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Emulsions

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] although Lissant first defined this minimum as 0.70.[4] HIPEs consisting of a continuous organic phase and an internal aqueous phase (w/o emulsions) 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 because of 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 emulsions (a continuous aqueous phase and an internal organic phase) 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 previous reports on particle-stabilized emulsions deal with emulsions that have internal phase levels below 70 vol %. Kralchevsky et al.[12] developed a thermodynamic model predicting that particle-stabilized emulsions will phase invert above internal phase volume fractions of 0.5, but added that, experimentally, kinetic factors mean that phase inversion is observed at volume fractions of 0.70. Binks and Lumsden[11] further stated that particle-stabilized emulsions phase invert between volume fractions of 0.65 and 0.70, which means the major phase becomes the continuous phase.

We report herein the stabilization of Pickering w/o HIPEs with volume fractions of up to 0.92 by using silica nanoparticles (SPs), which have been hydrophobized by adsorption of oleic acid (OA). 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 SPs (20–100 nm in diameter) were functionalized by adsorption of OA. The OA content of the functionalized SPs was determined by thermogravimetric analysis (TGA) to be 3.5 wt %. Binks and Lumsdon[11] prepared w/o emulsions by a high energy emulsification method using dichlorodimethylsilane-hydrophobized SPs, 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 SPs will act as a mechanical barrier for the phase inversion of HIPEs if the emulsions are produced simply by stirring.

We prepared HIPEs 1–4 (Table 1, entries 1–4) containing styrene/poly(ethylene glycol) dimethacrylate (PEGDMA; 1:1) as the oil phase with 70, 75, 80, or 85 vol % internal aqueous phase, with added functionalized SPs (1 wt % with respect to the monomers). The aqueous phase contained $CaCl_2 \cdot 2H_2O$ (0.27 M). The emulsification was carried out under gentle stirring at 400 rpm. Control experiments showed that neither oleic acid, unmodified SPs alone, nor a combination of free oleic acid and SPs are suited to stabilize w/o emulsions (see the Supporting Information for more details). The appearance of HIPEs 1–4 after 24 h is shown in Figure 1. HIPE 1 experienced significant sedimentation. HIPE 2 had only an ultrathin 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

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

Sample	Internal phase volume [vol %]	Amount of functionalized SPs 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.

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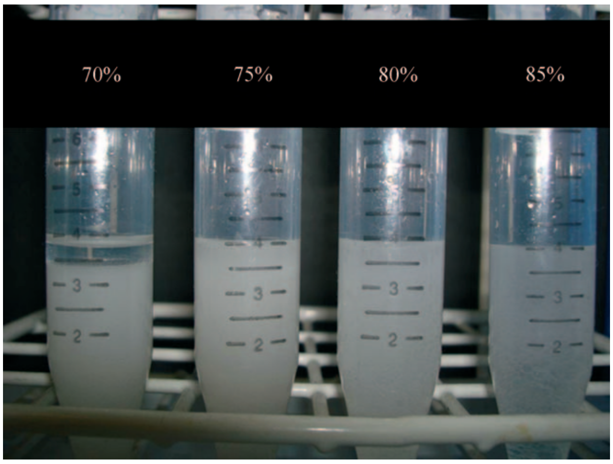

Figure 1. Photograph of HIPEs 1–4 stabilized by functionalized SPs (1 wt%) after 24 h and at 20°C.

droplets at higher internal phase volumes. The deformed droplets[13] in the HIPEs (Figure 2) and particle layer surrounding the droplet ensure the emulsion is mechanically stabilized against sedimentation.

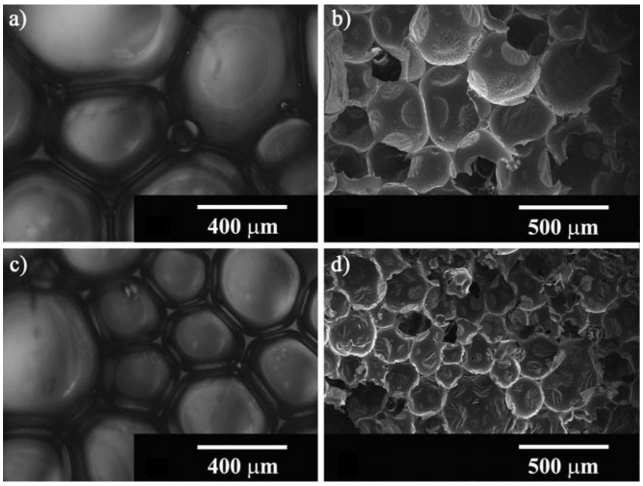

Figure 2. Optical microscope images of HIPE 5 (a) and 6 (c) and SEM images of PPH 5 (b) and 6 (d).

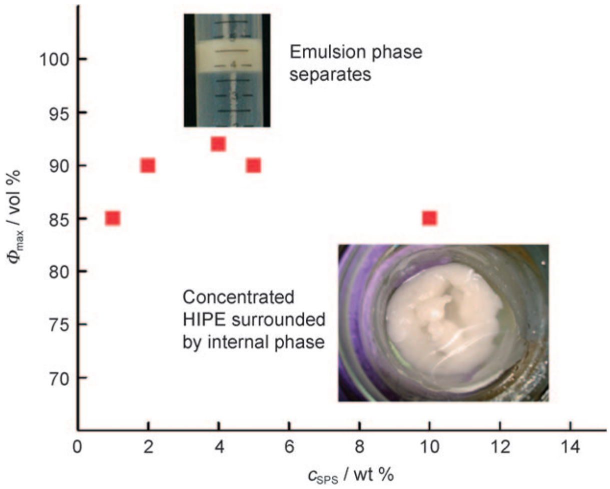

Figure 3. Upper limit of the internal phase volume Φ_{max} as function of SP concentration c_{SPs} used to stabilize the HIPEs.

These results show that functionalized SPs are suited to stabilize HIPEs and prove, contrary to previous reports,[6] that Pickering HIPEs (> 85 vol%) can be formed. Increasing the internal phase volume to 90 vol% resulted in phase separation of the HIPE, which most likely arises from the lack of sufficient numbers of particles (1 wt% with respect to the monomers, but less monomers and, 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 the Pickering HIPEs (Figure 3). 2 wt% functionalized SPs are sufficient to prepare a 90 vol% HIPE (5), while 4 wt% functionalized SPs allow stabilization of a 90 vol% HIPE (6) as well as 92 vol% HIPE (7; Table 1). However, only a 90 vol% HIPE (8) could be formed using 5 wt% functionalized SPs. Further addition of water to HIPE 8 resulted in a highly viscous emulsion surrounded by water (see inset in Figure 3). The increase in viscosity of HIPE 8 with increasing SP concentration may be attributed to the combination of two effects. Firstly, the increasing particle–particle interaction, which causes a 3D network of particles to form in the continuous phase,[11] leads to a significant increase of the organic phase viscosity. Secondly, the emulsion stability should be increased, which leads to an increasing number of smaller droplets, and hence increased droplet contact.

Free-radical polymerization was initiated by addition of azobisisobutyronitrile (AIBN, 1 mol% with respect to the monomers) to the organic phase of the HIPEs. The skeleton densities (SD) and foam densities (FD) of the PPHs were measured (Table 1). The porosity of PPH 1 confirms that the emulsion template experienced sedimentation as its porosity is higher than the initial internal phase volume of HIPE 1. 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 result suggests that the SPs are incorporated into the polymer matrix.

Microscope images of HIPEs 5 and 6 were taken 10 minutes after the emulsions were prepared. Figure 2 a,c shows that the droplet sizes of HIPEs 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 the gel point of the polymerization, it is not surprising that the pore sizes of PPHs 5 and 6 determined from scanning electron microscopy (SEM) images were 300–700 µm and 200–450 µm in diameter, respectively (Figure 2 b,d), which are similar to the diameter of the droplets in the emulsion.

We have shown that stable Pickering HIPEs with an internal phase of up to 92 vol% can be prepared using functionalized SPs and a low-energy emulsification method, namely, simple stirring. The functionalized SPs 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 accessible with surfactant-stabilized HIPEs. Our method allows for the preparation of tailor-made closed-celled poly-Pickering HIPEs.

Experimental Section

SPs (1 g) were suspended in a mixture of chloroform/OA (1:2 molar ratio), stirred for 3 h, and precipitated from solution with methanol. Excess OA was removed by repeated resuspension of SPs in chloroform and precipitation with methanol prior to drying at 120 °C. The OA content of functionalized SPs was determined by TGA (TA Q500) in air.

Styrene and PEGDMA were purified by filtration through basic and neutral Al_2O_3. The continuous emulsion phase was prepared by homogenizing the functionalized SPs in equal volumes of styrene and PEGDMA. The internal aqueous phase was added dropwise 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 microscope. Images of the HIPEs were taken with an Olympus BX51 M optical microscope. The SD and FD of PPHs were determined using Accupyc 1330 and Geopyc 1360 density analyzers, respectively.

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