Cement and Concrete Composites 88 (2018) 100–114

Contents lists available at ScienceDirect

Cement and Concrete Composites

journal homepage: www.elsevier.com/locate/cemconcomp

Micromechanics-based investigation of the elastic properties of polymer-modified cementitious materials using nanoindentation and semi-analytical modeling

Luise Göbel [a, c, *], Clémence Bos [b], Ruth Schwaiger [b], Alexander Flohr [c], Andrea Osburg [c]

[a] Research Training Group 1462, Bauhaus-Universität Weimar, Germany
[b] Institute for Applied Materials, Karlsruhe Institute of Technology, Karlsruhe, Germany
[c] F.A. Finger-Institute for Building Material Engineering, Bauhaus-Universität Weimar, Germany

ARTICLE INFO

Article history:
Received 27 January 2017
Received in revised form
11 January 2018
Accepted 14 January 2018
Available online 9 February 2018

Keywords:
Polymer-modified concrete
Microstructure
Nanoindentation
Elastic modulus
Continuum micromechanics

ABSTRACT

Cementitious materials are modified by the addition of polymers in order to improve the durability and the adhesive strength. However, polymer-modified mortars and concretes exhibit lower elastic moduli in comparison to unmodified systems. The macroscopic properties are governed by microstructural changes in the binder matrix, which consists of both cementitious and polymer components. Herein, different polymer-modified cement pastes were characterized using nanoindentation to better understand the microscopic origin of the macroscopic elastic modulus. By means of the statistical nanoindentation technique, the existence of three micromechanical phases in plain and polymer-modified cement pastes with a water-to-cement mass ratio of 0.40 is evidenced, illustrating that the polymer modification does not induce the formation of additional reaction products. Instead, the polymers adsorb on the hydration products as well as on unhydrated clinker grains and decrease the indentation moduli of the micromechanical phases. The link between the microscopic and macroscopic mechanical properties is established by means of a continuum micromechanics approach. A multiscale model aimed at the prediction of the elastic moduli of polymer-modified cementitious materials is developed with input parameters that are partially obtained from the nanoindentation tests. The comparison of the modeling results with the experimentally determined elastic (macroscopic) moduli at the scales of cement paste, mortar, and concrete is satisfactorily good, underlining the predictive capability of the modeling approach. The improvement of prediction models is essential for the application of polymer-modified cementitious materials in construction and will encourage their integration into design guidelines.

1. Introduction

During the past few decades, polymer-modified mortars and concretes (PCC) have been used in repair and restoration increasingly [1–3]. Their excellent durability, workability, and adhesive strength as well as the growing need for more durable and efficient building materials also promote the application of polymer-modified mortars and concretes in construction [4–7]. A fundamental understanding of the mechanical behavior of PCC is essential for their use in civil engineering structures. Mechanical properties and the durability of polymer-modified cementitious materials have already been investigated intensively [8,9]. The more pronounced creep activity and lower elastic moduli of PCC in comparison to conventional concrete have been investigated experimentally [10–12]. Furthermore, improvements regarding the waterproofness and the permeability have been reported [13,14], besides an enhanced chemical resistance and an increased freeze-thaw durability [15,16]. Several studies have also focused on the interaction processes between cementitious and polymer constituents and their effects on the cement hydration, revealing that the polymers slow down the hydration reaction due to physical and chemical retardation mechanisms [17–20]. In contrast, less information are available about the fundamental mechanisms underlying the microstructure and their influences on the macroscopic behavior of polymer-modified cementitious materials. The knowledge of micromechanical properties is not only essential for the

* Corresponding author. Bauhaus-Universität Weimar, F.A. Finger-Institute for Building Material Engineering, Coudraystraße 11 A, 99423 Weimar, Germany.
E-mail address: luise.goebel@uni-weimar.de (L. Göbel).

https://doi.org/10.1016/j.cemconcomp.2018.01.010
0958-9465/

improvement of the performance of the material at the macroscopic scale but it is also required for the development of prediction models which incorporate microstructural information.

Nanoindentation is a widely used technique for the determination of material properties at the microscale, allowing for the characterization of local regions in heterogeneous materials. Since 2001, several efforts have been directed towards characterizing the mechanical properties of the cement constituents, including the direct determination of the elastic modulus and hardness of the different cement clinker phases [21] and the application of statistical methods to evaluate a large number of indentations [22–24]. The concept of statistical grid nanoindentation has been refined and successfully applied in studies of hydrated cement pastes [25–27].

While the statistical nanoindentation technique aims at analyzing heterogeneous materials, it is also hampered by the presence of different phases, particularly of the hydration products. In several studies, the existence of two types of calcium-silicate-hydrate (C-S-H) phases, often referred to as low-density C-S-H and high-density C-S-H, with different mechanical properties has been reported due to the multipeak response in the frequency plots of the elastic modulus [23,28,29]. A third phase, the ultra-high density (UHD) phase, exhibits an elastic modulus higher than the two C-S-H phases [25,30]. This UHD phase was observed for substoichiometric cement pastes with a water-to-cement ratio lower than 0.40, while Chen et al. [31] recognized that the UHD phase is rather a mix of Portlandite and C-S-H crystals, so-called C-S-H/CH nanocomposites. However, the accuracy of the nanoindentation results depends significantly on the surface roughness [32–34] of the hardened cement pastes as well as on the size of the individual homogeneous phases [32]. Homogeneous C-S-H phases are too small to be measured separately, as it has been reported based on simulations [32]. According to Trtik et al. [32], the size of the nanoindentation interaction volume should be at least three times smaller than the homogeneous domains of the single phases; otherwise, the measured peaks correspond to the average moduli of different phases.

Recent activities aimed at coupling the mechanical nanoindentation tests with chemical measurements to improve the statistical nanoindentation technique and to obtain more realistic information on the phase identity [31,35–37], for example by combining scanning electron microscope/energy dispersive X-ray spectra (SEM-EDS) with grid nanoindentation. Therewith, it was shown that local regions with increasing fractions of Portlandite exhibited higher moduli than reported for high-density C-S-H [31].

One further important capability of nanoindentation testing is the measurement of basic creep properties. In particular, it was found that the logarithmic kinetics of the long-term creep of concrete can be quantitatively estimated based on minutes-long microindentations on cement pastes [30,38–41]. The creep rate of a cement paste was shown to increase significantly with increasing relative humidity [42].

Until recently, the focus has mainly been on Portland cement pastes. Currently, nanoindentation has been applied to alkali-activated cementitious materials [43,44] and to blended cement pastes including fly ash [45,46], slag [45,47], and silica fume [46,48]. The nanoindentation investigations revealed morphological changes of the hydration products and significant influences of the additives on the micromechanical properties of the cementitious phases. However, a comprehensive study of the micromechanical properties of polymer-modified cement pastes is missing, although a few attempts can be found. Wang et al. [49] investigated styrene-butadiene rubber (SBR) latex-modified cement pastes with varying polymer quantities added in the range of 0 %–20 % of the cement weight. The authors determined the average indentation moduli of the cement pastes as a function of the polymer content in order to identify the finer-scale origin of the macroscopic properties.

The objective of this paper is the quantification of the elastic properties on the microscale of polymer-modified cement pastes. Particularly, correlations between the micromechanical properties, the arrangement of the microstructural components, and the macroscopic mechanical behavior are derived. Results from nanoindentation tests on both polymer-modified cement pastes and films made of the modifying polymers are presented. Different cement pastes, mortars, and concretes are investigated, varying according to the type and quantity of the polymer. Furthermore, the experimental data are coupled with a multiscale model, which aims at the prediction of the elastic properties of polymer-modified cementitious materials. A continuum micromechanics approach is applied to highlight the significance of the micromechanical properties of PCC.

2. Materials and methods

In order to characterize the pure polymers, films were produced and investigated by means of the nanoindentation technique. Nanoindentation tests were also performed to determine the micromechanical elastic properties of polymer-modified cement pastes. Furthermore, the hydration kinetics of the cement pastes were investigated to evaluate the influence of the polymer modification on the cement hydration. A multiscale experimental study comprising mechanical tests with polymer-modified cement pastes, mortars, and concretes was carried out to provide data for the validation of the continuum micromechanics approach (see Section 4).

2.1. Materials

All specimens were made with Portland cement (CEM I 52.5 R) provided by HeidelbergCement (Germany). The chemical composition of the cement is shown in Table 1.

For the polymer modification, a re-dispersible powder (P1) and a dispersion (P2), both on the basis of a styrene/acrylate copolymer, as well as a dispersion (P3) on the basis of styrene/butadiene were used, see Table 2. The comparison between the minimum film formation temperatures (MFT) of the polymers reveals that P1 and P3 form continuous films in the hardened cement pastes for given processing and storage conditions (20 °C, 65% RH). P2 does not form load-bearing films under these conditions. However, the polymer particles have an adhesive bond to the hardened cement paste matrix [50]. Specimens with two polymer-to-cement mass ratios (p/c) amounting to 0.05 and 0.20 were prepared. For all mixtures, the water-to-cement mass ratio (w/c) was kept at 0.40. Deionized water was used. In total, seven different substoichiometric cement pastes, mortars, and concretes (with a w/c-ratio smaller than 0.42) were investigated, including a plain reference without polymer addition. In the following, the specimens are denominated according to the nomenclature *'polymer − p/c-ratio'*.

2.2. Hydration rate and degree of hydration

The hydration kinetics of the polymer-modified cement pastes were investigated using isothermal calorimetry (DSC Q200, TA

Table 1
Mass percentage of chemical components in the Portland cement.

Component	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO	K_2O	Na_2O
Content [%]	65.8	23.2	4.2	1.2	2.8	0.9	0.6	0.4