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Macroporous polymers from particle-stabilized emulsions

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ABSTRACT

Macroporous polymers are attractive materials due to their low density, low cost, recyclability and tunable mechanical and functional properties. Here, we report a new approach to prepare macroporous polymers from emulsions stabilized with colloidal polymeric particles in the absence of chemical reactions. Stable water-in-oil emulsions were prepared using poly(vinylidene difluoride) (PVDF), poly(tetrafluoroethylene) (PTFE), and poly(etheretherketone) (PEEK) as stabilizing polymeric particles in emulsions. The partial wetting of the polymeric particles by the two immiscible liquids drives particles at the water–oil interface during emulsification, leading to extremely stable water-in-oil emulsions. The particle-stabilized emulsions were processed into highly porous solid polymer components upon drying and sintering. The high stability of emulsions also allows for the preparation of hollow polymeric microcapsules. We describe the conditions required for the adsorption of particles at the liquid–liquid interface, we show the rheological behavior of the polymer-loaded wet emulsions and, we discuss the effect of the emulsions' initial compositions on the final sintered porous structures. This new approach for the fabrication of macroporous PVDF, PTFE, and PEEK polymers is particularly suited for the preparation of porous materials from intractable polymers but can also be easily applied to a variety of other polymeric particles.

1. Introduction

Porous polymers find numerous applications as for example mechanical dampers, supports for catalysis, thermal, acoustic and electrical insulators, piezoelectric electrets, furnishing and construction materials, scaffolds for tissue engineering, and encapsulants for drug delivery [1–5]. The main processing methods used for the preparation of macroporous polymers are foaming of a polymer melt or solution through incorporation of a gaseous phase [6,7], fibre bonding [8,9], phase separation [10], or sacrificial templating using ice crystals [11,12], emulsion droplets [13,14], wax [15], and salt particles [16] as fugitive phase.

The sacrificial template method enables tuning of the porosity, pore size distribution and pore morphology of the final material by adjusting the amount, size and shape of the fugitive phase. The use of volatile emulsion droplets as templates to produce porous polymers has been employed for many decades [17–21]. Macroporous polymers with pore sizes in the range of 1–100 μm have been produced by polymerization of the continuous phase of high (or medium) internal phase emulsions (HIPEs/MIPEs) followed by the subsequent removal of the internal phase by drying and heat treatment [13,22–28]. The preparation of porous polymers from poly(MIPEs/HIPEs) involves the stabilization of the internal droplet phase using conventional surfactants in a monomer solution. The volume fraction of the dispersed phase corresponds to 0.6 and >0.74 for MIPEs and HIPEs, respectively [21,26,27,29]. To increase the stability of the emulsions against collapse during liquid removal, the structure is locked by the polymerization of the continuous monomer phase. In addition to surfactants, the internal droplet phase of HIPEs has also been stabilized by colloidal particles adsorbed at the liquid interfaces, leading to particle-stabilized Pickering emulsions [30–32]. Macroporous polymers with porosities up to 90% and pore sizes in the range of 100–400 μm have been prepared by polymerizing the continuous phase of Pickering-HIPEs stabilized with carbon nanotubes [29], silica [33] and titania nanoparticles [34], and microgel latex particles [35], followed by evaporation of the dispersed phase.

Recently, particle-stabilized emulsions were used to produce porous polymeric structures in the absence of polymerization reactions. Porous membranes with pore sizes up to 20 μm were formed through phase inversion of a polymeric emulsion stabilized by zeolite nanoparticles [36].

Although emulsions have long been used as templates for the production of highly porous polymers, the technique has been mostly

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limited to polymers that can be polymerized in situ within the continuous phase or to polymers that are melt-processable. Hence, an emulsion templating approach that would not involve any chemical reactions and that could be easily applied to a wide variety of polymers, including "intractable" polymers that cannot be melt-processed would be highly desirable for the fabrication of macroporous polymers. Fluorinated polymers such as poly(vinylidene difluoride) (PVDF) and poly(tetrafluoroethylene) (PTFE) are particularly interesting due to their piezoelectric behavior (PVDF), and non-adherent properties combined with high temperature resistance (PTFE).

Powder processing routes are often used for shaping and consolidating intractable polymers such as PTFE. Therefore, a wide variety of intractable polymers are commercially available in powder form. Such polymeric particles can potentially be used to stabilize Pickering emulsions and also be the major constituent of macroporous polymers obtained after removal of the droplet templates. We recently developed a simple powder-based route to produce macroporous ceramics from emulsions stabilized with inorganic particles of various chemical compositions [37]. In that case, the adsorption of initially hydrophilic particles at the oil–water interface was achieved through the in situ adsorption of short amphiphilic molecules on the surface of particles. Here, we extend this powder-based approach for the preparation of macroporous polymers from emulsions stabilized by polymeric particles of different chemical compositions. The method relies on the adsorption of colloidal polymeric particles at the oil–water interface for the formation of stable water-in-oil emulsions that are subsequently used as templates for the preparation of porous polymers. The particles adsorbed at the liquid interface act as a barrier against extensive droplet coalescence, allowing for drying and sintering of the emulsions directly into macroporous polymers in the absence of any chemical reaction.

2. Experimental section

2.1. Materials

Poly(vinylidene difluoride) powder (PVDF) with average particle diameter, d_{50}, of 250 nm, specific density of 1.78 g/cm^3, and melting temperature of 160.5 °C was purchased from Polysciences, Inc. (Warrington, PA, USA). Poly(tetrafluoroethylene) powder (PTFE) with $d_{50} \sim 300$ nm, specific density of 2.15 g/cm^3, and melting temperature of 328.7 °C was obtained from Algoflon (Ausimont S.P.A., Italy). Poly(etheretherketone) powder (PEEK, VICOTE™ 707) with d_{50} of 16 μm, specific density of 1.3 g/cm^3, and melting temperature of 343 °C was acquired from Victrex plc (Rotherham, UK). The melting temperatures reported above were measured by differential scanning calorimetry (DSC). These values are comparable to those reported in the literature for the pure polymers, indicating that the commercial powders are surfactant-free. We also determined the contact angle of water droplets in air deposited on the surface of flat substrates made out of the commercial polymers. The contact angles measured through the water phase were 90°, 114°, and 77° for PVDF, PTFE, and PEEK particles, respectively, which are within the range accepted in literature.

Decane (≥98% pure, boiling temperature $T_b = 171–174$ °C, Fluka Chemie, Switzerland), octane (97% pure, $T_b = 125$ °C, Acros Organics, Belgium), hexane (96% pure, $T_b = 69$ °C, Scharlau, Spain), and toluene (99.99% pure, $T_b = 110.6$ °C, Acros Organics, Belgium) were used as-received. Diblock copolymer based on styrene and ethylene/propylene, G-1701E was purchased from Kraton Polymers LLC (Houston, TX, USA) and used as-received. The interfacial tensions of decane–water, octane–water, hexane–water, and toluene–water interfaces were measured to be 51.8, 51.4, 50.0, and 36 mN/m, respectively (PAT1, Sinterface Technologies, Berlin, Germany). Double deionized water with an electrical resistance of 18 MΩcm was used in all the experiments (Nanopure water system, Barnstead, USA).

2.2. Preparation of suspensions

Prior to emulsification, colloidal suspensions of particles were prepared by adding powders to oil under steady stirring in a conventional lab-scale mixer. In the case of hexane, the emulsion was cooled in an ice bath to prevent evaporation of hexane during mixing. The concentration of particles in the suspension varied between 5 and 17 vol% for the PVDF particles and was kept constant at 15 vol% and 26 vol% for the PTFE and PEEK particles, respectively. The detailed compositions of the investigated emulsions are shown in Table 1.

2.3. Preparation of emulsions

Emulsification was performed by vigorously stirring mixtures of water and concentrated suspensions of PVDF, PTFE, and PEEK particles in oil for 3 min using a household mixer at full power (Multimix 350W, Braun, Spain).

2.4. Rheology

Rheological tests were performed at 25 °C using a stress-controlled rheometer (Bohlin-Rheometer CS-50, Bohlin, England) with profiled parallel-plate geometry (25 mm plate diameter). Experiments were carried out with a mechanically-set gap of 1000 μm. Oscillatory measurements were conducted to determine the storage and loss moduli of the wet emulsions by gradually increasing the maximum applied stress from 10 to 1000 Pa at a constant frequency of 1 Hz. Steady-state experiments were carried out to measure the emulsion apparent viscosity as a function of shear rate by progressively increasing the applied stress from 200 Pa to 1000 Pa.

2.5. Drying and sintering

After emulsification, all emulsions were shaped and dried in air at 25 °C and ambient pressure for 2 days. Following drying, the PVDF samples were sintered at 177 °C for 4 h, the PTFE samples were sintered at 343 °C for 7 h, and the PEEK samples were sintered at 360 °C for 6 h to obtain polymeric macroporous structures.

2.6. Microstructural analysis

Optical micrographs were obtained by placing wet emulsion samples between two glass slides in an optical microscope (Polyvar MET, Reichert-Jung, Austria) connected to a camera (DC300, Leica, Switzerland) in transmitting light mode. The porous polymers

Table 1
Compositions of the emulsions stabilized by PVDF, PTFE, and PEEK polymeric particles.

Particle	Suspension solids content (vol%)	Oil	Water content (vol%)[a]
PVDF	5–17	Octane	30–65
PTFE	15	Hexane	50
PTFE	15	Octane	50
PTFE	15	Decane	50
PEEK	26	Octane	40

[a] The amount of the water phase was calculated with respect to the emulsion total volume (water + particles + oil).

obtained after sintering were investigated by scanning electron microscopy (SEM, LEO 1530). SEM samples were sputtered with platinum for 55 s at 60 mA. Droplet size distributions of the wet emulsions and pore size distributions of the sintered polymers were determined by evaluating a set of at least five microscope images for each composition using the linear intercept method (software Lince, TU Darmstadt, Germany). Average sizes and 68% confidence intervals were obtained by fitting lognormal distributions to the experimental data. Porosities of the sintered samples were determined from the geometrical dimensions of the samples, their weight and the theoretical density of the materials.

2.7. *Preparation of polymer capsules*

Colloidal capsules were formed by diluting the wet emulsions 500× by volume with the continuous oil phase. Prior to dilution, 0.05 mg/ml diblock copolymer was added to the oil phase to lock the particle layers that form the capsules' walls. Water capsules were harvested from the diluted emulsions by removing the upper oil phase with a pipette after sedimentation of the water droplets. Dry hollow capsules were prepared by depositing several drops of diluted wet capsules onto a clean, aluminum SEM sample holder, followed by drying in air at room temperature for 1 day.

3. Results and discussion

Water-in-oil emulsions stabilized by polymeric particles were obtained by dispersing the particles in the oil phase prior to emulsification. The initial hydrophobic nature of the polymeric particles allowed for the preparation of homogeneous suspensions of high particle concentrations in oil (Table 1).

Despite their predominantly hydrophobic nature, we observed that PVDF, PTFE, and PEEK particles readily adsorb at oil–water interfaces when water is mixed to the initial particle-containing oil suspension. This led to stable particle-coated water droplets dispersed throughout the continuous oil phase, as exemplified in Fig. 1 for the case of PVDF particles. Such results indicate that the particles are not fully wetted by the oil phase when their surface is also exposed to water, which results in a finite contact angle of the water–oil interface on the polymer surface. Our experiments showed that this condition is fulfilled when alkanes like hexane, octane and decane are used as oil phase. A finite contact angle in the range of 60–120° (measured through the aqueous phase) is also observed for water–air interfaces on most polymer surfaces [38]. The fact that water can partially wet the surface of polymers in contact with air or alkanes is probably due to the high interfacial tensions of water–alkane and water–air interfaces: 50.0–51.8 and 72.8 mN/m, respectively. According to Young–Laplace's force balance [39], a high interfacial tension of the water–alkane or water–air interfaces tend to hinder complete spreading of the hydrophobic fluid (alkane or air) on the polymer surface. Based on this argument, non-polar liquids of interfacial tension lower than that of alkanes (with respect to water) should wet the polymer surface to a larger extent and should thus make the adsorption of polymeric particles at the oil–water interface less favorable. Indeed, additional experiments using toluene as oil phase resulted in less stable emulsions, suggesting that the lower interfacial tension between toluene and water (36 mN/m) favors wetting on the polymer surface and thus inhibits the adsorption of polymeric particles on the surface of water droplets.

The results obtained here indicate that a high interfacial tension of the water–oil interface is a key requirement for the stabilization of

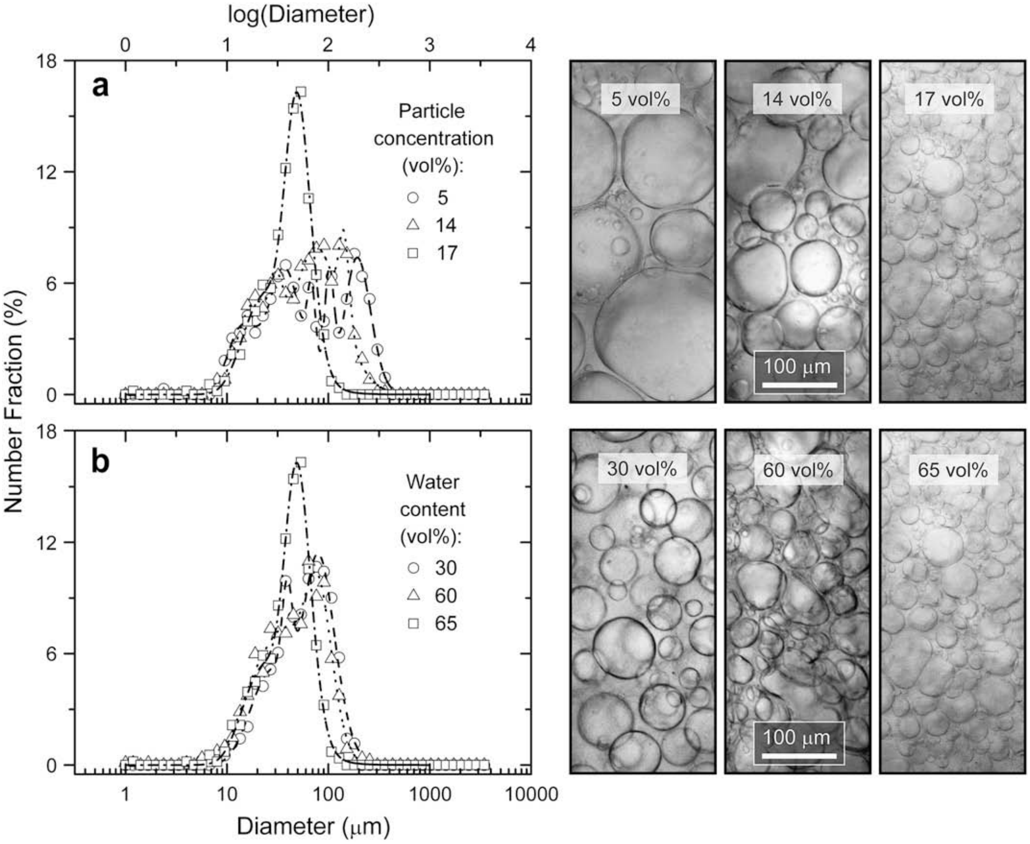

Fig. 1. Droplet size distributions and optical microscope images of water-in-oil emulsions prepared with (a) different concentrations of PVDF particles at a fixed water content of 65 vol%, (b) different water contents at a fixed particle concentration of 17 vol% in oil.

emulsions using polymeric particles, since this should lead to a finite contact angle of the water–oil interface on the polymer surface. Taking the water–air interface as an example of a high-energy interface at which most polymers form a finite contact angle between 60 and 120° [38], one should expect that particle-stabilized emulsions could be in principle obtained with a variety of other polymeric particles, as long as oils with a high interfacial tension with respect to water are used. The type of emulsions would then be determined by the exact contact angle of the water–oil interface on the polymer surface. Oil-in-water emulsions are expected for contact angles lower than 90°, whereas water-in-oil emulsions should result from contact angles larger than 90°. Emulsification would not be possible only close to a contact angle of 90° where the thin liquid film separating droplets might not be thick enough to prevent droplet coalescence [40].

The microstructure of wet emulsions stabilized by polymeric particles was varied by changing the amount of particles in the initial suspension and the water content in the emulsion (Fig. 1). For a fixed water content of 65 vol%, an increase in the concentration of PVDF particles from 5 to 17 vol% leads to a decrease in the cell size range of the wet emulsions from 11–266 μm to 16–69 μm, as indicated in the multimodal droplet size distributions shown in Fig. 1a. The decrease in the range of droplet sizes with increasing particle concentration results from the higher viscosity of the initial suspension, which induces higher shearing stresses on the droplets during mixing [37,41].

The influence of water content on the emulsion microstructure was investigated for PVDF-stabilized emulsions at a fixed particle concentration of 17 vol%. No significant change in the droplet size distribution was observed for water concentrations between 30 and 60 vol%. Interestingly, an increase in the water volume fraction from 60 to 65 vol% decreased the droplet size range from 19–121 μm to 16–69 μm, as illustrated in Fig. 1b. This reduction in droplet size range is probably due to a pronounced increase in the viscosity of the emulsion when the volume fraction of droplets approaches the condition of random close packing (∼64 vol% for monodisperse spheres). Water contents higher than 65 vol% resulted in emulsions with a phase-separated layer of water on the top of the mixture.

Emulsions comprising 65 vol% water and 17 vol% PVDF particles exhibited remarkable stability against coalescence, Ostwald ripening and sedimentation. No significant change was observed in the emulsion droplet size distribution within a time period of more than 1 year after emulsification. This long-term stability can be attributed to the irreversible adsorption of particles at the oil–water interface. Due to the high energies required to remove a particle from the oil–water interface, particles can impede the rupture of the thin liquid film between droplets, as well as inhibit the shrinkage of droplets induced by Ostwald ripening.

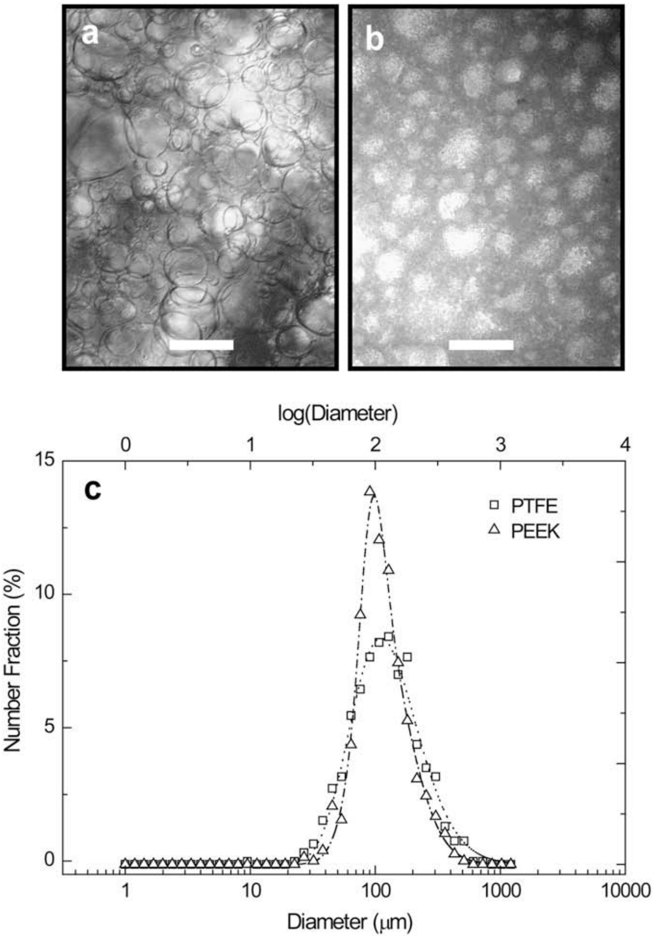

Fig. 2. (a, b) Optical microscope image and (c) droplet size distribution of water-in-oil emulsion stabilized with PTFE and PEEK particles. The emulsions were prepared by mixing suspensions of (a) 15 vol% PTFE particles in hexane with 50 vol% water, (b) 26 vol% PEEK particles in octane with 40 vol% water. The continuous lines correspond to the radial probability density functions used to describe the droplet size distributions. Scale bar: 200 μm.

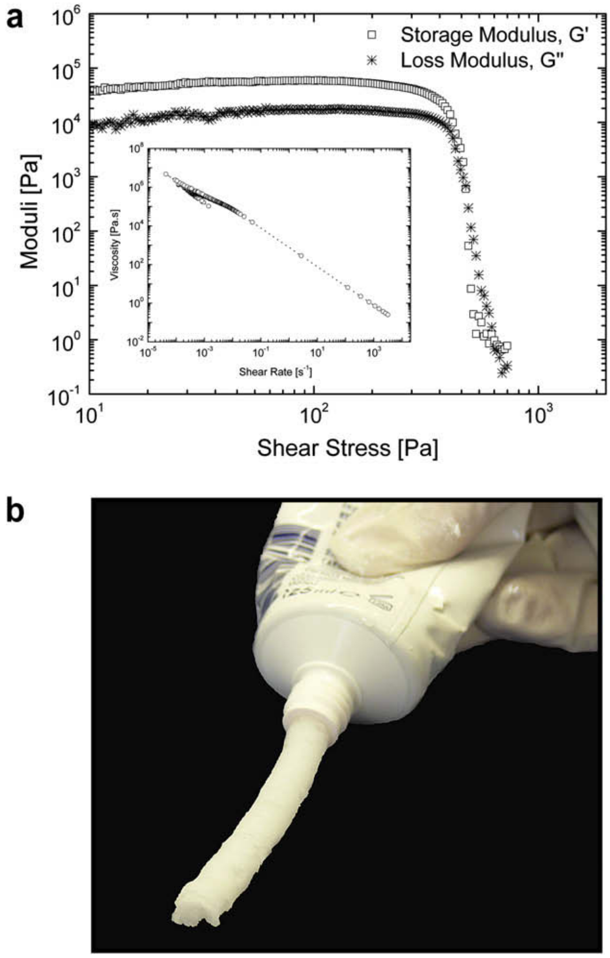

Fig. 3. (a) Storage (*G*′, □) and loss (*G*″, ∗) moduli as functions of applied shear stress for a water-in-octane emulsion containing 17 vol% PVDF particles and 65 vol% water. Inset: Apparent viscosity (○) of the same emulsion as a function of applied shear rate. (b) Image of the same water-in-oil emulsion extruded through a tube.

Similar to PVDF-stabilized emulsions, the adsorption of PTFE and PEEK particles at the oil–water interface resulted in stable particle-stabilized emulsions with water droplets dispersed throughout the continuous oil phase, as demonstrated in Fig. 2a and b. Emulsions stabilized by PTFE and PEEK particles exhibited broad droplet size distributions with sizes in the range from 67 to 234 μm and 77 to 203 μm, respectively (Fig. 2c).

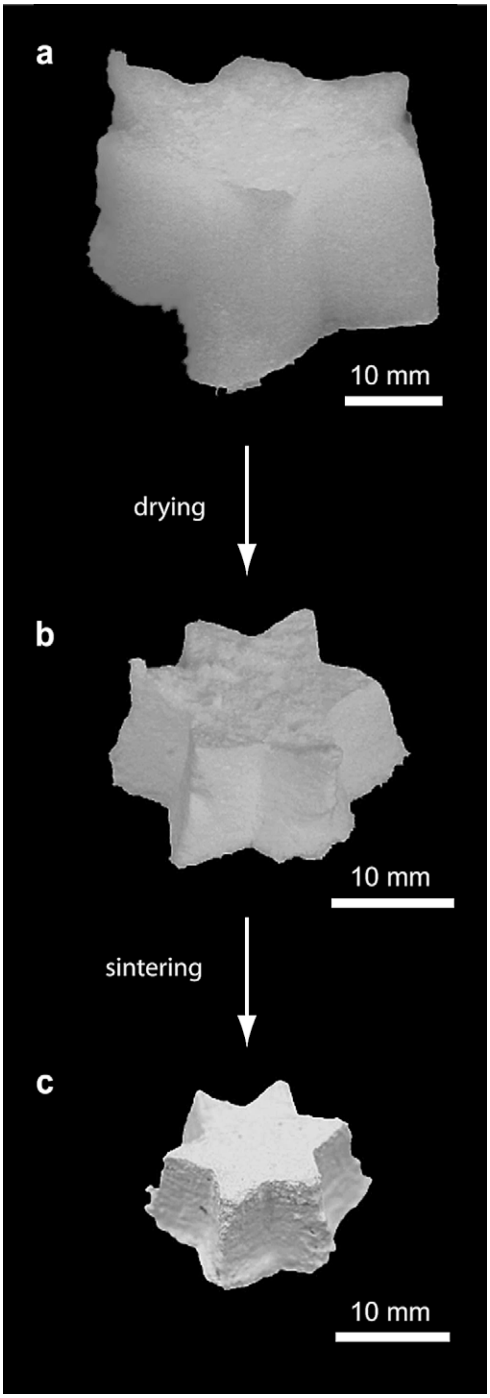

Fig. 4. Macroporous polymers obtained from PTFE-stabilized water-in-hexane emulsions. (a) Highly stable emulsions are formed through the adsorption of sub-micrometer-sized colloidal particles at the oil–water interface. The long-term stability of these emulsions allows for (b) drying and (c) sintering of the shaped materials directly into macroporous polymers without requiring any further gelation or strengthening reaction.

As a result of the densely packed water droplets and the high concentration of particles in the continuous phase, the wet emulsions exhibit viscoelastic behavior with a noticeable yield stress, as shown in Fig. 3 for a PVDF-stabilized emulsion. Under steady-shear conditions, the viscoelastic character led to a typical shear-thinning behavior with a marked decrease in the apparent viscosity as the shear rate is increased (Fig. 3, inset). This viscoelastic behavior enables shaping of the emulsions using conventional technologies such as injection molding and extrusion without requiring any

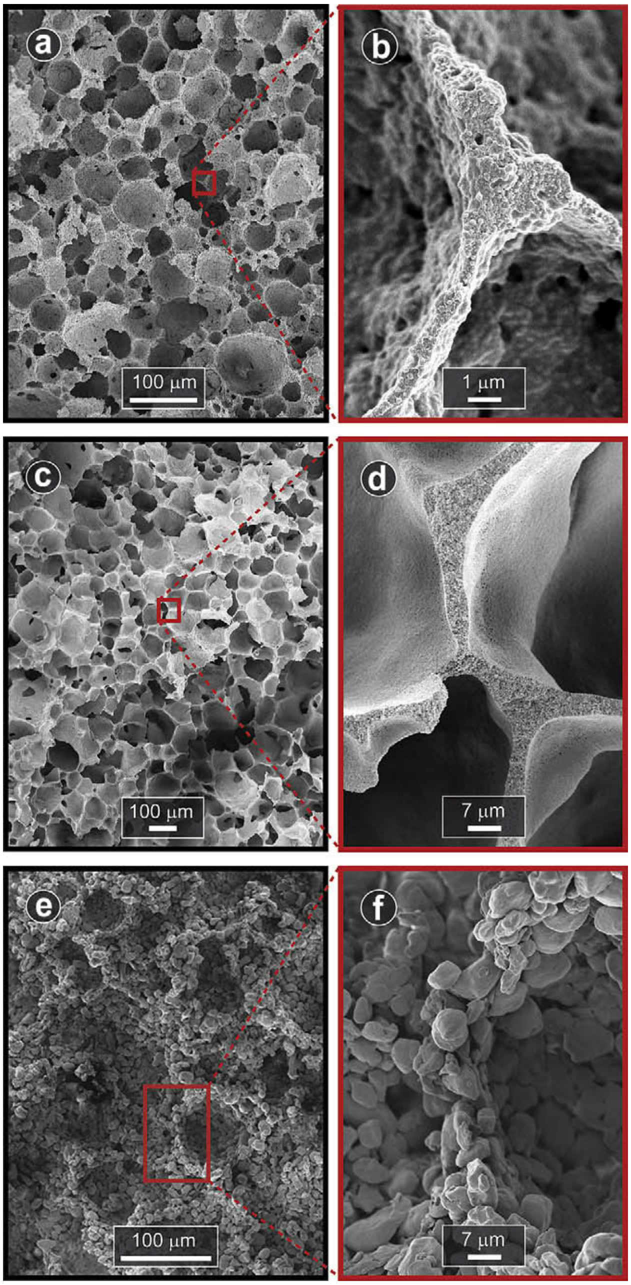

Fig. 5. Microstructures of sintered porous polymers prepared with PVDF, PTFE, and PEEK particles. (a) Porous PVDF obtained after sintering the water-in-octane emulsion with 65 vol% water and 17 vol% PVDF particles at 177 °C; (b) the dense strut of the sintered porous PVDF obtained after sintering; (c) porous PTFE obtained after sintering the water-in-hexane emulsion with 50 vol% water and 15 vol% PTFE particles at 343 °C; (d) the dense strut and the cell walls of the sintered porous PTFE formed after sintering. (e) Porous PEEK obtained after sintering the water-in-octane emulsion with 40 vol% water and 26 vol% PEEK particles at 360 °C; (f) the cell walls of the sintered porous PEEK.

further gelation or strengthening reaction. Water-in-oil emulsions containing 17 vol% PVDF particles and 65 vol% water for instance can be extruded without need of further strengthening to keep the shape of the material after the extrusion process (Fig. 3b).

The high stability achieved by the presence of particles adsorbed on the droplet surface and spanning throughout the continuous phase allowed for drying and sintering of the wet emulsions directly into macroporous polymers, as exemplified in Fig. 4 for a PTFE-stabilized emulsion.

Microstructures of porous polymers fabricated from PVDF, PTFE, and PEEK stabilized emulsions are shown in Fig. 5. Sintered PVDF structures obtained from emulsions containing 17 vol% PVDF particles and 65 vol% water showed pore sizes in the range from 16 to 100 μm (Fig. 6). Sintering of emulsions containing 15 vol% PTFE particles and 50 vol% water, and 26 vol% PEEK particles and 40 vol% water yielded porous structures with slightly larger pores in the range from 58 to 195 μm, and 80 to 180 μm, respectively (Fig. 6). To avoid the collapse of porous components upon heating, the samples were sintered slightly above the melting temperature within a narrow temperature range. At this temperature range, the viscosity of the polymers is presumably still sufficiently high to avoid the collapse of the structures. Fusion of particles in the continuous phase and at the pore surfaces during sintering led to the formation of dense struts and 1–5 μm thick walls (Fig. 5b and d). The porous PVDF and PTFE samples exhibited linear shrinkage of 30% and 13% during drying and sintering, respectively. The total porosity after sintering was 79% for the PVDF structures and 82% for the PTFE samples.

In addition to bulk macroporous polymers, the stability of wet emulsions enabled harvesting of semi-permeable particle-coated capsules. Wet capsules comprised of polymeric particles in the outer shell were obtained by diluting the PVDF-stabilized emulsions with the continuous oil phase. Locking the close-packed particle shells surrounding each water droplet with a diblock copolymer strengthened the particles outer layer and allowed for the production of polymeric hollow capsules upon drying, as shown in Fig. 7. Colloidal capsules coated with functional polymers such as PVDF, PTFE, and PEEK might be attractive materials for the encapsulation and delivery of active agents in food processing, pharmaceutics, agriculture and medicine.

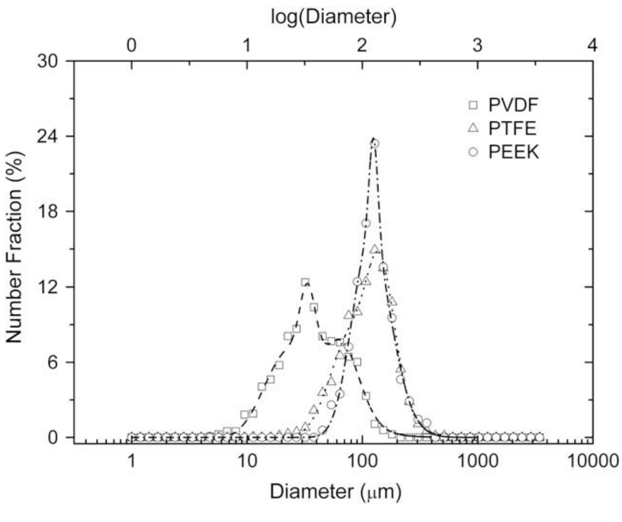

Fig. 6. Pore size distributions of sintered porous polymers prepared with PVDF, PTFE, and PEEK particles. (□) Porous PVDF obtained after sintering the water-in-octane emulsion with 65 vol% water and 17 vol% PVDF particles at 177 °C; (△) porous PTFE obtained after sintering the water-in-hexane emulsion with 50 vol% water and 15 vol% PTFE particles at 343 °C; (○) porous PEEK obtained after sintering the water-in-octane emulsion with 40 vol% water and 26 vol% PEEK particles at 360 °C.

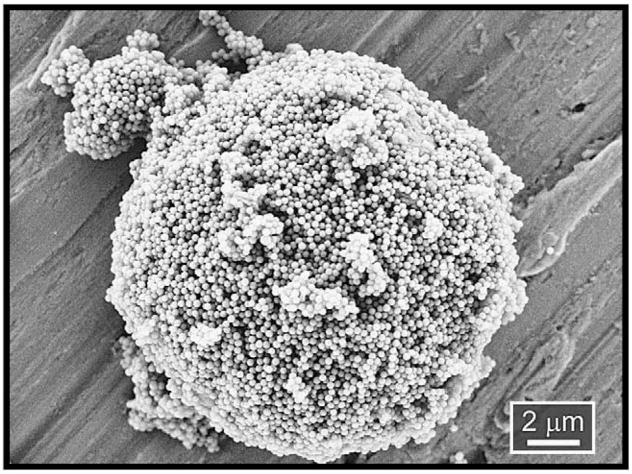

Fig. 7. SEM image of a dry PVDF capsule obtained after 500× dilution of PVDF-stabilized wet emulsion with a continuous oil phase containing 0.05 mg/ml diblock copolymer.

4. Conclusion

We described a simple and versatile approach to produce macroporous polymers from emulsions stabilized with polymeric particles of different chemical compositions. The adsorption of colloidal polymeric particles at the oil–water interface allows for the stabilization of water-in-oil emulsions that can be further processed into polymeric macroporous structures in the absence of any chemical reaction. Particle adsorption at the oil–water interface is accomplished by choosing oils that do not completely wet the surface of the polymeric particles. In the case of PVDF, PTFE and PEEK particles, for instance, this condition is valid when short alkanes exhibiting high interfacial tension with respect to water are used as oil phase. Taking poly(vinylidene difluoride), poly(tetrafluoroethylene), and poly(etheretherketone) particles as examples, we obtained bulk porous polymers with porosities up to 82% and pore sizes within a range from 16 to 200 μm. The high stability of the wet emulsions allows for harvesting of single hollow microcapsules composed of close-packed shells of polymeric particles. Macroporous polymers prepared by this approach may be used in many applications, as low-weight structural components, mechanical dampers, thermal and electrical insulating materials, piezoelectric electrets, scaffolds for tissue engineering and encapsulants for drug delivery.

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