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Tailoring mechanical properties of highly porous polymer foams: Silica particle reinforced polymer foams via emulsion templating

Kristina Haibach [a], Angelika Menner [a], Ronald Powell [b], Alexander Bismarck [a,*]

[a] *Polymer and Composite Engineering (PaCE) Group, Department of Chemical Engineering,*
Imperial College London, South Kensington Campus, London SW7 2AZ, UK
[b] *Halliburton Energy Services, 2600 South 2nd Street, P.O. Box 1431, Duncan, OK 73536-0470, USA*

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Abstract

The aim of this work was to synthesise highly open porous low-density polymer foams with superior mechanical properties by the polymerisation of the organic phase of concentrated emulsions. The continuous organic phase of the concentrated emulsion template occupying up to 40 vol% was polymerised leading to polymer foams with much improved mechanical properties. The Young's modulus as well as the crush strength of the foams was further increased dramatically by reinforcing the polymer phase with nanosized silica particles. To ensure that the silica particles were covalently incorporated into the polymer network, methacryloxypropyltrimethoxysilane (MPS) was added to the formulation, which reacts with the silica via hydrolysis reactions. The Young's modulus of silica reinforced foams increased by 280% and the crush strength by 218% in comparison to foams without reinforcement.

Keywords: Polymer chemistry; High internal phase emulsions; PolyHIPEs

1. Introduction

In recent years, open porous polymer foams obtained from high internal (ratio) phase emulsions (HIPEs) or concentrated emulsions gained increasing interest, due to their unique properties such as high porosity and high degree of interconnectivity. PolyHIPE materials are being considered for many applications such as filtration media [1] or support for heterogenic catalytic reactions [2]. PolyHIPEs are even explored for tissue engineering application, i.e. as scaffold to support the growth of osteoblast cells [3]. However, polyHIPEs have not yet found industrial applications because of undesirable properties, such as their brittleness and chalkiness.

HIPEs have been defined as emulsions where the internal phase occupies more than 74% of the volume; this corresponds to the maximum packaging fraction of monodispersed droplets [4–8]. The continuous organic phase of the HIPE contains monomers, such as styrene or acrylates, crosslinking components, i.e. divinylbenzene (DVB), and a surfactant to stabilise the emulsion. The internal phase of the emulsion is composed of an aqueous electrolyte solution. The addition of salt leads to an enhanced emulsion stability because Ostwald ripening is suppressed due to decreased solubility of organic compounds in the aqueous phase [9].

The most widely studied group of polyHIPEs are synthesised from HIPE formulations mainly containing styrene and divinylbenzene (DVB) as the organic phase of the emulsion [9–12]. By polymerising the continuous monomer phase of a HIPE and the removal of the dispersed water phase, a low-density solid foam with a highly interconnected pore network called polyHIPE is obtained. The pore volume fraction can be as high as 0.95. The pore size of the foams ranges between 5 and 100 μm and the average surface area of polyHIPEs was reported to be around 5 m^2/g [9]. The cellular structure and morphology of the polyHIPE depend strongly on the surfactant and salt concentration used in the formulation of the HIPE [10]. The pore size is inversely proportional to the surfactant level. An increase of the salt concentration in aqueous phase results in smaller pores. Based on the knowledge of polystyrene/DVB polyHIPEs various monomers, such as 4-vinylbenzyl chloride and 2-ethylhexyl acrylate [13], 4-nitrophenyl acrylate and 2,4,6-trichlorophenyl acrylate [14], were used to produce polyHIPEs.

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* Corresponding author. Tel.: +44 20759 45578; fax: +44 20759 45638.
E-mail address: a.bismarck@imperial.ac.uk (A. Bismarck).

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Tai et al. [15] have synthesised polyHIPEs consisting of an inorganic polysilsesquioxane network combined with an organic polystyrene network to enhance the thermal stability of the foams. They successfully copolymerised methacryloxypropyltrimethoxysilane (MPS) with styrene and divinylbenzene. The hydrolytic condensation of the trimethoxysilyl group forms the inorganic polysilsesquioxane network within the organic network. The hydrolytic condensation reaction of silane derivatives is also used for the synthesis of purely inorganic hierarchical porous monoliths [16].

We describe the synthesis of reinforced highly porous polymer foams with a highly interconnected pore network obtained from HIPE templates with varying amounts of MPS, styrene and DVB. Nanosilica particles were used as reinforcement for the inorganic network. The porous network structure of the polymer foams is studied using scanning electron microscopy (SEM). The surface area, density, porosity, elastic modulus and the thermal behaviour of the samples were characterise and compared to the values of samples without particles.

2. Experimental section

2.1. Materials

Styrene, divinylbenzene (DVB), methacryloxypropyltrimethoxysilane (MPS), α,α′-azoisobutyronitrile (AIBN) and $CaCl_2 \cdot 2H_2O$ were purchased from Sigma Aldrich (Gillingham, UK). The SiO_2 particles (200–300 nm) were kindly supplied by Rave Produkte und Dienstleistungen (Koblenz, Germany) and the non-ionic surfactant Hypermer 1070 by UNIQUEMA (Wirral, UK). All chemicals were used as received.

2.2. HIPE preparation

The concentrated emulsions and HIPEs were prepared in a reaction vessel and stirred by a glass paddle rod connected to an overhead stirrer. During the preparation of the emulsions the stirring rate was kept constant at 400 rpm. The continuous phase of the emulsion (16 or 40 vol%) contained up to three different monomers (styrene, DVB and MPS), always 20 vol% Hypermer 1070 as surfactant and 1 mol% AIBN as initiator. Up to 10 wt% SiO_2, in relation to the volume of the monomers, was added to the formulation of emulsions **2**, **4** and **5**. The composition of the emulsions is summarised in Table 1. The aqueous phase, which contained 0.034 mol/l $CaCl_2 \cdot 2H_2O$ as electrolyte, to suppress Ostwald ripening was slowly added to the homogeneous continuous phase. Once all of the aqueous phase had been added, the stirring rate was increased to 1000 rpm for a further 20 min to obtain a viscous homogeneous emulsion.

Table 1
Composition of the emulsion templates

Sample	Organic phase[a] (vol%)	Organic phase composition: DVB/MPS/S[b] (vol%)	SiO_2 content[c] (wt%)
1	16	50/17/13	0
2	16	50/17/13	1
3	40	60/20/0	0
4	40	60/20/0	1
5	40	60/20/0	10

[a] Volume of the organic phase relative to the total volume of the emulsion.
[b] Content of DVB, MPS and styrene (S) relative to the organic phase volume.
[c] wt% filler relative to the monomers.

2.3. PolyHIPE preparation

The concentrated emulsions were transferred into a flacon tube and sealed. The emulsions were polymerised at 70 °C for 24 h in an oven. The polymerised HIPEs were taken out of the tubes and extracted in a Soxhlet apparatus firstly with distilled water followed by methanol to remove any impurities. The polyHIPE was dried in a vacuum oven at 80 °C until constant weight.

3. Characterisation of the polymer foams

3.1. Microscopy/cell structure

To determine the internal structure, pore and pore throat size of each polymer foam, images of the fractured surfaces were taken using scanning electron microscopy (Jeol JSM 5610 LV, Jeol Ltd, Welwyn Garden City, UK). Therefore, approximately 1 cm^3 of each sample was fixed to a sample holder using a carbon black sticker. The sample was then placed inside an Emitech 550 (Emitech Ltd, Ashfort, UK) where it was gold sputtered in an argon atmosphere to achieve the necessary conductivity.

3.2. Surface area

The surface area of the polymer foams was determined from nitrogen adsorption isotherms at 77 K applying the Brunauer–Emmet–Teller (BET) model. The measurements were performed using a surface area analyser (Micromeritics ASAP 2010). Before performing the gas adsorption experiments, adsorbed impurities were removed via a 'degassing' step. Approximately, 0.2 mg (about 1 cm^3) of each polyHIPE was placed inside glass sample cells and heated under vacuum (heating temperature of 100 °C) overnight. For the analysis part, small amounts of nitrogen (the adsorbate) were admitted into the evacuated sample chamber.

3.3. Determination of the density and porosity

Density measurements were taken using a Helium Pycnometer (AccuPyc 1330, Micrometrics Ltd, Dunstable, UK). The samples are weighted initially and than placed into measuring chamber of known volume of the pycnometer. Helium is then expanded through a valve and its volume measured. As a result, the pressure in the cell will fall to an intermediate value. The polymer matrix density ρ_m can then be calculated using the following equation

$$\rho_{\mathrm{m}} = \frac{m_{\mathrm{S}}}{V_{\mathrm{C}} - \left(V_{\mathrm{EXP}}/\left((p_{1\mathrm{G}}/p_{2\mathrm{G}})-1\right)\right)} \tag{1}$$

where m_{S} is the sample mass, V_{C} the cell volume, V_{EXP} the expanded volume, $p_{1\mathrm{G}}$ the cell elevated pressure and $p_{2\mathrm{G}}$ the cell intermediate pressure. The envelope or foam density and porosity of the sample were measured using an envelope density analyzer (GeoPyc 1360, Micrometrics Ltd, Limited, Dunstable, UK). This instrument determines the external (envelope) volume of the sample so that the internal pores are considered to be part of the sample ($V_{\mathrm{P+M}}$). By subtracting the sample material volume, determined using the Helium pycnometer (V_{M}) (which does not consider the pores as part of the sample volume), the total pore volume (V_{P}) can be determined. This can be summarised by the following Eq. (2)

$$V_{\mathrm{P}} = V_{\mathrm{P+M}} - V_{\mathrm{M}} \tag{2}$$

The GeoPyc determines the external sample volume by measuring how far a plunger can be driven by a stepping motor into a cylinder containing a mixture of graphite powder and the sample. When the sample mass is divided by envelope volume, the envelope or foam density is obtained (ρ_{f}; Eq. (3)). The porosity (P) is found using Eq. (4)

$$\rho_{\mathrm{f}} = \frac{m_{\mathrm{S}}}{V_{\mathrm{P+M}}} \tag{3}$$

$$P = \left(1 - \frac{\rho_{\mathrm{f}}}{\rho_{\mathrm{m}}}\right) \times 100\% \tag{4}$$

3.4. Thermal analysis

The thermal behaviour of each sample was determined using a differential scanning calorimeter (DSC) (Pyris 1, Perkin–Elmer, Boston, USA). Approximately 5 mg of each polyHIPE were investigated in a temperature range from 20 to 200 °C at a heat rate of 10 °C min^{-1}. The heat flow was measured. Two heating and two cooling curves were recorded.

3.5. Elastic modulus

A Lloyds Universal Testing Machine (Lloyds EZ50, Lloyds Instruments Ltd, Fareham, UK) equipped with a 50 kN load cell was used to measure mechanical properties in compression. The samples were loaded at a rate of 1 mm/min. Five samples of 25 mm in diameter and 10 mm in height were tested for each polyHIPE. The samples were loaded until a displacement of half the height of the examined sample was reached. The elastic modulus was determined from the initial linear slope of the stress/strain plot.

4. Results and discussion

In addition to the monomers DVB, MPS and styrene (**1** and **2**), the continuous organic phase of all emulsions contained the non-ionic, polymeric surfactant Hypermer 1070 to stabilise the emulsions. The emulsions were prepared and polymerised following the commonly used preparation protocol [10,17–21]. The hydrolytic condensation of MPS leads to the formation of an inorganic network reinforcing the organic network formed by radical polymerisation. Due to the high content of the crosslinker DVB within the continuous phase, all resulting polymer foams were chalky, i.e. the foams crumble easily. The high degree of crosslinking explains the absence of a glass transition in the temperature region of 20–200 °C. PolyHIPE **1** and foam **3** did not contain any reinforcement. They were synthesised as reference samples to underline the effect of the reinforcement on the foam properties. Table 2 and 3 summarises the properties of the resulting polymer foams.

The polymerisation of HIPEs **1** and **2** containing 16 vol% organic phase leads to solid porous foams with an open porous network structure (Figs. 1 and 2) characteristic for polyHIPEs. The pore diameter of polyHIPE **1** ranges from 3 to 8 μm (Fig. 1(a) and (b)). The pores were interconnected via pore throats of 1.5–2.5 μm in diameter. The high porosity of 89% and the low foam density of 0.138 g/cm^3 are typical for polyHIPEs [6].

The SEM micrograph of polyHIPE **2** (Fig. 2(a)–(c)) containing 1 wt% nanosized $\mathrm{SiO_2}$ particles also showed the characteristic open porous structure of polyHIPEs. The $\mathrm{SiO_2}$ particles are incorporated into the polymer structure without affecting the open porous structure of the foam. However, pore size and pore size distribution have changed significantly if compared to polyHIPE **1**. Due to the addition of $\mathrm{SiO_2}$ to the organic phase of the emulsion, HIPE **2** was observed to be more viscous than HIPE **1**. The high viscosity of **2** may reflect the onset of the formation of the inorganic network triggered by the rapid reaction between MPS and $\mathrm{SiO_2}$ particles. At high viscosities, the shear stress of mixing is insufficient to break up all large droplets of the internal aqueous phase in the emulsion. Therefore, it is difficult to generate a uniform, fine dispersion of the droplet phase in highly viscous HIPEs [15]. This leads to the formation of polymer foam **2** with large (30 μm) pores (Fig. 2(a)), which are surrounded by many small pores (2 μm) (Fig. 2(b)). Pore throats form during polymerisation in the area

Table 2
Properties of the polyHIPEs and foams

Sample	Pore size (μm)	Pore throat size (μm)	Matrix density (g cm^{-3})	Foam density (g cm^{-3})	Porosity (%)	Surface area (g m^2)
1	3–8	2±0.5	1.241±0.007	0.138±0.001	89±1	3.60±0.13
2	2–30	1±0.2	1.211±0.004	0.155±0.080	85±1	5.19±0.05
3	1–5	1±0.2	1.150±0.001	0.309±0.003	70±1	2.03±0.04
4	2–8	1.5±0.5	1.209±0.002	0.360±0.020	68±3	2.13±0.03
5	9±1	1.5±0.5	1.126±0.004	0.350±0.010	69±1	7.60±0.12

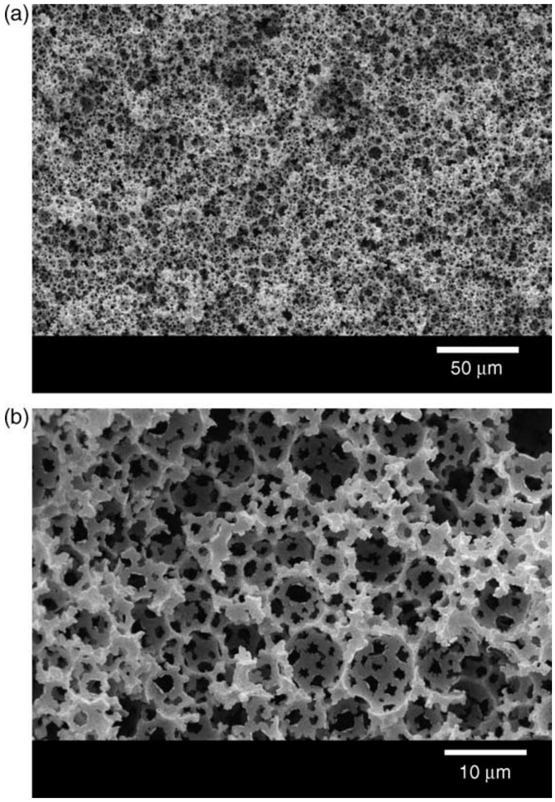

Fig. 1. SEM-micrographs of polyHIPE **1**.

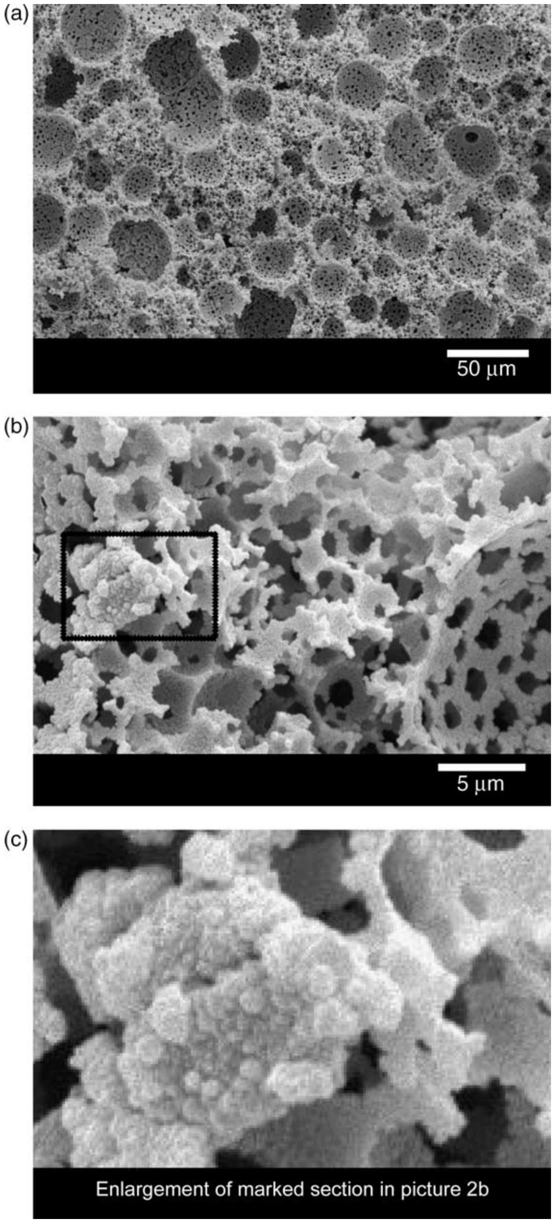

Fig. 2. SEM-micrographs of polyHIPE **2**.

of contact points of neighbouring droplets. Their formation is a complex process and believed to depend on many parameters, such as the volume fraction of the internal phase, the concentration of the surfactant, the droplet size, the tendency for Ostwald ripening and the nature of the polymer forming throughout the polymerisation [19]. The pores of polyHIPE **2** are highly interconnected via many pore throats of approximately 1 μm in diameter. At a larger magnification it can be seen that **2** (Fig. 2(c)) has a different internal surface structure than polyHIPE **1**. The added SiO_2 particles are more hydrophilic than the rest of the organic phase. Consequently they consequently are orientated towards the o/w interface in the liquid HIPE **2**. As a result, the internal surface of polyHIPE **2** appears to be ‘rougher’ than the surface of **1**. This leads to an increase in surface area of **2** (5.19 m^2/g) compared to **1** (3.60 m^2/g). The polymer matrix density of 1.211 g/cm^3, foam density of 0.155 g/cm^3 and porosity of 85% of **2** is not significant different compared to polyHIPE **1** (Fig. 3).

The emulsions **3** and **4** contained 40 vol% organic phase and 60 vol% aqueous phase, respectively. PolyHIPEs have been defined as polymer foams synthesised from HIPEs, where the internal phase occupied slightly more than 74% of the volume [4–8]. Emulsions with internal volume fractions from 20 to 70 vol% are commonly classified as medium internal phase (ratio) emulsions [22]. It is commonly believed that emulsion templates such as **3** and **4** having 60 vol% internal phase are not suitable to synthesise highly porous polymer foams with a highly interconnected pore network structure. Nevertheless the resulting polymer foams **3** and **4** (Figs. 3 and 4) possess a highly interconnected pore network structure, which is characteristic for polyHIPEs [17]. The pore size of **3** ranges from 1 to 5 μm and the pore throat size is approximately 1 μm (Fig. 3(a)). The polymer foam **4** contains additionally 1 wt% SiO_2 particles (Fig. 4(a)–(b)) and possesses the same ‘rough’ surface structure as **2**. The SiO_2 particles in foam **4** have been successfully integrated into the pore walls without affecting the pore structure. The pore diameter in foam **4** ranges from 2 to 8 μm. The pores are interconnected via pore throats of about 1.5 μm in diameter. Due to the high organic phase level of 40 vol%, the foam density of **3** (0.309 g/cm^3) and **4** (0.360 m^3/g) increased and the porosity of **3** (70%) and **4** (68%) decreased in comparison to **1**. The slight increase in surface area of **4** (2.13 m^2/g) in comparison to **3** (2.03 m^2/g) is a result of the ‘rough’ surface caused by the SiO_2 particles. All properties of

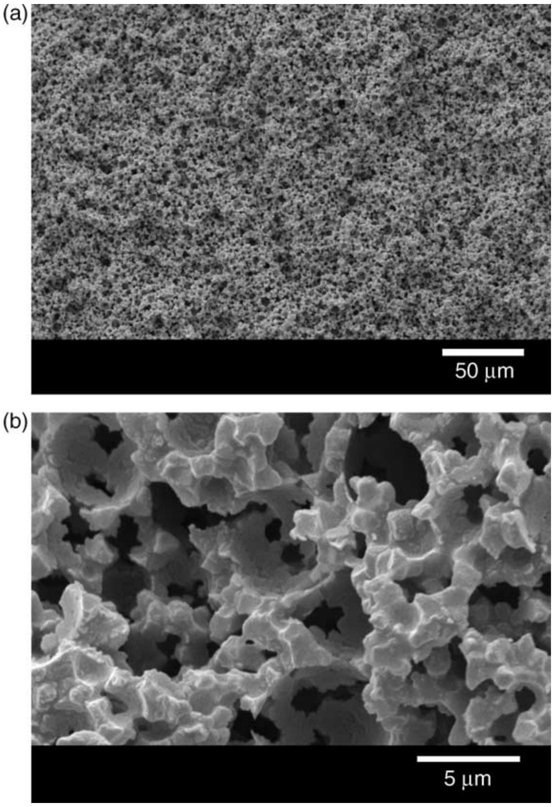

Fig. 3. SEM-micrographs of polymer foam **3**.

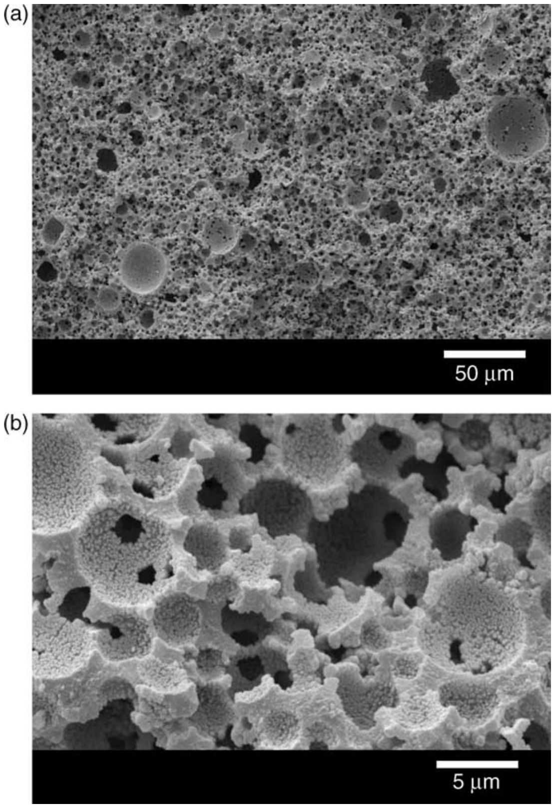

Fig. 4. SEM-micrographs of polymer foam **4**.

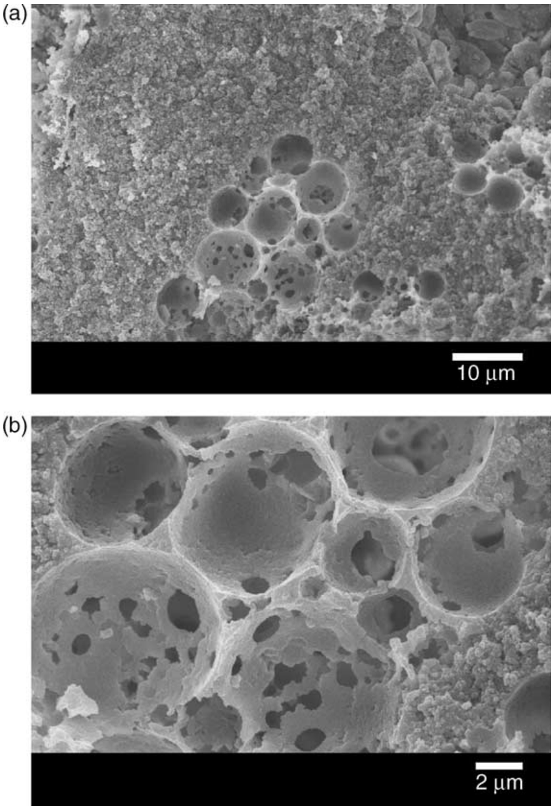

Fig. 5. SEM-micrographs of polymer foam **5**.

the foams **3** and **4** match the characteristics reported for polyHIPEs [6].

The HIPEs with greater continuous phase levels can be stabilised with high molecular weight, non-ionic surfactants, such as Hypermer 1070. Hypermer 1070 enables emulsions to be stabilised with a continuous phase of up to 40% relative to the total volume of the emulsion [23].

10 wt% SiO_2 particles have been added to the organic phase of the emulsion **5**, which also possessed an organic phase level of 40 vol%. Due to the increased SiO_2 concentration, more methanol was produced during the formation of the inorganic network, which destabilises the emulsion. The SEM micrographs (Fig. 4(a)–(b)) of the resulting polymer foam **5** show that the porous network structure is almost completely collapsed. There are only a few pores (9 µm) left, which are interconnected via pore throats (1.5 µm). Foam **5** is very brittle and has a foam density of 0.350 g/cm^3 and a porosity of 69%.

Fig. 6 shows representative compressive stress–strain curves and Table 3 summarises the mechanical properties for all foams (**1**–**4**). The stress–strain curve has an initial elastic region from which the Young's modulus of the samples was determined. For the less porous foams **3** and **4** it can be seen that at higher applied stresses the pore structure collapses if the crush strength is exceeded and the samples eventually fail. The Young's modulus of polyHIPE **1** is 3 MPa and its crush strength 0.26 MPa. The Young's modulus is low in comparison to the polyHIPEs **2**–**4** but not unusual for polyHIPEs [3,15]. The relatively low modulus and crush strength is caused by the high degree of pore interconnectivity, which inversely affects

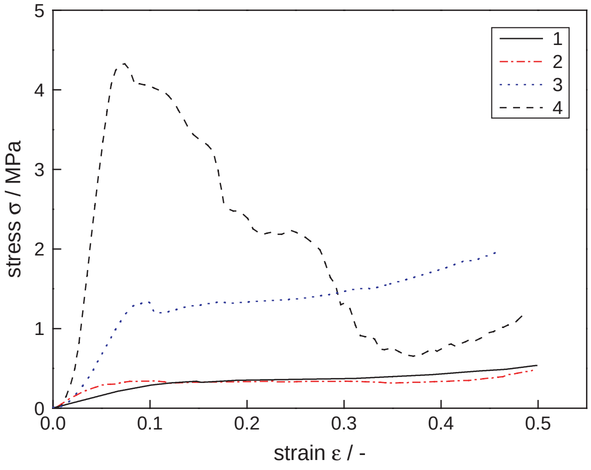

Fig. 6. Representative stress–strain curves for the polyHIPEs **1** and **2** as well as the polymer foams **3** and **4**.

the structural integrity of the foams. The addition of 1 wt% SiO_2 particles to the formulation acts as reinforcement of the inorganic network formed by MPS, which causes a remarkable increase of the Young's modulus of polyHIPE **2** (6 MPa) by more than 100% compared to **1**. The crush strength of polyHIPE **2** increases only marginally as compared to polyHIPE **1**. This is a result of the rather broad pore size distribution of polyHIPE **2** (Fig. 2(a)). Foams with inhomogeneous pore sizes are more likely to fail at low applied compressive loads as compared to foams with a narrower pore size distribution. Due to the increase in foam density, the Young's modulus of 25 MPa as well as crush strength of 1.35 MPa of foam **4**, which was obtained from an w/o emulsion template containing 40 vol% organic phase, was significantly higher than the Young's moduli and crush strengths of polyHIPE **1** and **2** obtained from typical HIPEs containing only 16 vol% organic phase. Foam **4** has with 95 MPa the highest Young's modulus; an increase of 280% compared to foam **3**. The dramatic increase of the Young's modulus as well as the crush strength of the foam containing nanoSiO_2 particles shows that the particles have been successfully integrated in the inorganic polysilsesquioxane network via the formation of covalent bonds. Therefore, the nanosized SiO_2 particles act as reinforcement of the polymer phase, where it is needed, without damaging the pore structure of the polyHIPE. However, the degree of pore interconnectivity of foam **4** is reduced as compared to foam **3**. This too might have an impact on the increased Young's modulus as well as crush strength. Sample **5** containing 10 wt% SiO_2 is too brittle to even manufacture the sample discs required for mechanical tests.

Table 3
Mechanical properties: Young's modulus and crush strength as well as specific Young's modulus and crush strength of the polyHIPEs and foams

Sample	Young's modulus (MPa)	Specific Young's modulus (MPa $(kg\,m^{-3})^{-1}$)	Crush strength (MPa)	Specific crush strength (MPa $(kg\,m^{-3})^{-1}$)
1	3 ± 0.5	0.022 ± 0.004	0.26 ± 0.03	0.002 ± 0.0002
2	6 ± 0.7	0.039 ± 0.005	0.31 ± 0.05	0.002 ± 0.0003
3	25 ± 2	0.081 ± 0.006	1.35 ± 0.17	0.004 ± 0.0005
4	95 ± 5	0.264 ± 0.013	4.30 ± 0.23	0.012 ± 0.0005
5	–	–	–	–

5. Conclusion

The poor mechanical properties of the polyHIPEs have so far hindered any major industrial application. Our aim was to improve the mechanical properties of such materials. We chose two strategies to achieve our objective: firstly the increase of the organic phase level in order to increase the monomer concentration and secondly the reinforcement of the inorganic network formed by MPS with nanosilica particles.

The polymer foams **1–4** possess the characteristic interconnected pore structure and properties of typical polyHIPEs. The continuous phase of the emulsions **3**, **4** and **5** occupied 40% of the emulsion volume. The non-ionic polymeric surfactant Hypermer 1070 was well suited to stabilise such emulsions. The samples were highly porous although the porosity decreased and the foam density rose with the increase of the continuous phase level. The low loading fraction of SiO_2 particles did not affect the density of the polymer and porosity of the foams. However, the increase of the silica content causes the porous network structure of foam **5** to collapse almost completely due to the destabilisation of the emulsion triggered by the rapid production of methanol induced by grafting of the inorganic MPS network onto the silica particles.

Nanosized SiO_2 particles have been successfully integrated in the polymer matrix of polyHIPE materials. The nanosized SiO_2 particles are well suited to enhance the stability of the inorganic polysilsesquioxane network formed by MPS. The increased organic phase volume leads to an increase in density, which improves the elastic modulus of the foams **3** and **4** compared to **1–2**. The addition of SiO_2 particles increased the elastic modulus dramatically in comparison to samples without reinforcement. **2** showed an increase of 100% and the elastic modulus of **4** has improved by 280%.

Future work will focus on an increase of the nanosilica loading fraction and improvement of the overall mechanical performance namely a reduction of chalkiness via the use of better suited monomers and crosslinkers.

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