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The influence of porogen type on the porosity, surface area and morphology of poly(divinylbenzene) PolyHIPE foams

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The type of porogen added to the continuous phase of HIPEs containing divinylbenzene strongly influences the morphology of the resulting PolyHIPE foam. The cell size was reduced as the solvent became a better cosurfactant, as inferred from surface pressure measurements of films representative of each HIPE continuous phase. In addition, this caused the windows connecting adjacent cells to increase, to such an extent in two cases that the cellular morphology was apparently lost. The surface area increased as the solubility parameter of the solvent approached that of the polymer, however the materials with highest surface areas also had a non-cellular morphology and were very weak mechanically. This could be rectified by the use of mixtures of the solvents investigated, producing materials with surface areas up to 554 $m^2\ g^{-1}$, a cellular morphology and good mechanical properties.

Introduction

PolyHIPE polymers (PHPs) are highly porous materials obtained by polymerising the continuous phase of a high internal phase emulsion (HIPE).[1–3] Such an emulsion has a volume fraction of droplets of at least 0.74, and can exceed 0.99. Its formation depends critically on the nature of the surfactant, which must be soluble only in the continuous phase (otherwise emulsion inversion will occur). The foams obtained by this process have a well-defined cellular morphology (Fig. 1a and b), which is strikingly different from that of foams prepared by other methods (*e.g.* gas-blowing). In addition, features of the morphology such as cell size,[4,5] interconnecting hole size[6] and porosity can be efficiently controlled. This, together with their superior mechanical properties,[7] potentially gives PHPs a significant advantage over gas-blown foams for a number of applications.

Over the past two decades a considerable amount of work on PolyHIPEs has been carried out by researchers at Unilever,[1,6,8–10] although these workers were not the first to describe such systems (notable examples were prepared earlier by Bartl and von Bonin[11,12]). Nevertheless, highly significant advances in PolyHIPE technology were made during this period and several groups to the present day have continued this. Some resulting developments in applied PolyHIPE materials science worthy of mention include solid phase peptide supports (in granular form),[13] supports for a variety of heterogeneous catalytic systems (granular and monolithic),[14–16] uniformly functionalised monoliths as precursors to supported species,[17] sulfonated materials as superadsorbents,[18] solid-phase acid catalysts (monolithic)[19] and ion-exchange resins,[20] monolithic supports for cells[21] and enzymes,[22] membrane filters for the removal of particulates from aerosols,[23] elastomeric materials,[24,25] porous carbon precursors,[26] monoliths for heavy metals separation[27,28] and polycondensation materials of high thermo-oxidative stability.[29,30]

Many applications of porous materials, such as reverse-phase HPLC and solid-phase extraction, require high surface areas. Moderately porous monolithic polymers with sufficient surface areas for such applications have been prepared and described extensively by Svec, Frechet and coworkers.[31] PHPs have significantly higher porosity but tend to possess low surface areas (around 5 $m^2\ g^{-1}$) due to their relatively large cell size (5–100 μm), which has hampered their performance in such applications. Hainey *et al.*[32] reported that the surface area of PHPs could be increased up to 350 $m^2\ g^{-1}$ by a combination of three factors: an inert diluent (porogen) added to the monomer phase; a high crosslinker level; and a high surfactant concentration (33 wt% relative to total organic phase). The highest surface areas were obtained when a solvating porogen, such as toluene, was used in conjunction with a crosslinker level of 80%.

As part of our work on the preparation of novel PHPs for materials applications, we required materials of high surface area together with sufficient mechanical strength to allow their use in applications involving, for example, the flow of liquids. An initial investigation of the materials described by Hainey *et al.* indicated that their mechanical properties were insufficient for our needs, and were only improved at the expense of surface area when the surfactant level was dropped. For this reason, we decided to investigate fully the influence of the porogen type on the porous characteristics, morphology and mechanical properties (in a qualitative sense) of the resultant PolyHIPE foams. We wish to describe our results in this article.

Experimental

Materials

Divinylbenzene (Aldrich; 80 vol% *m*- and *p*-divinylbenzene, the remainder *m*- and *p*-ethylstyrene), was purified by passing through a column of basic alumina to remove the inhibitor. Potassium persulfate (Aldrich), sorbitan† monooleate (Aldrich; Span 80, HLB = 4.3), calcium chloride dihydrate (Avocado), toluene (T) (FSLC), chlorobenzene (CB) (Aldrich), 2-chloroethylbenzene (CEB) (Aldrich) and 1-chloro-3-phenylpropane (CPP) (Aldrich) were used as supplied.

PolyHIPE preparation

We chose to employ a number of solvents as porogens in PHP preparation (Table 1). Typically the organic phase (10 ml) comprised DVB (and ethylstyrene impurities) and porogen(s)

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†The IUPAC name for sorbitan is 2-(1-hydroxyethyl)-3,4-dihydroxytetrahydrofuran.

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(1 : 1 ratio by volume), and to this was added Span 80 (20 vol% to monomer–porogen mixture, 2 ml). The aqueous phase (90 ml) contained potassium persulfate (0.2 g) and calcium chloride (1.0 g). The separate organic and aqueous phases were purged with argon for 15 min, after which the latter phase was added dropwise to the former under argon with constant mechanical stirring. Full details of the procedure for preparing PolyHIPE materials have been described elsewhere.[32] All foams prepared were nominally 90% porous, based on aqueous phase content, and 80% crosslinked.

Electron microscopy

Scanning electron micrographs (SEMs) were obtained using a Hitachi S2400 electron microscope operating at 25 kV. Fractured samples were prepared for SEM by mounting on aluminium stubs using a carbon paste, either to make specimens adhere better or to increase the conductivity. All samples were sputter coated with a thin layer of gold prior to viewing, to enhance conductivity. Samples were prepared for TEM by embedding in a support resin: small pieces of material were cut then placed in CO94 embedding capsules (TAAB Laboratories Equipment Ltd.). Emix (medium) Resin TO28 (TAAB Laboratories Equipment Ltd.) was poured into the embedding capsules, and penetration of the embedding resin into the foam structure was facilitated by vacuum. Curing of the resin was carried out for 36 h at 60 °C. Ultrathin sections (90 nm) of the resulting composite were cut using a Diatome 45° diamond knife (TAAB Laboratories Equipment Ltd.) on a Ventana (RMC) MT-XL Ultramicrotome (Ventana Medical System Inc.). The sections were mounted on uncoated 400 mesh copper Gilder grids G400, of 3.05 mm diameter. The grids were examined using a Philips CM100 (compustage) Transmission Electron Microscope (TEM) operated at 100 kV. Micrographs were recorded at 620 ×, 7900 × and 19000 × magnification.

Surface area measurements

Surface areas were calculated from gas adsorption data obtained on a Micromeritics Accusorb 2100E instrument, which were treated with the Brunauer–Emmet–Teller (BET) model.[33] The instrument was calibrated using silica–alumina and kaolinite standards.

Surface pressure–area (π–A) curves

Surface pressure *vs.* molecular area data were obtained using a Langmuir film balance supplied by NIMA Technologies. Measurements were carried out as follows: 30 μl of a Span 80 solution (2.33×10^{-3} mol dm^{-3}) either alone or including porogen (1.17×10^{-2} mol dm^{-3}) in chloroform was spread on an aqueous solution containing 6.1×10^{-2} mol dm^{-3} of $CaCl_2 \cdot 2H_2O$. Surface pressure was recorded immediately after the deposition of the organic solution as the porogens show some tendency to dissolve in the aqueous phase. Barrier closing speed was adjusted to 200 cm^2 min^{-1} to minimise the dissolution of porogen in the water phase during measurement.

Results and discussion

All HIPEs prepared during the course of this work employed sorbitan monooleate (Span 80) as the surfactant, which is insoluble in water (low HLB value surfactants are hydrophobic). The HIPEs were prepared with 20% (v/v) surfactant concentration relative to the continuous phase (minus surfactant), using well established procedures. No difficulties were encountered, and all HIPEs were stable up to the point of polymer gelation. Therefore, the changes in structure discussed in the forthcoming section are not due to emulsion breakdown. As the morphology of the materials is quite complex, it is worthwhile at this point to define some of the terminology that will be used in the subsequent discussion. The foams are open-cell, therefore the large (on the order of microns) spherical cavities in the materials (see Fig. 1) are termed cells. The circular holes connecting adjacent cells are referred to as

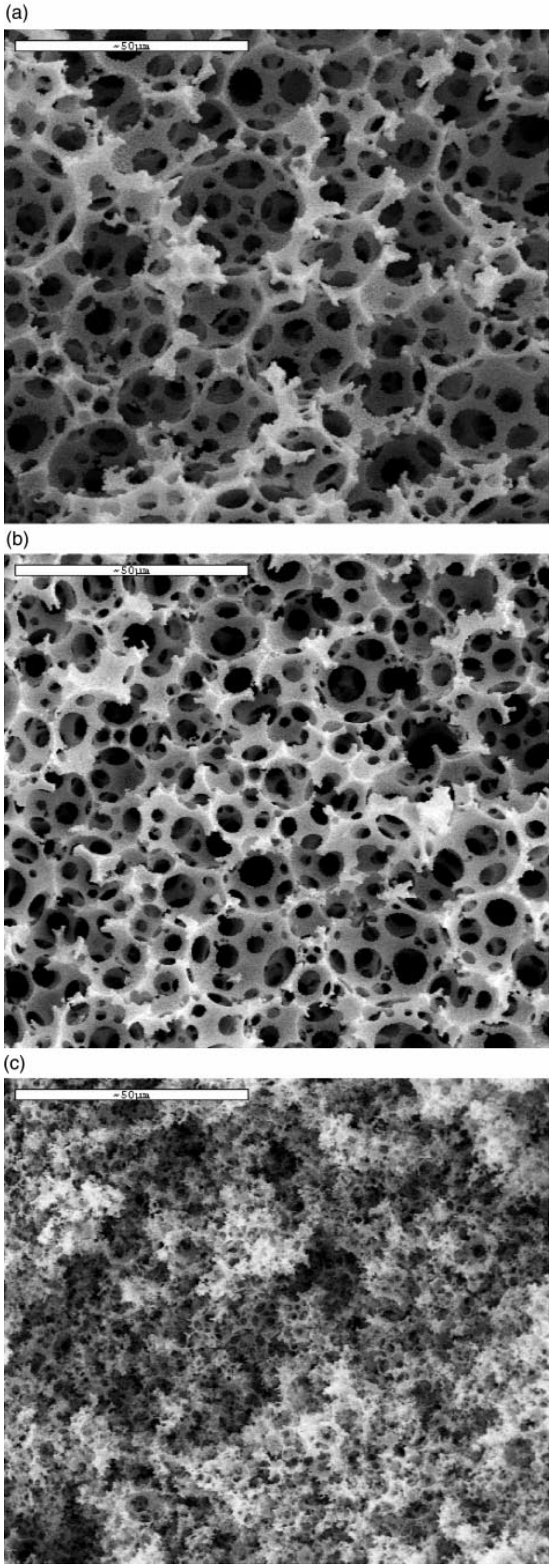

Fig. 1 SEMs of PHPs prepared with porogens: a) T; b) CB; c) CEB. Scale bar = 50 μm.

Table 1 Characterisation of PolyHIPE foams[a]

Porogen[b]	$\delta/(\mathrm{MPa})^{1/2}$	Surface area/$\mathrm{m^2\ g^{-1}}$	Sample characteristics
T	18.2	312 ± 2	chalky; moderately tough
CB	19.6	401 ± 4	chalky; moderately tough
CEB	20.1[c]	543 ± 5	crumbles easily into fine powder
CPP	23.0[c]	399 ± 6	crumbles easily into fine powder
T–CEB	19.4[d]	369 ± 4	chalky; moderately tough
T–CPP	21.3[d]	314 ± 3	chalky; moderately tough
CB–CEB	19.9[d]	554 ± 4	chalky; moderately tough
CB–CPP	21.6[d]	261 ± 5	chalky; moderately tough

[a] All samples were nominally 90% porous and 80% crosslinked (see Experimental section for details). [b] See text for full names of porogens. [c] Values calculated[43] by the methods of Hoptyzer–Van Krevelan and Hoy, and average taken. [d] Values calculated using eqn. (3).

windows. Finally, the use of inert porogens in the monomer phase results in the formation of pores. These may be micro-, meso- or macropores, according to their size as defined by IUPAC.[34]

Single component porogenic solvents

Examination of SEMs at low magnification (Fig. 1) indicates an influence of the porogen type on the foam morphology on a large scale. Changing from T (Fig. 1a) to CB (Fig. 1b) causes a marked decrease in cell diameter. In work previously communicated,[5] we presented data obtained on a Langmuir trough for monolayers of Span 80 alone and Span 80 plus DVB, 4-vinylbenzyl chloride (VBC) and mixtures of DVB and VBC at different mole fractions, spread on an aqueous $CaCl_2$ solution (equivalent to the HIPE dispersed phase). These showed that VBC was adsorbed at the (air–water) interface along with Span 80, and that adsorption of VBC was greater than for DVB when the latter was mixed with Span 80. Moreover, the results also indicated that mixtures of DVB and VBC displayed adsorptions intermediate between the values of the pure components, dependent on the mixture composition. The trough data were obtained since simple Wilhelmy plate interfacial tension experiments resulted in non-reproducible data, due to the interface being curved as a result of similar densities of aqueous and chlorinated organic phases. The trough proved a simple and reliable method of investigating the adsorption of organic liquids at the interface under compression, conditions most likely to represent the condensed surfactant layer present at the oil–water interface on the droplet surface in HIPEs. These data correlated well with the observed reduction in VBC–DVB PHP cell size as the content of VBC was increased. Since smaller cells are produced by smaller emulsion droplets, which in turn are found in more stable emulsions, this suggested that the chlorinated monomer was influencing the HIPE interfacial properties. Consequently, we used the trough data to infer that the VBC was also adsorbed at the HIPE oil–water interface along with Span 80 (*i.e.* it is a cosurfactant), which would lower interfacial tension and produce smaller droplets and foam cells. Since both air and oil are hydrophobic phases, we felt we were justified in applying the trough data to emulsion interfaces.

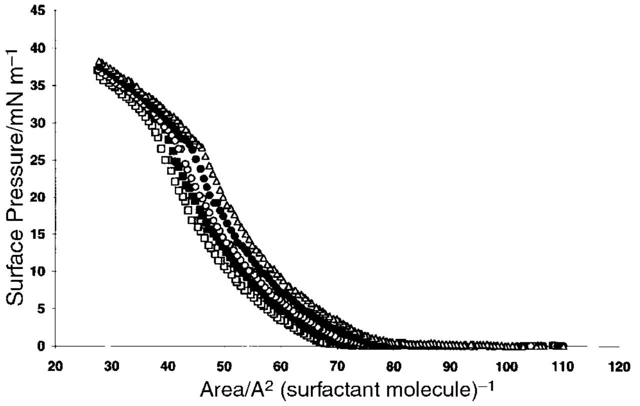

Fig. 2 π–A curves of films containing Span 80 alone (open squares) and Span 80 (17 mol% relative to total oil phase) plus T (filled squares), CB (open circles), CEB (open triangles) and CPP (closed circles).

Further evidence to support this general hypothesis is provided in Fig. 2, which shows the results of spreading and compressing solutions that mimic the HIPE continuous phases employed in the present work. Again, this clearly demonstrates that the adsorption of solvent with Span 80 at the interface increases as the solvent is varied from T to CB to CPP to CEB and implies a decrease in interfacial tension. The data also correlates well with the difference in cell size between foams prepared with T and CB. It is worth pointing out that these π–A curves were all reproducible (six times), and that steps were taken to prevent dissolution of the solvents in the aqueous phase (see Experimental). We believe this has been successful, since the curve of CEB is shifted to the right of CPP, despite the former being less hydrophobic and therefore more likely to be removed from the monolayer by dissolution. Furthermore, the curve for CB is shifted to the right of T. Similarly, with the possible exception of T, we would anticipate that minimal evaporation of each solvent would occur over the short timescale of each experiment.

Fig. 1c provides further information on the influence of porogen on foam morphology, and indicates that the characteristic open-cellular PolyHIPE structure is absent when the porogen is CEB (the specimen prepared with CPP showed a similar morphology). The morphology of this material resembles more closely that of monoliths prepared by Svec and Frechet,[31] albeit with higher porosity. It is conceivable that the HIPE has collapsed prior to polymer gelation, resulting in a non-cellular structure, however no evidence of emulsion breakdown such as separated aqueous phase was observed. On the contrary, the trough evidence (Fig. 2) seems to suggest the opposite, that CEB (and CPP) increases emulsion stability (more condensed interfacial layer). We wondered whether this morphological transition could be due to an influence of the porogen on the size of the windows connecting adjacent cells, in addition to an influence on cell size. If the window diameter increased to a sufficiently high extent, only polymer struts would remain giving the impression of a loss of cellular structure.

Williams and coworkers[4] observed a loss of cellular structure at very high surfactant levels (75% relative to total oil phase including surfactant) for poly(styrene/DVB) PHPs, although this was not rationalised fully. Also reported in that work, and separately by workers at Unilever,[6] was an increase in window size as the concentration of electrolyte in the aqueous phase was increased. Both these observations imply that window size increases as interfacial tension decreases. The explanation is that as the interfacial tension decreases, the films separating adjacent emulsion droplets become thinner. Previously, using cryo-SEM experiments, we showed that the point at which the windows appear coincides with the polymerisation gel point, implying that shrinkage due to the conversion of monomer to

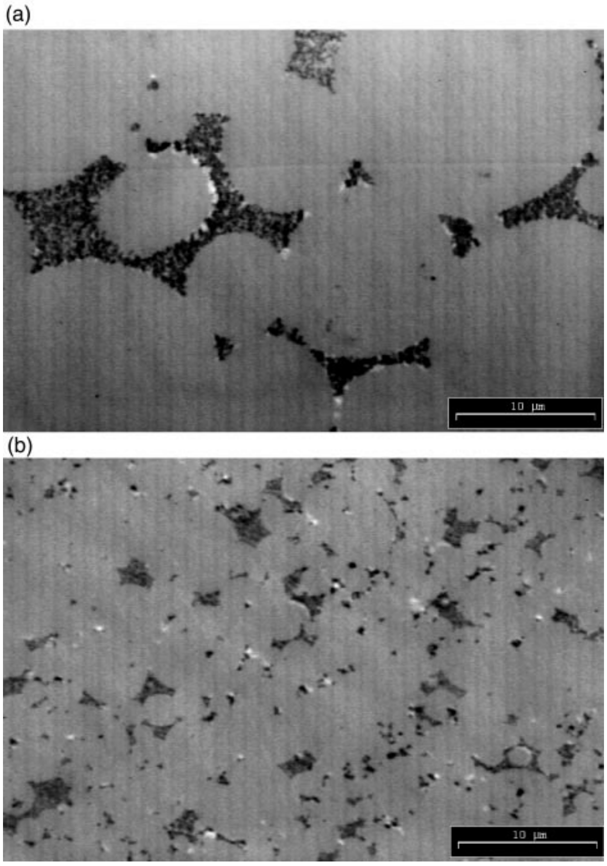

Fig. 3 TEMs of PHPs prepared with porogens: a) T; b) CEB. Scale bar = 10 µm.

higher density polymer is the probable cause of window formation. Thinner films undergoing shrinkage would result in a larger window, and one can imagine that if the windows were very large the cellular structure would not be obvious. The lowering of interfacial tension inferred from the π–A curves shown in Fig. 2 is indeed greatest with the solvents CEB and CPP, which seems to support our hypothesis. Further evidence is provided by TEM at low magnification of the foam prepared with CEB (Fig. 3b), which indicates that the cellular morphology has indeed been retained, and that the originally spherical droplets merge to a greater extent when the solvent is CEB (CPP produced a similar morphology). This TEM shows much more clearly the retention of the cellular structure than the corresponding SEM (Fig. 1c), and proves that the HIPE has been stable up to the gel-point. Therefore, these data seem to confirm the suggestion that the apparent loss of cellular structure is due to extremely large interconnecting holes appearing due to excessive thinning of surfactant films between adjacent emulsion droplets, as a result of a progressive lowering of interfacial tension as the solvent becomes a better cosurfactant. The high levels of surfactant required by Williams *et al.*[4] to achieve a similar effect rules out the possibility that our results are due to small changes in Span 80 concentration due to experimental technique.

The surface areas (plus associated errors in their measurement) and visual characteristics of the foams prepared during the course of this work are given in Table 1. Examination of the first four entries clearly demonstrates that the porogen influences the foam surface area dramatically, which increases on changing from toluene (T) to chlorobenzene (CB) to 2-chloroethylbenzene (CEB), from 312 $m^2 g^{-1}$ to 543 $m^2 g^{-1}$. Changing the solvent to 1-chloro-3-phenylpropane (CPP) causes a reduction in surface area to 399 $m^2 g^{-1}$.

The solubility parameter (δ) values of the four solvents are also given in Table 1. Comparison of the values with that of the polymer gives an idea of the extent of interaction between the two; the smaller the difference, the greater the interaction and so the better is that solvent at solvating the polymer chains. This is expressed quantitatively in eqns. (1) and (2), known as the Hildebrand solubility parameter approach:

$$\frac{\Delta H_m}{V} = (\delta_1 - \delta_2)^2 \phi_1 \phi_2 \tag{1}$$

$$\Delta G_m = \Delta H_m - T \Delta S_m \tag{2}$$

where ΔH_{m}, ΔG_{m} and ΔS_{m} are the enthalpy, free energy and entropy of mixing, respectively, V is the molar volume of the solvent, and δ and ϕ are the solubility parameter and volume fraction, respectively, of the solvent (1) and polymer (2). Thus, when δ_1 and δ_2 are similar, ΔH_{m} is small and ΔG_{m} is negative.

Polymer resins are generally divided into two classes; gel-type and macroporous.[34] The former are lightly crosslinked ($<2\%$), are prepared without added diluent and have porosity only in the swollen state, whereas the latter are more highly crosslinked ($>5\%$), are prepared in the presence of porogenic solvents and possess permanent porosity in the dry state. The class of resin obtained is a function of several factors, including crosslinker content, nature and concentration of diluent and temperature. The morphology and surface area of macroporous resins is profoundly influenced by the nature of the porogen. If a good swelling solvent is employed, phase separation of the polymer gel phase is delayed until late in the polymerisation. This produces a large number of small microparticles, which remain discrete until complete conversion since the residual monomer level is low, and results in a material of high surface area (if the polymer is sufficiently crosslinked). A less efficient swelling solvent, however, causes precipitation of polymer microparticles at an earlier stage when monomer levels are higher. This residual monomer will locate in the polymer gel phase and cause "filling in" of the gaps between microparticles as it polymerises. The result is a lower surface area material. Poly(styrene-divinylbenzene) (PSDVB) macroporous resins have been prepared using a wide range of porogens, including swelling and non-swelling solvents (as individual components or mixtures)[35–37] and linear polymers.[38]

The δ value for PSDVB quoted in the literature[39] is 18.6 $(\mathrm{MPa})^{1/2}$; comparison of this value with those in Table 1 for the various solvents indicates that there is not a good correlation between difference in δ and polymer surface area. However, the value of δ for PSDVB has been found to vary depending on the class of solvent used to determine it, as described by Errede.[40–42] In that work, δ was determined from swelling studies in several homologous solvent series. Using substituted aromatic solvents (Ph-Z), δ was found[40] to be 19.4 $(\mathrm{MPa})^{1/2}$, whereas in chloroalkanes[41] it was 20.5 $(\mathrm{MPa})^{1/2}$. The former value is most meaningfully compared with δ of T and CB (as they belong to the same class as the solvent series in which it was determined); CB is a better swelling solvent than T as its value of δ is closer to 19.4, in agreement with Errede's findings. The behaviour of α-chloro-ω-phenylalkane solvents (CEB and CPP) is more difficult to explain; their performance does not correlate well with the homologous series of alkylbenzenes ($Ph(CH_2)_n$-H),[42] since the swelling in that solvent series was greater when $n = 3$ than when $n = 2$. However, the reported δ value determined in chloroalkanes ($Cl(CH_2)_n$-H)[41] was closer to that of CEB than CB or CPP and does correlate with the trend reported here. However, the reliability of this comparison may be questionable as δ for CEB and CPP in this work were calculated[43] with an estimated error of ±10%, experimental values being unreported.

Further evidence to suggest that CB and CEB are better porogens than T is provided by high magnification SEMs of the various foams (Fig. 4). It can be seen quite clearly that the size

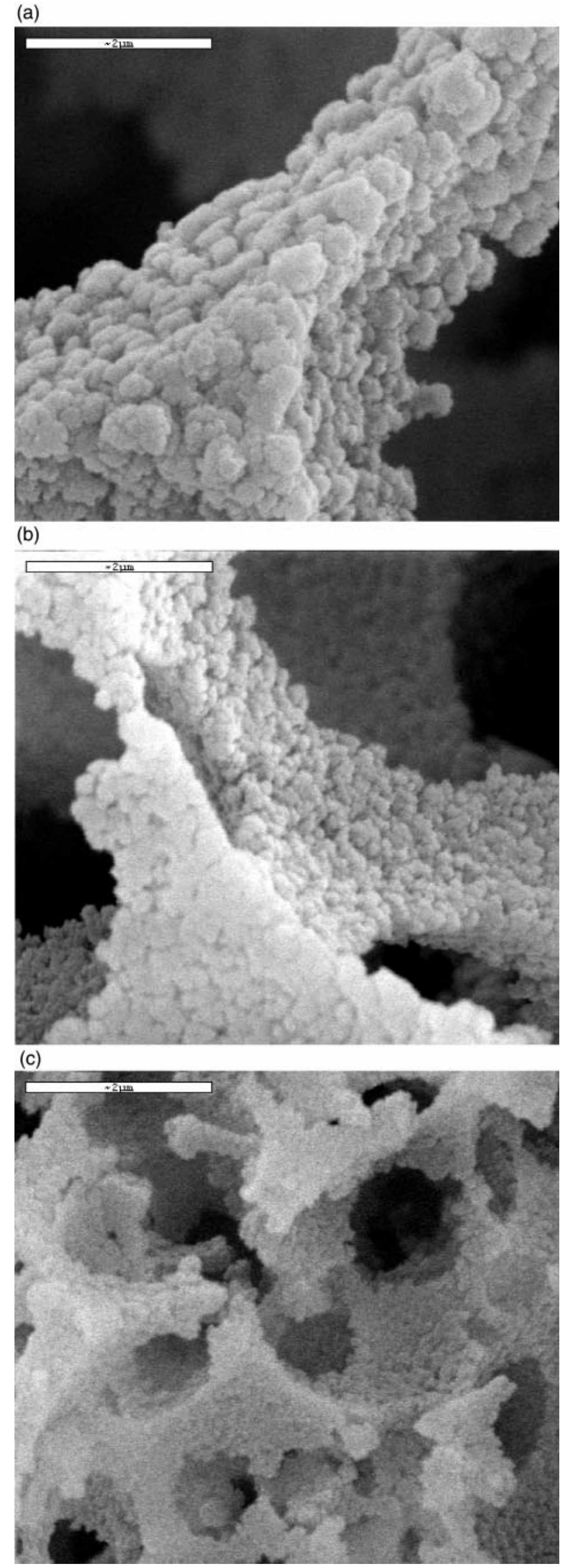

Fig. 4 SEMs of PHPs prepared with porogens: a) T; b) CB; c) CEB. Scale bar = 2 μm.

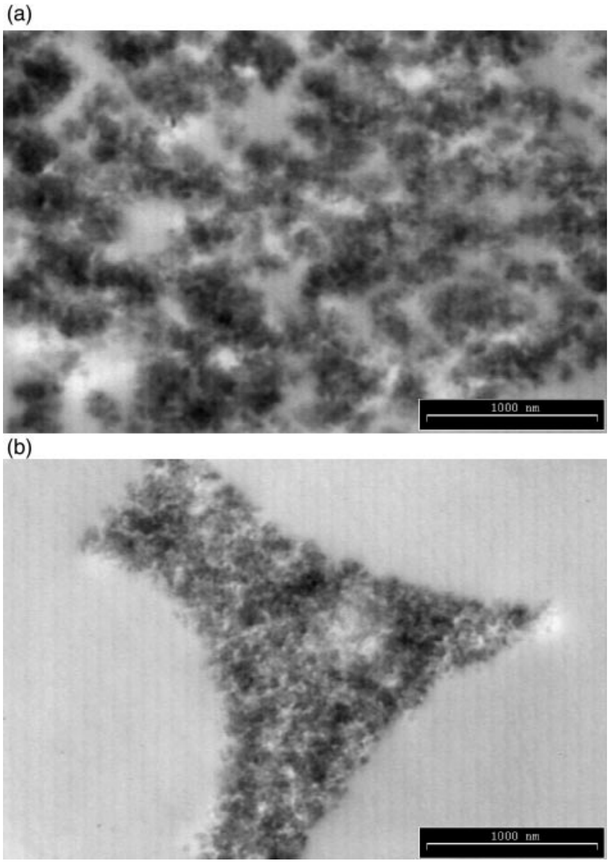

Fig. 5 TEMs of PHPs prepared with porogens: a) T; b) CEB. Scale bar = 1000 nm.

of the microparticles comprising the foam decreases as the solvent is changed from T (Fig. 4a) to CB (Fig. 4b) to CEB (Fig. 4c) (there was no discernible difference in microparticle size between PHPs prepared with CEB and CPP). This indicates that CB and CEB are solvating the polymer network until late in the polymerisation, resulting in small microparticles. This trend is more evident from high magnification TEM pictures (Fig. 5). The decrease in both microparticle size (dark regions) and interstitial voids (light/white regions) as the solvent is changed from T to CEB (Figs. 5a and b) is indeed marked. These findings are in direct agreement with the micrographs shown in Fig. 4.

One of our initial goals was to increase surface area without compromising mechanical stability. Table 1 gives an indication of the mechanical stability of the various foams and, unfortunately, those with the highest surface areas prepared

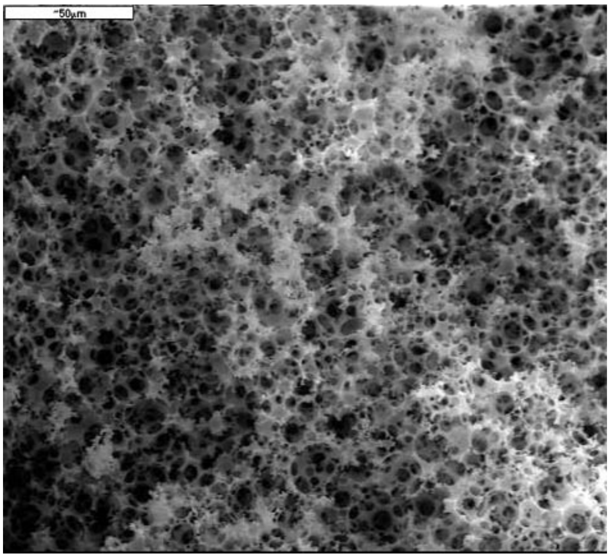

Fig. 6 SEM of a PHP prepared with T–CEB (50 : 50 volume ratio). Scale bar = 50 μm.

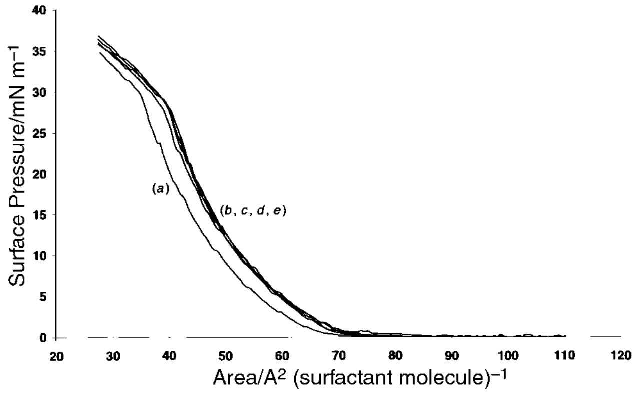

Fig. 7 π–A curves of films containing a) Span 80 alone and Span 80 (17 mol% relative to total oil phase) plus mixed porogens (50 : 50 volume ratio): b) T–CEB; c) T–CPP; d) CB–CEB; e) CB–CPP.

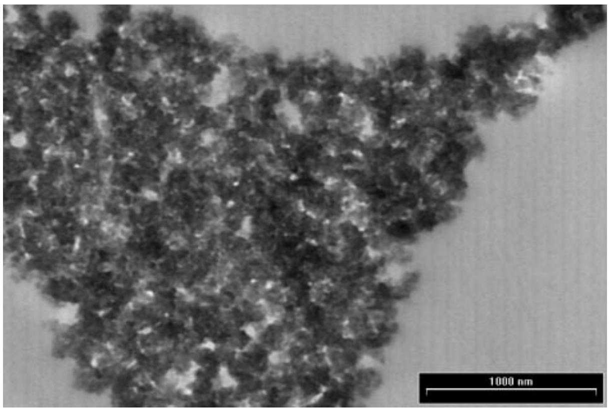

Fig. 8 TEM of a PHP prepared with CB–CPB (50 : 50 volume ratio). Scale bar = 1000 nm.

with single porogens (CEB or CPP) are extremely fragile and so unlikely to be of much practical use. However, the foam prepared with CB has a surface area 33% higher than that prepared with T, together with similar handling properties. This is due mainly to the presence in the former of smaller polymer microparticles and, to a lesser extent, a smaller cell size.

Mixed porogenic solvents

The results from foams prepared with single porogens indicate that varying the solvent can increase the surface area, arguably as δ of the solvent approaches that of the polymer. However, there is also an influence on foam morphology on a larger scale; the cell size decreases and the interconnect size increases. In two cases, this latter parameter increases to such an extent that the cellular morphology is apparently lost and poor mechanical properties result.

We wondered if it would be possible to strike a balance between these factors (porosity and cellular structure), by using mixed porogenic solvents to prepare PHPs. In particular, it was hoped that we could prepare foams of very high surface area but that retained a PolyHIPE morphology. SEMs at low magnification demonstrate clearly that each foam prepared from mixed solvents has a recognisable PolyHIPE cellular structure (Fig. 6 is representative). This suggests that the mixed porogens have a different effect on HIPE interfacial behaviour than the single components. The π–A curves of films of the various mixed solvents, shown in Fig. 7, appear to confirm this. Curves for all mixed solvents are shifted to the right of the curve for Span 80 alone and are more or less coincident, indicating that each solvent pair produces a monolayer packed to a similar extent. In addition, comparison of Figs. 2 and 7 indicates that the mixed porogens do not have as great a cosurfactant effect as CEB and CPP alone. This correlates well with the differences in morphologies of the various materials; CEB and CPP have the greatest influence on π and also produce the non-cellular morphology, whereas the mixed solvents have less of an influence on π and retain the PHP structure. Further differences compared to foams prepared from single components can also be observed in Fig. 6. For example, there appears to be an influence on interconnect size, as shown by the presence of regions where the foam structure is more closed-cell. In addition, the cell size distribution is more polydisperse with mixed porogens. These are all indications that HIPEs prepared with mixed porogens are less stable, *i.e.* the solvent mixtures do not lower the interfacial tension to the same extent as single solvents such as CEB and CPP. These conclusions are supported by the surface pressure experiments (Figs. 2 and 7).

The influence of the cellular structure on foam mechanical properties is evident from Table 1, in a qualitative sense. All of the foam samples prepared with mixed porogens were much tougher and less brittle than those prepared with either CEB or CPP single solvents. We ascribe this to the retention of the PolyHIPE cellular morphology with these mixed porogens, which undoubtedly lends the materials greater mechanical strength.[7]

The surface area values of the foams prepared from mixed porogens (Table 1) are also rather interesting: T with CEB produces a material of surface area intermediate between those of the individual components; whereas T with CPP gives a surface area similar to T alone; CB with CEB results in a surface area as high as that of CEB alone; and CB with CPP leads to a value lower than that of either component. The δ values of the mixed solvents (δ_{mix}) were calculated according to eqn. (3),[44] where x_i and V_i are the mole fraction and molar volume of component i, respectively; these are also reported in Table 1.

$$\delta_{\mathrm{mix}} = \frac{x_1 V_1 \delta_1 + x_2 V_2 \delta_2}{x_1 V_1 + x_2 V_2} \qquad (3)$$

For entry 5, there is a good correlation between δ and the surface area obtained as both parameters lie between the values of the individual components. However, the surface areas in entries 6 to 8 do not relate simply to the calculated δ values for the mixed solvents. It would appear that in these cases either the solubility parameter of the mixture is not a simple function of the values of the individual components, or the surface area is influenced by some other unforeseen parameter. A further possibility is the presence of errors in the calculation of δ or CEB and CPP ($\pm$10%). However, TEM (Fig. 8) clearly demonstrates the presence of pores within the PHP polymer walls, which are responsible for the high surface areas (the micrograph shown is representative of the foams prepared).

It should be pointed out that all of the materials prepared in this study were derived from HIPEs containing 20% surfactant, as opposed to 33% used by previous workers.[32] The high surfactant content of materials in the latter case reduces their mechanical stability. By varying the porogen type and maintaining surfactant level at 20%, we have achieved an increase in surface area of almost 100% without compromising mechanical stability. Thus, we have succeeded in our original objective of producing PolyHIPE materials of high surface area and sufficient strength to permit their use in certain applications. We believe this will allow the development of a new generation of highly porous, high surface area monolithic materials for a variety of applications involving fluid flow. We are currently in the process of evaluating these materials for such applications.

Conclusions

We have prepared highly porous open-cell polyDVB foams in the presence of various porogenic solvents, either as single components or mixtures. The nature of the solvent has a profound influence on the foam morphology on both a large and small scale. By SEM, CB was found to reduce the foam cell size compared to T, whereas CEB and CPP seemed to destroy the characteristic PolyHIPE cellular morphology. From surface pressure data, we inferred that the solvents were packing with the surfactant to a greater or lesser extent at the interface, *i.e.* behaving as cosurfactants. This would both reduce HIPE droplet (and thus PolyHIPE cell) size and increase the diameter of the interconnecting windows. The trough data indicated that the order of solvent packing at the interface was CEB > CPP > CB > T, and this correlated well with the difference in cell size between foams prepared with CB and T. TEM (Fig. 3) indicated that the material prepared with CEB consisted of highly compressed cells (difficult to identify by SEM), confirming that this solvent had retained the cellular morphology but produced extremely large windows. This explains the morphology observed by SEM.

In addition, the solvents also influence foam surface area. As the solubility parameter (δ) approaches that of polyDVB, the structure produced contains a larger number of small microparticles, which results in a high surface area. This effect was greatest with CEB as porogen; however, due to the morphology described above, this material (and that prepared with CPP) is mechanically very weak and is not likely to be usable in any practical situation. This situation can be remedied by employing mixed porogens. The surface areas of the resulting materials were not predictable in a simple fashion from the values of foams produced from their individual components, and in one case (CB/CEB) the surface area was equal to the highest value for a single porogen (CEB). The morphology of each sample prepared with porogen mixtures resembled that of conventional PolyHIPE materials, and the mechanical properties were significantly better than for the foams prepared from CEB or CPP. Consequently, these materials have a real possibility of use in a wide range of applications requiring high surface areas.

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