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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

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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 then pure cement and showed also no shrinkage when exposed to xylene and dodecane.

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,

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* Corresponding author. Tel.:+44 2075945578.
E-mail address: a.bismarck@imperial.ac.uk (A. Bismarck).

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cement is used during well-drilling operations to fill the annular space between the casing and the wall of the borehole. In this case, cement has to provide support for further drilling as well as preventing gas and fluid migration into and through the annular space. The set cement has to withstand extreme temperatures, pressures and chemical attack, but still needs to have a low permeability. Moreover, the cement slurry has to have good workability and must set in a certain period of time. Currently setting times for cement slurries can vary widely depending on the water to cement ratio and retarder content. Long waiting times (often up to 24 h) are disadvantageous considering that waiting times are non-productive and costly.

The approach we are introducing in this paper comprises the synthesis of a polymer hybrid material using high internal phase emulsion templates and an *in situ* polymerisation technique to produce a scaffold within hydrating cement. We adopted this approach because emulsion templating using high internal phase emulsions (HIPE) allows for the production of macroporous polymers, commonly known as polymerised HIPEs (polyHIPEs) possessing a very porous interconnected structure with tailorable mechanical properties [16–20]. The organic continuous (monomer) emulsion phase can be rapidly and controllably hardened/cured (polymerised) into a solid, rigid material with tuneable properties. It is expected that the resulting porous but continuous polymer phase created within the dispersed cement phase will act as a scaffold for the cement and provide enough strength to allow proceeding with for instance drilling operations while the retarded cement slurry is still slowly setting. The feasibility of the synthesis of polymer cement hybrid materials, the morphology as well as physical and mechanical properties of the obtained polymer-cement hybrid materials was studied.

2. Experimental part

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 non-ionic surfactants Hypermer 1083, 2296 and 1031 (kindly provided by CRODA, Wirral, UK), Portland cement (Class A, Hanson Ltd, UK), lignosulfonic acid sodium salt (LSASS) (kindly provided by Halliburton, USA), carboxymethylcellulose (CMC) (M_w = 90 kDa, Sigma-Aldrich), sucrose (table sugar), Borax (Sigma-Aldrich), nitrilotri (methylphosphonic acid) (Dequest 2000) (purum, >97.0% Sigma-Aldrich), $CaCl_2 \cdot 2\ H_2O$ and Na_2SO_4 (Sigma-Aldrich), acetic acid (100%, VWR UK). All chemicals were used as received without further purification. Analytical grade deionised water (DI water) was used for all experiments.

2.2. Preparation of high internal phase emulsions

HIPEs 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 vol.% monomer (St):crosslinker (DVB)), 30 vol.% of surfactant and 1 mol% initiator (AIBN) with respect to the monomers. The initiator was first dissolved in half the amount of monomer and then added to the rest of the organic phase. The aqueous phase containing 0.5 wt.% $CaCl_2 \cdot 2H_2O$ solution was added dropwise into the organic phase at a stirring rate of 400 rpm. After complete addition of the aqueous phase, the stirring rate was increased to 2000 rpm for a further 10 min to homogenise the emulsion. Afterwards, the emulsion was transferred into polypropylene standing centrifuge (Falcon®) tubes, sealed and placed into an oven for 24 h at 70 °C for polymerisation. Afterwards, the polymerised samples were removed from the Falcon tubes, cut using a band saw (STARTRITE Bandsaw 502s, UK) and dried in a vacuum oven at 50 °C until constant weight.

2.3. Preparation of cement containing HIPEs

Cement containing HIPEs (CHIPE) with an internal 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 vol.% monomer (St): crosslinker (DVB)), 30 vol.% (if not stated otherwise) surfactant and 1 mol% initiator with respect to the monomers (Table 1). The initiator was first dissolved in half of the amount of monomer and added to the rest of organic phase. The aqueous phase was divided into two parts with a volume ratio of 1:6. The smaller part was a 0.5 wt.% aqueous solution of $CaCl_2 \cdot 2 \cdot H_2O$, which was added dropwise at a constant mixing speed of 400 rpm into the organic phase to form a primary emulsion. A cement slurry was prepared by adding cement and retarder into deionised water at constant agitation speed using a hand mixer followed by final homogenisation for 35 s. The cement to water ratio was kept constant 1/0.38. This slurry was then added into the prepared primary emulsion at 400 rpm and the formulation was mixed for another 35 s at an agitation speed of 2000 rpm using the overheard stirrer. Finally, the CHIPE was transferred into standing polypropylene centrifuge (Falcon®) tubes, sealed and placed into an oven at 70 °C for polymerisation. $CaCl_2$ in sufficient concentration is an accelerator for cement setting; however because of the negligible amount of $CaCl_2$ in the final CHIPE it can be safely assumed that it was not acting as an accelerator in this case.

The polymerised CHIPEs or polymer-cement hybrids (PCH) were kept in the oven for 3 days before any tests were performed. After removal from the oven, the PCHs were removed from the Falcon tube, cut using a band saw and dried in vacuum oven at 50 °C overnight if required for analysis (such as SEM). Three different surfactants from

Table 1
Composition of the traditional and cement containing HIPEs.

Surfactant used in organic phase*	Aqueous phase	Observations
Organic: aqueous phase ratio = 20: 80 vol.%		
Hypermer 2296	0.5 wt.% solution $CaCl_2 \cdot 2H_2O$ in DI water, cement	
Organic: aqueous phase ratio = 30 : 70 vol.%		
Hypermer 2296	0.5 wt.% solution $CaCl_2 \cdot 2H_2O$ in DI water	Discussed in text as polyHIPE 2296
Hypermer 1031	0.5 wt.% solution $CaCl_2 \cdot 2H_2O$ in DI water	Discussed in text as polyHIPE 1031
Hypermer 2296	0.5 wt.% solution $CaCl_2 \cdot 2H_2O$ in DI water, cement, 0.1 wt.% Borax	Discussed in text as PCH 2296
Hypermer 2296	0.5 wt.% solution $CaCl_2 \cdot 2H_2O$ in DI water, cement, 0.1 wt.% sucrose	Phase separated as soon as homogenisation stopped
Hypermer 2296	0.5 wt.% solution $CaCl_2 \cdot 2H_2O$ in DI water, cement, 0.1 wt.% LSASS	
Hypermer 2296	0.5 wt.% solution $CaCl_2 \cdot 2H_2O$ in DI water, cement, 0.1 wt.% CMC	
Hypermer 2296	0.5 wt.% solution $CaCl_2 \cdot 2H_2O$ in DI water, cement, 0.1 wt.% Dequest 2000	
Hypermer 2296	0.5 wt.% solution Na_2SO_4 in DI water, cement, 0.1 wt.% sucrose	
Hypermer 1031	0.5 wt.% solution $CaCl_2 \cdot 2H_2O$ in DI water, cement, 0.1 wt.% sucrose	
Hypermer 1031	0.5 wt.% solution $CaCl_2 \cdot 2H_2O$ in DI water, cement, 0.1 wt.% Borax	Discussed in text as PCH 1031
Hypermer 1083	0.5 wt.% solution $CaCl_2 \cdot 2H_2O$ in DI water, DI water, cement, 0.1 wt.% Borax	Discussed in text as PCH 1083
–	DI water, cement, 0.1 wt.% Borax	Discussed in text as pure set cement

* For all samples St was used as monomer; DVB as crosslinker and AIBN as initiator.

the Hypermer family were used for the stabilisation of CHIPEs: Hypermer 2296, 1083 or 1031. The PCHs made using different surfactants have been named PCH 2296, PCH 1083 and PCH 1031, respectively. In case a very large amount of retarder, i.e. 1 wt.%, was used the number "1" was added to the sample name, for example PCH 2296-1.

The concentration of the cement ([cement]) in the polymer–cement hybrid material was calculated as a percentage of total weight of the system ([cement + monomers]).

2.4. Preparation of cement paste

A mixture of dry cement and 0.3 wt.% retarder with respect to the cement weight was added to water (cement/water ratio 1/0.38) and homogenised using an electrical hand mixer for 1 min. The prepared cement slurry was then transferred into Falcon tubes, sealed and placed into an oven for 3 days at 70 °C. Afterwards samples were removed from the Falcon tube, cut using a band saw and dried in a vacuum oven at 50 °C overnight if required for analysis (SEM).

2.5. Ultrasound transit time measurements

A cement containing HIPE 1031 and a pure cement slurry with and without Borax, used as retarder, were examined by measuring ultrasound transition times. The ultrasound transit time measurement is a non-destructive *in-situ* characterisation technique, which has been previously employed to study the hydration of cement at an early age [21,22]. It was also used to examine the influence of silica rich mineral additives on the hydration of Class H cement at 180 °C [23].

The cement paste and CHIPE 1031 were prepared as described in Sections 2.3 and 2.4. Transit times were measured on a Halliburton Ultrasonic Cement Analyzer with Chandler modifications for data acquisition. Samples were kept at a temperature of 70 °C for 72 h and then compression tests were performed to determine the mechanical properties of the set cement. The samples for crush tests were cut into cylinders with a diameter of 50 mm and a height 55.9 mm.

2.6. Characterisation of polyHIPEs, polymer–cement hybrids and hydrated cement paste

The *morphology* of fracture surfaces of polyHIPEs, PCHs and hydrated cement pastes was studied by scanning electron microscopy (SEM; Jeol JSM 5610 LV, Jeol Ltd., Welwyn Garden City, UK). The accelerating voltage was 15 kV. Samples were fixed to a sample holder using a carbon black sticker. All samples were gold coated for 120 s in argon atmosphere (Emitech 550, Emitech Ltd., Ashfort, UK) to guarantee sufficient electrical conductivity.

The *skeletal density* ρ_s of the samples was determined using a Helium Pycnometer (AccuPyc 1330, Micromeritics Ltd, Dunstable, UK). This method measures the pressure change resulting from displacement of helium by a solid object. A dry and pre-weighed sample is placed into pycnometer cell with known volume V_c. After sealing, the pressure within the sample chamber P_{1g} is measured. This is followed by the introduction of helium via a valve and its expanded volume V_{exp} is measured. Then pressure in the system P_{2g} is allowed to equilibrate and is measured again. The skeletal density ρ_s is calculated as follows:

$$\rho_s = \frac{m_s}{V_c - \frac{V_{exp}}{\left(\frac{p_{1g}}{p_{2g}} - 1\right)}}[\mathrm{g/cm^3}], \tag{1}$$

where m_s is the weight of the sample (g), V_c is the pycnometer volume (cm^3), V_{exp} is the expanded volume (cm^3), p_{1g} is the elevated pressure, p_{2g} is the equilibrated pressure. To obtain an average value for each sample the measurement was repeated on at least three pieces taken from different parts of a sample.

The *envelope density* ρ_e of the samples was measured using a GeoPyc 1360 analyser (Micromeritics Ltd., Dunstable UK). This technique relies on the displacement of a solid object immersed in a bed of much smaller solid particles. The external (envelope) volume V_e of the sample is determined so that the internal pores are considered to be part of the sample. The measurements are done on pieces of a specimen mixed with graphite powder in a glass cylinder containing a plunger. V_e of the sample is determined by measuring how far the plunger can be moved into the cylinder. The envelope density ρ_e is determined by:

$$\rho_e = \frac{m_s}{V_e}.$$

To obtain an average value for each sample the measurement was repeated on at least three pieces taken from different parts of a sample.

The *porosity P* of the sample was calculated using the following equation:

$$P = \left(1 - \frac{\rho_e}{\rho_s}\right) \times 100(\%).$$

The *mechanical properties*, namely the crush strength and elastic modulus, of the polyHIPEs and PCHs were investigated by compression tests, which were carried out in accordance to 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. In accordance to CIP 35 the dimensions of the specimens were chosen in such a way that height of the specimen was twice its diameter [24]. The elastic modulus was determined from the slope of the initial linear part of the stress–strain plot. The compliance of the testing machine was taken into account for all calculations. The reported crush strength and elastic modulus values are the average of five to eight measurements and the errors presented are standard errors.

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

2.6.1. Chemical resistance

To determine the *oil resistance*, weighed specimens with recorded dimensions were placed in to *p*-xylene and n-dodecane, respectively, in which they were stored at 100 °C. The dimensions of the specimens were measured in 7 day intervals over a period of four weeks.

Acid degradation of the PCHs was performed in a 1 wt.% sugar solution in 1 M acetic acid. After the weight and the dimensions of samples were recorded, they were placed into glass bottles with screw caps, where they were submerged into the sugar in acetic acid solution. The weight ratio of PCH or pure set cement to acid solution was 1:1. The samples were stored in the sugar acetic acid solution for 40 days. The acid solution was changed regularly to keep the pH of the system below 7. After 40 days the samples were removed and washed with distilled water, which was followed by washing in acetone to replace water, and then filtered and dried in a vacuum oven at 40 °C. SEM, pycnometry and TGA were used to determine the effect of the acid treatment on morphology and properties of the PCHs.

3. Results and discussion

We attempted to synthesise a scaffold for setting or hydrating cement within the cement itself using a high internal phase emulsion (HIPE) templating approach. Potentially a fast polymerisation of the continuous monomer phase of the HIPE within the cement results in an interconnected polymer network that acts as a scaffold for the setting cement phase providing sufficient strength to the cement. Initially, we conducted a set of experiments to determine the optimal formulation; choosing a suitable retarder and determine the maximum cement concentration which still allows the introduction of a cement slurry as internal phase into a HIPE without causing the emulsion to destabilise, which could occur because of an increased sedimentation rate caused by the high density of the cement slurry used as internal phase. To select a retarder we explored a wide range of retarders, such as sucrose, LSASS, Dequest 2000 and Borax. However, surprisingly only Borax did not adversely affect the emulsion stability. When using the other three retarders, a sudden destabilisation of the emulsion and the formation of two immiscible phases, the organic monomer phase (on top of the mixture) and the cement slurry (on the bottom of the reaction vessel) was observed as soon as the homogenisation process stopped.

Initially, we investigated the feasibility of producing HIPEs consisting of only 20 vol.% organic phase and 80 vol.% cement slurry to produce the polymer cement hybrids. Stable CHIPEs with a cement content of up to 86 wt.% could be prepared and polymerised. As expected, the incorporation of cement into a polyHIPE led to an increase of both the skeletal and envelope densities and to a significant reduction of the porosity of the PCHs as compared to pure polyHIPEs; both envelope density and porosity of PCHs approach the value of hydrated set cement. However, the compression properties of the produced PCHs were extremely poor; the elastic modulus was lower than 1 GPa for a PCH containing 86 wt.% of non-retarded set cement.

3.1. Morphology, density and mechanical properties of polymer cement hybrids

Based on the results obtained for the PCH containing an 80 vol.% internal cement phase it was decided to decrease the internal phase volume to 70 vol.%. The properties of the pure polyHIPE controls, synthesised PCHs and pure cement are summarised in Table 2. As expected, the density of the PCH material as well as the elastic modulus are much higher than that of the pure polyHIPE. However, the compressive properties are still well below those of pure set cement. A possible explanation for this could be found in the morphology of the hybrid material (Fig. 1c). The pure polyHIPE without any cement (Fig. 1a) is a macroporous polymer with pores of a diameter ranging from 2.5 μm to 6 μm, which are interconnected by pore throats with diameters of 1–2 μm. It was expected that cement, which by itself, when set, forms a continuous network (Fig. 1b), will fill the empty space of these pores and the polymer pore walls will give support, i.e. act as scaffold, to the setting cement. However, we found that two distinct morphologies of the cement and polyHIPE coexist within the material (Fig. 1c). This means that during the CHIPE preparation the cement slurry formed a separate phase rather than being incorporated into the dispersed emulsion droplets. This observation could be explained by the small size of the emulsion droplets and the affinity of cement to water or aqueous salt solutions. It is also possible that the solution of $CaCl_2 \cdot 2H_2O$ inside the emulsion droplets is used for further cement hydration but diffusion of cement slurry into the droplets is limited because of the viscosity of cement slurry and thickness of the oil phase surrounding the emulsion droplets.

Table 2

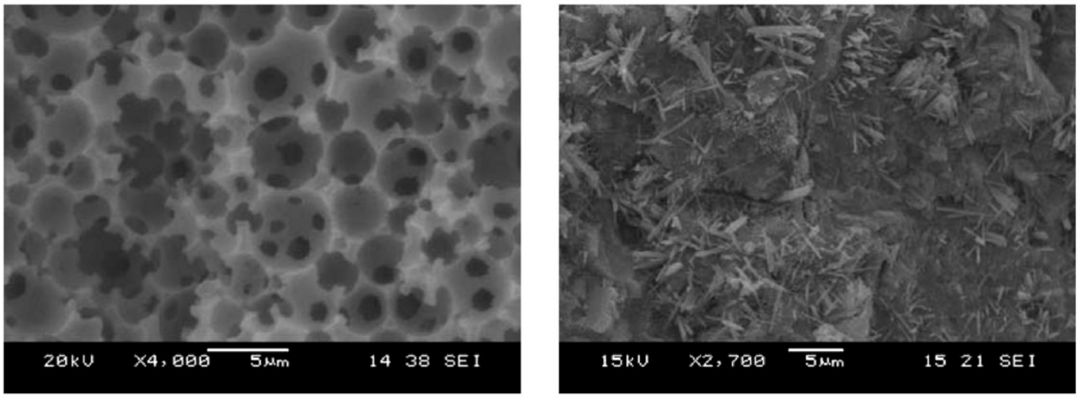
Skeletal ρ_s, envelope density ρ_e, porosity P as well as elastic modulus E and crush strength σ of a polyHIPE, polymer hybrid materials and pure set cement.

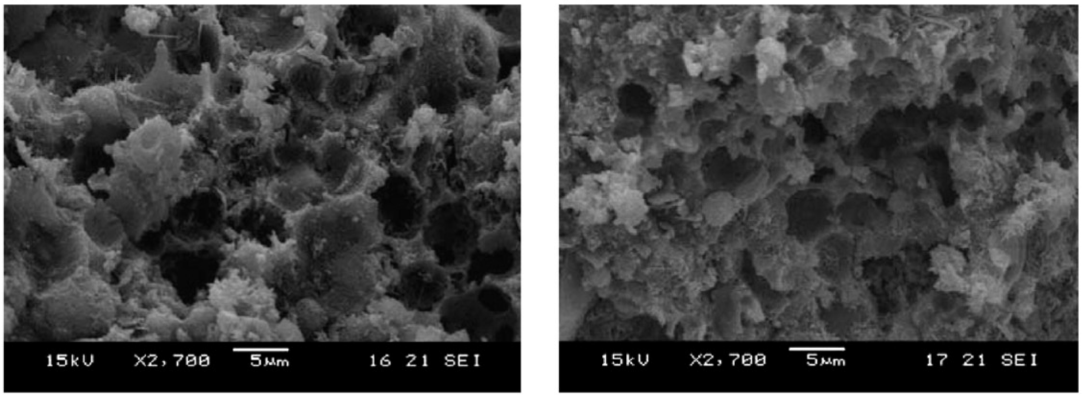
Sample	ρ_s/g/cm^3	ρ_e/g/cm^3	P/%	E/GPa	σ/MPa
PolyHIPE 2296	1.226 ± 0.007	0.249 ± 0.016	79 ± 3	0.062 ± 0.001	3.4 ± 0.2
PCH 2296	2.170 ± 0.004	1.430 ± 0.055	35 ± 1	1.5 ± 0.1	11.5 ± 1.3
PCH 1031	2.240 ± 0.003	1.410 ± 0.025	37 ± 1	1.7 ± 0.4	10.6 ± 2.5
PCH 1083	2.210 ± 0.005	1.470 ± 0.025	33 ± 1	1.4 ± 0.6	12.2 ± 3.1
Pure set cement	2.590 ± 0.004	1.690 ± 0.078	34 ± 3	5.1 ± 0.8	25.5 ± 1.1

Surfactants play an important role in the formation of high internal phase emulsions, affecting its stability and as a result the pore size and interconnectivity of polymerised HIPEs, which reflects the structure of the emulsion at the gel point during polymerisation [25]. In order to increase the droplet size, two other surfactants with similar hydrophilic–lipophilic balance (HLB) values were explored to formulate polymer cement hybrids. The morphology of the PCHs and polyHIPEs is presented in Fig. 1a, c–f. The morphology of the polyHIPEs obtained using Hypermer 2296 (Fig. 1a) and Hypermer 1083 (not shown) are very similar with clearly-identifiable pores and pore throats. However, when Hypermer 1031 was used as surfactant the resulting macroporous polymers had rather thick pore walls, non-uniform pores and ill-defined pore throats (Fig. 1f). It is known that the morphology of a polyHIPE depends on the structure of the emulsion (HIPE) template at the gel point of the polymerisation [18]. It seems that the surfactant Hypermer 1031 results in the formation of a bicontinuous emulsion, which after polymerisation results in a bicontinuous polyHIPEs.

The difference in morphology between the PCH samples and hydrated set cement is obvious (Fig. 1b–e). The needle-like morphologies in the hydrated cement could be calcium silicate hydrate (known as C–S–H) or ettringite. It would be expected that the hydrated set cement contains mainly C–S–H, which has a fibrous structure and only a small amount of ettringite ($(CaO)_6(Al_2O_3)(SO_3)_3$ 32 H_2O), which usually forms small needles at this relatively high curing temperature of 70 °C. This is consistent with the literature [26] reporting that ettringite is transforming into calcium monosulphoaluminate above 40 °C. Decomposition of ettringite in the samples leads to an increase of the porosity. However, there was no major difference in the morphology of the PCHs, i.e. between samples PCH 2296 and PCH 1083. However, PCH 1031 exhibited a more uniform morphology. It is much harder to distinguish the polyHIPE structure from the cement structure. Some flakes which could be seen on the broken surface of PCH 1031 could represent both calcium hydroxide (known as portlandite or CH) and C–S–H [27].

As expected all PCHs have much higher skeletal and envelop densities than the pure polyHIPE, which contains 79% air, but the PCHs have also slightly lower densities than pure set cement. The high porosity for the pure polyHIPE of 79%, even if only 70 vol.% internal phase was used as template, were also observed by others [17,19]. The reason for the discrepancy could be that i) the polymerisation yield was not 100% and ii) the surfactant is structurally parasitic as it is not incorporated into the polymer walls during polymerisation of the emulsion template leading to a greater porosity, especially since continuous emulsion phase contains 30 vol.% surfactant. All PCHs have almost identical skeletal and envelop densities and, therefore, almost the same porosity, which gives rise to near identical compressive properties of the obtained hybrids too (Table 2), which however, are significantly lower than those measured for pure set cement. Although, the obtained data are very promising, further improvement of the mechanical performance of the hybrid materials is required to achieve values approaching those for pure set cement.


(a) polyHIPE 2296
(b) pure set cement


(c) PCH 2296
(d) PCH 1083

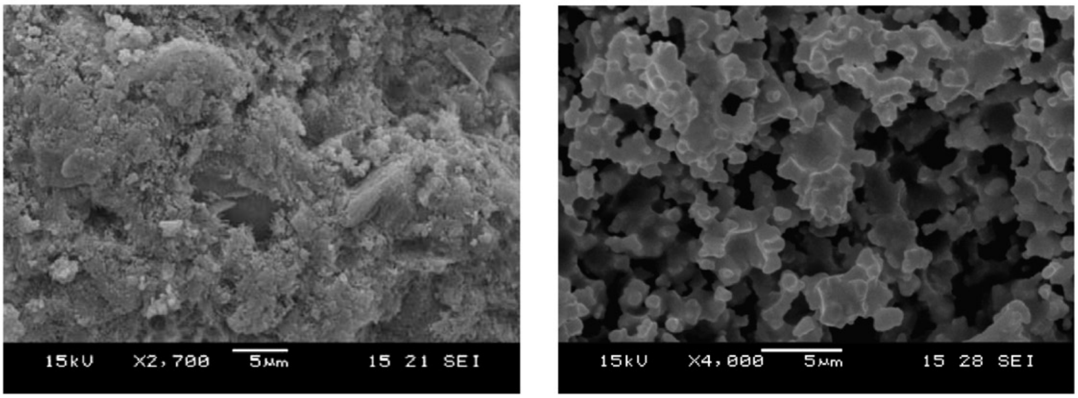

(e) PCH 1031
(f) polyHIPE 1031

Fig. 1. SEM micrographs of pure polyHIPE 2296 (a) and polyHIPE 1031 (f), hydrated cement (b) and PCHs containing different surfactants (c–e).

The setting behaviour of PCH 1031 and cement slurries containing retarded and non-retarded cement was studied using the non-destructive measurement of the transit time of ultrasound through our formulations. With increasing setting time the strength of either the cement or our polyHIPE or PCHs increases resulting in smaller transit times of the ultrasound through the samples. The transit time of ultrasound compression waves propagating through the slurry is presented in Fig. 2. In both samples not containing an organic phase, Neat Class A and borax retarded Class A, once the setting is initiated, it continues until the composition is fully set. However, in the cases in which the samples contain an organic phase, CHIPE 1031 and CHIPE 1031-1, a brief setting period occurs, in this case for about 1 to 2 h, followed by a pause in the setting for about 5 h, followed by the resumption of setting until the mixture is fully set. In addition, for both CHIPEs (1031 and 1031-1), the initial setting resulted in a 15–30% reduction in transit time (μs/m), with the remaining reduction in transit time occurring during the second setting period (when the setting resumes). This first setting is a result of the polymerisation of the monomer component of the organic phase. The polymerised organic phase acts as a scaffold or lattice that supports the cement slurry until the cement slurry finally sets.

As expected the addition of 1 wt.% of retarder to both systems (pure cement and CHIPE 1031) resulted in an increased setting time. However, in case of the CHIPE 1031 system the effect of the retarder was less pronounced, which could be due to the influence of the polymeric surfactant on the setting behaviour of the cement. An additional drop in the transit time was detected for both CHIPE 1031 samples which is the result of polymerisation of organic continuous phase, i.e. changing the physical state of the sample from viscous liquid into solid. The decrease in ultrasound transit time through the

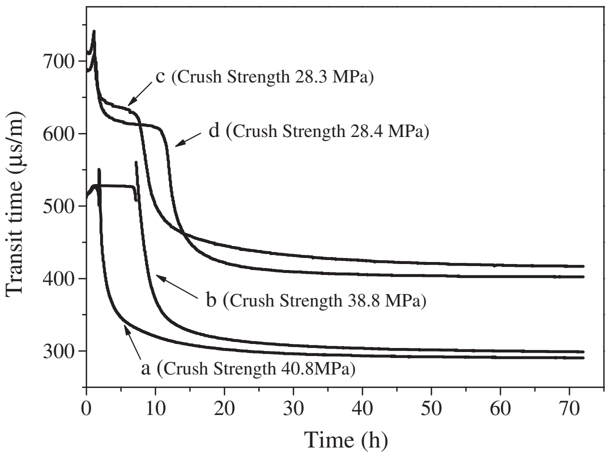


Fig. 2. Development of transit times for ultrasonic compression waves propagating through a) Class A Portland cement; b) Class A Portland cement slurry retarded with 1 wt.% of Borax; c) CHIPE 1031 and d) CHIPE 1031-1 retarded with 1 wt.% of Borax, which were all kept at 70 °C. In brackets shown is the crush strength of fully set formulations.

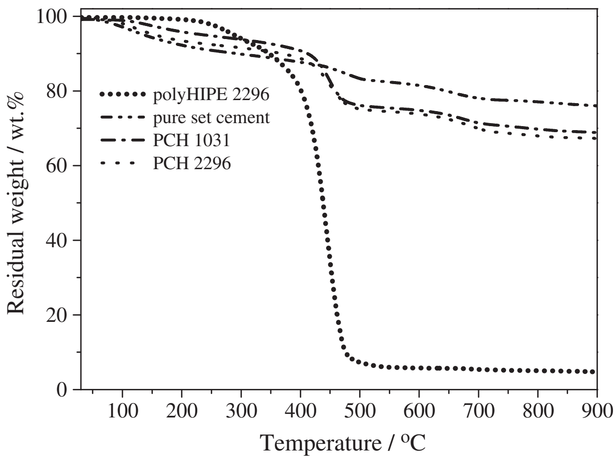


Fig. 3. Weight loss as function of temperature curves of PCHs, pure set cement and pure polyHIPE.

CHIPE, indicating the onset of significant setting, occurs later than for the pure cement slurry, which means that the compressive strength in this system develops later then in pure cement. Crush tests were performed on the set samples after 72 h. It was found that for pure cement the stress at breaking was 40.8 MPa at a strain of 0.014, while for PCH 1031 the stress at breaking was 28.3 MPa at a strain of 0.018. Introduction of 1 wt.% of Borax into the CHIPE did not significantly affect the performance of the set PCH (breaking point at a stress of about 28.4 MPa and a breaking point at a strain of 0.017). The obtained results show that, as expected, the introduction of a weaker material, i.e. of a polymer scaffold (polyHIPE), into cement led to a reduction of the crush strength of the polymer cement hybrid compared to pure cement. However, while the absolute compression strength of the PCH dropped, the PCHs have a larger strain to failure compared to pure cement and thus a higher resiliency to impact. In oil well applications a cementitious material with a low modulus can be supported by the surrounding rock formation only if the strain resistance is high enough and a higher resiliency allows for greater protection of the casing/cement/wellbore bonding during working conditions.

Thermogravimetric analysis was performed to characterise the impact of the organic phase on the thermal behaviour of the PCHs. Four main processes are known to take place during the thermal decomposition of set cement [9,28,29]; from about 70 °C to 120 °C unbound water is lost, which is followed by the decomposition of ettringite and C–S–H at around 200 °C. The decomposition of portlandite (CH) occurs usually at temperatures of around 440 °C and, finally, the decomposition of carbonate phases (calcium carbonate) occurs above 550 °C. The weight loss as function of temperature curves for the PCHs, pure set cement and polyHIPE 2296 are presented in Fig. 3. The total weight loss for the pure set cement was found to be 25%, which is in a good agreement with literature [9,28,29]. The TGA curve for polyHIPE 2296 is characterised by a single step degradation of the polymer in the temperature range from 220 °C to 500 °C.

We found that the free (unbound) water content in the PCH samples was slightly lower compared to the pure set cement and the slope of the weight loss is very shallow. This could be due to presence of the continuous hydrophobic polymer network within the cement, which makes it also more difficult to remove the water from the PCH. It was impossible from the TGA results to distinguish between C–S–H, C–H and polymer decomposition, due to the fact that all three processes occur simultaneously. However, the existence of the ettringite and C–S–H phases in PCH samples could be proven by the weight loss in the temperature range between 200 °C and 500 °C, in this temperature range all samples lost more than 14 wt.%, which is the theoretical polymer content assuming 100% conversion. Moreover, the SEM micrographs (Fig. 1c–e) showed clearly the presence of a needle-like morphology which could be due to both the ettringite and C–S–H. The decomposition of the carbonate phase for all studied samples was observed at ~600 °C. However, the weight loss occurring in this temperature range for the pure cement was around 3% but the PCH samples lost about 6% irrespectively of the surfactant used.

3.2. Chemical resistance of the polymer cement hybrids

One important characteristic of cement for civil engineering and oil industry applications is its chemical resistance. To establish how the presence of the organic phase influences the chemical resistance of the cement, PCHs and pure set cement were exposed to dodecane and *p*-xylene at elevated temperatures. The change in specimen dimensions with time in *p*-xylene and n-dodecane is presented in Fig. 4. It was found that pure set cement after 2 weeks in *p*-xylene at 100 °C started to shrink below its initial size. A slight shrinkage of pure set cement was also observed after initially swelling when it was exposed to dodecane but the dimensions did not reach the initial values.

All PCH specimens exposed to both *p*-xylene and dodecane at 100 °C exhibited significant swelling behaviour. A significant increase in volume of the PCHs was detected after the first week. However, the extent of swelling of the PCHs in dodecane and p-xylene depended significantly on the surfactant used to make them. PCH 1083 showed the greatest volume increase in *p*-xylene but in dodecane it swelled the least. The swelling behaviour of PCH 2296 and PCH 1083 in both dodecane and *p*-xylene follow the same trend leading to a plateau. The presence of the organic polymer network, although highly crosslinked, explains the ability of the specimens to swell. The swelling behaviour will provide the ability of a damaged cement sheath to seal against flow in the presence of liquid hydrocarbons.

Unhydrated and hydrated cement is severely attacked by acids which results in the decomposition of the cement material. To evaluate the effect of the incorporation of a polymer into cement on the stability of cement against acid attack, the PCH samples and pure set cement were treated with 1 wt.% sugar solution in 1 M acetic acid. Even though, acetic acid is a weak organic acid with a dissociation constant K_a of $1.8 \cdot 10^{-5}$ at 25 °C, it is often used in acid corrosion tests

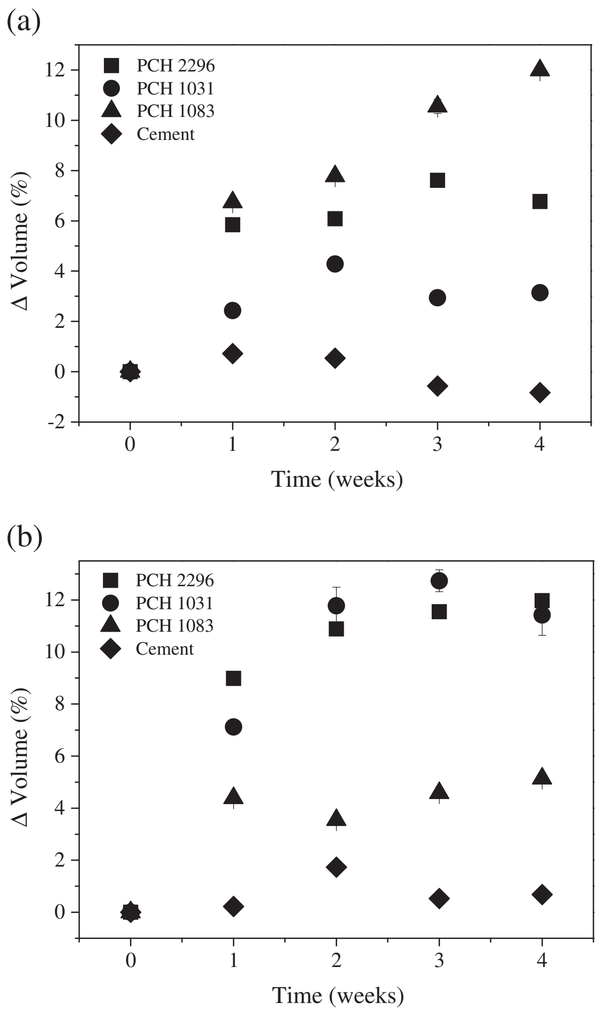


Fig. 4. Volume change of PCHs and pure set cement as a function of time when exposed to *p*-xylene (a) and n-dodecane (b) at 100 °C.

[30–32]. Acetic acid attack results in the formation of a brownish skin on the surface of all samples which differs in intensity of the colour. The formed skin is a mixture of iron and aluminium hydroxides, which are products of cement corrosion. The main reason for the corrosion of the cement is the dissolution of the calcium compounds. CH is the first compound to react if the pH drops below 12.6 [31]. When pH drops even further eventually, the C–S–H and ettringite start to degrade as well. The initial corrosion process of hydrated cement in acid is very fast, but the rate is suppressed as the formation of the less soluble hydroxides ($Fe(OH)_3$, $Al(OH)_3$, silica gel) forms a protective layer. This layer is responsible for slowing down the diffusion of acid in to the cement. The presence of the iron and aluminium hydroxides, which have a higher density compared to C–S–H, could explain the increase of the skeletal density of the samples after being exposed to the sugar acetic acid (see Table 3).

It is worth mentioning that set cement lost its shape; it disintegrated into smaller pieces during acid corrosion. However, the PCHs held their shape, because of the presence of the continuous open macroporous polymeric network throughout the cement which acted as scaffold for the setting cement (Fig. 5a).

The morphologies of the PCHs and set cement after exposure to sugar in acetic acid solutions are presented in Fig. 5. The appearance of PCH 1031 and PCH 1083 is similar. It is clear that the PCH 2296 (Fig. 5a), even after the acid corrosion test, consists of continuous porous polymer structure, which was still partially filled with some inorganic degradation debris. In contrast the pure set cement lost its structural integrity completely (Fig. 5b).

The TGA results (Table 3) of the acid treated and original PCHs showed that in case of the acid treated PCH 2296 the weight loss is higher than for the original PCH 2296. This is explained by the increasing polymer fraction in the PCHs after partial dissolution of the cement. The shape of the TGA curves for both PCHs and pure set cement differs significantly after acid corrosion (the TGA curves are not presented here). Only one significant weight loss step at a peak temperature of 90 °C is observed for pure set cement after acid corrosion, which probably corresponds to the loss of free water. This peak weight loss is followed by a further but shallow decrease in weight. For the PCHs, two clear weight losses can be seen, one occurs in the temperature range between 60 °C and 70 °C and the other in the temperature range between 460 °C and 470 °C, corresponding to the loss of acetone, which was used after washing the sample to make the drying process more efficient, and water followed by polymer decomposition, respectively. Set cement lost 78% of its weight but the PCHs lost only about 66% of their weight independently of the surfactant used to make them, which shows that the PCHs are more resistant against (acetic) acid attack compared to pure set cement.

The results of the acid corrosion test proved conclusively that synthesised PCH materials consisted indeed of two interpenetrating networks; a polymer network, which has the typical structure of a conventional polyHIPE (Fig. 1a) and network consisting of hydrated set cement. The polymer scaffold could be used as a support for setting retarded cement, providing enough strength to proceed with, for instance, a drilling operation if used to cement an oil well without losing time waiting for cement to set. Moreover, being chemically resistant, the presence of the organic phase would protect the setting cement from attack by aggressive media.

4. Conclusions

We demonstrated the feasibility of formulating cement containing high internal phase emulsions, which can be used as a template to create novel polymer cement hybrid materials. PCHs with different polymer/cement ratios have been synthesised by polymerising the

Table 3
PCHs and set cement after acid degradation of cement.

Sample	Weight loss* (wt.%)	Skeleton density (g/cm^3)		Total weight loss** (wt.%) at			
		Before	After	500 °C	900 °C	500 °C	900 °C
				Before acid degradation		After acid degradation	
PCH 2296	67	2.170 ± 0.004	2.210 ± 0.050	23	32	46	51
Set cement	78	2.590 ± 0.004	2.860 ± 0.040	22	23	23	26

*—weight loss after acid treatment;
**—weight loss according to TGA.

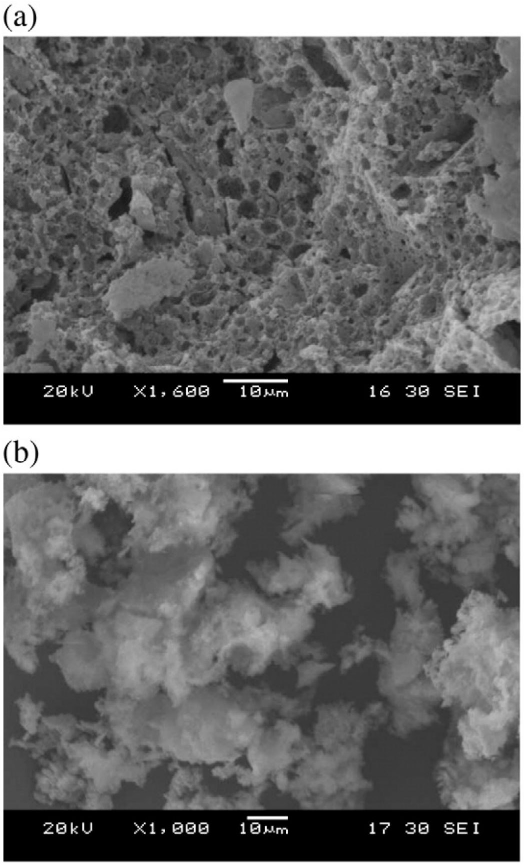


Fig. 5. SEM images of PCH 2296 (a) and set cement (b) after acid treatment.

continuous monomer phase of the emulsion and their structural, physical and mechanical properties in compression have been studied. We found that a continuous polymer network formed within the setting or retarded cement. The polymer network acts as a scaffold for setting retarded cement slurries. The synthesised polymer cement hybrids have crush strength up to 28 MPa, which is significantly lower than the crush strength of set cement (around 40 MPa). However, the strain to failure of the PCH materials is 30% larger than that of set cement, which makes them attractive materials for oil industry applications. Moreover, polymer cement hybrids provide an improved resistance against chemical attack.

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