

High Internal Phase Emulsions Stabilized solely by Functionalized Silica Particles**

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High Internal Phase Emulsions (HIPEs) are important for a wide range of applications in the food, cosmetic, pharmaceutical and petroleum industries.^[1] If the continuous phase is polymerizable, HIPEs can be used as templates^[2] for the synthesis of highly porous polymers with potential applications as low weight structures or scaffolds in tissue engineering.^[3] HIPEs are characterized by a minimum internal phase volume ratio of 0.74^[2] but Lissant first defined this minimum as 0.7.^[4] HIPEs consisting of a continuous organic phase and an internal aqueous phase (w/o emulsion), are commonly stabilized by large amounts of surfactants.^[5] Particle-stabilized emulsions also known as Pickering-emulsions have recently attracted much interest.^[6] Unlike surfactants, particles irreversibly adsorb at the interface of emulsions due to their high energy of attachment which makes them good emulsifiers.^[7] The ability of particles to adsorb at the interface between the two phases is primarily dependent on the wettability of the particles.^[8] Hydrophilic particles such as metal oxides tend to stabilize o/w emulsion while hydrophobic particles such as carbon tend to stabilize w/o emulsions.^[9] Nevertheless, it is possible to modify the wettability of particles by adsorbing surfactant molecules onto the particle surfaces^[10] or by silanation.^[11]

All reports on particle-stabilized emulsions deal with emulsions having internal phase levels below 70 vol.-%. Kralchevsky *et al.*^[12] developed a thermodynamic model, which predicts that

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particle-stabilized emulsions will phase invert above internal phase volume fractions of 0.5 but added that experimentally, phase inversion is observed at volume fractions of 0.7 due to kinetic factors. Binks *et al.*^[11] further stated that particle stabilized emulsions phase invert between volume fractions of 0.65 and 0.7 meaning the majority phase becomes the continuous phase.

We report on the stabilization of Pickering-HIPEs with volume fractions up to 0.92, using silica nanoparticles (SP), which have been hydrophobized by adsorption of oleic acid (OA) in order to use them as emulsifier for w/o HIPEs. We studied the influence of the particle concentration on the emulsion stability, the droplet size and the upper limit of the internal phase volume fraction within the emulsion. Furthermore, we polymerized the Pickering-HIPEs to produce highly porous poly-Pickering-HIPEs (PPH).

Hydrophilic SP (20-100 nm in diameter) were functionalized by adsorption of OA. The OA content of the functionalized SP was determined by TGA to be 3.5 wt.-%. Binks and Lumsdon^[11] prepared w/o emulsions via a high energy emulsification method using dichlorodimethylsilane hydrophobized SP and observed a catastrophic inversion of the emulsions from w/o to o/w at internal phase levels between 60 and 70 vol.-%. The question of interest here is if OA functionalized SP will act as a mechanical barrier to phase inversion of HIPEs if the HIPEs are produced simply by stirring.

In order to answer this question we prepared HIPEs 1 - 4 containing styrene/poly(ethylene glycol) dimethacrylate (PEGDMA; 1:1 by vol.) as oil phase and 70, 75, 80 and 85 vol.-% internal aqueous phase, respectively, using 1 wt.-% functionalized SP with respect to the monomers. The aqueous phase contained 0.27 M CaCl₂·2H₂O. The emulsification was carried out under gentle stirring at 400 rpm. It is worth noticing that neither oleic acid nor unmodified SP alone nor a combination of free oleic acid and SP are suited to stabilize w/o emulsions as

control experiments revealed.[†] The appearance of the HIPEs 1 – 4 after 24 h is shown in Figure 1. HIPE 1 experienced significant sedimentation. HIPE 2 had only an ultra thin layer of the oil phase above the sedimented emulsion whereas HIPEs 3 and 4, which possess even higher internal phase volumes, were stable against sedimentation. This trend can be attributed to the compressed packing of droplets at higher internal phase volumes. The deformed droplets^[13] in the HIPEs (Figure 3) and particle layer surrounding the droplet ensures the emulsion is mechanically stabilized against sedimentation. These results show that the functionalized SP are suited to stabilize HIPEs and prove contrary to previous reports^[6] that Pickering HIPEs (> 85 vol.-%) can be made. Increasing the internal phase volume to 90 vol.-% resulted in phase separation of the HIPE most likely due to the lack of sufficient number of particles (1 wt.-% with respect to the monomers but less monomers, therefore, less particles if compared to a 85 vol.-% HIPE) required to act as a mechanical barrier to droplet coalescence. To test our hypothesis, we increased the particle concentration and determined the upper limit of the internal phase volume within our Pickering-HIPEs (Figure 2). 2 wt.-% functionalized SP are sufficient to prepare a 90 vol.-% HIPE (5), while 4 wt.-% functionalized SP allow to stabilize a 90 vol.-% (6) as well as 92 vol.-% HIPE (7). However, only a 90 vol.-% HIPE (8) could be made using 5 wt.-% functionalized SP. Further addition of water to HIPE 8 resulted in a highly viscous emulsion surrounded by water (Figure 2). The increase in viscosity of the HIPE with increasing SP concentration may be attributed to a combined effect of the increasing particle-particle interaction (causing a 3d network of particles to form in the continuous phase),^[11] which leads to a significant increase of the organic phase viscosity, and an increasing number of droplets, and hence droplet contact.

[†] Please see supplementary information for more details

1 mol.-% AIBN (with respect to the monomers) was added to the organic phase of the HIPEs to initiate free radical polymerization. The skeleton densities (SD) and foam densities (FD) of the PPHs were measured (Table 1). The porosities of PPHs 1 and 2 confirm that the emulsion templates experienced some degree of sedimentation as porosities of the PPHs are higher than the initial internal phase volume of HIPE 1 and 2. The porosities of the other PPHs are identical (within error) to the internal phase volume of the HIPE templates. The SD increases with increasing particle concentration while the FD reduces with increasing internal phase volume of the HIPEs. This suggests that the SP are incorporated into the polymer matrix.

Microscope images of HIPEs 5 and 6 were taken 10 min after the emulsions were prepared. Figures 3a, c show that droplet sizes of HIPE 5 and 6 are 400 - 700 μm and 250 - 500 μm in diameter, respectively, which demonstrates that the droplet size reduces with increasing SP concentration. Since poly-Pickering-HIPEs are a replica of the emulsion templates at gel point of the polymerization, it is not surprising that the pore sizes of PPHs 5 and 6 determined from SEM images were with 300 - 700 μm and 200 - 450 μm in diameter, respectively (Figures 3b, d), identical within error to the droplets in the emulsion.

Table 1. *Emulsion compositions, porosity and density of the PPHs.*

Sample ID	Internal phase volume [vol.-%]	Amount of functionalized SP used ^{a)} [wt.-%]	Porosity ^{b)} [%]	SD ^{c)} [g/cm ³]	FD ^{d)} [g/cm ³]	
1	70		1	74	1.178	0.302
2	75		1	77	1.185	0.273
3	80		1	80	1.187	0.235
4	85		1	84	1.215	0.190
5	90		2	87	1.198	0.158
6	90		4	89	1.285	0.144
7	92		4	90	1.316	0.131
8	90		5	-	-	-

a) With respect to the continuous phase; b) Value ± 2 ; c) Value ± 0.002 ; d) Value ± 0.022

We show that stable Pickering-HIPEs with up to 92 vol.-% internal phase can be prepared using functionalized SP and a low energy emulsification method, i.e. simple stirring. The functionalized SP act as a mechanical barrier and prevent droplet coalescence and phase inversion in Pickering-HIPEs. This means it is now possible to prepare Pickering-HIPEs, which can be used as templates for the manufacturing of highly porous polymer foams if the continuous phase consists of suitable monomers. This route was previously only assessable with surfactant stabilized HIPEs. Our method allows for the preparation of tailor-made closed-celled poly-Pickering-HIPEs.

Experimental section

1g of SP were suspended in a 1: 2 molar mixture of chloroform and OA, stirred for 3 h and precipitated from solution with methanol. Excess OA was removed by repeated re-suspending of SP in chloroform and precipitation in methanol prior to drying at 120°C. The OA content of functionalized SP was determined by TGA (TA Q500) in air. Styrene and PEGDMA were purified by filtration through basic and neutral Al₂O₃. The continuous emulsion phase was prepared by homogenizing the functionalized SP in equal volumes of styrene and PEGDMA. The internal aqueous phase was added drop wise to the organic phase under gentle stirring at 400 rpm for 5 min. HIPEs were transferred into falcon tubes and polymerized at 70°C for 24 h. PPHs were dried at 120°C for 24 h in vacuum. SEM images of Au coated PPHs were taken with a Jeol JSM-5610 LV. Images of the HIPEs were taken with an optical microscope (Olympus BX51M). The SD of PPHs was determined using Accupyc 1330 and FD using Geopyc 1360.

Keywords: emulsion template, polyHIPE, foam, polymers, colloids

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Figure 1. Photograph of HIPEs 1-4 stabilized by 1 wt.-% functionalized SP after 24 h and at 20°C.

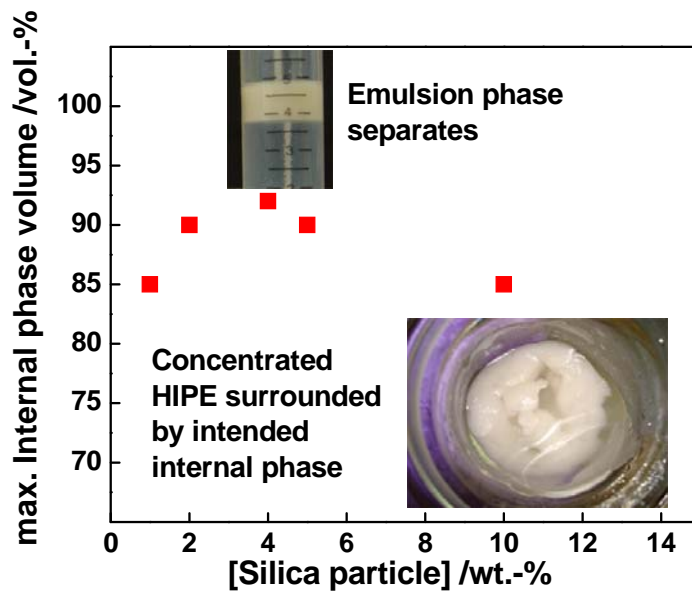


Figure 2. Upper limit of the internal phase volume as function of SP concentration used to stabilize the HIPEs.

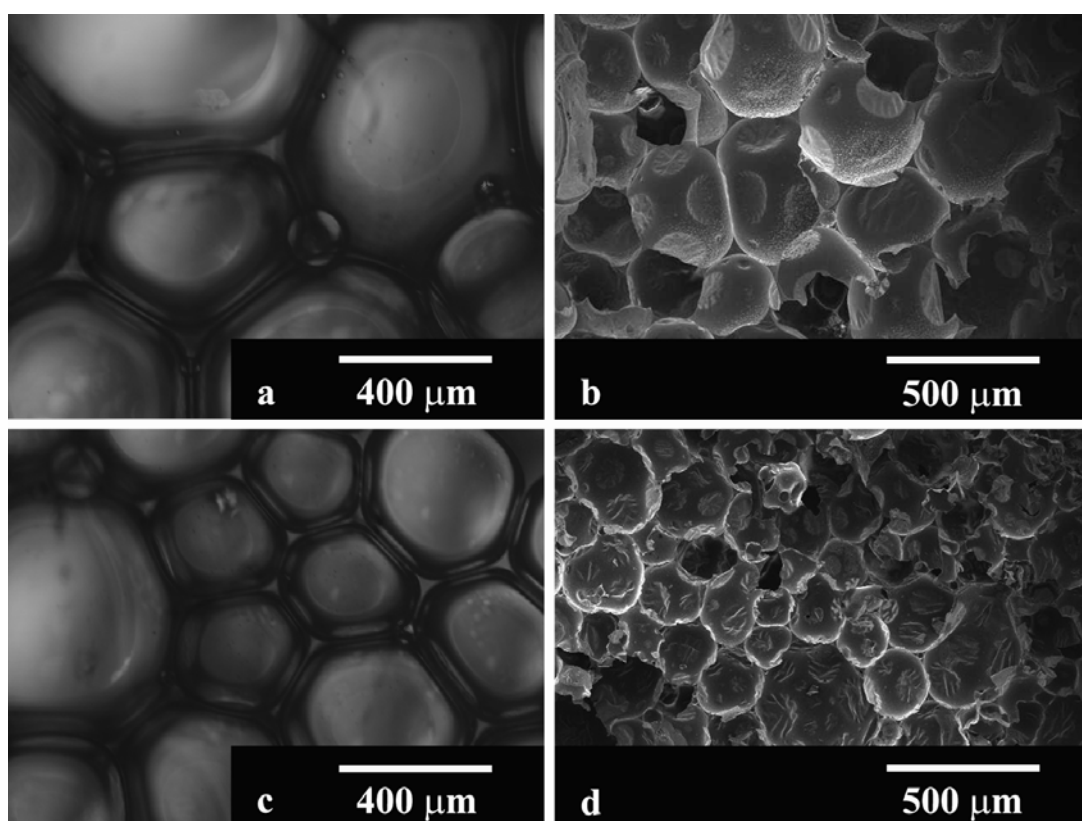


Figure 3. *Optical microscope images of HIPE 5 (a) and 6 (c) and SEM images of PPH 5 (b) and 6 (d).*