High internal phase emulsion templates solely stabilised by functionalised titania nanoparticles†

Angelika Menner,[a] Vivian Ikem,[a] Mariely Salgueiro,[a] Milo S. P. Shaffer[b] and Alexander Bismarck*[a]

Received (in Cambridge, UK) 13th June 2007, Accepted 27th July 2007
First published as an Advance Article on the web 9th August 2007
DOI: 10.1039/b708935j

Porous polymer foams (poly-Pickering-HIPEs) have been synthesised from stable high internal phase emulsion templates solely stabilised by low concentrations of functionalised titania nanoparticles.

Highly porous, open-celled, low density polymer foams are very attractive materials for a wide range of applications due to their low density and interconnected structure. Emulsion templating using high (or medium) internal phase emulsions (HIPEs/MIPEs) has emerged as an effective route to prepare such polymer foams known as polyHIPEs.[1] HIPEs are often defined as very concentrated emulsions where the internal phase occupies more than 74% of the emulsion volume.[1] Conventional polyHIPEs are prepared by polymerising water in oil (w/o) HIPEs where the organic continuous phase consists of monomers and crosslinkers.[1] The continuous phase is the minority phase but is stabilised against coalescence by non-ionic surfactants such as Span 80 (sorbitan monooleate, Sigma, Aldrich, Gillingham, UK)[2] or Hypermers (Uniquema, Wirral UK).[3] The emulsion stability is further increased by suppressing Ostwald ripening, using an aqueous electrolyte as the dispersed phase to minimise mutual solubility of the two-phase mixture. It has been shown that HIPEs can act as templates during the polymerisation, producing polymer foams that are a replica of the pore structure of the emulsion at the gel point.[1,2]

The potential applications of polyHIPEs vary from filter membranes,[4] ion exchange resins[4] and supports for solid-phase chemistry[4] to matrices for cell culture and scaffolds for tissue engineering.[5] However, industrial applications of these materials have been limited particularly by poor mechanical properties of conventional polyHIPEs. The most common polyHIPEs, based on styrene/DVB formulations, tend to be extremely brittle with low shear resistance[3] which can, however, be mitigated by the use of more flexible monomers or crosslinkers.[1,3] Furthermore, large fractions of expensive surfactant (5–50%) are required to stabilise HIPEs effectively,[2] although there have been claims of using $<2\%$ surfactants containing an oxy-alkylene component to stabilise HIPEs.[6] In this communication we propose an alternative strategy based on replacing the surfactant altogether by using small particles to stabilise HIPEs. Particle-stabilised emulsions, also known as Pickering or Ramsden emulsions, are extremely stable due to the adsorption of particles at the interface between the continuous and dispersed phases which provides a barrier to droplet coalescence.[7] It is known that the extent to which the particles are wetted by the two immiscible phases largely determines the stability of the emulsion, although particle size, concentration, and mutual interaction between the particles are all important.[7] In order to stabilise water-in-oil (w/o) emulsions, more hydrophobic particles are required.[7]

The addition of titania nanoparticles (TNPs) not only potentially stabilises Pickering emulsion templates but may also introduce other benefits to the resulting nanocomposite foams including, for example, catalytic activity, UV-absorption or enhanced surface roughness which may lead to a variety of applications in the future.[8] Commercially available TNPs (ESI†) are very hydrophilic. To reduce the hydrophilicity, the particles were functionalised with oleic acid. 1 g of 'as received' TNPs were suspended in a 1 : 2 molar mixture of chloroform and oleic acid. The suspension was stirred for 3 h, after which methanol was added to precipitate the nanoparticles before centrifugation. Excess oleic acid was then removed during a purification step in which the nanoparticles were re-suspended in freshly distilled chloroform using an ultrasonic nozzle. Methanol was added to precipitate the nanoparticles before centrifugation. This process was repeated five times after which the purified TNPs were dried under vacuum at 120 °C for 24 h. The oleic acid content of TNPs was 2.5 wt%, as determined by TGA in air (ESI†).

The titania nanoparticles were used to stabilise Pickering-MIPE **1** and Pickering-HIPEs **2–4** having an internal aqueous phase volume of 70, 75, 80 and 85%. The continuous phases of all mixtures consisted of 1 wt% of nanoparticles suspended in a 50 : 50 mixture of styrene and DVB (ESI†) (by volume) using a high speed stirrer at 15000 rpm for a period of 15 min. The initiator, 1 mol% azobisisobutylonitrile (AIBN), was then introduced with stirring at 400 rpm, followed by the gradual addition of the aqueous phase, consisting of 0.03 mol l^{-1} $CaCl_2 \cdot 2H_2O$. Finally, the stirring rate was increased to 2000 rpm in order to obtain stable emulsions after which approximately 5 ml of each emulsion was poured into smaller falcon tubes to study the emulsions. Pickering-MIPE **1** and Pickering-HIPEs **2–3** were w/o emulsions which sedimented slowly over 24 h after preparation. The volume of the organic continuous phase expelled from the sedimented emulsions **1–3** was determined after 24 h and the new internal phase volume calculated to be 79, 81 and 85%, respectively. It was noted that the volume of separated organic phase decreased with increasing internal phase

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[a] *Department of Chemical Engineering, Polymer & Composite Engineering (PaCE) Group, Imperial College London, South Kensington Campus, London, UK SW7 2AZ.*
E-mail: a.bismarck@ic.ac.uk; Fax: +44 20759 45638;
Tel: +44 20759 45578
[b] *Department of Chemistry, Imperial College London, South Kensington Campus, London, UK SW7 2AZ*

† Electronic supplementary information (ESI) available: Details of preparation techniques and characterisation methods. See DOI: 10.1039/b708935j

volume. Nevertheless, the preparation of Pickering-HIPE **4** having 85% internal volume phase was impossible because of immediate phase separation (see ESI,† Fig. 1). These results suggest that for emulsions stabilised by functionalised TNPs having an oleic acid content of 2.5 wt%, the emulsion stability increases with increasing internal phase volume but an upper limit for internal phase volume exists between 80 and 85%. Until now, the prevailing view has been that only molecular surfactants are able to stabilise HIPEs; particle stabilised emulsions are expected to phase invert so that the majority phase is always continuous at volume fractions above between 0.65 and 0.70.[7] As a result, the minority phase becomes the internal phase and the formation of Pickering-HIPEs was thought to be impossible. Menner *et al.*[9a] reported on the first successful preparation of poly-Pickering foams synthesized by the polymerisation of a MIPE with 60% internal phase volume stabilised solely by carbon nanotubes. Colver *et al.*[9b] also reported on the preparation of poly-Pickering foams from emulsion templates stabilised by polymer microgels. However, these emulsion templates were prepared by forced sedimentation and centrifugation of Pickering emulsions with original internal phase volume <50%.[9b] In the current experiments, only 1 wt% of nanoparticles have been used to stabilise a dispersed phase with volume fraction up to 0.80, proving that Pickering-HIPEs are possible. The oleic acid adsorbed at the surface of the titania cannot be directly responsible, in a molecular sense, for this stabilisation. First, the total oleic acid content is extremely low ~0.03 wt% and secondly, attempts to stabilise HIPEs solely with 0.2 wt% oleic acid failed. Oleic acid adsorbed to TiO_2 does not act as a molecular surfactant, since its polar head group is bound tightly to the surface but it turns the titania more hydrophobic, by attaching long alkyl chains. A Pickering-HIPE **5** with 80% internal aqueous phase volume was prepared with untreated titania but it phase separated immediately since the particles are completely wetted by the aqueous phase, they prefer to remain in the bulk water rather than at the interface. On the other hand, oleic acid modified titania prefers the organic phase but retains sufficient polarity (perhaps through incomplete coating) that it remains at the interface. The particle layer at the interface protects the droplets of the Pickering-HIPE against coalescence. The treated TNPs prevented successfully the phase inversion of Pickering-HIPEs despite the high volume fraction (up to 0.80) of the internal majority phase. For comparison, a 'traditional' surfactant-stabilised HIPE **6** with an internal phase volume of 80% was made using similar conditions to Pickering-HIPEs **3** and **5** but using 20 vol% of the non-ionic polymeric surfactant Hypermer 2296 (ESI†).

The emulsion templates were transferred into Flacon tubes, which were sealed and polymerised in an oven at 70 °C for 24 h. The resulting polymer monoliths were removed from the tubes, dried in an oven at 110 °C for 24 h and then transferred to a vacuum oven for further drying at 110 °C for 24 h.

The polymerisation of the continuous phase of Pickering emulsions **1–3** resulted in porous but very brittle polymer monoliths. The matrix densities (ESI†) of polymer foams **1–3** are identical, within error, at 1.12 ± 0.01 g cm^{-3}. However, the average foam densities (ESI†) are 0.234 ± 0.001 g cm^{-3} (**1**), 0.229 ± 0.001 g cm^{-3} (**2**) and 0.206 ± 0.001 g cm^{-3} (**3**) with porosities of 79 ± 1% (**1**), 80 ± 1% (**2**) and 82 ± 1% (**3**). The experimentally determined porosities of poly-Pickering HIPEs **2** and **3** are slightly lower than the final internal phase volume of the sedimented emulsion templates due to the slow sedimentation process. It is thought that this difference is a result of the completion of the polymerisation before total sedimentation occurred. In the case of the polyHIPE prepared from the traditional HIPE template (**6**) with 80% internal phase volume the same as Pickering-HIPE **3**, the foam density is 0.144 ± 0.003 g cm^{-3} and porosity 87 ± 1%. However, unlike poly-Pickering-HIPE **3**, this high porosity can also be attributed to the loss of molecular surfactant during washing/drying.

Turning to the microstructure, SEM studies (ESI†) show that polymer foam **6** (see Fig. 1) has a open porous network structure typical for polyHIPEs. Pores of 6–12 μm in diameter are interconnected *via* pore throats of about 3 ± 1 μm. However, poly-Pickering foams **1–3** have much larger closed cell pores. The pore size was generally in the range of 100–400 μm for all poly-Pickering-foams, although a few bigger pores (600–700 μm) and smaller pores (20–100 μm) were observed. The smaller pores were evident in the pore walls (See Fig. 1 and ESI,† Fig. 2). The main difference between the foams made from Pickering or surfactant stabilised emulsions is the degree of pore interconnectivity. Although the pores of the poly-Pickering-foams **1–3** are mostly closed, areas in the pore walls covered by an extremely thin polymer layer are visible. These areas represent the contact faces between closest neighbouring droplets in the emulsion template where usually pore throats form. The pore throat formation in traditional polymer foams is supported by large amounts of surfactants.[2,10] In the case of poly-Pickering-foams, the thin polymer films are relatively stable but as they are put under stress by the mechanical forces arising during the vacuum drying, some are forced to rupture as can be seen in Fig. 1. This gives rise to some degree of interconnectivity to neighbouring pores and allows for the complete removal of the trapped aqueous phase. Of further interest was the fact that some polymer balls were found within some pores as seen in Fig. 1. This suggests that although most of the functionalised TNPs were relatively hydrophobic, a minority were still hydrophilic enough to form an o/w emulsion within some of the droplets of the w/o emulsion. Following polymerisation and drying, these o/w emulsions in the w/o droplets became trapped polymer balls within the pores. This coincidental discovery highlights an opportunity for poly-Pickering-HIPEs to be made with a substructure within another structure. By suitably choosing particles with different wettability, it will be possible to formulate deliberately an emulsion template based on one emulsion within another.

To summarise, very low loading fractions (1 wt%) of TNPs functionalised with oleic acid (2.5 wt%) were successfully used to stabilise HIPEs with an internal phase volume fraction up to 0.80 against coalescence and phase inversion. The polymerisation of these HIPE templates resulted in poly-Pickering-HIPEs with high porosities. The poly-Pickering-HIPEs were partially open due to the mechanical stress on the thin film regions in the poly-Pickering-HIPEs during drying. Although we report a proof of concept, it can be seen that the strategy could be extended to a range of other particulate fillers as long as the correct balance of surface wetting characteristics can be obtained. There is also potential to adjust particles architecture as well as composition. The use of nanoparticles with varying size, shape and hydrophobicity should allow control of the droplet size in the emulsion template and

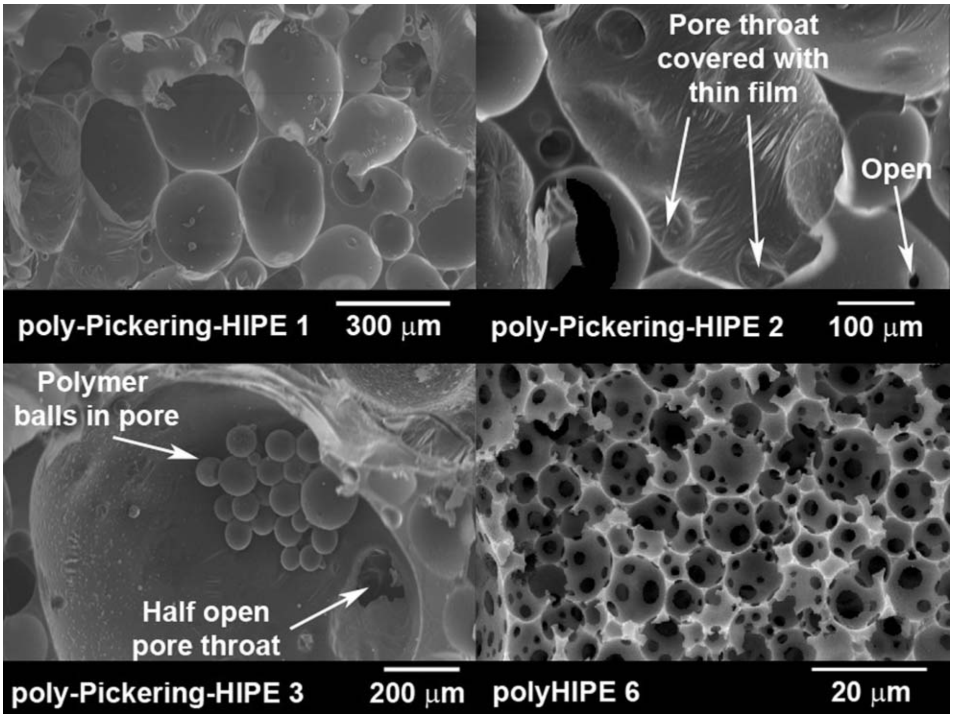

Fig. 1 SEM images of poly-Pickering-HIPEs **1–3** and the traditional (control) polyHIPE **6**.

hence structure in the resulting poly-Pickering-HIPEs. By using anisotropic particles with specific crystallography, different crystalline faces may ultimately be presented at the internal surfaces of the polymer foam, providing potential benefits in catalytic and other applications.

The authors are grateful for the financial support of the Challenging Engineering Programme (EP/E007538/1) of the UK Engineering and Physical Science Council (EPSRC), Halliburton Energy Services and V. I. also for an ORS Award.

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