

Cement paste–epoxy adhesive interactions

Fatma Djouani^a, Carole Connan^a, Michel Delamar^a, Mohamed M. Chehimi^{a,*}, Karim Benzarti^{b,*}

^a Interfaces, Traitements, Organisation et Dynamique des Systèmes (ITODYS), University Paris Diderot & CNRS (UMR 7086), 15 rue Jean de Baïf, 75013 Paris, France

^b Université Paris Est, Laboratoire Central des Ponts & Chaussées (LCPC), PCM, 58 Bld Lefebvre, 75015 Paris, France

ARTICLE INFO

Article history:

Available online 25 March 2010

Keywords:

Cement paste
C–S–H
Ettringite
Portlandite
Adhesives
Adhesion
Wetting
Surface energy
Glass transition

ABSTRACT

In the field of civil engineering, the durability of concrete assemblies using adhesives is widely conditioned by the properties of the interface between the resin and the mineral support (concrete). In this context we studied first the molecular interactions at the interface between an epoxy resin and cement pastes by several approaches based on XPS and IR spectroscopies, DSC, and inverse gas chromatography (IGC). XPS showed evidence of crosslinking of the polymer at the surface of hardened cement pastes. XPS chemical shifts of the N1s peak from the adsorbed hardener testified for the existence of interfacial donor–acceptor interactions between the cement and hardener. Such a specific interaction is probably responsible for the increase in the of glass transition temperature (T_g) of the adhesive near the cement substrate surface. FTIR study of the interactions of the epoxy adhesive with the main hydrates taken separately (namely C–S–H, ettringite and portlandite) permitted to better understand the complex cement paste–adhesive interfacial system. The IGC-determined dispersive and acid–base components of the surface energy of the cement pastes were found to be depressed after coating, a result that correlates with surface chemical composition data. Small area XPS analysis of cement paste/adhesive interphase revealed, on a prototype of cement paste–adhesive joint, modifications of the Ca2p and N1s regions, which suggests that this zone is the locus of chemical reactions that favour mineral substrate–resin adhesion. Small area XPS firmly showed the existence of a diffuse interphase rather than a sharp cement paste–adhesive interface.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

The science and technology of adhesion and adhesives witnessed a quantum jump in the number of studies pertaining to the particular fields of civil and off-shore engineering [1–3]. Epoxides are the adhesives which have been by far the most investigated for applications in building applications. For example, they were applied for adhesively bonding precast decks on ultra high performance concrete (UHPC) upper chords [4]. These systems offer a broad range of advantages, such as cure at ambient temperature, good adhesion properties on most substrates, relatively high mechanical strength and environmental resistance, low shrinkage [3]. Common epoxy formulations for assembly applications in civil engineering are based on diglycidylether of bisphenol A resins (DGEBA) (Fig. 1) that can be crosslinked with a wide variety of hardeners such as amines, organic acids, anhydrides and catalysts [5].

When applied to substrates, it is of fundamental and technological importance to understand how the formulated (epoxy-based)

adhesive interacts with and adheres to mineral and other surfaces. In this respect, high-resolution surface and interface analytical tools such as XPS and ToF-SIMS are essential to monitor specific interfacial interactions [6].

It is well known that the hydration of Portland cement is a chemical process involving several simultaneous reactions and leading to the formation of hydrates from the anhydrous cement powder and water. This complex process has thermodynamic, kinetic and structural features depending on both chemical and physical parameters.

The water-to-cement ratio (w/c) influences hydration kinetics. It has been found that a higher water-to-cement ratio leads to a higher hydration rate after the middle period of hydration, but only has a small effect on the hydration rate in the early stage [7]. The w/c ratio also determines the ultimate degree of hydration. Theoretically, a w/c ratio of about 0.4 is sufficient for the complete hydration of cement.

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 [8,9]. Therefore, the surface interactions of cementitious substrates, and especially the dispersion and acid–base properties, are of great importance.

* Corresponding authors.

E-mail addresses: chehimi@univ-paris-diderot.fr (M.M. Chehimi), Karim.benzarti@lcpc.fr (K. Benzarti).

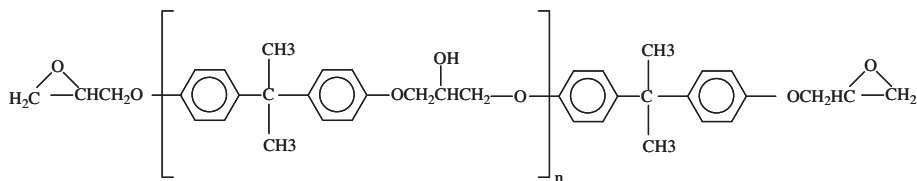


Fig. 1. Chemical structure of DGEBA oligomers.

Surprisingly, only a few studies are available in the literature on the surface properties of cementitious materials.

However, the cement–adhesive interface was studied at the LCPC laboratory by micro-thermal analysis μ TA [10,11]. This sample was a prototype of cement paste embedded in an epoxy cylinder. This study has revealed indirectly the variations in the glass transition temperature (T_g) of the polymer at the interface due to the decrease in the macromolecular chain mobility resulting from possible interactions between the mineral and organic components.

Additional work has been carried out to investigate the penetration of adhesive into the cement substrate using a fluorescent dye incorporated into the epoxy adhesive. Observations by optical microscopy under ultraviolet (UV) light illumination (Fig. 2) showed that the epoxy adhesive can penetrate the porous structure of the cementitious substrates up to depths of 100–200 μ m, depending both on the porosity and the degree of water saturation of the cementitious substrate, and on the viscosity of the resin. Such an interpenetrated region can be considered as a transition zone between the pure polymer and cementitious phases.

In this context, we have developed systematic studies of molecular interactions of structural adhesive components with mineral substrates [12–15]. An epoxy resin based on DGEBA oligomers was chosen with an average polycondensation degree of 0.14, and triethylenetriamine (TETA) was selected as the hardener amine. The mineral substrate of interest in construction was a hardened cement paste from an Ordinary Portland Cement (OPC), and its surface properties were characterized by XPS (chemical composition) and inverse gas-phase chromatography (IGC) at infinite dilution (surface energy). The surface energy of the cement pastes was found to be gradually minimized by organic coatings consisting of either the epoxy resin or the hardener [14,15].

In the present work, we investigate the effect of an epoxy resin and hardener mixtures on the surface and interface physicochemical properties of powder particles obtained from grinded OPC cement pastes. Stoichiometric and non-stoichiometric mixtures were

coated from fresh chloroform solutions onto cement paste powder particles. XPS and FTIR were used to study the surface and interface chemistry of the cement paste–(cross-linked epoxy resin) systems; IGC was used to monitor surface energy changes of the cement pastes after coating; and DSC was used to determine the glass transition temperature of the resin at the substrate–adhesive interface. Complementary experiments were also conducted on synthetic hydrates representative of the main hydration products formed in the OPC cement paste, i.e., portlandite, ettringite and calcium silicate hydrate (C–S–H), in order to assess the contributions of individual components to the interaction behaviour with epoxy formulations.

In addition, a more realistic sample, i.e., a prototype of a cement paste–adhesive joint, was examined by small area XPS in the interfacial region in order to account for the gradual changes of the chemical composition in this critical interfacial zone.

2. Experimental section

2.1. Materials

2.1.1. Hardened cement pastes

Hardened cement pastes were prepared from commercial cement, an Ordinary Portland Cement OPC (CEM I 52.5 PMES from Lafarge, Le Havre, France) made of pure reactive clinker. A fresh mixture with a water-to-cement weight ratio (w/c) of 0.5 was poured into cylindrical PVC moulds (diameter 35 mm and height 80 mm). Hardened specimens were removed from their moulds after 24 h, hermetically wrapped with an adhesive aluminium sheet, and stored at room temperature for 28 days to complete the hydration process. The hardened cement pastes were then manually grinded using a hammer in order to obtain a coarse powder. A drying treatment was then achieved by solvent exchange: the cement paste powder was stored for 1 month in a glass vessel filled with methanol and the solvent was then removed by heating the vessel at 40 °C under vacuum. A mass loss of 8.2% was observed after the drying processes.

The previous material was then pressed, ground and finally sieved to give the particle diameter in the 250–400 μ m range which is adequate for GC measurements. Fig. 3 shows the aspect of the powders of OPC hardened cement paste after preparation.

These powder particles were used to study the interaction of epoxy resin/hardener formulations, coated as ultrathin films from chloroform onto the cementitious substrate, using XPS, FTIR, IGC and DSC techniques.

In the more realistic situation, a 1 \times 2 cm-sized cement paste block was embedded in an epoxy resin/hardener mixture (without any solvent) and the system left to cure at room temperature. After cure, the sample was sliced to 1 mm thickness using a Struers Accutom 50 precision cut-off machine, and the resulting cement paste/adhesive joint samples were examined by XPS in the interfacial region (see Fig. 4).

2.1.2. Epoxy adhesive and coated cementitious substrates

The epoxy resin used was DGEBA (Epikote 828 Shell with a concentration of 5.34 mol of epoxy groups per kg) and will be

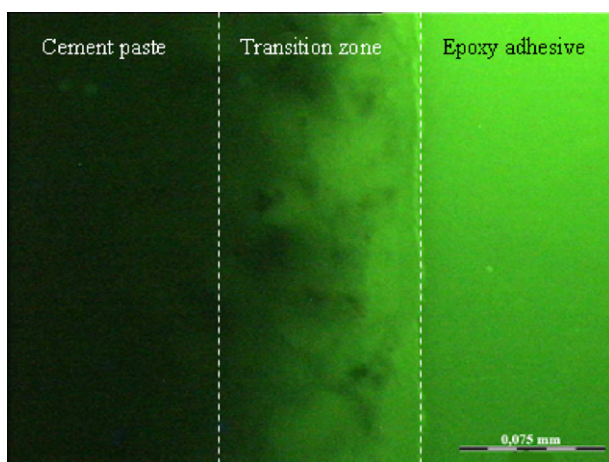


Fig. 2. Hardened cement paste–epoxy adhesive interface image obtained by optical microscopy under UV light illumination.

Download English Version:

<https://daneshyari.com/en/article/259921>

Download Persian Version:

<https://daneshyari.com/article/259921>

[Daneshyari.com](https://daneshyari.com)