, no studies have been reported concerning the use of biopolymers on hybrid cement based mortars. This paper reports experimental results regarding the study of the influence of mix design of 43 hybrid cement mortars containing two different biopolymers on its mechanical performance. The results show that the use of the biopolymer carrageenan is much more effective than the biopolymer xanthan concerning the increase in compressive strength. An optimum biopolymer content was found.

Keywords—Waste reuse, fly ash, waste glass, hybrid cement, biopolymers, mechanical strength.

I. INTRODUCTION

WASTE reuse is crucial not only to avoid putting pressure on non-renewable raw materials but also the environmental degradation associated to waste landfill [1]. Some wastes like fly ash (FA) deserve an especial attention because they are generated in high amount and have a very low reuse rate [2]. Waste soda lime silicate glass is also generated in relevant quantities and that merits increase recycling efforts. In Hong Kong, approximately 373 tons of waste glass are generated daily in 2010. It was estimated that the total amount of waste glass generated in the EU-27 in 2007 was 25.8 Mt [3]. Hybrid cements involve the activation of industrial wastes with alkaline activators, usually composed by hydroxide, silicate, carbonate, or sulfate leading to co-precipitation of two gels (C-S-H + N-A-S-H), but over time a C-A-S-H type gel would be the most thermodynamically stable product [4], [5]. These materials have a particular ability for the reuse of several types of wastes [6], [7]. Therefore, the valorization of FA and waste glass in hybrid cement would have obvious environmental benefits. In this context, this paper reports results of compressive strength of several FA and waste glass hybrid mortars containing two biopolymers.

II. EXPERIMENTAL PROGRAM

A. Materials and Design

The raw materials used for the preparation of the hybrid cement mortars were FA (FA), calcium hydroxide (CH), fine aggregate, milled glass (MG) and sodium hydroxide solution. The FA was obtained from The PEGO Thermal Power Plant in Portugal and it was classified as class F according to ASTM-C618 standard. The chemical composition of the FA

Fernando Torgal is with the University of Minho Portugal (e-mail: torgal@civil.uminho.pt).

selected for this study is presented in Table I.

TABLE I
CHEMICAL COMPOSITION AND PHYSICAL PROPERTIES OF FA

Composition	(wt. %)
SiO ₂	60.81
Al ₂ O ₃	22.68
Fe ₂ O ₃	7.64
MgO	2.24
Na ₂ O	1.45
CaO	1.01
TiO ₂	1.46
K ₂ O	2.70
Physical properties	
Specific gravity	2.30
Specific surface (cm ² /g)	3430

The CH used in this study had a commercial name of Lusical H100 and chemical composition of Ca(OH)₂ ≥ 93% and MgO ≤ 3. Waste glass was provided by the use of glass bottles that were ground for 1h in a ball mill. The density of the MG was 1.27 g/cm³. Solid sodium hydroxide which was obtained from commercially available product of ERCROS, S.A., Spain, was used to prepare three solutions with different concentration (4 M and 12 M). The chemical composition of the sodium hydroxide was composed of 25%Na₂O and 75%H₂O. A sand/binder ratio of 4 was used. The sand was used as inert filler provided from the MIBAL, Minas de Barqueiros, S.A. Portugal. Two activator/binder ratios were used (0.4 and 0.5). Two biopolymers carrageenan and xanthan were provided by Melbourne Food Depot. Xanthan is a natural polysaccharide, which is produced by a biotechnological process involving fermentation of glucose or sucrose by the *Xanthomonas campestris* bacterium. Carrageenan is a natural high-molecular-weight polysaccharide, purified extract from red seaweed. Different contents of biopolymers were used in the mix compositions, including 0.05%, 0.1%, 0.15% (in weight of binder). The 43 mix compositions are listed in Table II.

B. Production and Testing

During production, FA was mixed with fine aggregate, CH, milled waste glass and biopolymer powder for 2 min. Then, the alkali activator solution was added and mixed for 5 min. Mortars were cast into cubic molds (50×50×50 mm³). After 24h, specimens were demolded and cured in laboratory conditions (25 °C and 65%RH). Compressive strength testing was carried out after seven days with respect to the recommendations of the European standard EN1015-11.

TABLE II
MIX COMPOSITIONS (KG/M³)

Mixtures	FA	Sand	SS	SH
90FA_10CH_4M_2SS/SH_0.8A/B	379	1685	269	134
90FA_10CH_4M_1SS/SH_0.8A/B	379	1685	169	169
80FA_10CH_10MG_4M_2SS/SH_0.8A/B	332	1664	222	111
90FA_10CH_8M_2SS/SH_0.8A/B	379	1685	269	134
90FA_10CH_8M_1SS/SH_0.8A/B	379	1685	169	169
80FA_10CH_10MG_8M_2SS/SH_0.8A/B	332	1664	222	111
90FA_10CH_4M_2SS/SH_0.8A/B_0.05CAR	379	1685	269	134
90FA_10CH_4M_1SS/SH_0.8A/B_0.05CAR	379	1685	169	169
80FA_10CH_10MG_4M_2SS/SH_0.8A/B_0.05CAR	332	1664	222	111
90FA_10CH_8M_2SS/SH_0.8A/B_0.05CAR	379	1685	269	134
90FA_10CH_8M_1SS/SH_0.8A/B_0.05CAR	379	1685	169	169
80FA_10CH_10MG_8M_2SS/SH_0.8A/B_0.05CAR	332	1664	222	111
90FA_10CH_4M_2SS/SH_0.8A/B_0.1CAR	379	1685	269	134
90FA_10CH_4M_1SS/SH_0.8A/B_0.1CAR	379	1685	169	169
80FA_10CH_10MG_4M_2SS/SH_0.8A/B_0.1CAR	332	1664	222	111
90FA_10CH_8M_2SS/SH_0.8A/B_0.1CAR	379	1685	269	134
90FA_10CH_8M_1SS/SH_0.8A/B_0.1CAR	379	1685	169	169
80FA_10CH_10MG_8M_2SS/SH_0.8A/B_0.1CAR	332	1664	222	111
90FA_10CH_4M_2SS/SH_0.8A/B_0.15CAR	379	1685	269	134
90FA_10CH_4M_1SS/SH_0.8A/B_0.15CAR	379	1685	169	169
80FA_10CH_10MG_4M_2SS/SH_0.8A/B_0.15CAR	332	1664	222	111
90FA_10CH_8M_2SS/SH_0.8A/B_0.15CAR	379	1685	269	134
90FA_10CH_8M_1SS/SH_0.8A/B_0.15CAR	379	1685	169	169
80FA_10CH_10MG_8M_2SS/SH_0.8A/B_0.15CAR	332	1664	222	111
90FA_10CH_4M_2SS/SH_0.8A/B_0.05XAN	379	1685	269	134
90FA_10CH_4M_1SS/SH_0.8A/B_0.05 XAN	379	1685	169	169
80FA_10CH_10MG_4M_2SS/SH_0.8A/B_0.05 XAN	332	1664	222	111
90FA_10CH_8M_2SS/SH_0.8A/B_0.05 XAN	379	1685	269	134
90FA_10CH_8M_1SS/SH_0.8A/B_0.05 XAN	379	1685	169	169
80FA_10CH_10MG_8M_2SS/SH_0.8A/B_0.05 XAN	332	1664	222	111
90FA_10CH_4M_2SS/SH_0.8A/B_0.1 XAN	379	1685	269	134
90FA_10CH_4M_1SS/SH_0.8A/B_0.1 XAN	379	1685	169	169
80FA_10CH_10MG_4M_2SS/SH_0.8A/B_0.1 XAN	332	1664	222	111
90FA_10CH_8M_2SS/SH_0.8A/B_0.1 XAN	379	1685	269	134
90FA_10CH_8M_1SS/SH_0.8A/B_0.1 XAN	379	1685	169	169
80FA_10CH_10MG_8M_2SS/SH_0.8A/B_0.1 XAN	332	1664	222	111
90FA_10CH_4M_2SS/SH_0.8A/B_0.15 XAN	379	1685	269	134
90FA_10CH_4M_1SS/SH_0.8A/B_0.15 XAN	379	1685	169	169
80FA_10CH_10MG_4M_2SS/SH_0.8A/B_0.15 XAN	332	1664	222	111
90FA_10CH_8M_2SS/SH_0.8A/B_0.15 XAN	379	1685	269	134
90FA_10CH_8M_1SS/SH_0.8A/B_0.15 XAN	379	1685	169	169
80FA_10CH_10MG_8M_2SS/SH_0.8A/B_0.15 XAN	332	1664	222	111

III. RESULTS AND DISCUSSION

A. Compressive Strength

The results of the compressive strength after seven days curing of hybrid cement mortar mixtures without biopolymers are shown in Fig. 1, The mixture 80FA_10CH_10MG_2SS/SH_0.8A/B shows the highest compressive strength of around 9 MPa. It is worth remembering that this mechanical performance is high enough for several construction applications, like for use in renders and for masonry units. The explanation lies in the fact that, for low sodium hydroxide concentrations, the main hydration product formed is a CSH gel [8], [9]. The replacement of 10% FA by milled waste glass shows a relevant increase on the short term compressive

strength of around 30%. The waste glass provides reactive silica that contributes to the increase of the compressive strength. The reduction of sodium silicate/sodium hydroxide ratio from 2 to 1 shows no influence on the compressive strength for both sodium hydroxide concentrations. Increasing the replacement of FA from 10% to 20 wt.% by the MG as well as decreasing the ratio of sodium silicate to sodium hydroxide from 2 to 1, reduced the compressive strength of the mix composition of 80FA_10CH_10MG_4M_2SS/SH_0.8A/B about 30%. This is because silica from waste glass is not as reactive as liquid Na₂SiO₃. Fig. 2 shows the compressive strength of hybrid cement mortar mixtures with biopolymer carrageenan and cured at ambient temperature during seven days. The biopolymer carrageenan increased compressive

strengths of mixtures 90FA_10CH_2SS/SH_0.8A/B and 90FA_10CH_1SS/SH_0.8A/B. This increment was higher for these mixtures with 4 M sodium hydroxide concentration. Due to addition of carrageenan, the maximum compressive strength and the maximum increase of compressive strength was about 17 MPa and 3 times, respectively for the mix mixture 90FA_10CH_2SS/SH_0.8A/B with 0.15% of carrageenan. For mixture 80FA_10CH_10MG_2SS/SH_0.8A/B with molar concentration of 4 mol/L, the compressive strength increased by increasing the content of carrageenan up to 0.1%, while increasing the content of carrageenan to 0.15% reduced the compressive strength. Conversely, by increasing the molar concentration from 4 mol/L to 8 mol/L, increasing the content of carrageenan up to 0.15% resulted in recording the maximum compressive strength (16.2 MPa for mixture 80FA_10CH_10MG_2SS/SH_0.8A/B. Fig. 3 shows the compressive strength of AACB mixtures with biopolymer xanthan and cured at ambient temperature during 7 days. Xanthan is not as effective as carrageenan to enhance compressive strength. With the exception of 90FA_10CH_8M_1SS/SH_0.8A/B_0.1XAN, addition of Xanthan has no significant effect on increasing the compressive strength of mix compositions. The maximum compressive strength and increase of compressive strength due to addition of Xanthan were recorded about 13 MPa and 2 times, respectively for mixture 90FA_10CH_8M_1SS/SH_0.8A/B_0.1XAN. Concerning the mixture 80FA_10CH_10MG_2SS/SH_0.8A/B, 75FA_10CH_15MG_1.5SS/SH_0.8A/B, the addition of Xanthan biopolymer as even reduced its compressive strength.

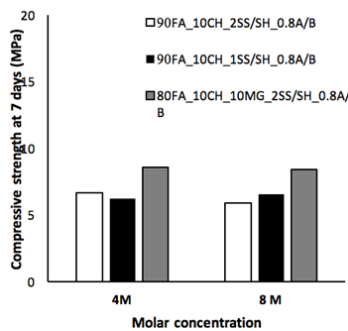
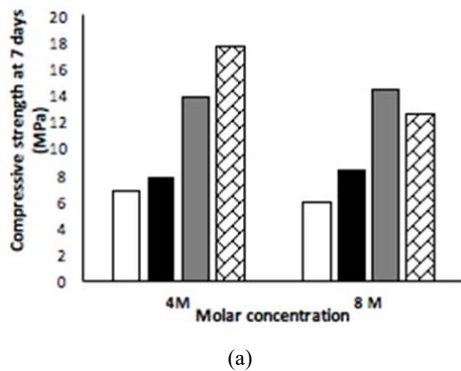
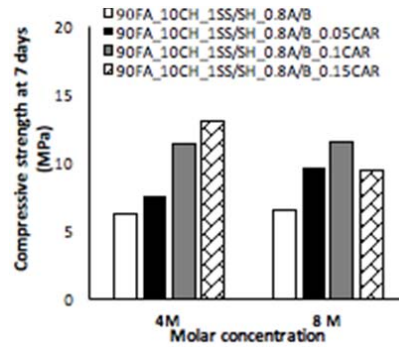


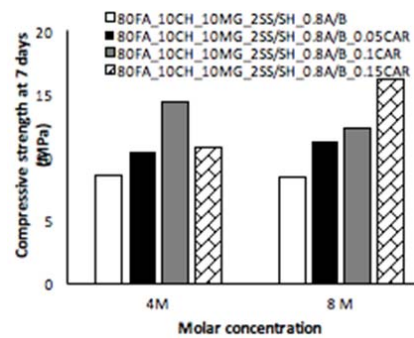
Fig. 1 The compressive strength after 7 days curing of hybrid cement mortars without biopolymers



(a)

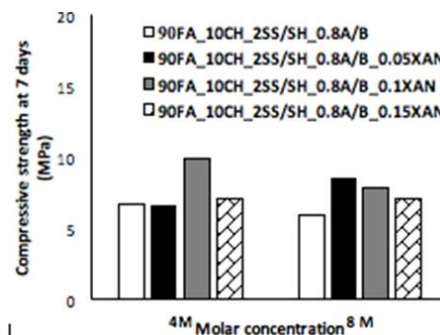


(b)

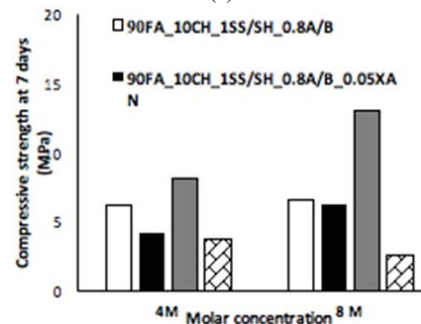


(c)

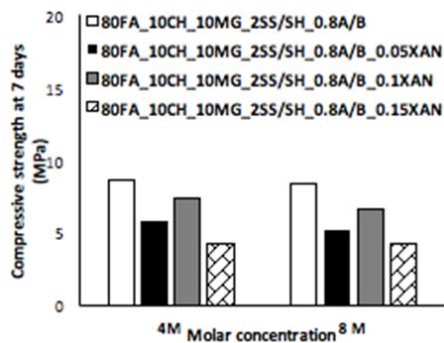
Fig. 2 Compressive strength of AACB mixtures with biopolymer carrageenan: a) 90FA_10CH_2SS/SH_0.8A/B; b) 90FA_10CH_1SS/SH_0.8A/B; c) 80FA_10CH_10MG_2SS/SH_0.8A/B



(a)



(b)



(c)

Fig. 3 Compressive strength of AACB mixtures with biopolymer xanthan: a) 90FA_10CH_2SS/SH_0.8A/B; b) 90FA_10CH_1SS/SH_0.8A/B; c) 80FA_10CH_10MG_2SS/SH_0.8A/B

IV. CONCLUSIONS

The results of the present investigations are as follows. The results show that a mixture of 80% FA, 10% waste glass and 10% CH activated with an alkaline activator based on a 4-M sodium hydroxide shows the highest compressive strength. The reduction of the sodium silicate content is associated with a reduction of compressive strength that is slightly compensated by the replacement of FA by waste glass. The mixtures containing carrageen show better workability in comparison with mix compositions containing xanthan. The results show that the increase of biopolymer carrageenan content is associated to an increase in compressive strength and that the use of 0.1% of carrageenan leads to optimum compressive strength. The use of xanthan shows no beneficial effects on the compressive strength of AACB mortars. Several mixtures with xanthan even show a reduction in the compressive strength.

ACKNOWLEDGMENT

The authors would like to acknowledge the financial support of the Foundation for Science and Technology (FCT) in the frame of project IF/00706/2014-UM.2.15

REFERENCES

- [1] COM (2011) 571, "Roadmap to a Resource Efficient Europe, European Commission, Brussels, 2011.
- [2] COM (2014) 398 final, "Towards a circular economy: A zero waste programme for Europe," Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions. Brussels, 2014.
- [3] J. Van Deventer, J. Provis, P. Duxson, D. Brice, "Chemical Research and Climate Change as Drivers in the Commercial Adoption of Alkali Activated Materials," *Waste Biomass Valor* vol. 1:pp.145–155, 2010.
- [4] J. Provis, "Geopolymers and other alkali activated materials: why, how, and what?" *Materials and Structures* vol. 47, pp.11-25, 2014.
- [5] J. Provis, Y. Muntingh, R. Lloyd, H. Xu, L. Keyte, L. Lorenzen, P. Krivenko and J. Van Deventer, "Will geopolymers stand the test of time?," *Ceramic Engineering and Science Proceedings* Vol.28, pp.235-248, 2008.
- [6] F. Pacheco-Torgal, Z. Abdollahnejad, A. Camões, M. Jamshidi and Y. Ding, "Durability of alkali-activated binders. A clear advantage over Portland cement or an unproven issue?," *Construction and Building*

Materials Vol.30, pp.400-405, 2012.

- [7] F. Pacheco-Torgal, Z. Abdollahnejad, S.Miraldo, S. Kheradmand, "Alkali-activated cement-based binders (AACB) as durable and cost competitive low CO₂ binders: Some shortcomings that need to be addressed," in *Handbook of low carbon concrete*, 1st A. Nazari, J. Sanjayan, , Elsevier Science and Tech, Waltham, 2016, pp.195-216.
- [8] S. Alonso, A. Palomo, "Calorimetric study of alkaline activation of calcium hydroxide-metakaolin solid mixtures," *Cement and Concrete Research*, vol.31, p.25-30, 2001.
- [9] S. Alonso, A. Palomo, "Alkaline activation of metakaolin and calcium hydroxide mixtures: influence of temperature, activator concentration and solids ratio," *Materials Letters*, vol.47, p.55-62, 2001.