O U R N A L O F

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Adhesion as a tool for in-built nanotechnology design in cementitious materials

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Confined water, such as those molecules in nanolayers of 2-3 nm in length, plays an important role in the adhesion of hydrophilic materials, mainly in cementitious ones. In this study, the effects of water containing kosmotropic substances on adhesion, known for their ability of enhancing the hydrogen bond (H-bond) network of confined water, were evaluated using mechanical strength tests. Indeed, to link adhesion provided by water confined in nanolayers to a macro-response of the cementitious samples, such as the bending strength, requires the evaluation of local water H-bond network configuration in the presence of kosmotropes, considering their influences on the extent and the strength of H-bonds. Among the kosmotropes, trimethylamine and sucrose provided a 50% increase in bending strength compared to the reference samples, the latter just using water as an adhesive, whereas trehalose was responsible for reducing the bending strength to a value close to the samples without any adhesive. The results attained opened up perspectives regarding exploring the confined water behavior which naturally occurs throughout the hydration process in cement-based materials.

Key words: Adhesion, Confined Water, Mechanical Properties.

Introduction

Portland cement is the commodity with the largest consumption in the world, mainly because cement-based materials are inexpensive, easy to handle, and suitable for complex building structures. Nowadays, building trends and architectural designs are challenging the intrinsic properties of Portland cement. Additionally, environmental issues address further requirements concerning the production of cementitious materials and their performance. This implies a great opportunity for innovation in Portland cementbased materials.

By casting techniques and microstructural designs, materials engineering have seen the greatest known advances in the mechanical performance of cementitious materials in previous decades. Water-cement ratio (w/c) reduction was one of the first techniques to improve their mechanical strength, due to a porosity decrease. Roy and Gouda showed that cement pastes with w/c = 0.10 could attain a compressive strength up to 330 MPa, after having been compacted under 345 MPa for 1 h [1]. Birchall et al. also pointed out that a low w/c ratio plus the addition of polymers in solution allowed their plastic casting by techniques such as roll pressing and extrusion [2]. Thereby, the resulting mechanical performance was much improved. Bending strengths in the range of 40 MPa to 150 MPa were accredited to smaller defect sizes within such pastes, called Macro-Defect Free Cements. These results have shown that a low mechanical strength should not be inherent to cement-based materials. This latter statement was further reinforced by Richard and Cheyrezy who enhanced the dispersion and the packing of particles, increasing the compressive strength of cementitious materials close to 600 MPa [3].

Over two decades ago, Double had already pointed out these materials engineering trends, but highlighted another parameter able to lead to further innovations: adhesion [4]. Nevertheless, since then, available information on this subject has been scarce, except by Kendall's work, which correlated microstructural features and adhesion to mechanical strength of cementitious materials (σ). Part of his achievements is summarized by the equation below, where the microstructural parameters are represented by the packing fraction (f), particle size (D), and critical defect size (c), whereas the physical-chemical parameter is related to the work of adhesion forces (W) [5]:

$$\sigma = \left[\frac{15.6\phi^4}{\sqrt{Dc}}\right] W \tag{1}$$

However, what are the adhesion forces present in cementitious pastes? Pellenq and van Damme related adhesion to the presence of water molecules [6]. More recently, Rossetto *et al.* have shown elsewhere that adhesion in cementitious pastes is ruled by water molecules confined in nanolayers (2-3 nm) by their hydrated surfaces, the socalled *confined water* [7]. Indeed, what makes water a special substance is the number of hydrogen bonds (Hbonds) which each molecule can make: two as acceptors and the other two as donors [8]. This aspect gives water the capability to organize itself in a tetrahedral structure, implying that each water molecule would make four H-bonds

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with other surrounding water molecules. Actually, this tetrahedral structure only prevails at temperatures as low as 228 K, in the absence of impurities, when the structural defects in the H-bond network tends to be zero [9, 10].

Confining the water molecules in nanolayers (no more than 2-3 nm) renders a similar effect to decreasing the temperature, making their dynamic behavior and viscosity quite different from that of bulk water [11, 12]. The adhesive power of confined water inspired Jinesh and Frenken to compare it to a *glue* [13]. Interestingly, this sort of water was experimentally verified by both inelastic neutron scattering and a computer simulation in Portland cementbased materials [14, 15]. Another feasible way to verify the adhesion would be by fracture mechanics. Considering that W is related to K_{IC} and that in the lower part of both equations (1 and 2) the critical crack length (c) is dominant, the adhesion changes (W or K_{IC}) could be, at first, evaluated by the tensile strength (σ) values. This would avoid the direct measurement of the different variables in equation 1 or the K_{IC} (Eq. 2) in a low toughness and notch sensitive material, such as cement:

$$\sigma = \frac{1}{Y_{\sqrt{\pi c}}} \frac{K_{IC}}{V_{\sqrt{\pi c}}}$$
(2)

This is how this study aims to measure the adhesion afforded by *kosmotropic* substances, providing insights in order to improve the mechanical performance of cementbased materials. Kosmotropes are known by their ability of enhancing the H-bond network of confined water, and they can split into two groups: ionic and non-ionic. The latter group is more efficient in making strong H-bonds with water than the ionic one, usually named *anti-chaotrope*. In addition to the strength of H-bonds, some of these nonionic kosmotropic substances, namely the macromolecules, are able to arrange the water molecules at a greater distance than that by self-structuring, acting like a *scaffold*. Thus, to link these confined water features, considered by the present authors as an *in-built nanotechnology* of the cementitious materials, to the mechanical strength, a macro response, this study makes use of samples where slightly spray moistened (kosmotropes added) pre-hydrated cement were compacted under high pressure. Using previously hydrated cement as a starting material inhibits changes in the hydration process and in the hydrated phases, as would be expected by adding the kosmotropic substances from the beginning. On the other hand, it demands pressing such a material in order to: (i) improve the fraction of water confined in nanolayers which contribute to adhesion; and (ii) renders similar microstructure in the samples, i.e. parameters in brackets in equation 1.

Experimental Procedure

A Brazilian type V cement (64.50 wt% C₃S; 3.78 wt% C₂S; 11.50 wt% C₃A; 7.05 wt% C₄AF; 7.68 wt% gypsum, where, C = CaO, S = SiO₂, A = Al₂O₃, F = Fe₂O₃ and H = H₂O-Holcim, São Paulo) was gradually spray moistened with deionized water until a w/c ratio of 0.15 was attained. Thereafter, this slightly moistened cement was sieved (Tyler #30, < 500 μ m) and then allowed to hydrate in a loose way for 7 days inside a sealed plastic bag. Hydration was attested by nuclear magnetic resonance (²⁹Si MAS-NMR, see reference 16 for NMR measurements setting) after this time, as shown in Figs. 1(a) and 1(b). This *pre-hydrated* cement is the starting material for the experiments, which were designed to test different kosmotropic substances as adhesives among the hydrated cementitious surfaces.

Each set of samples, with at least five specimens, was prepared by rewetting the pre-hydrated cement with 10 wt% either of plain deionized water (*reference*) or of a kosmotropic aqueous solution, which led to a final w/c ratio of 0.265. This is followed by their compaction under a pressure of 100 MPa applied for 10 minutes in order to obtain rectangular plates ($20 \times 70 \times 15 \text{ mm}^3$). A three-point bending strength was measured (span = 45 mm, according to ASTM C-1161), using an MTS (model 810) universal



Fig. 1. ²⁹Si-NMR-MAS results for: (a) anhydrous Portland cement powder; (b) pre-hydrated Portland cement powder (w/c = 0.15), socalled starting material; (c) sample prepared by the compaction (100MPa for 10 minutes) of the starting material sprayed with further water (till a final w/c ratio of 0.265). Solid lines represent the Direct Polarization of ²⁹Si (DP), whereas the dashed ones (Cross Polarization of ¹H-²⁹Si, CP) stands for the hydrated sites. DP curves can distinguish the CSH populations (i.e. Q^0 , Q^1 , and Q^2) and, hence, the degree of hydration (x) of the sample; whereas CP illustrates which populations are the hydrated ones (Q^1 and Q^2).



Fig. 2. Non-ionic kosmotropic substances: (a) sucrose; (b) trehalose; (c) glycine; (d) proline; (e) trimethylamine.

testing equipment. Before the mechanical testing, the compacted samples were kept for 24 h at room temperature in a relative humidity of 50%.

In order to draw conclusions regarding the role of Hbonds in adhesion and, as a consequence, in the mechanical strength of cementitious materials, aqueous solutions (0.5 M and 1.0 M) of the following kosmotropic substances were used: sucrose ($C_{12}H_{22}O_{11}$, MW = 342.3 g/mol, commercial grade), trehalose ($C_{12}H_{22}O_{11}.2H_2O$, MW = 378.3 g/mol), glycine ($C_2H_5NO_2$, MW = 75.1 g/mol), proline ($C_5H_9NO_2$, MW = 115.1 g/mol), and trimethylamine (C_3H_9N , MW = 59,11 g/mol), whose chemical structures are shown respectively in Figs. 2(a) to 2(e). Except for the sucrose, all other kosmotropic substances were laboratory graded (Synth, Brazil).

The effect of the kosmotropic substances were evaluated based on the mechanical strength of the cementitious samples in order to highlight how they affect the adhesion by confined water. Nevertheless, it is worth noticing that: (i) this study focuses on presenting the adhesive effects on a comparative basis; (ii) rewetting the pre-hydrated cement with water resulted in a small increase in its degree of hydration (x), as presented in Fig. 1(c), but not sufficient to change the cementitious microstructure and, consequently, to inhibit the correlation of adhesion and mechanical strength of cementitious samples.

Results and Discussion

Table 1 summarizes the results for cementitious samples with different kosmotropic substances and their concentrations. Firstly, it is shown that for most of the compositions the apparent density cannot account for the variations in the bending strength. Secondly (not shown in Table 1), when the pre-hydrated cement was compacted after no rewetting, the resulting bending strength ($\sigma_B = 3.0 \pm 0.5$ MPa) was nearly 1/3 of that compacted with water, although the apparent density of both was nearly the same. This shows that water is a good adhesive when confined in nanolayers, mainly with the help of a high compaction pressure (100 MPa), as stated by Jinesh and Frenken [13], who concluded (by atomic force microscopy) that confined water acts as a glue. Thirdly, most kosmotropic substances had different influences on adhesion when compared to reference samples. Glycine, despite its known

Table 1. Apparent density (d) and 3-point bending strength (σ_B) of cementitious samples

Sample	d (g/cm ³)	$\sigma_{\rm B}$ (MPa)	
		0.5M	1.0M
Reference	1.86 ± 0.02	8.0=	± 1.3
Sucrose $(C_{12}H_{22}O_{11}, MW^* = 342.3 \text{ g/mol})$	1.92 ± 0.02	12.7 ± 1.5	8.7 ± 1.3
Trehalose $(C_{12}H_{22}O_{11}.2H_2O, MW = 378.3 \text{ g/mol})$	1.88 ± 0.02	6.6 ± 0.8	3.3 ± 0.3
Glycine ($C_2H_5NO_2$, MW = 75.1 g/mol)	1.87 ± 0.02	7.9 ± 1.0	7.7 ± 1.0
Proline ($C_5H_9NO_2$, MW = 115.1 g/mol)	1.87 ± 0.02	12.4 ± 1.2	7.0 ± 1.1
Trimethylamine (C_3H_9N , MW = 59.11 g/mol)	1.87 ± 0.02	11.3 ± 1.2	11.2 ± 1.2

*MW = Molecular Weight.

role in the constitution of collagen, was an exception: regardless of its concentration, the bending strength of samples was nearly the same as that of the reference sample. In fact, the amine group in the glycine structure might have been balanced by its carbonyl one in terms of the water ordering-disordering effect, respectively.

The main difference between glycine and proline is the presence of the amide group $(R-C(=O)-N-R_2)$ in the latter instead of the amine (NH₂) one, as shown in Fig. 2. Because proline lacks hydrogen in the amide group, it cannot act as a H-bond donor, but only as an H-bond acceptor. As defined by Jeffrey, H-bonds are formed when the electronegativity of element A, covalently bonded to H, attracts the hydrogen electron and leaves it as a partially unshielded proton. This configures a donor A-H bond, so that acceptor B must have lone-pair electrons or polarizable ones in order to make the H...B bond [17]. In this case, as nitrogen presents more lone-pair electrons than oxygen, it implies that the strength of H-bonds that proline makes with water is expected to be higher than those just with water molecules. In fact, this feature is observed in the adhesion of proline samples and, consequently, in their bending strength: $12.4 \pm$ 1.2 MPa versus 8.0 ± 1.3 MPa for the reference samples. This result was attained when the proline concentration in rewetting solution was 0.5 M. As the proline concentration was increased to 1.0 M, the bending strength of their samples was close to the reference sample $(7.0 \pm 1.1 \text{ MPa})$. It should be considered that water tends to arrange itself in a tetrahedral manner because two H-bonds act as donors and the other two H-bonds as acceptors. Thus, when the proline concentration increases in solution, it is likely that its deficiency of donating H-bonds may account for this bending strength reduction. Trimethylamine was used in order to isolate these effects. In this group of samples, only amine was present, so that the increase in the strength of H-bonds prevailed and the bending strength was higher than the reference sample, regardless of its concentration in the aqueous solution (Table 1).

Up to now, it has been shown that the strength of H-bonds

could be changed according to the kosmotropic substance present in the rewetting solution, and so the adhesion of cementitious samples. Nevertheless, as previously mentioned, the extent of H-bonds can also be influenced by the kosmotropic substances. That is why the influence of sucrose on the adhesion of compacted pre-hydrated cement samples was evaluated. Indeed, each -OH sucrose group generates almost two H-bonds - one as a weaker acceptor and the other as a stronger donor - which poorly fit into the local water tetrahedral network [18]. When the sucrose concentration in the rewetting solution was 0.5 M, it is most likely that its ability to structure water molecules beyond the condition of water self-structuring, i.e. 2-3 nm, was present. In other words, its *scaffold* effect prevailed and, hence, the bending strength of these cementitious samples was nearly 50% higher than that of the reference sample. Nevertheless, when the sucrose concentration was increased to 1.0 M in the rewetting solution, it was noticed that the bending strength of these samples dropped. Apparently, the lesser H-bonds which sucrose makes with the available water might explain this drop, as occurred with proline. In order to check this hypothesis, trehalose was used.

Trehalose is one of the most important kosmotropes. However, trehalose greatly interferes in the local tetrahedral network of water: most of its hydroxyl groups make only one H-bond with water molecules which, in turn, are unable to form H-bonds with any other surrounding water or even with the trehalose molecules. This explains the decrease of the bending strength for the 0.5 M trehalose containing samples $(6.6 \pm 0.8 \text{ MPa} \text{ versus } 8.0 \pm 1.3 \text{ MPa} \text{ of the reference}$ ones). The bending strength of trehalose samples kept decreasing $(3.3 \pm 0.3 \text{ MPa})$ with its increasing concentration. Again, as the trehalose concentration increased, almost all the confined water might have been associated to trehalose and the ability of water to form four H-bonds per molecule nearly vanished. In other words, water molecules within the 1.0 M trehalose solution lost their power to adhere to hydrated cementitious surfaces, as the bending strength of these samples was nearly the same as for those samples where pre-hydrated cement was compacted without rewetting ($\sigma_B = 3.0 \pm 0.5$ MPa; $d = 1.78 \pm 0.02$ g/cm³).

Conclusions

The results presented show that adhesion in cementbased materials is very sensitive to the action of kosmotropic substances and, in addition, that the bending strength is a feasible way to evaluate the effect of kosmotropes on the adhesion. In fact, this study relates to the adhesion of cementbased materials by confined water, which is provided by the high pressure applied to the cement powder plus the effect of kosmotropic aqueous solutions.

Concerning the degree of water-structuring of the kosmotropes hereby evaluated, some aspects of their molecular structure could account for different influences on adhesion. In particular, trimethylamine was effective in improving the adhesion, and, as a consequence, the bending strength of cementitious samples, regardless of its concentration in the aqueous solution. Nonetheless, it was shown that a carbonyl group may counter-balance such an amine adhesion improvement, shown by using glycine. Indeed, amine owes its performance on adhesion to the nitrogen, which strengthens H-bonds with water. This was confirmed by evaluating a kosmotrope containing the amide group, such as proline. At a lower concentration (0.5 M), prolineadhered samples showed a 50% increase in the bending strength, whereas at a higher concentration (1.0 M), the bending strength dropped close to the reference sample value. The same thing happened with sucrose-adhered samples, besides the sucrose adhesion improvement was attributed to the scaffold effect instead of H-bond strengthening. Both proline and sucrose have something in common: the ability to make less H-bonds with water than the water with itself. This feature was further observed with trehalose-adhered samples, provided this kosmotrope tightly binds one water molecule per -OH group and inhibits them to make any other H-bond. The results showed that when the trehalose concentration was high (1.0 M), the bending strength of cementitious samples was nearly the same as those samples compacted in the absence of water.

To conclude, the results presented some insights to further enhance the power of adhesion of confined water and open perspectives for selecting other kosmotropes. This in-built nanotechnology could be a suitable alternative to design cement microstructures containing nanometric particles, which are expensive and make cement processing steps a very difficult task.

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