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In-situ preparation of polymer scaffolds in retarded cement slurries: An emulsion templating approach for rapid, on-demand strength development

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ABSTRACT

We demonstrate in this communication that stable high internal phase emulsions consisting of a majority dispersed cement slurry as aqueous phase and a continuous but minority monomer oil phase can be produced. Polymerisation of the monomer phase using both a conventional thermal method as well as by fast setting using carbon fibres as resistance heaters results in bicontinuous polymer cement hybrid materials. We found that a reduction of the polymerisation time from 24 h to 90 min did not affect the physical characteristics, such as density and porosity, of the polymer–cement hybrids but results in a decrease of the crush strength and a significantly reduced elastic modulus.

1. Introduction

Portland cement is used in a wide variety of applications, ranging from civil engineering to the oil and gas industry because of its unique ability when mixed with water to form a flowable slurry or paste, which subsequently reacts to produce a durable solid with high compressive strength [1,2]. In the oil industry cement is used mainly during drilling for oil and gas operations where to fill the annular space between the casing and the wall of the borehole. The purpose of the set cement is to provide support for the drill pipe to allow further drilling as well as preventing gas and fluid migration into and through the annular space. However, the time when drilling can continue depends on the setting time of the cement, which varies depending on temperature, the water/cement ratio and the retarder (or other modifier) content and can take more than 24 h [3,4]. These very long setting times are disadvantageous considering that waiting times during drilling operations are not only non-productive, but very costly.

Extensive research focused not only on existing cement compositions and the rheological behaviour of pastes, ageing and mechanical performance of cementious materials [1,2,5–7] but also on the modification of cement formulations to improve the rheology of the paste, [8] the mechanical performance and morphology [9–11], as well as physical and chemical stability [12] but also in reducing the permeability [8] of set cement. However, a major unsolved research challenge is the ability to actively control the setting time of cement pastes. Cement compositions have been modified by adding various additives [13], including polymers, which resulted in improved crack resistance and bending strength [14], improved rheology of the cement paste or reduced the porosity of set cement. However, generally the addition of polymers does usually not provide mechanical strength to a cement paste during setting. Our hypothesis is that it should be possible to control the development of strength in setting cements by introducing a second phase into the cement formulation, which can be controllably set/cured into a solid material independently of the cement hydration to form a continuous scaffold within (retarded) cement. Earlier we demonstrated [15] the feasibility of using a high internal phase emulsion (HIPE) approach to synthesise novel polymer cement hybrid (PCH) materials and discussed their properties. Polymerised HIPEs (polyHIPEs) are macroporous polymers with an interconnected pore structure and controllable porosity, morphology, physical and mechanical properties [16]. The pore structure of polyHIPEs can be tailored by varying the content (phase volume ratio) and composition of the continuous emulsion phase [17–19]. The continuous (organic) emulsion phase can be polymerised and once the template (water) phase is removed high porosity macroporous, rigid polymers are produced.

In this communication we are presenting the first evidence that it is indeed possible to significantly decrease the polymerisation time of the continuous organic phase of HIPEs containing a retarded cement slurry internal/dispersed phase. Furthermore, we describe the effect of the heating method used to initiate the polymerisation of the organic phase on morphology, physical (density) and

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mechanical (compression) properties as well as thermal stability of the resulting polymer–cement hybrids.

2. Experimental work

2.1. Materials

The following materials were used: styrene (St) (99%, Fluka), divinylbenzene (DVB) (technical grade, Fluka), 2,2′-azobis(isobutyronitrile) (AIBN) (97%, Fisher Scientific UK), the nonionic surfactant Hypermer 1031 (kindly provided by CRODA, Wirral, UK), Portland cement (Class A, Hanson Ltd., UK), Borax (Sigma–Aldrich) and $CaCl_2{\cdot}2H_2O$ (Sigma–Aldrich). All chemicals were used as received without further purification. Analytical grade deionised water (DI water) was used for all experiments.

2.2. Preparation of cement containing high internal phase emulsions, cement paste and polymerisation procedure

Cement containing High Internal Phase Emulsions (CHIPE) with an internal (or dispersed) phase volume of 70% were prepared in a glass reaction vessel equipped with a glass paddle rod connected to an overhead stirrer. The organic phase of the emulsion contained 70 vol.% monomers (50:50 styrene (St)/divinylbenzene (DVB) as a crosslinker), 30 vol.% surfactant Hypermer 1031 and 1 mol.% initiator 2,2′-azobis(isobutyronitrile) (AIBN) with respect to the monomers. The aqueous phase was divided into two parts with a volume ratio 1:6. This was necessary as the direct addition of the cement slurry into the organic phase caused the emulsion to phase separate immediately already during emulsification. The smaller part was a 0.5 wt.% aqueous solution of $CaCl_2$. This $CaCl_2$ concentration (0.3 wt.% with respect to cement) in the final CHIPE is much too low to act as accelerator. Typical concentrations of $CaCl_2$ when used as an accelerator are in the range of 2–4 wt.%, depending on the conditions to which the cement paste shall be exposed [3]. The smaller part of the aqueous phase was added dropwise at constant mixing speed of 400 rpm into the organic phase to form a primary emulsion. The cement slurry was prepared by adding Portland cement (Class A) and retarder (Borax) into deionised water at constant agitation speed using a hand mixer. After all cement was added the slurry was homogenised using hand mixer for 35 s. The cement to water ratio was kept constant 1/0.38. The cement slurry was then poured into the primary emulsion while stirring it using a overheard stirrer at 400 rpm. The formulation was mixed for another 35 s at a stirring speed of 2000 rpm. The compositions of the samples prepared are listed in Table 1.

For conventional polymerisation, the prepared CHIPEs were transferred into polypropylene standing centrifuge tubes, sealed and placed into an oven at 70 °C for polymerisation of the organic phase. The samples were kept in the oven for 3 d to ensure complete polymerisation (although this takes much less time) and for ageing of the cement prior to any testing. The polymerised CHIPE is called PCH.

In order to prove that it is possible to rapidly set the organic phase of the CHIPE independently of the Portland cement phase, the polymerisation was initiated using carbon fibres as resistance heaters for the CHIPE. The prepared CHIPEs were transferred into a glass vessel ($d = 2.54$ cm) which was helically wrapped with one layer of carbon fibres (M40B, 12,000-50B, SOFICAR Torayca, France) with the space between convolutions about 0.6–1.0 cm to ensure that the fibre bundles were well apart (Fig. 1a). Glass vessels were necessary in this case as the polypropylene started melting when a current was passed through the fibres, which acted as resistance heaters. Alternatively, it was also possible to initiate the polymerisation simply by submerging one U-shaped loop of carbon fibres (about 10 cm long) into a CHIPE (Fig. 1b). Later method was not further used as the conditions to polymerise the entire organic phase of CHIPEs using this method could not easily be optimised. It was observed that the CHIPE in direct contact with the carbon fibres overheated, which led to coalescence of emulsion droplets and partial water evaporation. As a result large voids, which could be seen by naked eye, formed. Moreover, some organic phase of CHIPE in the middle of the vessel (farthest from the submerged carbon fibres) did not polymerise and remained liquid. Such a temperature gradient was not observed when using a glass vial helically wrapped with carbon fibres. The carbon fibres were used as resistance heaters to locally heat the reaction mixture and so initiate the free radical polymerisation. 11–13 W h was used to polymerise the organic phase of a CHIPE with a volume of 30 cm^3. However it is important to note that most of the heat generated by the carbon fibres was lost to the environment during the process because polymerisation vessel was not insulated and the experiment conducted in an open laboratory atmosphere. We believe that optimisation of the setting process, i.e. by using appropriate insulation, will allow to significantly reduce the energy

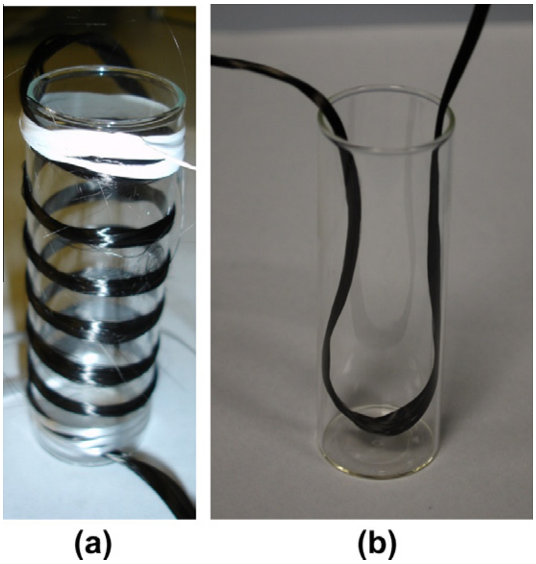
(a) (b)

Fig. 1. Photographs of the setups used for rapid setting of CHIPE; a – glass vial which was helically wrapped with carbon fibres, glass fibres were used to hold the carbon fibres in position at the top and bottom of the glass vial; b – glass vial containing one loop of carbon fibres. The glass vials were filled with CHIPE and a current passed through the carbon fibres, which acted as resistance heaters supplying the heat to initiate the free radical polymerisation of the continuous organic/monomer phase.

Table 1
PolyHIPE and PCH made from HIPEs and CHIPEs with the following compositions polymerised in a convection oven or *via* rapid heating using carbon fibres as resistance heaters.

Sample	Organic phase (30 vol.%)	Aqueous phase (70 vol.%)	Heating method used
PolyHIPE	St, DVB, Hypermer 1031, AIBN	0.5 wt.% solution $CaCl_2$, DI water	Convection oven
PCH	St, DVB, Hypermer 1031, AIBN	0.5 wt.% solution $CaCl_2$, DI water, cement, 0.1 wt.% Borax	Convection oven
PCH RS	St, DVB, Hypermer 1031, AIBN	0.5 wt.% solution $CaCl_2$, DI water, cement, 0.1 wt.% Borax	Resistance heating
Hardened cement paste	–	DI water, cement, 0.1 wt.% Borax	Convection oven

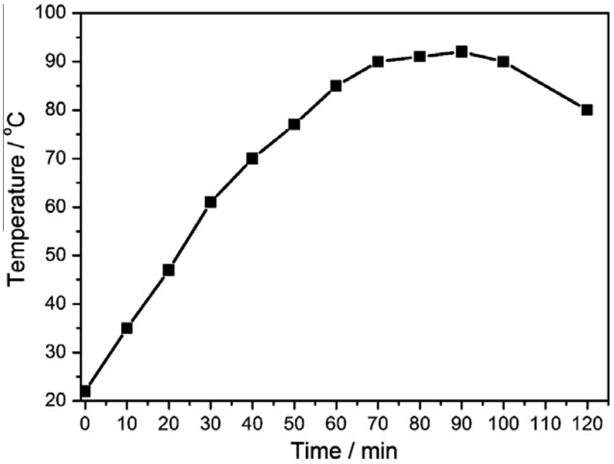

Fig. 2. Typical temperature profile measured using a thermocouple in the centre of the curing CHIPE. Please note that the heat required to initiate the exothermic free radical polymerisation was supplied by carbon fibre resistance heaters.

lost to the environment. The polymerisation of most of organic phase of the CHIPE was complete after 90 min. This was determined by recording the temperature during the polymerisation process at the top and bottom of the reaction mixture. The maximum recorded temperature reached 93 °C. The decrease of the temperature was considered as an indicator of the completion of the polymerisation reaction (Fig. 2). Moreover, the physical state of the CHIPE changed from a paste to a solid material. This was verified simply by trying to push a wooden stick into the setting CHIPE. Even so, the samples were solid prior to placing them into the oven; they were not strong enough to be removed from the glass reaction vessel without damage as the cement adhered rather well to the glass. Therefore, after complete polymerisation, the polymerised CHIPE were transferred into an oven at 70 °C and kept there for 3 d before any tests were performed to complete cement setting and allow its ageing. CHIPE polymerised using this method are called PCH RS (rapidly set). Afterwards, the PCH were removed from the reaction vessels by smashing the glass tubes, cut using a band saw (STARTRITE Bandsaw 502s, UK) and dried in vacuum oven at 50 °C overnight if required for analysis (such as SEM). The compositions of the studied samples are listed in Table 1.

2.3. Characterisation of polymer–cement hybrids and hydrated cement paste

The time of hydration at the moment of testing was 3 d for all cement containing samples.

The morphology of the polymer cement hybrids was studied using scanning electron microscopy (SEM; Jeol JSM 5610 LV, Jeol Ltd., Welwyn Garden City, UK) using accelerating voltage of 15 kV. All samples were gold coated for 120 s in argon atmosphere (Emitech 550, Emitech Ltd., Ashfort, UK) to guarantee sufficient electrical conductivity.

Skeletal, envelope density and porosity of the samples was determined by pycnometry using a helium pycnometer (AccuPyc 1330, Micrometrics Ltd., Dunstable, UK) and a GeoPyc 1360 analyser (Micrometrics Ltd., Dunstable UK). For each specimen the measurement was repeated at least on three samples taken from different parts of a specimen to obtain an average value.

Mechanical properties of the samples were investigated by compression tests, following the industrial standard BS ISO 844 using a Lloyds Universal Testing Machine (Lloyds EZ50, Lloyds Instruments Ltd., Fareham, UK) equipped with a 50 kN load cell. The samples were loaded at a rate of 1 mm/min until the specimen failed. The dimensions of the cylindrical specimens were chosen in such a way that height of the specimen (50 mm) was twice its diameter, which was 25 mm.

The thermal stability of the synthesised materials in a nitrogen atmosphere was determined using thermogravimetric analysis (TGA) using Q500 Thermogravimetric Analyser (TA Instruments, USA) in the temperature range from 30 °C to 850 °C at a heating rate of 20 °C/min. TGA was performed on 10–15 mg of the material. The obtained data were analysed using integrated Universal analysis 2000 software.

3. Results and discussion

The choice of surfactant was made based on earlier research [15] were three non-ionic surfactants were used (Hypermer 2296, Hypermer 1083 and Hypermer 1031) to produce stable cement containing high internal phase emulsions (CHIPE). Our results showed that polymer cement hybrids (PCH) could be synthesised using all three surfactants. Moreover, all three PCH exhibited similar physical and mechanical properties. However, the PCH obtained after setting both monomers and cement in the CHIPE template stabilised by Hypermer 1031 had a much more uniform morphology; it was not possible to distinguish the polymer (Fig. 3a) and cement (Fig. 3b) phases. Therefore, Hypermer 1031 was chosen to study the possibility to rapidly set a CHIPE.

In order to rapidly provide strength in retarded cement we had to identify a suitable curing method for the continuous organic phase of the CHIPE. Taking into account the nature of initiation of a free radical polymerisation, we had to identify a method of providing enough energy for the initiation step of the polymerisation. A frontal polymerisation approach [20] was not feasible for our system because the majority cement slurry internal phase was too big a heat sink, which led to a premature termination of the polymerisation. However, resistance heating using electrically conducting carbon fibres [21], which are readily available in large quantities and have a high electrical resistance, meant that the CHIPE can easily be heated on demand by passing a current through the carbon fibres, which were wrapped around the reaction vessel. The heat irradiated from carbon fibres caused the initiator to decay which started the polymerisation.

The SEM images of the PCH (Fig. 3c) and PCH RS (Fig. 3d) show that the morphology of the materials, obtained using either method, was identical. It is difficult to identify any differences between these two PCH. Needle-like morphologies can be seen in all PCH irrespectively of the method used to heat the CHIPE to initiate the polymerisation. These needle-like structures could represent both calcium silicate hydrate (C–S–H) [22] and ettringite ($(CaO)_6(Al_2O_3)(SO_3)_3 \cdot 32H_2O$) [22]. Compared to C–S–H, which has a fibrous structure, ettringite forms small needles at this relatively high curing temperature (70 °C or higher) [1]. As a result the hydrated hardened cement paste in PCH contains mainly C–S–H.

The porosity of PCH, PCH RS and hardened cement paste are 37%, 33% and 34%, respectively. The method of heating used to initiate the polymerisation did not affect the skeletal and envelope densities of obtained PCH. Skeletal densities were 2.240 g/cm^3 and 2.180 g/cm^3 and envelope densities were 1.410 g/cm^3 and 1.480 g/cm^3, for PCH and PCH RS, respectively. These values are significantly lower compared to those for hardened cement paste (values for skeletal and envelope densities of hardened cement paste are 2.590 g/cm^3 and 1.690 g/cm^3), due to incorporation of the less dense polymer phase into cement.

Compression tests were performed on cylindrical test specimens, with a height to diameter ratio of 2, to determine the influence of the heating method used to produce the PCH on the mechanical performance. Hydration times for all samples prior to

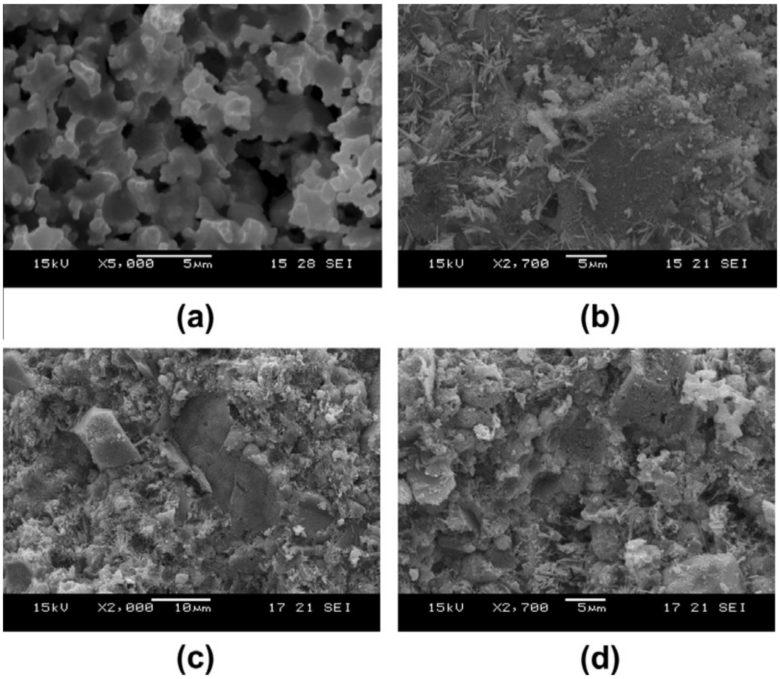

Fig. 3. SEM micrographs of pure polyHIPE (a), hardened cement paste (b), PCH (c) and PCH RS (d).

compression tests was 3 d. Typical stress strain curves for PCH are presented in Fig. 4. The rapid setting of CHIPE led to a reduction of the mechanical properties of the resulting PCH; the elastic modulus of the PCH RS was 0.56 ± 0.03 GPa as compared to 0.85 ± 0.08 GPa for PCH. The elastic modulus for hardened cement paste was determined to be 2.04 ± 0.1 GPa. The crush strength, determined from the first point of failure, i.e. initial drop in the stress *vs.* strain curve, for PCH RS was 2.6 ± 0.1 MPa, which is half of that the conventionally cured PCH (6.3 ± 0.45 MPa). The measured crush strength for hardened cement paste was 9.6 ± 1.3 MPa. It is important to mention that strain to failure of the PCH (0.57–0.77%), determined from the first point of failure, was equal or higher than that for the hardened cement paste (0.57%). This is especially important as cement with a higher strain resistance allows for greater protection of the casing/cement/borehole bonding during dynamic loading.

The significant drop in the compressive strength and modulus for the PCH RS could be caused by formation of lower amount of C–S–H compared to PCH due to the evaporation of water near the walls of the vessel which were exposed to the highest temperatures during the setting process, which affected the amount of water available for cement hydration in CHIPE. This could happen because the polymerisation took place in an open vial at ambient pressure with a centre point temperature reaching up to 93 °C.

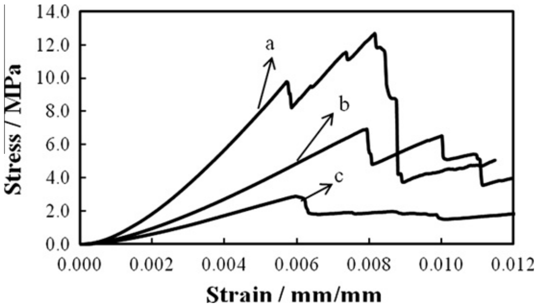

Fig. 4. Representative stress–strain curves for hardened cement paste (a), PCH (b) and PCH RS (c).

According to the literature on thermal stability of cementious materials [23–25] at temperatures exceeding 70 °C one of the processes taking place is the evaporation of non-bonded water.

The thermal behaviour of the PCH was studied using thermal gravimetric analysis. Three main weight loss areas were observed in the thermograms (Fig. 5) of all studied PCH which are due to the following processes: from about 70 °C to 230 °C unbound water evaporates as well as dehydration reaction of C–S–H and ettringite takes place, which is followed by polymer decomposition in the temperature range from 250 °C to 550 °C but this overlaps with the decomposition of portlandite (CH) (440 °C) and eventually carbonate phases (calcium carbonate) decompose at temperatures above 550 °C [23–25]. Due to overlap of polymer decomposition and the decomposition of ettringite and C–S–H it was not possible to determine amount of C–S–H in the PCH obtained using different heating techniques. However, the heating method used to initiate the polymerisation of the monomer phase of the CHIPE did not affect overall thermal stability of the PCH, the total weight loss at 850 °C for all PCH was about 33 wt.%. The total weight loss for the hardened cement paste was found to be 25 wt.%, which is in

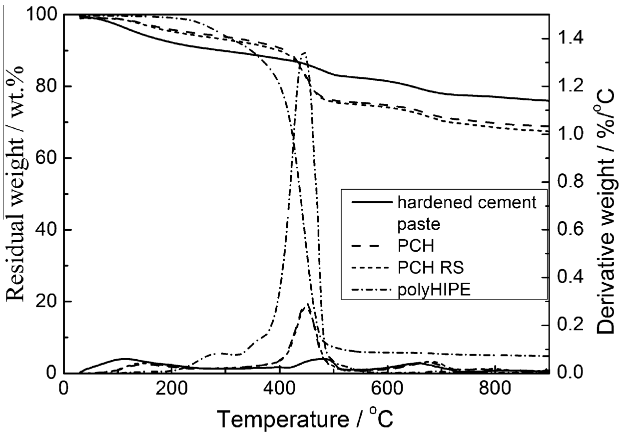

Fig. 5. TGA curves of pure polyHIPE, PCHs and hardened cement paste.

a good agreement with literature [23–25]. The difference in the total weight loss is due to the presence of the polymer phase.

4. Conclusions

We demonstrated that it is possible to produce sufficiently stable high internal phase emulsions (HIPEs) with a (retarded) cement slurry as dispersed phase and a continuous monomer emulsion phase, which could be polymerised via free radical polymerisation initiated not only at a constant temperature of 70 °C but also set rapidly into solid polymer cement hybrids, within 90 min, using carbon fibres as resistance heaters. The densities and porosities of the PCH produced by the rapid heating technique were similar to those obtained using conventional thermal free radical polymerisation of the continuous phase. Even though, mechanical performance of the rapidly set PCH was inferior compared to conventionally set PCH, their morphology was the same as observed for conventionally set PCH, which suggests that optimisation of the rapid setting process will result in improved materials.

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