1. Materials:

Styrene, divinylbenzene (DVB), oleic acid, α,α'-azoisobutyronitrile (AIBN), methanol, chloroform and $CaCl_2 \cdot 2H_2O$ were purchased from Sigma Aldrich (Gillingham, UK). The non-ionic surfactant Hypermer 2296 was kindly supplied by UNIQUEMA (Wirral, UK) and spherical titania particles (P25; 20 nm in diameter) by DEGUSSA AG (Frankfurt, Germany). All chemicals were used as received.

2. Experimental procedure

2.1 Preparation of functionalised Titania nanoparticles (TNP)

1 g of "as received" hydrophilic titania nanoparticles were suspended in 7 ml of chloroform in a conical flask. Oleic acid (8 ml) was added to the suspension and the mixture was stirred using a magnetic stirrer. After 3h, about 30 ml methanol was added to precipitate the particles prior to centrifugation. The excess oleic acid was then removed in a purification step whereby the nanoparticles were re-suspended in about 10ml chloroform and sonicated for 10 mins using the ultrasound nozzle. Afterwards, the particles were precipitated via the addition of methanol before centrifugation. In total, this process was repeated 5 times. The nanoparticles were dried for 24 h at 120 °C.

2.2 Preparation of poly-Pickering-HIPEs: PolyHIPE from 80% internal phase emulsion template stabilised by 1wt. % functionalised TNP

50 ml Pickering-HIPE were prepared as followed; 0.10 g of functionalised TNP were suspended in a mixture of 5 ml styrene and 5 ml DVB using a high speed stirrer at 15000 rpm for 15 min before being transferred into a reaction vessel. The continuous phase was formed via the addition of 0.15g AIBN to the stirred (400rpm) monomer/TNP suspension. Afterwards, 40 ml of the internal aqueous phase consisting of 0.03mol/l $CaCl_2 \cdot 2H_2O$ (250 ml electrolyte consisted of 1.25 g $CaCl_2 \cdot 2H_2O$ dissolved in water) was gradual added. The stirring rate was increased to 2000 rpm for 5mins to obtain a stable emulsion.

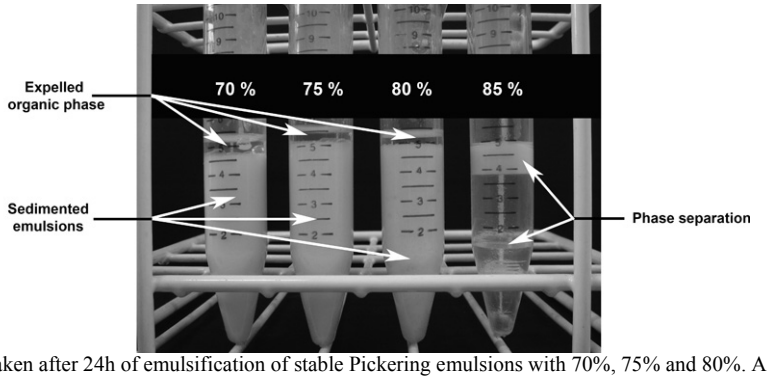

Fig. 1 Photograph taken after 24h of emulsification of stable Pickering emulsions with 70%, 75% and 80%. A small amount of organic phase was expelled after 24h of sedimentation. A Pickering-emulsion with 85% internal phase phase separated immediately. All emulsions were solely stabilised by functionalised TNP particles containing 2.5 wt.% oleic acid.

The emulsion was transferred into a flacon tube, sealed and polymerised at 70°C for 24h. The resulting poly-Pickering-HIPE was removed from the tubes and dried at 70°C under vacuum to weight constancy.

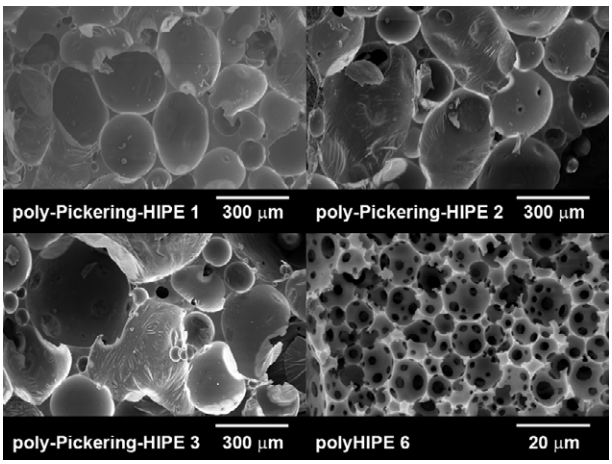

Fig. 2 SEM images of the Poly-Pickering-HIPEs **1-3** and a traditional (control) polyHIPE **6**

3. Characterisation Techniques

3.1 Thermo gravimetric analysis (TGA):

The amount of oleic acid adsorbed at the surface of the titania nanoparticles was determined using a Thermogravimetric Analyser (Pyris 1 TGA, Perkin Elmer, Beaconsfield, UK). Approximately 8 mg of the particles were placed on a platinum holder and heated to 600°C at a heating rate of 10°C min^{-1} under a flow of 20 ml min^{-1} air. The oleic acid content equals the weight loss in the temperature range between 180 °C and 500 °C (evaporation and degradation of oleic acid).

3.2. Determination of density and porosity:

Density measurements were taken using a Helium Pycnometer (AccuPyc 1330, Micrometrics Ltd., Limited, Dunstable, UK). Therefore, the samples are weighted initially and than placed into measuring chamber of known volume of the pycnometer. The pressure will rise above the atmospheric value. The 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.

$$\rho_m = \frac{m_S}{V_C - \frac{V_{EXP}}{\left(\frac{p_{1G}}{p_{2G}} - 1\right)}} \qquad [g\ cm^{-3}] \qquad (1)$$

where is m_S the sample mass, V_C the cell volume, V_{EXP} the expanded volume, p_{1G} the cell elevated pressure and p_{2G} 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_{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:

$$V_P = V_{P+M} - V_M \qquad [cm^{-3}] \qquad (2)$$

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 (ρ_f) is obtained (Eq. 3). The porosity (P) is found using Eq. 4:

$$\rho_f = \frac{m_S}{V_{P+M}} \qquad [g\ cm^{-3}] \qquad (3)$$

$$P = \left(1 - \frac{\rho_f}{\rho_m}\right) \cdot 100 \qquad [\%] \qquad (4)$$

3.3. Scanning electron microscopy:

The SEM micrographs of cryo-fractured surfaces of all samples were taken using a Leo Gemini (FEGSEM). 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. The images were analysed using ImageTool software where Feret's diameter was considered as the pore size. Prior to the analysis the pores were traced manually and a grey-scaled image was obtained from scanning the outlined structure. The image was skeletonised in order to thin down boundaries that may appear broad. This process produces a slightly larger cell size due to the reduction of the wall thickness. Two images were analysed with a total of 100 pores per foam.