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High Internal Phase Pickering Emulsions as Template for Lightweight Foam Cement

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Abstract

Styrene high internal phase emulsion (HIPE) with 80 vol.% of water as internal phase was prepared using organophilic laponite as Pickering stabilizer. High volumes of HIPE were admixed separately with cement to prepare macroporous polyHIPE-cement composite via heat driven polymerization. Scanning electron microscopy (SEM) confirmed a shift in the morphology of the admixed cement with HIPE upon setting in comparison with the pristine cement. It was also confirmed that the polymeric network of HIPE built up an interconnected network structure incorporating the set cement particles and polyHIPE, which is responsible of the developed macrporosity. The compressive strength of the resulting foamed concrete was reasonable even in presence of high extent of macrporosity as compared to similar composite structures admixed with HIPE stabilized by classical surfactants. Interestingly, the presence of polyHIPE network caused limitation of the shrinkage associated with the setting of the cement particles leading to a decrease in the developed cracks with respect to comparable cement samples prepared in absence of these additives.

Keywords: Pickering high internal phase emulsions; Foam Cement; Laponite; Polymerization; Composite.

1. Introduction

It is well known that the tensile and flexural strength of hardened cementitious materials are dependently developed according to the nature of the space between cement particles during and after hydration process [1-3]. Hence, the ratio of water to cement should be adjusted to reach ultimate properties.

Additives, such as superplasticizers, can improve the workability of cement [3], whereas particles with appropriate size to fill the gaps between cement particles can play a role to enhance the performance of cementitious materials. The early beginning of the last century witnessed the practical start of using polymers additives and modifiers for cement and relevant materials like mortar and concrete, which was found to cause advance of the workability of the cement paste [3], and adhesion to other substrates [4, 5]. In parallel, the flexural strength and impact toughness [3, 6],

resistance to dynamic loads, durability [7], physical and chemical stability [4], all of which were remarkably improved. This was also associated with a significant reduction of the cement permeability [5].

Polymeric additives were integrated into cement in different forms, mostly as emulsion latexes, powders or resins [6-10], where it was recognized that latexes provided the most effective form due to their high capacity of film formation on the surface of anhydrous cement grains. Monomers, as precursors of polymers, can also be employed as admixtures for cements. Nevertheless, their polymerization can only occur after mixing with the cement by undergoing suitable activation via temperature, addition of a hardener or UV irradiation. A limited penetration depth was unfortunately found as a major drawback [4, 11].

Systematic studies performed on polymer addition into cement indicated that it can have a

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strong impact on the hydration process, which, in most cases, a prolongation of the hydration time [7, 12-14]. This was explained by some researchers to result from a film forming ability of the dissolved polymers around the particles of cement in addition to their presence in vacant gaps between the particles leading to development of capillaries. Accordingly, the hydration water follows longer path to reach unhydrated cement particles [9, 12, 15].

The slow setting associated with some cement formulations can endow good workability of the cement slurry before it acquires its full set state in a reasonable time and satisfactory strength of the resulting structures, which render them useful for various applications. This is mainly determined by the response of the set cement to factors such as temperature, pressure, resistance to chemical attack and extent of permeability. The setting times for cement slurries are highly dependent on the water to cement ratio. Long setting times are unfavourable bearing in mind that prolonged waiting is costly and less-productive.

A heterogeneous system of two immiscible liquid phases ('oil' and 'water') can be defined as an emulsion; in which one of the phases is dispersed in the other as microscopic or colloidal droplets (typically around 1 μm). Simple emulsions are classified as either oil-in-water (o/w) or water-in-oil (w/o), depending on which phase comprises the droplets [16, 17].

When two immiscible liquids are agitated together, an exceedingly unstable emulsion forms, which quickly separates into the bulk phases. The inclusion of an emulsifying agent, which protects the freshly produced droplets from re-coalescence, can stabilize such emulsions. Many emulsifying agents can be used for the emulsion stabilization i.e. surfactants, polymers, and solid particles.

The usage of fine solid powders in the emulsion stabilization (was first investigated by Pickering [18], afterward it became well-known as 'Pickering emulsions'. In Pickering emulsions, the colloidal particles wetted by water (at the interface between oil and water) can stabilize o/w emulsions, however w/o emulsions can be stabilized with the colloidal particles wetted by the oil phase than the water. [19-21] Many solid particles can be used for such purpose, i.e. Laponite [22], Fe_3O_4 [23, 24], SiO_2 [25], and ZnO [26]. Pickering emulsion has a number of advantages, including reduced foaming, decreased toxicity, and lower cost due to the absence of classical surfactants [3, 20, 21].

High internal phase emulsion (HIPE) is a colloidal concentrated system with high internal phase ratio, which has a volume fraction above 0.74. Compared to HIPE stabilized with conventional surfactants; HIPE stabilized with solid particles (Pickering HIPE) has many advantages i.e. higher stability, usage of lower amount of stabilizer as well as less environmental pollution [27-29].

The current work testifies the approach of incorporating polymerizable HIPE template into cement followed by in situ polymerization to generate foamed cement composite. It is worthy to note that the adopted approach provides controlled hydration source for cement from its aqueous high internal dispersed phase, while the minor monomer continuous phase (polymerizable phase) constitutes a soft phase that allows for the production of macroporous polyHIPEs upon polymerization [30-34]. This is likely to create a macroporous polymer phase within the cement host, thus can act as a scaffold to afford reasonable strength to the cement, which allows for expansion of its use into varied fields of applications. This will be justified by conducting intensive characterizations to investigate the consequences of using such approach on the morphological, physical and mechanical properties of the obtained polymer-cement composite.

2. Materials, Methods and Characterizations
2.1. Materials

Styrene (99 %) was purchased from Merck KGaA, Germany. Laponite® RD was provided by ROCKWOOD Clay Additives GmbH, Germany. Extra pure benzoyl peroxide (with iodometric assay of 75 %) was supplied from LOBA Chemie, India. Cationic surfactant, cetyltrimethylammonium bromide (CTAB) (≥ 98%, molecular wt. = 364.45 g/mol), calcium chloride dihydrate (≥ 99%) as well as anhydrous ethylene glycol (99.8%) were provided from Sigma-Aldrich Chemie GmbH, USA. The amorphous fumed silica powder (23 % SiOH and 2.49 % Carbon content) was obtained from Wacker-Chemie (Burghausen), Germany. Acetone (99 %) was purchased from El-Nasr Pharmaceutical Chemicals Co. (ADWIC), Egypt.

Ordinary Portland Cement (OPC) samples (standard strength class 42.5 N) were supplied from National Cement Company (NCC), Egypt. Chemical requirements for this cement type are limited to magnesia and sulfur-trioxide contents and loss on ignition, since the cement is adequately defined by its physical and mechanical characteristics. The main characteristics of the used cement samples are illustrated in Table 1.

2.2. Methods
2.2.1. Surface modification of laponite® RD

To increase the surface hydrophobicity of laponite® RD particles; the laponite surface was treated with cetyltrimethylammonium bromide (CTAB) as follows: 20 g of hydrophilic laponite was dispersed in 500 mL deionized water containing 6 g of CTAB. The mixture was then

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heated at 80 °C for 6-8 hours under vigorous stirring. The resultant product was then collected after cooling, filtration, washing several times with

deionized water, dried overnight at 60 °C and finally kept for further use

Table 1. Physical and mechanical characteristics* of the used cement samples

Strength Class	Compressive Strength, MPa				Initial setting time	Soundness (Expansion)
	Early Strength		Standard Strength			
	2 days	7 days	28 days		min.	mm
42.5 N	≥ 10	-	≥ 42.5	≤ 62.5	≥ 60	≤ 10

* Mechanical requirements of cements include early strength (the compressive strength determined in accordance with EN 196-1 at either 2 days or 7 days) and standard strength (the compressive strength determined in accordance with EN 196-1 at 28 days). However, physical requirements of cement (determined in accordance with EN 196-3) include the initial setting time and soundness (or expansion).

2.2.2. Preparation of high internal phase emulsion (HIPE)

For the preparation of HIPE, styrene monomer as an organic dispersion phase, deionized water as a dispersed internal phase, modified laponite as a stabilizer, benzoyl peroxide as an initiator and calcium chloride dihydrate as an accelerator for cement setting, were used, and the procedure proceeded following a method described elsewhere with a slight modification [35], in which an aqueous internal phase with a volume of 80 % was employed. Thus, 3 wt% of modified laponite, with respect to the monomer phase, and 1 wt % of benzoyl peroxide (with respect to monomer) were charged into 20% volume of styrene as an organic phase. The organic phase mixture was then stirred for 10 minutes till complete dispersion and/or dissolution of the stabilizer and initiator, respectively. Afterward, 80% volume of the aqueous phase including 0.5 % wt. of calcium chloride was added dropwise to the organic phase and the stirring rate was increased after the complete addition of the aqueous phase for another 10 minutes. The resultant HIPE was tested by drop test as of w/o type where the oil was ensured as the continuous phase. In addition, the preparation process was monitored by checking the emulsion formation using optical microscopy.

2.2.3. Preparation of HIPE-Cement Hybrids (HIPEC)

The HIPE-cement hybrids (HIPEC) were prepared following a reported procedure [35] with slight modification. Firstly, the cement slurry was prepared by mixing cement (316 g) with deionized water (120 mL) under constant agitation rate so that a cement:water ratio of 1:0.38 was attained. Afterward, the prepared slurry was then mixed with the prepared emulsion (25 mL) under higher stirring rate to produce the HIPE-cement hybrid (HIPEC). The as-prepared HIPEC was then transferred to handmade ASTM standard steel three gang mold (Fig. 1a, supplied from Technoline, Co., Egypt) and placed into an oven at 70-80 °C for 24 hours to

provoke polymerization. The polymerized HIPEC cubes were then removed from the oven, cooled to room temperature, immersed in acetone for 3 hours, in deionized water for 24 hours then reheated again for another 24 hours at 90 °C. Finally, the prepared HIPEC cubes were kept dry for further characterization.

Using the above-mentioned protocol, the experimental work was continued by keeping the slurry amount constant and increasing the HIPE volume in order to decrease the HIPEC density while monitoring the characteristics of the produced hybrids (i.e. morphology, density as well as mechanical properties). Another series of experiments was also undertaken by fixing the HIPE amount while decreasing the amount of the cement slurry, prepared by the same cement:water ratio i.e. 1:0.38, and the characteristics of the produced hybrids were also monitored.

2.2.4. Polymerization of HIPE

In order to use it as a control for comparing the bare poly-HIPE with the HIPEC hybrid, the HIPE was then polymerized thermally as follows; the resultant HIPE was transferred into handmade one gang glass mold (made of 3 mm thickness glass, Fig. 1b) and heated at 70-80 °C for 24 hours to produce the poly-HIPE. The resultant polyHIPE (monolith) was then carefully released from the glass mold and kept dry for further characterization.
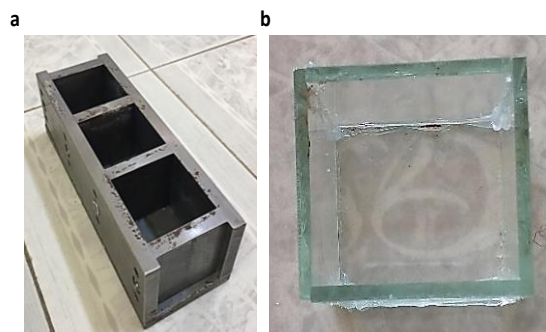

Figure 1. Digital photos for **a)** the handmade ASTM standard steel three gang mold, with dimensions (5×5×5 Cm³) for each gang, **b)** the handmade one gang glass mold with dimensions (5×5×5 Cm³).

2.3. Characterizations

Fourier transform infrared (FTIR) spectra were recorded on a Bruker Optik spectrometer (Vertex70, GmbH), Germany, within the wavenumber range of 500 - 4000 cm^{-1}. The optical microscopic images were recorded using WiLL/Leitz (A. I. O Egypt) optical microscope, fitted with a digital camera PHD-5MP (MicroCam, Egypt) and the images processing was done via Microvision 2.0 software. Scanning electron microscopy (SEM) images were taken using a JOEL JSM-5400 LV electron microscopy, Japan. Before characterization, the samples were dispersed in absolute ethanol, dried in air, then coated by gold using JOEL, JES-1100 E ion sputtering device, Japan.

Compressive strength of samples was evaluated using Shimadzu universal testing machine UMH-30 (type UH-A, No.600283-03), assembled in Japan. The machine is designed for measuring the tension, compression, transverse and bending tests on metallic materials as well as non-metallic materials i.e. plastic, rubber, rubber molding, wood, ceramic products and concrete. The machine is working using a loading method that employs hydraulic transmission system in which the loading rate should be widely adjustable, smooth while simple operation remote control, higher mechanical efficiency and greater load handled properly are available. With the load weighing mechanism a load (30-ton capacity) is being applied to a specimen, which is transformed into a change in the oil pressure whose force is balanced with the lever system and amount of the rise of the pendulum, and the moment of a force of the pendulum are further transformed into an angle of rise of the pendulum or sin θ, therefore rotating the pointer whose indication is of equi-division scale is accomplished.

Setting time of cement slurries is defined as the interval during which the cement slurry loses its plasticity after adding water to cement. Cement setting time can be measured (using Vicat apparatus which is also used to determine the required quantity of water to produce a cement slurry of normal or standard consistency) during two stages i.e. initial setting time, t_1 (the time within which the cement can be moulded in any desired shape without losing its strength) and final setting time, t_2 (the time taken for the cement paste to become hard and attain the mould shape). The initial setting of the cement is the difference between t_2 and t_1.

3. Results and Discussion
3.1. Surface modification of laponite nanoparticles

Pickering emulsions are, in contrary to conventional emulsions, involving the use of finely dispersed solids instead of classical surfactants, to

generate of solid-stabilized emulsions. This depends upon the capacity of the particles to wet both oil and water phases. [18, 19] It is realized that the traditional emulsion route requires rather higher amount of surfactants to serve as emulsifiers. However, the recycling of these surfactants after polymerization is quite tiresome, which raises the advantage of Pickering emulsion system over the other route from the environmental concern from one side. Further, it does not suffer from foaming problem from another side.

For this purpose, it was decided to use laponite particles as solid stabilizer for HIPE that involves a polymerizable monomer as continuous oil phase (minor part, 20%) while the internal aqueous dispersed phase was major (80%). This means that the originally hydrophilic particles of laponite should be converted into organophilized form to be effectively dispersible in the polymerizable oil phase. Fig. 2 displays the FTIR spectra of laponite before and after organophilization.
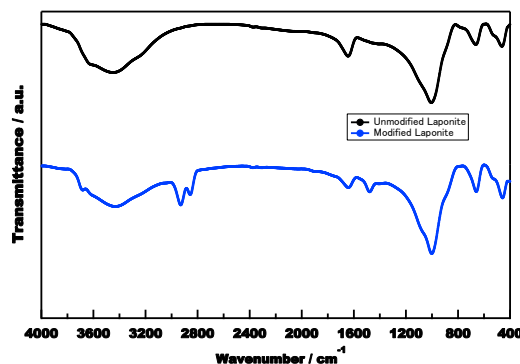

Figure 2. FTIR Spectra of laponite before and after organophilization

The FTIR spectrum of neat laponite shows bands at around 3450 cm^{-1} and 1644 cm^{-1}, referring to adsorbed water while the shoulder at around 3650 cm^{-1}, can be attributed to the surface hydroxyls. As this band is poorly resolved, this may indicate overlapping of two bands corresponding to stretching vibrations of Si–OH and Mg-OH, respectively. In addition, a strong band at 1010 cm^{-1} can be assigned to Si-OH stretching. This agrees with our reported results for laponite nanoparticles. [22] After reaction of laponite with cetyltrimethylammonium bromide, new peaks appeared in the relevant FTIR spectrum, namely at 2927 cm^{-1} and 2855 cm^{-1} corresponding to asymmetric and symmetric C-H stretching, respectively. Also, the emerged band at 1478 cm^{-1} is corresponding to the deformation vibration of C-H groups. The emergence of a peak at 3685 cm^{-1} dictates the insertion of alkyl amine groups to the clay structure after organophilization.

3.2. Preparation and/or polymerization of high internal phase emulsion (HIPE)

Before all it was necessary to check the validation of using the organophilic particles successfully as Pickering stabilizer for preparation of emulsion. The formed emulsion in Fig. 3a is lacking any sign indicating un-stability of the emulsion, which was confirmed by the light microscopy images in Fig. 3 b-e. It is obvious that droplets in the size range 40-110 μm were formed. The droplets were semi regular-shaped with apparent deformations, likely due to exceeding the close packed density of the dispersed phase. The larger magnification revealed that the droplets are well surrounded probably by a thick strict darker layer of the organophilic laponite particles, which helped to allow the droplets to be kept away from approaching each other and ensured stabilization of the formed emulsion. Furthermore, the surrounding layer appears swelled by the minor content of the continuous polymerizable monomer. This shows that this stabilizing layer, while in its swelled form, can act as a template for post polymerization of the monomer continuous phase.
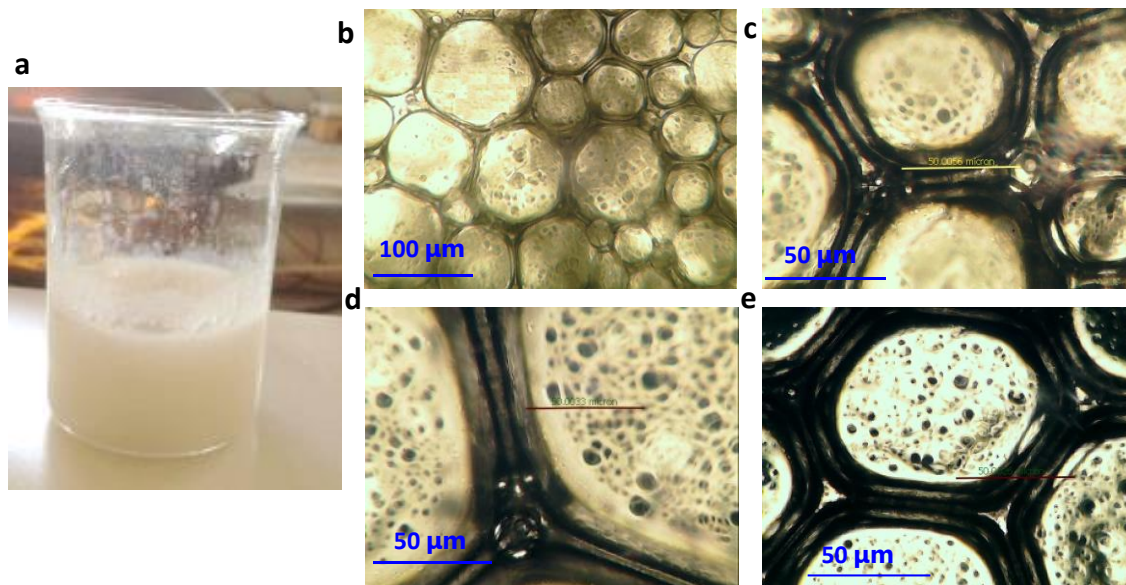

Figure 3. a) A digital image, and **b-e)** Optical microscopic images of the formed HIPE.

To check for this, the formed HIPE was exposed to polymerization conditions and the resulting structure is displayed in Fig 4, which gives rise to a visually-clear highly macroporous polymer foam with very low density (i.e. 92.2 kg/m^3). This corroborates that the continuous styrene phase is liable to efficient polymerization which opens the door for use of HIPE as additive for cement to create well-balanced foam structure with controlled properties. Interestingly, such a highly porous foam structure with low density to appear so robust and not easily destructible proves that the originally stabilizing layer of laponite acted as a reinforcing template, especially after plasticization by swelling of the monomer continuous phase followed by the polymerization.
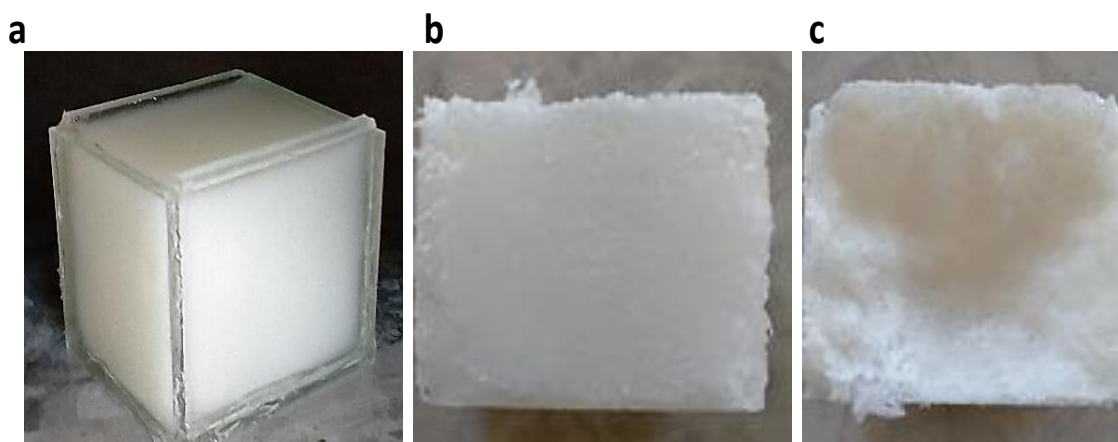

Figure 4. Cubic samples of the polymerized HIPE.

3.3. Preparation of HIPE-Cement Hybrids (HIPEC)

PolyHIPE-Cement hybrids were formulated by adding different volumes of HIPE (25-175 mL) to a fixed cement amount, prepared by mixing 316 g of cement with 120 mL water. In the meantime, a neat cement samples were prepared in absence of any emulsion additive for comparison. As expected, the density of cementitious hybrids decreased systematically from 1700 kg/m^3 with increasing the volume of the added emulsion to reach 977 kg/m^3 for 175 mL addition, as shown from Fig. 5. However, the drop-in density was much faster for the larger additions (125 & 175 mL) since this was presumably a result of a remarkable increase in volume of the cementitious structure, which is indicative of a high content of developed pores following the polymerization of HIPE. The low density in the last sample is very good as it will be more suitable for the real applications of the foam cement, namely thermal and sound insulation and for walls fillers and others. [36]
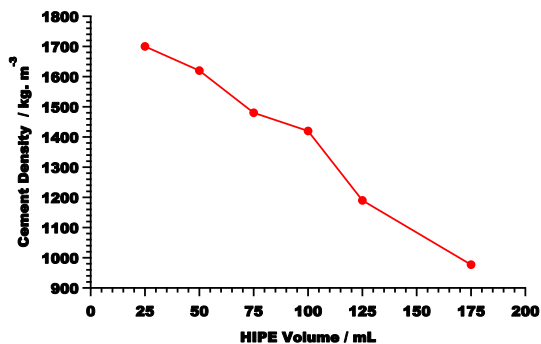

Figure 5. Variation of density (in kg/m^3) of foamed cement as a function of the volume of HIPE additive.

SEM micrographs of the hybrid samples as well as the neat cement (Fig. 6a-h) ensured this assumption and showed the samples porosity increased tremendously by increasing the volume of HIPE. It can be also noticed that the morphology of the neat set cement changes with the insertion of the polymerized emulsion and the cement samples disappeared and enveloped by the emulsion network, especially at higher volumes of the emulsion. Thus, porous network structures with varied degrees of connectivity are formed.

Interestingly, the detected cracks were found to decline with increasing the emulsion volume. This effect is thought to be induced by the provoked decrease in rigidity of the cementitious hybrid as a result of the polyHIPE presence, assisted by the gained expansion at higher added volume (125 & 175 mL).

As expected, the compressive strength changed with increasing the volume of emulsion additive and followed a typical trend for a material undertaking an increase in free volume and low extent of shrinkage during hardening (Fig. 7). Thus, it decreased regularly as the content of the polymerized emulsion enlarged in the hybrid. The elevated free volume and enveloping of the cement particles by the polymerized HIPE to generate connected network of the polymerized emulsion and cement particles are further supported from SEM images in Fig. 6, which resulted in compacted hybrid structure with superior compressive strength compared to other similar studies despite the high extent of porosity. [35]
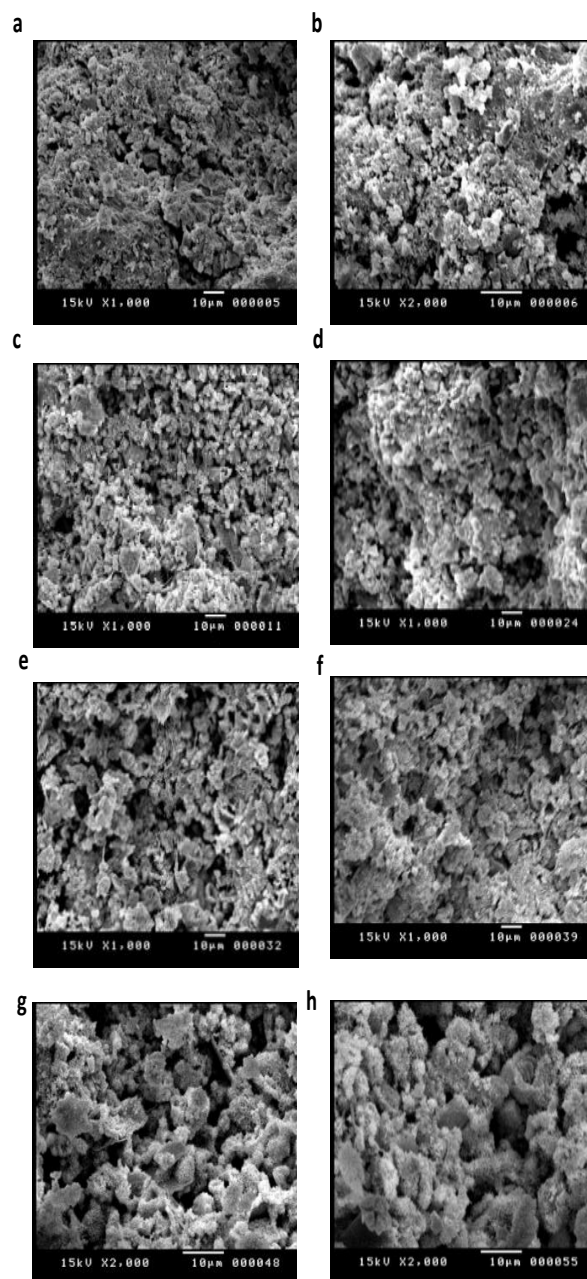

Figure 6. SEM images of **a)** Neat cement without HIPE, **b-h)** the HIPE-cement hybrids with different HIPE volumes, **b)** 25 ml, **c)** 50 ml, **d)** 75 ml, **e)** 100 ml, **f)** 125 ml **g)** 150 ml, and **h)** 175 ml
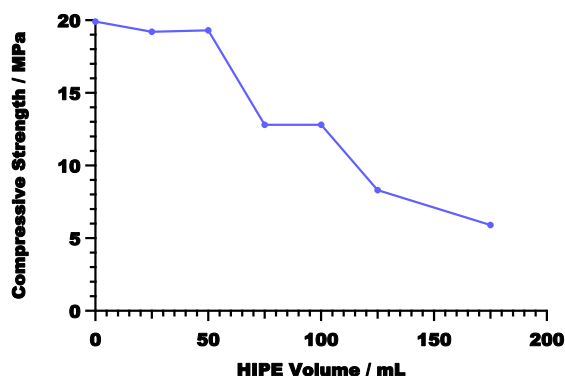
Figure 7. Changes in the compressive strength (MPa) of foamed cement as a function of the volume of HIPE additive.

Setting time of cement slurries is defined as the interval during which the cement paste loses its plasticity after adding water to cement. Figure 8 shows that the initial setting regularly increases by increasing the volume of emulsion additive (no setting time was determined with the highest volume of HIPE i.e. 125 mL and 175 mL).
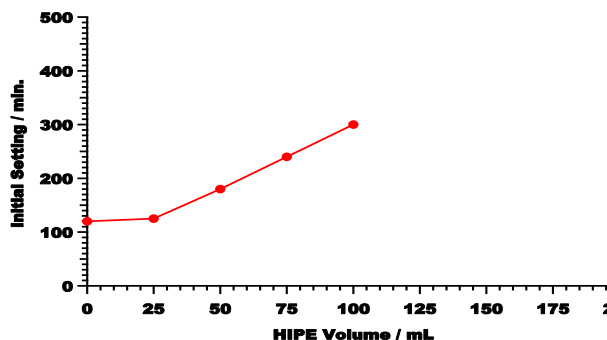

Figure 8. Variation of cement initial setting as a function of the volume of HIPE additive.

4. Conclusions

Admixing cement with polymerizable high internal phase Pickering stabilized emulsion containing up to 80 vol.% of water as internal phase can act in case of polymerization as a polymeric template to yield macroporous polymer cement composite. The extent of formed macrporosity is determined according to addition level of HIPE, which also affects the compressive strength as well as crack development. It can be demonstrated that the presence of polyHIPE network covering the surface of the set cement particles allowed connectivity between the cement particles and compactness of their composite. This caused reasonable compressive strength from one side and limitation of the shrinkage associated with the setting of the cement particles from another side, which accounts for the drop in the developed cracks with respect to comparable cement samples admixed with HIPEs stabilized by classical surfactants.

5. Conflicts of interest

The authors declare no conflict of interest.

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