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Surface energetics of cementitious materials and their wettability by an epoxy adhesive

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Abstract

The surface thermodynamic properties of cementitious materials and the wettability of these substrates by an epoxy adhesive were investigated using various surface analysis techniques.

In a first step, surface energies of hardened cement pastes were assessed either by contact angle measurements using the Owens and Wendt approach, or by inverse gas chromatography (IGC). A good correspondence was found between the two techniques for the dispersion contribution γ_s^d, and a strong amphoteric behavior of these materials was also demonstrated. Additionally, a surface carbonaceous contamination detected by X-ray photoelectron spectroscopy (XPS) was found to lower the surface energy of as-received samples, whereas an acetone cleaning treatment resulted in increased γ_s^d values.

In a second part, surface characterizations were performed on three synthetic compounds, representative of the main hydration products of hardened cement pastes, i.e. calcium hydroxide, ettringite and calcium silicate hydrate (C-S-H). IGC experiments provided γ_s^d values ranging from 45.6 up to 96.3 mJ m^{-2} at 35 °C, and the acid–base behavior was correlated to the water content.

Last, XPS and IGC analyses were performed on cement paste powders coated either with an epoxy resin (R) or with an amine hardener (H), separately, at mass loadings up to 10 wt.%. Changes in the dispersion contribution to the surface energy (γ_s^d) and Lewis acid–base interaction energy were found to be significantly dependent on the adsorption of both H and R, showing a substantial wetting of the mineral substrate by the adhesive components. In addition, XPS evidenced interfacial hydrogen bonding between the hardener and the cementitious substrates.

Keywords: Cement pastes; Epoxy resins; Wettability; Contact angles; Inverse gas chromatography; XPS

1. Introduction

Cementitious materials, such as concrete or mortars, are used worldwide in construction and civil applications. In margin of these traditional materials, polymer applications have grown during the last decades and are promised to further developments [1]. At the moment, polymeric materials are used as concrete or mortar additives in order to control the rheological properties or to improve the toughness [2,3], as protective coatings for civil structures [4], as adhesives for the reinforcement of bridge structures by bonded composites [5,6], and as sealing resins for injecting cracks in concrete [5]. Epoxy adhesives are even intended for structural bonding of precast concrete elements [5]. In most of these applications, a good wettability of the cementitious substrate by the polymer is required in order to promote physico-chemical interactions and ensure an optimal level of adhesion between the mineral and organic phases. Therefore, the surface energetics of cementitious substrates, and especially the dispersion and acid–base properties, are of great importance.

Surprisingly, only a few studies are available in the literature on the surface properties and wettability of cementitious materials [7–12].

Courard [7] used a Wilhelmy plate tensiometer for the estimation of the surface energies of nine liquid cement slurries and obtained values between 50 and 71 mN/m. Then, he estimated the surface energy (γ_s) of hardened cement pastes, by measuring the contact angles between these solids and drops of the previous cement slurries with an optical goniometer. Using

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Nomenclature

$a_{\mathrm{CH_2}}$	cross-sectional area of an adsorbed CH_2 group (6 Å^2)
BC	blended cement
BC 0.5	hardened BC cement paste (W/C = 0.5)
BC 0.5-AC	hardened BC cement paste (W/C = 0.5) washed with acetone
BC 0.5-R *y*%	hardened BC cement paste (W/C = 0.5) coated with *y* wt.% of resin R
BC 0.5-H *y*%	hardened BC cement paste (W/C = 0.5) coated with *y* wt.% of hardener H
BET	gas sorption analysis using Brunauer, Emmet and Teller's method
C_{org} and C_{mine}	organic and mineral contributions to the total carbon content
C-S-H	calcium silicate hydrate
$\Delta G_{\mathrm{a}}^{AB}$	acid–base contribution to the free energy of adsorption
ΔG_{a}	free energy of adsorption of 1 mol of solute from a reference state
$\Delta G_{\mathrm{CH_2}}$	free energy of adsorption per methylene group
H	amine hardener based on triethylene tetramine (TETA)
IGC-ID	inverse gas chromatography at infinite dilution
I_{sp}	specific interaction parameter
N	Avogadro number
OPC	ordinary portland cement
OPC 0.5 or OPC 0.3	hardened OPC cement pastes with W/C ratio of 0.5 or 0.3
OPC *x*-AC	hardened OPC cement paste washed with acetone, *x* stands for the W/C ratio (*x* = 0.5 or 0.3)
OPC *x*-R *y*%	hardened OPC cement paste coaded with the resin R, *x* stands for the W/C ratio (*x* = 0.5 or 0.3) and *y* for the mass loading of R
OPC *x*-H *y*%	hardened OPC cement paste coaded with the hardener H, *x* stands for the W/C ratio (*x* = 0.5 or 0.3) and *y* for the mass loading of H
R	epoxy resin based on diglycidyl ether of bisphenol A (DGEBA)
R	gas constant
SFE	surface free energy of a solid
TGA	thermo-gravimetric analysis
T	temperature
T_{b}	boiling temperature
V_{N}	net retention volume
$V_{\mathrm{N,ref}}$	net retention volume of an hypothetical *n*-alkane that boils at the same temperature than the test polar probe
V_{g}	net retention volume per gram of packed material
W/C	water to cement ratio
$\gamma_{\mathrm{L}}^{\mathrm{d}}$ and $\gamma_{\mathrm{L}}^{\mathrm{p}}$	dispersion and polar contributions to the surface tension γ_{L} of a liquid
$\gamma_{\mathrm{S}}^{\mathrm{d}}$ and $\gamma_{\mathrm{S}}^{\mathrm{p}}$	dispersion and polar contributions to the surface energy γ_{S} of a solid
$\gamma_{\mathrm{CH_2}}$	Surface free energy of a methylene group
$\gamma_{\mathrm{IGC}}^{\mathrm{AB}}$	IGC descriptor
χ	surface chemical descriptor

a multi-liquid graphical resolution method, he obtained γ_{s} values in the range 15–44 mN/m with a high accuracy. The value of the dispersion contribution to the surface energy ($\gamma_{\mathrm{s}}^{\mathrm{d}}$) of the hardened cement paste was found to be about twice that of the polar contribution ($\gamma_{\mathrm{s}}^{\mathrm{p}}$). After hydrophobic treatment, the cement paste did not exhibit any $\gamma_{\mathrm{s}}^{\mathrm{p}}$ component. Additionally, Courard found that goniometric measurements were not directly adaptable to porous concrete since the surface heterogeneities of such a material provided a high level of dispersion.

Momber [8] performed measurements of contact angles to cement and concrete surfaces with the sessile drop method and noted a pronounced effect of the surface preparation method on the contact angles. All angles changed from hydrophobic to hydrophilic after mechanical treatment. The problem was addressed in terms of a highly porous layer that forms on a cement sample surface during the curing process.

Momber [9] also performed contact angle measurements on powders made of cement paste and concrete by applying the Washburn method (imbibition tests). He did not find a notable effect of the aggregate material in case of the concrete samples (the contact angle shifted from 72°–80°), although the basalt used as the aggregate had a very low contact angle of 5°. He concluded that hydration products had a dominating influence on wettability.

Other authors measured contact angles by mercury intrusion porosimetry [10] or imbibition tests [11,12], but the results were not correlated to the surface energetics of materials. All of them underlined the practical difficulty in characterizing the wettability of cementitious materials, which exhibit a multi-scale porous structure and a substantial surface roughness.

The characterization of hardened cement pastes by inverse gas chromatography was reported for the first time in a previous paper [13]. In this preliminary study, the experimental protocol was optimized in order to characterize powdery cementitious materials at a working temperature of 35 °C, which corresponds to realistic conditions on building sites. In further papers, we correlated the dispersion component of the surface energy of cement pastes to the surface chemical composition as determined by XPS [14], and studied the interactions at the molecular level between cement pastes and adhesive components [15].

The present article reports recent studies in the ongoing research program devoted to the surface energetics and the wettability of cementitious materials.

The first part is concerned with the surface thermodynamic properties of hardened cement pastes. Dispersion and acid–base contributions to the surface free energy evaluated by IGC on powdery materials have been compared to those derived from contact angle measurements performed on polished flat samples, using the Owens and Wendt method [16]. The influence of the cement composition and the water-to-cement ratio on the