



Polymerised high internal phase emulsion cement hybrids: Macroporous polymer scaffolds for setting cements

Natasha Shirshova^a, Angelika Menner^a, Gary P. Funkhouser^b, Alexander Bismarck^{a,*}

^a Department of Chemical Engineering, Polymer and Composite Engineering (PaCE) Group, Imperial College London, South Kensington Campus, London, SW7 2AZ, UK

^b Halliburton Energy Services, Duncan Technology Center, 2600 South 2nd Street, Duncan, OK 73536-0470, USA

ARTICLE INFO

Article history:

Received 29 June 2010

Accepted 20 January 2011

Keywords:

Portland cement (D)

Polymer (D)

Polymer cement hybrid materials

Mechanical properties (C)

Oil well cement (E)

ABSTRACT

We polymerised the continuous styrene/divinylbenzene monomer phase of high internal phase emulsions (HIPEs) containing 70 vol.% cement slurry as internal phase to synthesise polymer cement hybrid materials. These novel cement containing poly(merised)HIPEs have an interconnected bi-phasic structure consisting of an interpenetrating network of set cement and polymer. Incorporating 14 wt.% of polymer into the cement resulted in an increased compressive strain to failure as compared to pure set cement but both elastic modulus and crush strength decreased. These novel polymer cement hybrid materials have a better chemical resistance against acetic acid than pure cement and showed also no shrinkage when exposed to xylene and dodecane.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

The strength of cementitious materials is determined by the space between cement particles which is filled as a result of the cement hydration process. This is the reason for the low tensile and flexural strength of hardened cement [1–3]. The properties of cement can be adjusted by varying the water to cement ratio and the addition of admixtures (superplasticizers) to improve the workability of cement [3]. Furthermore, the performance of cementitious materials can be improved by the addition of particles that are small enough to fill the gaps between cement particles. Polymers have been used as additives and modifiers for cement and cement based materials, such as mortar and concrete, as early as 1909 [4]. Combining cement based materials with polymers leads to an improvement of a number of important properties, such as the rheology of the paste [5], adhesion strength to substrates and mechanical properties; polymer addition especially improves the resistance to dynamic loads, impact toughness [6] and flexural strength [3], durability [7], physical and chemical stability [4] and it reduces the permeability of cement [5]. In polymer modified cements (PMC), polymers are incorporated in several forms: as latex (in this case both monomers and polymers have been used), powders or epoxy or unsaturated polyester resins [7–9]. Latexes have been found to be more effective compared to dry powders because they more easily create a film on the surface of anhydrous cement grains. Polymers that are mainly used as cement admixtures

are styrene-acrylic ester emulsions [10], epoxy resins [4,9], polyester-styrene copolymers [4,6] and vinyl-acetate/ethylene copolymers [5]. If monomers are used as an admixture, polymerisation takes place after mixing with the cement. The polymerisation is typically activated by a variety of methods, for instance by temperature, addition of a hardener or UV irradiation, which however has a limited penetration depth [4,11]. Monomers for cement modification are used mainly for renovation and restoration purposes or in situations where high adhesion, durability and weatherability are required [4,11].

The mechanism of cement hydration, its rheological behaviour and mechanical performance as well as microstructure of set cement are topics of ongoing research [5,7,10,12–14]. Nevertheless, it was shown that addition of polymer strongly affects the hydration process of cement [7,14]. Usually, the use of polymers as an admixture leads to an increase of the hydration time. Detailed studies [9,12,15] suggest a reason for this observation, which could be described as follows: the dissolved polymer forms a film, which not only covers the cement particles but also fills the space between cement particles and bridges capillary pores. In this case it takes longer for the free water to access unhydrated cement compared to unmodified cement paste.

It was our aim to develop a method that would allow producing quickly a scaffold within non-hydrated or retarded cement, which could provide sufficient mechanical strength to support the hydrating (retarded) cement. Cement formulations that provide sufficient strength during the slow setting of cement may be useful for various applications in civil engineering and the oil industry, where it will allow continuing certain operations, such as drilling, before the cement is fully set. In the oil industry,

* Corresponding author. Tel.: +44 2075945578.

E-mail address: a.bismarck@imperial.ac.uk (A. Bismarck).