Hydrogen bond assisted adhesion in Portland cement-based materials

(Adesão assistida por ligação de hidrogênio em materiais à base de cimento Portland)

H. L. Rossetto[1,2], V. C. Pandolfelli[1]
[1]Departamento de Engenharia de Materiais - DEMa, Universidade Federal de S. Carlos - UFSCar,
Rod. Washington Luiz, km 235, S. Carlos, SP 13565-590
[2]Instituto de Física de S. Carlos, Universidade de S. Paulo - IFSC-USP, Av. Trabalhador São-Carlense 400,
S. Carlos, SP 13566-590
hebert@if.sc.usp.br

Abstract

Adhesion is a physical-chemical parameter able to render innovations to Portland cement-based materials. However, this concept still lacks experimental evidence to underlie further developments in this subject. This work has demonstrated how distinct substances can impart different adhesion forces after evaluating the hydration degree and the mechanical strength of non-reactive cementitious materials. The substances capable of making tridimensional hydrogen bonds, such as water, for instance, were the most effective in providing cementitious samples with improved bending strength. It implies that water is not only important because of its role in cement hydration, but also because it develops adhesion between hydrated cementitious surfaces. More than speculating the fundamental understanding on adhesion in Portland cement-based materials, the present paper intends to stimulate thinking on how to take the benefits of the water confined between the hydrated cementitious surfaces as an in-built nanoadhesive, so far little explored, but at the same time so prone to yield high performance materials.
Keywords: adhesion, hydrogen bond, mechanical properties, Portland cement.

Resumo

Adesão é um parâmetro físico-químico que pode promover inovações em materiais à base de cimento Portland. Este conceito, entretanto, ainda requer evidência experimental para propiciar mais desenvolvimentos neste assunto. Este trabalho tem demonstrado como diferentes substâncias podem promover diferentes forças de adesão após a avaliação do grau de hidratação e a resistência mecânica de materiais cementícios não reativos. As substâncias capazes de produzir ligações de hidrogênio tridimensionais como, por exemplo, a água, foram as mais eficazes para produzir amostras cementícias com melhor resistência mecânica. Isso significa que a água não é importante somente por causa de seu papel na hidratação do cimento, mas também porque ela desenvolve adesão entre as superfícies cementícias hidratadas. Mais que especular sobre o entendimento fundamental na adesão de materiais cementícios à base de cimento Portland, este artigo tem a intenção de estimular a discussão como aproveitar a água confinada entre as superfícies cementícias hidratadas como um nanoadesivo interno, até agora pouco explorado, mas ao mesmo tempo com tendência de fornecer materiais de alto desempenho.
Palavras-chave*: adesão, ligação de hidrogênio, propriedades mecânicas, cimento Portland.*

INTRODUCTION

Over two decades ago the adhesion, as a key parameter in terms of breakthroughs in Portland cement-based materials, was highlighted [1]. More recently, Kendall [2] pioneered in correlating this parameter to tensile strength (σ), as follows

$$\sigma_f = \frac{15.6W\phi^4}{(Dc)^{1/2}} \qquad (A)$$

where packing fraction ϕ, particle diameter D, and crack length c represent the microstructural parameters, whereas W is related to the work of adhesion. The mechanical strength accounts for the broad use of Portland cement-based materials, and it is often attributed to the hydration of clinker with water. Indeed, hydration occurs by a process known as dissolution-precipitation, firstly described by Le Chatelier. However, even for the cement pastes with the highest water-to-cement ratios (w/c) [3], water is not completely consumed during hydration. Thus, could the remaining water, i.e., the water which did not take place in hydration reaction and got adsorbed on the hydrated surfaces, contribute to joining these cementitious surfaces? Could other substances replace water in this role of adhering Portland cement-based materials? Additionally, how is someone supposed to study the adhesion itself in a system where these substances could interfere in the hydration? To deal with these peculiarities, an experimental procedure was used where hydrated (non-reactive) Portland cement powder was compacted with different substances in order to evaluate their effect on the adhesion among the cementitious surfaces.

EXPERIMENTAL

A Brazilian type V cement (Holcim: 64.50 wt.% C_3S; 3.78 wt% C_2S; 11.50 wt.% C_3A; 7.05 wt.% C_4AF; 7.68 wt.% gypsum, where, C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3 and H = H_2O) was gradually moistened by water spray until a water-to-cement ratio (w/c) of 0.15 was attained. Thereafter, this slightly moistened cement powder was sieved (Tyler #30, <500μm) and then allowed to hydrate in a loose way inside a sealed plastic bag. Hydration was attested by nuclear magnetic resonance (^{29}Si MAS-NMR, see [4] as a reference for NMR measurements) after 7 days, as shown in Figs. 1a and 1b. This pre-hydrated (that is, no longer reactive) cement was the starting material for our experiments, designed to test the ability of the different substances as adhesives for the hydrated cementitious surfaces.

The adhesive substances were chosen according to their capability of making hydrogen bonds (H-bonds). In the previous research carried out by the authors [5], it was shown that some substances, known as H-bond structure breakers, strongly influenced the mechanical strength

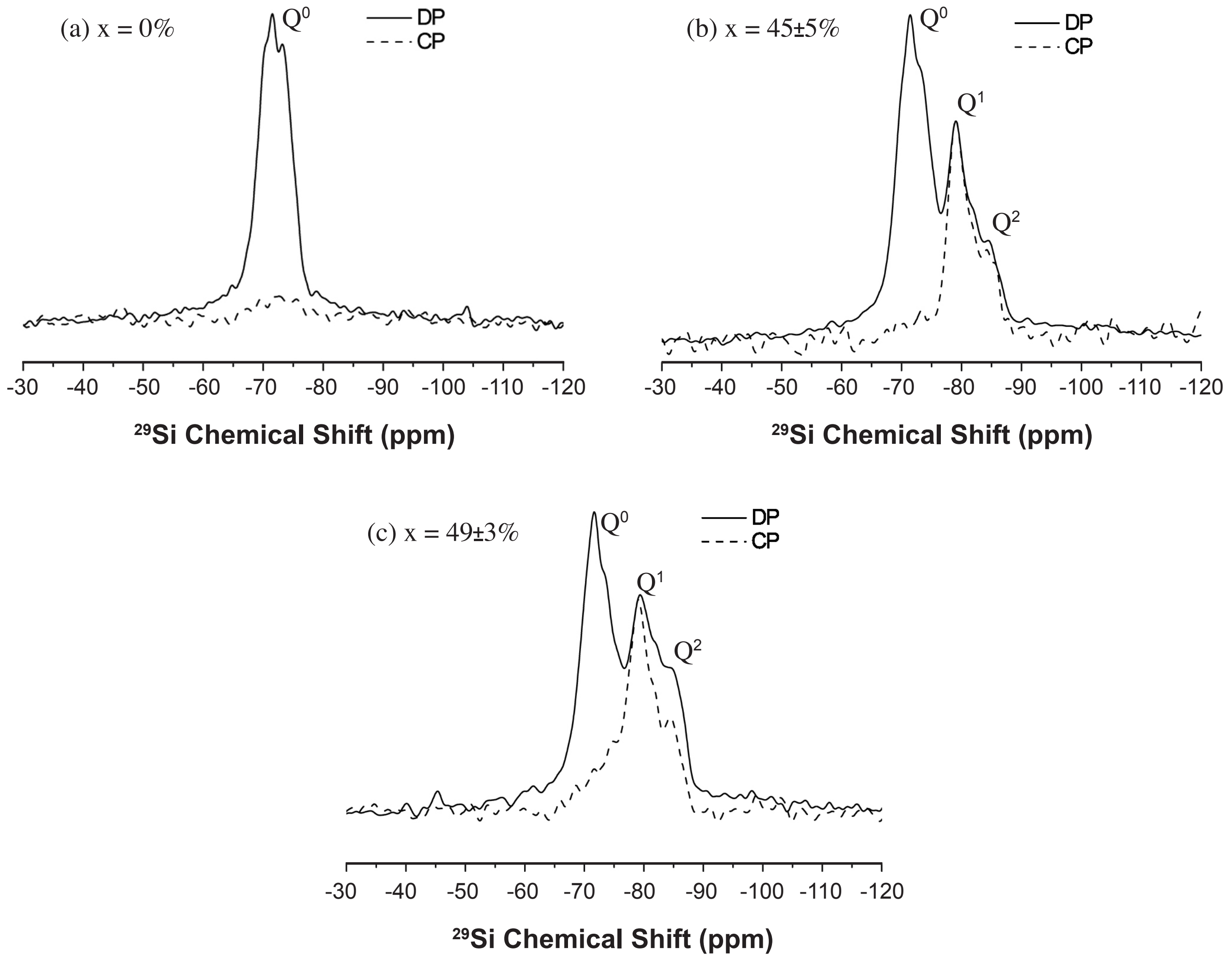

Figure 1: ^{29}Si-NMR-MAS results for: (a) anhydrous Portland cement powder; (b) pre-hydrated Portland cement powder (w/c = 0.15); (c) sample prepared by the compaction (100 MPa for 10 min) of the starting material sprayed with water (10 wt.% relative to the starting material). Solid lines represent the Direct Polarization of ^{29}Si (DP), whereas the dashed ones (Cross Polarization of ^{1}H-^{29}Si, CP) represent the hydrated sites. DP curves can distinguish the CSH populations (i.e. Q^0, Q^1, and Q^2 [14]) and, consequently, the degree of hydration (x) of the sample; whereas CP illustrates which populations are the hydrated ones (Q^1 and Q^2).

[Figura 1: Resultados de ^{29}Si-NMR-MAS para: (a) pó de cimento Portland anidro; (b) pó de cimento Portland pré-hidratado (w/c = 0,15); (c) amostra preparada por compactação (100 MPa por 10 min) do material de partida borrifado com água (10 peso% relativo ao material de partida). Linhas sólidas representam a polarização direta de ^{29}Si (DP), enquanto que as tracejadas (polarização cruzada de ^{1}H-^{29}Si, CP) representam os sítios hidratados. As curvas DP podem distinguir as populações CSH (i.e. Q^0, Q^1, e Q^2 [14]) e, conseqüentemente, o grau de hidratação (x) da amostra; por outro lado, CP ilustra quais populações são as hidratadas (Q^1 e Q^2).]

of the cementitious plates. In order to draw conclusions regarding the role of H-bonds on the mechanical strength of the cement-based materials and, consequently, on their adhesion, the following substances were used: water, ethyl alcohol, ethylene glycol, and a vegetable oil (extracted from soy bean). All samples were measured under 3-point bending (span = 45 mm), using MTS (model 810) universal testing equipment. Before the mechanical tests, the samples were kept for 24 h at room temperature.

Each set of samples (containing at least five specimens) was prepared by spraying the above mentioned pre-hydrated cement with 10 wt.% of a particular substance (1M aqueous solution in the case of ethyl alcohol and ethylene glycol), followed by their compaction under a pressure of 100 MPa applied for 10 min in order to obtain rectangular plates (20 x 70 x 15 mm^3). The high compaction pressure tends to induce similar critical defect sizes (c, in Equation A) among the samples, for the same initial particle size (D, in Equation A). Thus, the packing fraction (ϕ) and the adhesion (W) would be the only parameters commanding the mechanical strength, provided each different adhesive substance can impart distinct degrees of lubrication to the system being compacted.

RESULTS AND DISCUSSION

Firstly, it is worth noticing that re-wetting the pre-hydrated cement with water resulted in a small increase in its degree of hydration x, as shown in Fig. 1c, whereas for those adhered with other substances, x remained unaltered when compared to the pre-hydrated cement (Fig. 1b). It confirms the non-reactive character of the starting material used in this work to test our hypothesis, that is, that the water which did not take place in hydration reaction and got adsorbed on cementitious hydrated surfaces could contribute to join them. On the other hand, it further confirms that the chosen adhesive substances do not interfere in the hydration degree of the starting non-reactive cement. Thus, the only way these substances can impart different influences on the bending strength of the cementitious samples derives from their impacts either on packing fraction or on adhesion of such samples. Secondly, it is well known that water owes its peculiarities to its incredible capacity of making H-bonds [6]. As defined by Jeffrey [7], H-bonds are formed when the electronegativity of element A, covalently bonded to H, attracts the H electron and leaves it as a partially unshielded proton. This configures a donor A-H bond, so that the acceptor B must have lone-pair electrons or polarizable ones in order to make the H···B bond.

Concerning water, each molecule is capable of donating two H-bonds and accepting two others. This allows water molecules to be arranged in a tetrahedral manner, which implies that a tridimensional network among the molecules can be formed. According to Table I, such water feature might be responsible for the best adhesion of the cementitious surfaces. Besides the highest density, water adhered samples presented more than twice the bending strength of the ethyl alcohol adhered samples and the reference ones. Ethyl alcohol (CH_3CH_2OH, MW = 46 g/mol) has only one possibility to make H-bond, which most likely reduces its power of adhering the cementitious hydrated surfaces. Furthermore, the bending strength of ethyl alcohol adhered samples is nearly the same as the one of the reference samples (without any adhesive).

Based on these results, it is apparent that the density differences among those samples, even with the fourth power of the packing fraction in Equation A, cannot account for the large differences of their bending strength. If the reference sample were normalized to the density of the water adhered one by multiplying its bending strength by 1.192 [as a result of $(1.86/1.78)^4$] even though its new bending strength (3.5 MPa) would be inferior to that of a water adhered sample (8.0 MPa). This result reinforces the role of water in the adhesion of cementitious surfaces. This is also shown in the experiments with ethylene glycol ($HOCH_2CH_2OH$, MW=62 g/mol) and vegetable oil (MW=884 g/mol) as adhesives. According to Table I, the samples adhered with both substances were denser than the water adhered ones, due to their lubricating effect. Nevertheless, water adhered samples presented nearly threefold and fivefold the bending strength of ethylene glycol and vegetable oil adhered samples, respectively. Ethylene glycol has two possibilities for making H-bonds, nevertheless, both of its OH- bounds might be attached to the same surface, instead of connecting two distinct hydrated surfaces [8]. Finally, the substance with the least possibilities to make H-bonds with hydrophilic hydrated cementitious surfaces was the vegetable oil, which provided the lesser adhesion to the sample.

Table I - Apparent density d and 3-point bending strength σ_B of cementitious rectangular plates compacted with the particular distinct adhesives, except by the reference sample, compacted with no adhesive.
[Tabela I - Densidade aparente d e resistência à flexão em 3 pontos σ_B de placas retangulares cementícias compactadas com diferentes adesivos, exceto a amostra de referência, compactada sem adesivo.

Adhesive substance	σ_B (MPa)	d
Reference (only pre-hydrated cement without adhesive)	3.0±0.5	1.78±0.02
Deionized water (H_2O, MW=18g/mol)	8.0±1.3	1.86±0.02
Ethyl alcohol (CH_3CH_2OH, MW=46g/mol)*	3.1±0.5	1.73±0.02
Ethylene glycol ($HOCH_2CH_2OH$, MW=62g/mol)*	2.7±0.3	2.01±0.02
Vegetable oil (extracted from soy bean)&	1.7±0.3	2.02±0.02

(*) Laboratory graded products; (&) commercial product.

These results match those presented for another hydrophilic material: silica [9]. Although it is early to discuss in-depth the origins of adhesion by water, a great H-bond maker, it has been shown that its behavior in the vicinity of most hydrophilic surfaces, at a distance range of 1.0-1.5 nm from the surface (the so-called confined water), is quite similar to that of supercooled water at lower temperatures [10]. In other words, the hydrophilic surfaces tend to structure the water molecules into a particular distance, and the effect of such confinement has been measured in terms of viscosity: close to seven orders of magnitude higher than that of bulk water [11]. This means that confined water behaves as a solid phase and that it can connect two hydrated surfaces. Recently, it has been shown by computer simulations [12] and by inelastic neutron scattering [13] that hardened cement-based materials present the confined water among their particles' surfaces, which further validates the results of the experiments presented in this work. On the other hand, our results also stimulate future studies on how to further explore this in-built nanoadhesion of cement-based materials, provided that the remaining water, i.e., the water which did not take place in hydration reaction and got adsorbed on hydrated cementitious surface, contribute to their adhesion and can yield high performance materials.

CONCLUSIONS

The results of the mechanical strength tests revealed that the substances having a higher ability of establishing tridimensional hydrogen bonds were the best adhesives for the cementitious materials, once the starting material for the experiments was a pre-hydrated (non-reactive) Portland cement. Among the substances investigated, water yielded the best results, and behaves completely different when confined between two hydrated surfaces which are apart from each other by few nanometers. In the experiments herein presented, this condition was provided by the high compaction pressure applied to the material being molded into rectangular samples, so that water could act as a singular adhesive among the previously hydrated phases. These results show that the importance of water for cement-based materials is beyond the hydration itself, and is decisive when joining the resultant hydrated cementitious surfaces. These results also stimulate thinking on how to take the benefits of the water confined between the hydrated cementitious surfaces as an in-built nanoadhesive, so far little explored, but at the same time so prone to yield high performance materials.

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