

Highly Permeable Macroporous Polymers Synthesized From Pickering Medium And High Internal Phase Emulsion Templates**

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Various applications require macroporous materials with high permeability and a significant compressive strength. For instance, the oil servicing industry is interested in utilizing a liquid medium that can be placed within the annulus between the oil bearing natural formation and a screen wrapped perforated pipe, which turns into a macroporous permeable and mechanically stable solid during a curing step.^[1] The minimum requirements for the solid macroporous material are a permeability of 1 D (10^{-12} m²) and a compressive strength ≥ 3.5 MPa. This challenge could be addressed by employing high internal phase emulsions (HIPE), whose continuous phase consists of monomers, as a template to produce macroporous polymers, commonly known as poly(merized)HIPEs,^[2] with a well defined controllable pore structure. However, conventional polyHIPEs synthesized from surfactant stabilized water-in-oil (w/o) HIPEs have poor mechanical properties^[3, 4] and low permeabilities^[5] due to the rather small pore and pore throat sizes.^[2] Here we present a new approach for synthesizing polyHIPEs with much higher permeabilities and sufficient mechanical properties. We utilize the ability of w/o particle-stabilized HIPE templates (Pickering-HIPEs) to produce closed-cell macroporous polymers with large pores as reported recently by us.^[6] We demonstrate that small amounts of

non-ionic polymeric surfactant added to such Pickering-HIPE templates lead to the formation of poly-Pickering-HIPEs with an open porous structure and greatly enhanced permeability (more than 5 times) compared to conventional polyHIPEs. The further development of this approach will allow the synthesis of a novel class of permeable particle reinforced macroporous polymers with a significant potential for practical exploitation.

It was shown that the poor mechanical properties usually observed for polyHIPEs can be improved by increasing the continuous organic phase volume, using particle reinforcements or by changing the composition of the monomer phase.^[4, 7] However, little is reported on methods for improving the permeability of polyHIPEs. Biasetto et al.^[8] stated that the permeability of microcellular foams is limited by the pore throat size and showed that gas permeability increases with increasing pore and pore throat sizes, which is in agreement with our findings on conventional polyHIPEs.^[5] PolyHIPEs are a replica of the emulsion structure at the gel point of polymerization,^[2, 3, 9] therefore, the pore structure of polyHIPEs can only be tailored by adjusting the emulsion template.^[4, 10] The pore size of polyHIPEs depends largely on emulsion stability, which is strongly influenced by the surfactant and salt concentrations in the emulsion template.^[11] The pore and pore throat sizes in conventional polyHIPEs can be increased by increasing the internal phase volume or destabilizing the emulsion template in a controlled manner by adding additives such as methanol.^[12] This nonetheless resulted in thinning of the pore walls, which is detrimental to the mechanical performance.^[12, 13] In contrast to traditional surfactant stabilized HIPEs, the droplet size of Pickering-HIPEs is already much larger.^[6] However, the polymerization of Pickering-HIPEs results in mainly closed-cell macroporous polymers^[6, 14] with a few pores interconnected by pore throats formed during drying.^[15] So far no successful route to control the interconnectivity of poly-Pickering-HIPEs has been reported.

The gas permeability of conventional polyHIPE 1 (Table 1), made from a surfactant stabilized emulsion template having 74 vol.-% internal phase, with pore and pore throat sizes

(**Figure 1a**) of $4.9 \pm 1.9 \mu\text{m}$ and $1.5 \pm 0.5 \mu\text{m}$, respectively was $0.46 D$.^[5] Since it is not possible to increase pore size and hence the permeability of conventional polyHIPEs while maintaining adequate mechanical properties^[6, 12] we decided to explore Pickering emulsion templating. Poly-Pickering-HIPE 2 (Table 1) was synthesized from a 3 w/v% oleic acid modified silica particle stabilized w/o emulsion template having 75 vol.-% internal phase.^[7a] SEM images (**Figure 1b**) showed poly-Pickering-HIPE 2 has a closed-cell pore structure typical of poly-Pickering-HIPEs, having a pore size of $210 \pm 8 \mu\text{m}$ but no evidence of pore throats. Therefore poly-Pickering-HIPE 2 was impermeable.

This is an indication of the extreme stability of the films separating the emulsion droplets. The conventional approach of using additives, such as methanol, to destabilise the films, thus opening the pores did not help (see supplementary information). Assuming a hexagonal close packing of the particles at the deformed o/w interface in Pickering-HIPE 2 one can easily calculate^[16] that significant amounts of the particles ($>2.6 \text{ w/v } \%$) remain in the continuous phase unattached to the o/w droplet surface (see supplementary information). Therefore one can expect that the excess and attached particles aggregate, thus leading to the formation of thicker particle layers around the droplets and very stable emulsion films similar to those already reported.^[17] The closed-cell pore structure exhibited by poly-Pickering-HIPE 2 can thus be explained by these thick particle layers and hence extremely stable films, which do not easily rupture during or after polymerisation.^[17b]

If the excess particles stay well dispersed in the continuous phase, they could easily be squeezed out of the thinning films between the emulsion droplets into Plateau-Gibbs borders. This should result in much thinner films more vulnerable to break during the polymerization or subsequent purification/drying of the poly-Pickering HIPEs.^[15] To prevent the excess particles from aggregating, we added the oil soluble dispersant Hypermer 2296 to ready-made Pickering emulsion templates and investigated the pore structure of the poly-Pickering HIPEs

made from them. Hypermer 2296 is a viscous liquid non-ionic polymeric surfactant used in the oilfield and other industries as an effective dispersing agent and w/o emulsifier.

When 5 vol.-% Hypermer 2296 with respect to the oil phase was added to the Pickering emulsions 3 - 6 they did not coalesce but their viscosity detectably decreased. We also observed significant sedimentation (approx. 10% organic phase was expelled) in Pickering-MIPE 4 containing 70 vol.-% internal phase, slight sedimentation in Pickering-HIPE 3 and little to no sedimentation in Pickering-HIPEs 5 and 6. The polymerization of these Pickering-emulsions resulted in poly-Pickering-M/HIPEs 3 – 6 (Table 1), which have a pore structure very similar to that of conventional polyHIPEs (**Figure 1a**) but with much larger pores and pore throats (**Figure 1c - f**). These macroporous polymers have an average pore size of around 100 μm and pore throat sizes in the range 19 - 26 μm (Table 1). Hence, the addition of Hypermer 2296 to the Pickering emulsion templates has a remarkable effect on the properties of both the templates and poly-Pickering-M/HIPEs obtained from them. The surfactant causes a detectable reduction of the emulsion viscosity, sedimentation of the emulsion droplets and decrease of their size. As a result the pore diameters in the polymeric foams ($\sim 100 \mu\text{m}$) are significantly smaller than those without surfactant ($\sim 210 \mu\text{m}$) and, more importantly, macroporous polymers with open porous structures are formed irrespective of the internal phase volume fraction of the original emulsion template.

The mechanisms of pore throat formation in polyHIPEs are still under debate in the literature, but it is accepted that the films separating the droplets in the emulsion templates must be sufficiently thin in order to break and form pore throats.^[15] The actual mechanism and role of the added surfactant in the pore throat formation presented here is still unclear and needs further investigation. Nevertheless, our results give some vital clues about the interplay between the particles and surfactant in the synthesis of open porous poly-Pickering-HIPEs. It is important to note that the Hypermer 2296 alone does not allow for the preparation of stable M/HIPEs under the investigated conditions. Hence, the particles act as the primary stabilizer

of Pickering emulsions in the presence of this surfactant. When added to an already made Pickering-M/HIPE, the surfactant adsorbs at the free o/w interface between the particles at the droplet surface, thus reducing the interfacial tension. At these conditions, the original droplets break up to smaller ones during agitation, resulting in the smaller pore sizes obtained for the poly-Pickering-HIPEs (cf. **Figure 1b** and **d**). The surfactant also adsorbs at the particle surface, thus changing its wetting properties and imparting steric repulsion, thereby disaggregating the particles, leaving them well dispersed in the organic phase and reducing the viscosity of the continuous phase. This reduced viscosity leads to the sedimentation of the less concentrated emulsions and results in thinner droplet films in comparison to the original Pickering-HIPE without surfactant. The results from wetting experiments on a model macroscopic system have also provided evidence for surfactant adsorption. Microscopic slides have been treated with oleic acid in the same way as silica particles used in the emulsions and the contact angle of water drops on the slides in toluene were measured. The addition of surfactant to the oil decreased the contact angle measured through water from $141^\circ \pm 5^\circ$ in pure toluene to $111^\circ \pm 7^\circ$ in the presence of 5 vol.-% Hypermer 2296, thus indicating a significant change of wettability due to surfactant adsorption. The contact angle in the presence of surfactant, however, remained bigger than 90° , which is an important condition for the formation of stable w/o emulsions.^[18] This is in agreement with our findings that the addition of Hypermer 2296 to Pickering emulsion templates does not impart coalescence. As a consequence of surfactant adsorption at the o/w interface, pore throats might form during polymerization in the manner described by Menner et al.^[15]

The pore throat size is directly dependent on the pore size; the larger the pores the larger the pore throats. Therefore, the dramatic increase of the average pore size of the poly-Pickering-HIPEs leads to a dramatic increase in their average pore throat size compared to conventional polyHIPEs, thereby resulting in the large gas permeabilities of poly-Pickering-M/HIPEs 3 – 6, more than 5 times that of conventional polyHIPE 1 (Table 1 and **Figure. 2**).

The porosity of all open porous poly-Pickering-HIPEs is nearly the same (Table 1) although very different internal phase volumes have been used in the emulsion templates. This can first be attributed to the sedimentation experienced by the Pickering emulsion templates in the presence of Hypermer 2296, which leads to an effective increase of the internal phase volume in the less concentrated emulsion templates. Secondly, it is possible that polymerization was incomplete leaving unreacted monomers, which after purification also results in an increased porosity. The gas permeability of the open porous poly-Pickering-HIPEs 3, 5 and 6 are identical within the error. This can be explained by the similar pore throat diameters and almost identical porosities of these poly-Pickering-HIPEs. Even poly-Pickering-MIPE 4 made from an emulsion template with an internal phase volume less than the critical limit of 74 vol.-% has a gas permeability of 1.4 ± 0.1 D, which is 3 times larger than that of the conventional poly-HIPE 1. The lower permeability of poly-Pickering-MIPE 4 in comparison to the other open porous poly-Pickering-HIPEs is due to the lower porosity, reduced pore throat diameter and lower number of pore throats per pore (4.8) in comparison to that of poly-Pickering-HIPEs 3, 5, 6 (5.8 – 6.3). The lower number of pore throats in poly-Pickering-MIPE 4 could be due to the fact that a MIPE rather than a HIPE was used as a template. Although Pickering-MIPE 4 underwent sedimentation, there was less contact between neighbouring droplets, which resulted in smaller and fewer pore throats.

The mechanical properties of macroporous polymers can be also tailored by varying the internal phase volume of the Pickering-emulsion templates (Table 1). The mechanical properties, crush strength and Young's modulus, of Poly-Pickering-HIPE 2 were lower than those measured for conventional polyHIPE 1, which can be explained by the increased pore size and weaker pore structure of poly-Pickering-HIPE 2 in comparison to polyHIPE 1. As expected, opening up the pore walls and increasing the overall porosity of poly-Pickering-HIPEs led to a significant reduction of crush strength and Young's modulus of the macroporous polymers. It is however worth noting that poly-Pickering-HIPEs 3, 5, 6 with

very similar porosities (87 – 90 %) and interconnectivities also have almost identical crush strengths and Young's moduli. It is important to note that despite the low mechanical properties generally measured for the macroporous polymers presented in this study, the materials with porosities exceeding 85% did not fail (i.e. were not blown out of the gas permeability apparatus) during gas permeability tests as experienced for conventional polyHIPEs with porosities > 82%.^[5] These poly-Pickering-M/HIPEs 3 – 6 did not fail during the gas permeability test because of (i) the lower resistance to flow and (ii) the reinforcement of the polymer by the hydrophobized silica particles used to stabilize the emulsion templates. Nevertheless, these materials were still brittle and chalky, shattering during the compression test, which is commonly observed for styrene/DVB based polyHIPEs.^[4] Further improvement of their mechanical properties could be achieved by changing the polymer matrix and/or via particle reinforcement following the approach described here.

In summary, we have presented a new and versatile emulsion templating approach for synthesizing highly permeable macroporous polymers with average pore sizes of 100 μm and average pore throat sizes of 19 - 26 μm . The macroporous polymers have permeabilities of up to 2.6 D in contrast to conventional polyHIPEs with permeabilities of up to 0.46 D.^[5] By varying the internal phase volume of the Pickering emulsion template, we have shown that the pore structure, permeability and mechanical properties of the resulting macroporous polymers can be tailored. The approach presented here can be further optimized to fulfil the requirements on highly permeable particle reinforced macroporous polymers, which can be used as a permeable barrier in oil wells, porous media for chemical and biological separation or scaffolds for tissue engineering.

Experimental

Materials: Styrene, divinylbenzene (DVB), oleic acid (OA), α,α' -azoisobutyronitrile (AIBN), toluene, methanol, acetone, chloroform and calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) were purchased from Sigma Aldrich (Gillingham, UK). Silica particles (20 nm in diameter) were

kindly supplied by Ortwin Rave Produkte + Dienstleistungen, Germany and Hypermer 2296 by Croda, US. All chemicals were used as received.

Preparation and characterization: The conventional polyHIPE 1 was prepared and characterized by Manley et al.[5]. Prior to emulsification, silica particles were surface functionalized with oleic acid as described in our earlier work.[6] Emulsions were prepared in volumes of 50 ml, with the organic phase consisting of styrene and divinylbenzene (DVB) (50:50 by volume). The continuous phase was prepared by suspending the oleic acid functionalized silica particles in the organic phase using a Polytron 1600 homogenizer (Kinematica, Luzern, CH) at 15000 rpm for 15 min. It is important to note that particle concentrations used as well as surfactant concentrations are based on the monomer volume and not the total emulsion volume. The particle suspensions were transferred into a reaction vessel and AIBN (1 mol.-%; with respect to the monomers) dissolved in the suspension under gentle stirring at 400 rpm. Varying amounts of the internal aqueous phase containing $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (0.27 M; 10 g in 250 ml distilled water) was added gradually under continued stirring at 400 rpm for 2 min. The emulsion templates for the highly permeable macroporous polymers were prepared by later adding Hypermer 2296 (5 vol.-%; with respect to the organic phase) to the stable Pickering-emulsions under continued stirring for 30 s. M/HIPES were transferred into free standing polypropylene centrifuge tubes and polymerized at 70°C for 24 h in an oven (LTE) to yield the poly-Pickering-M/HIPES. Poly-Pickering-M/HIPES were purified by Soxhlet extraction first in distilled water followed by acetone for 24 h to remove residual surfactant and finally dried at 120°C for 24 h. Pore structures of the poly-Pickering-M/HIPES were investigated by scanning electron microscopy (Hitachi science systems, S-3400N VP SEM). Porosities were determined using Geopyc 1360 after measuring the absolute skeletal density using Accupyc 1330. Mechanical tests were carried out according to BS ISO 844 using Lloyds EZ 50. Gas permeability was measured with a home built sample cell using the pressure rise technique. Nitrogen was passed through the macroporous polymer and Darcy's law used to determine the viscous permeability (for more details see [5]). The contact angles of water on microscope slides in toluene were measured using the sessile drop method using the DSA 10 (Krüss GmbH, Germany).

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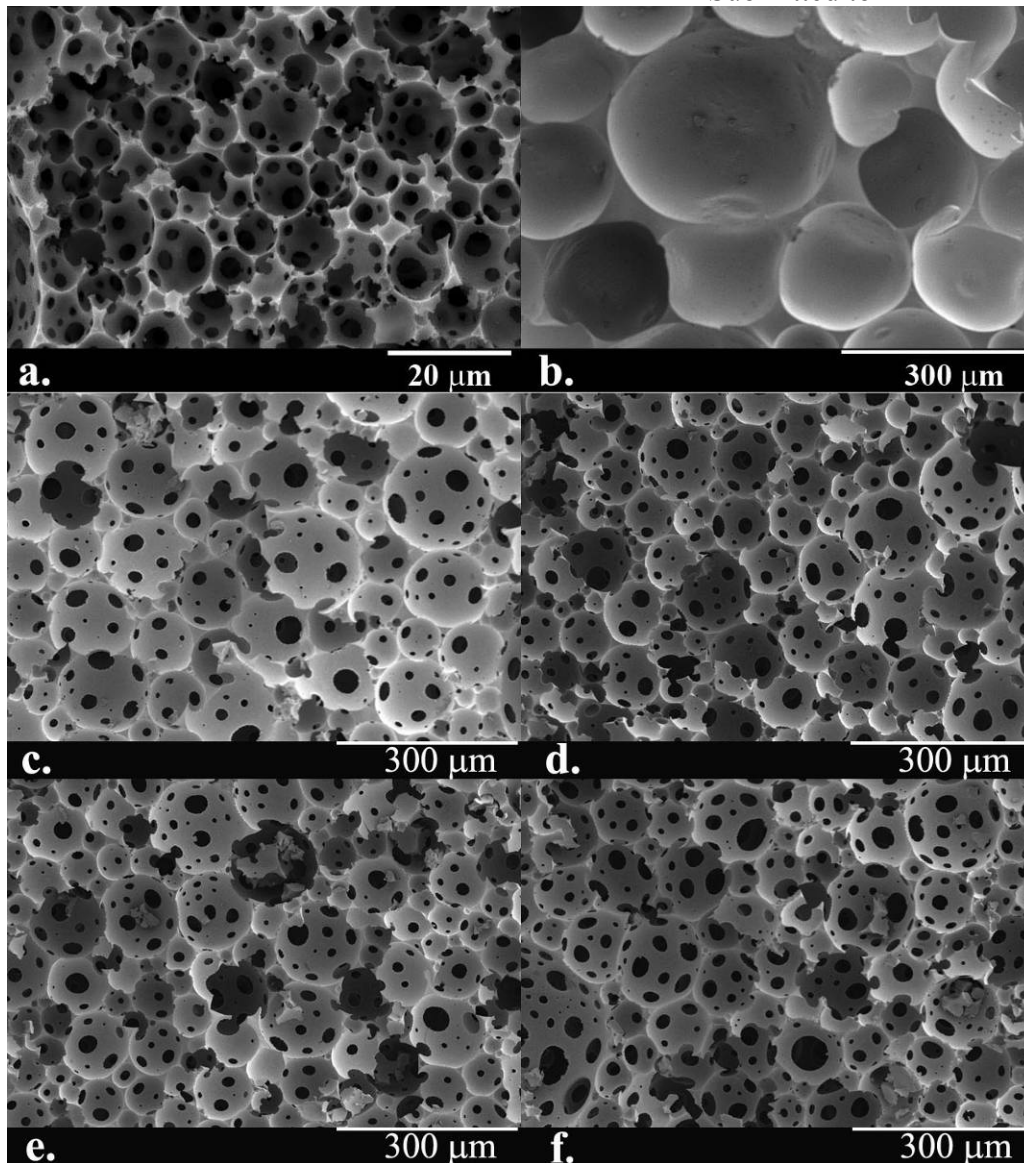


Figure 1. SEM images of a) conventional polyHIPE 1 synthesized from a surfactant stabilized HIPE template containing 74 vol.-% internal phase, b) poly-Pickering-HIPE 2 synthesized from a Pickering-HIPE template containing 75 vol.-% internal aqueous and poly-Pickering-M/HIPEs 3 – 6 containing c) 70 vol.-% internal phase (sample 4) d) 75 vol.-% internal phase e) 80 vol.-% internal phase and f) 85 vol.-% internal phase, to which 5 vol.-% of Hypermer 2296 was later added.

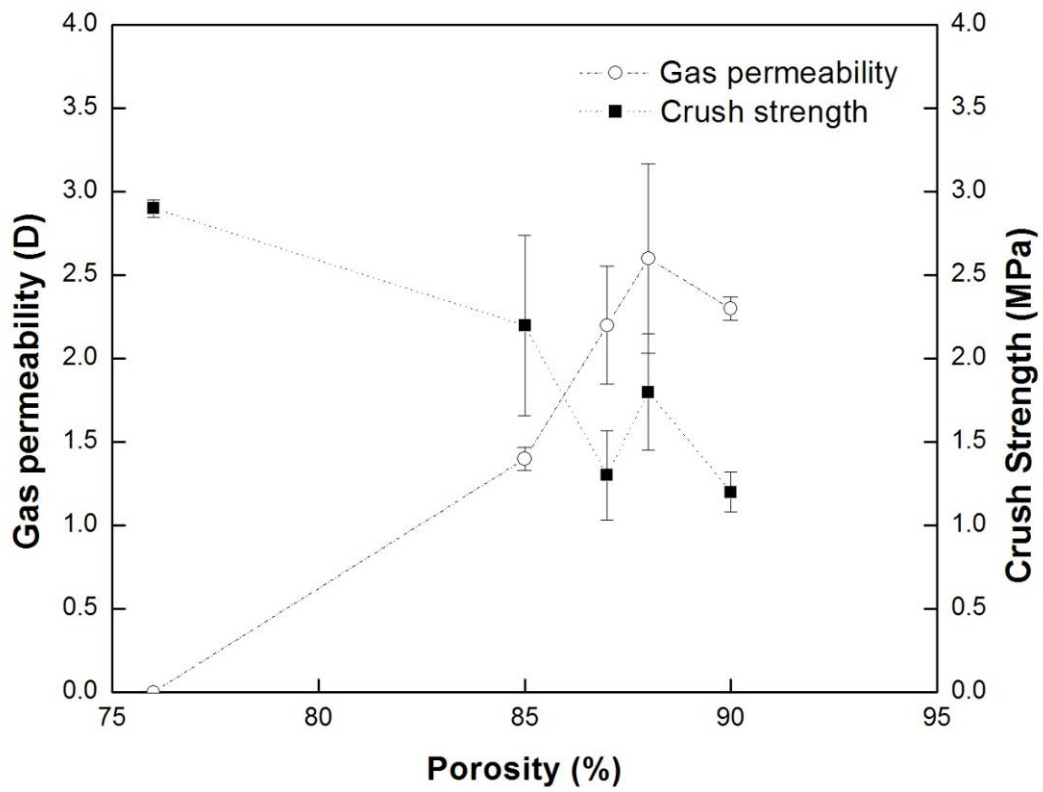


Figure 2. Graph illustrating gas permeability and crush strength of poly-Pickering-M/HIPES 2–6 as a function of the emulsion template internal phase volume.

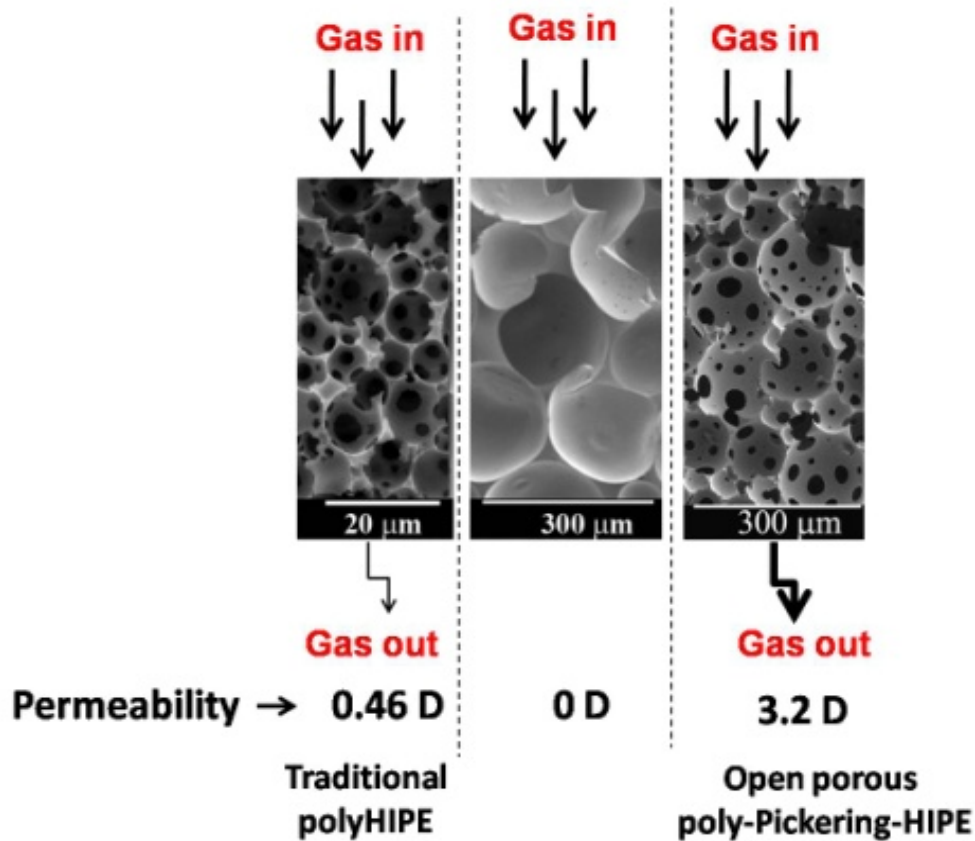
Table 1. Composition of emulsion templates characterized by internal phase volume fraction (ϕ_i), particle (C_p) and surfactant (C_s) concentration and porosity (P), pore diameter (d_p), pore throat diameter (d_t), gas permeability (k), crush strength (σ) and Young's modulus (E) of the macroporous polymers.

Sample	ϕ_i [vol.-%] [a]	C_p [w/v%] [b]	C_s [vol.-%] [b]	P [%]	d_p [μm]	d_t [μm]	k [D]	σ [MPa]	E [MPa]
PolyHIPE 1 [c] ^[b]	74	0	20	82 ± 2	4.9 ± 2	1.5 ± 0.5	0.46 ± 0.04	3.6 ± 0.6	72 ± 9
Poly-Pickering- HIPE 2 [c]	75	3	0	76 ± 1	210 ± 8	0	0	2.9 ± 0.1	49 ± 7
Poly-Pickering- HIPE 3	75 (74)	3	5	87 ± 2	100 ± 3	26 ± 2	2.20 ± 0.40	1.3 ± 0.3	27 ± 8
Poly-Pickering- MIPE 4	70 (69)	3	5	85 ± 2	100 ± 4	19 ± 1	1.41 ± 0.07	2.2 ± 0.5	32 ± 13
Poly-Pickering- HIPE 5	80 (79)	3	5	88 ± 2	100 ± 3	26 ± 2	2.60 ± 0.60	1.8 ± 0.4	30 ± 14
Poly-Pickering- HIPE 6	85 (84)	3	5	90 ± 2	98 ± 5	23 ± 2	2.32 ± 0.07	1.2 ± 0.1	18 ± 6

[a] Internal phase consists of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (0.27 M). The numbers in brackets are calculated taking into account the increase of the external (oil) phase volume due to the addition of Hypermer 2296. [b] Particle concentration and surfactant concentration with respect to monomer phase. [c] Control samples

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Open porous poly-Pickering-M/HIPEs with permeabilities of up to 3.2 D were prepared by polymerisation of Pickering-M/HIPEs to which small amounts of surfactant were added. The permeability of these poly-Pickering-M/HIPEs is more than 5 times that of conventional polyHIPEs. This approach allows the synthesis of a novel class of permeable particle reinforced macroporous polymers with significant potential for practical exploitation.