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SHORT COMMUNICATION

Study of the formation of the open-cellular morphology of poly(styrene/divinylbenzene) polyHIPE materials by cryo-SEM

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Abstract The formation of the interconnected morphology of open-cell styrene/divinylbenzene (DVB) PolyHIPE copolymers has been studied by scanning electron microscopy on frozen HIPE samples at different stages of polymerisation, a technique known as cryo-SEM. The transition from discrete emulsion droplets to interconnected cells was observed to occur around the gel-point of the polymerising system. This would suggest that the formation of holes between adjacent cells is due to the contraction of the thin monomeric films on conversion of monomer to polymer, as a result of the higher density of the latter.

Key words Styrene/divinylbenzene copolymers – PolyHIPE – open-cell – cryo-SEM

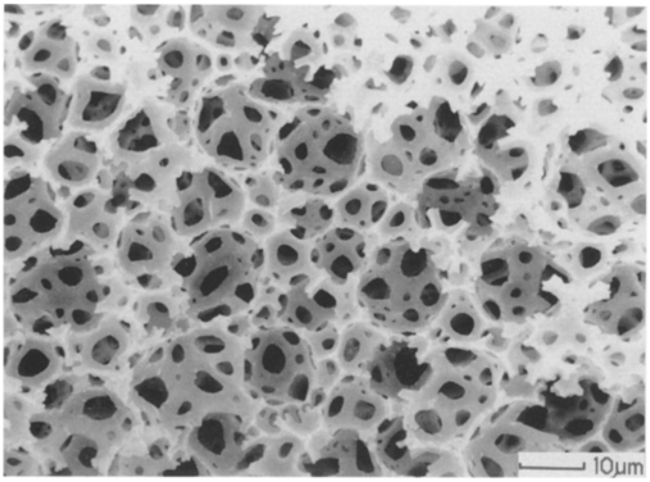
Introduction

The internal phase volume ratio (ϕ) of an emulsion is the volume fraction of the internal phase relative to the total emulsion volume. High internal phase emulsions (HIPEs), possessing an internal phase volume ratio of greater than 0.74, can readily be prepared from two immiscible liquids, one of which is generally, but not necessarily, water or aqueous solution [1]. These concentrated systems are stabilised by careful choice of surfactant, such that it is soluble exclusively in the continuous phase solution of the emulsion. This prevents emulsion inversion.

Perhaps one of the most important applications of HIPEs is their ability to be used as template systems for the synthesis of a range of polymeric materials. By polymerisation of either, or both, phases of the emulsion, novel materials with a variety of fascinating properties can be produced. The literature on HIPEs and their use in the preparation of novel polymer materials has been the subject of a recent review [2].

If a high internal phase emulsion is prepared in which the continuous phase contains one or more monomeric species, and polymerisation is initiated, a novel type of highly porous material is produced. Polymers of this type are referred to as PolyHIPE, using the nomenclature devised by Unilever scientists [3].

By far, the most studied PolyHIPE system is the styrene/divinylbenzene (DVB)-based material. This was the main subject of the patent of Barby and Haq for Unilever in 1982 [3]. HIPEs of an aqueous phase in a mixture of styrene, DVB and nonionic surfactant were



Polystyrene polyhipe ×2000

Fig. 1 SEM of poly(styrene/DVB) PolyHIPE

prepared and polymerised by heating in a sealed container, typically for 24 h at 50 °C. This yielded a solid, crosslinked, monolithic polymer material which, on exhaustive extraction with a lower alcohol in a Soxhlet apparatus, followed by drying *in vacuo*, produced a low-density polystyrene foam of very high porosity, with a permanent, macroporous, open-cellular structure (Fig. 1).

For many potential applications an open-cellular structure is vital, and so understanding and controlling the mechanism of hole formation is of considerable interest. An investigation into this mechanism has previously been carried out [4] but direct evidence was difficult to obtain.

The present communication describes our attempts to use scanning electron microscopy (SEM) to "observe" hole formation directly. This has been achieved by examining frozen, fractured samples of a styrene/DVB HIPE at different stages of polymerisation, by SEM, a technique known as cryo-SEM. It was thought that this might allow the identification of the transition point from discrete droplets to interconnected cavities, and thus aid the elucidation of the mechanism of hole formation.

Experimental

Materials

Styrene (Fisons), divinylbenzene (Aldrich, tech. grade), sorbitan monooleate (Span 80, Koch-Light, HLB = 4.3), $K_2S_2O_8$ (Fisons) and $CaCl_2 \cdot 6H_2O$ (Fisons) were all used as received.

Instrumentation

SEM on frozen HIPE samples was performed with a Cambridge Instruments S360 scanning electron microscope equipped with a cold stage and evacuation chamber. Samples were fractured and coated with gold prior to examination.

HIPE preparation and SEM studies

A HIPE consisting of an aqueous solution (90 ml) of potassium persulfate (0.2 g, 0.7 mmol.) and calcium chloride hexahydrate (1.0 g, 4.5 mmol.) in an organic phase of styrene (9 ml, 80 mmol.), DVB (1 ml) and Span 80 (2 g) was prepared as detailed previously [3, 5]. A small sample (about 0.5 ml) was taken (time = 0) and immediately frozen in liquid nitrogen slush (∼ − 210 °C) . The bulk sample was heated at 60 °C in an oven. The initial frozen sample was fractured and examined at liquid nitrogen temperature by SEM. Further HIPE samples were taken at various time intervals (until the HIPE solidified) and treated and examined as above.

Results and discussion

Researchers at Unilever [3] discovered that the surfactant used to form the HIPEs must have a low hydrophile–lipophile balance (HLB) value (between 2 and 6), as would be expected for w/o emulsions. The optimum surfactant was sorbitan monooleate (Span 80), which has an HLB value of 4.3. The concentration of the surfactant in the monomer phase was found to be critical to the formation of a stable polymer foam [4, 6]. At least 4% surfactant, relative to the total oil phase, was required for PolyHIPE formation, whereas formulations containing above 80% surfactant (%w/w relative to total organic phase) resulted in the formation of an unconnected material. Surfactant levels between 20 and 50% were deemed to be optimum at all internal phase volumes.

Williams [4] discovered that the surfactant level also had a profound effect on the cellular structure of PolyHIPE materials. From 4 to 5% surfactant, the polymers produced had a closed-cell structure, i.e., each cell was discrete from its neighbours. The aqueous phase remained trapped inside the structure, resulting in a high density polymer. Between approximately 7 and 50% surfactant, however, an open-cell foam was produced, with an entirely interconnected microstructure. The aqueous phase could easily be removed, yielding a dry, low density polymer matrix.

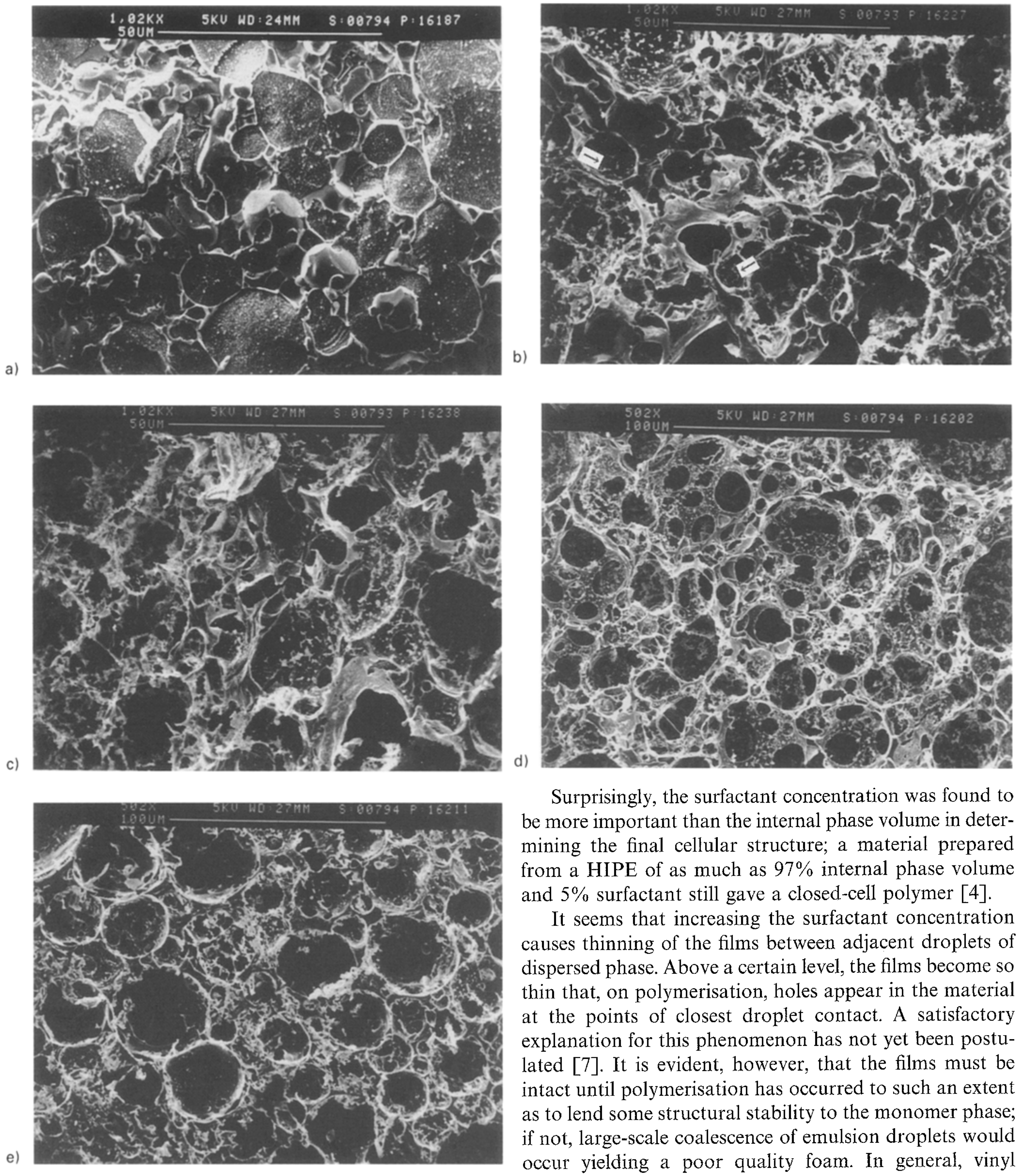


Fig. 2 SEMs of styrene/DVB HIPEs at different stages of polymerisation: a) unpolymerised HIPE; b) polymerised for 2 h 10 min; c) polymerised for 2 h 40 min; d) polymerised for 4 h; e) polymerised for 5 h

Surprisingly, the surfactant concentration was found to be more important than the internal phase volume in determining the final cellular structure; a material prepared from a HIPE of as much as 97% internal phase volume and 5% surfactant still gave a closed-cell polymer [4].

It seems that increasing the surfactant concentration causes thinning of the films between adjacent droplets of dispersed phase. Above a certain level, the films become so thin that, on polymerisation, holes appear in the material at the points of closest droplet contact. A satisfactory explanation for this phenomenon has not yet been postulated [7]. It is evident, however, that the films must be intact until polymerisation has occurred to such an extent as to lend some structural stability to the monomer phase; if not, large-scale coalescence of emulsion droplets would occur yielding a poor quality foam. In general, vinyl monomers undergo a volume contraction on polymerisation (i.e., the bulk density increases) and in the limits of a thin film, this effect may play a role in hole formation, especially at higher conversions in the polymerisation process. In principle, therefore, the areas of the holes in the cell walls should correlate with the ratio of the specific volumes of the monomer/surfactant mixture and crosslinked polymer phase, although producing quantitative data in this respect is very difficult.

Electron micrographs of frozen HIPE samples at various stages of polymerisation are shown in Figs. 2a–e.

The structure of the unpolymerised HIPE can be seen in Fig. 2a. The droplet size distribution is relatively polydisperse and ranges from approximately 5 to 25 μm. The thin films surrounding each droplet are clearly visible, and the polyhedral nature of the droplets is also evident. In particular, there are a small number of frozen droplets which have remained intact after fracturing, which display quite clearly a polyhedral structure with flat faces.

After heating for slightly over 2 h (Fig. 2b), the films surrounding the aqueous droplets are more or less intact, although one or two holes (→) are starting to appear. The lighter, powder-like material in the micrographs is residual (frozen) water. The aqueous phase is partially removed by a sublimation technique, known as etching, to allow the cell walls to be seen. This process unfortunately also removes some of the frozen monomer solution, causing small, irregular holes to appear in some places. Their irregularity makes them quite distinct from the circular holes which form during polymerisation.

Continuing polymerisation for a further 30 min (Fig. 2c) increases the number of circular holes between adjacent dispersed phase droplets. This behaviour continues with time (Figs. 2d and 2e) until, after 5 h (Fig. 2e) the structure starts to resemble a fully polymerised open-cell PolyHIPE material.

The holes, therefore, would seem to begin to appear after 2 to 2.5 h. This corresponds approximately to the gel-point of the polymerising styrene/DVB HIPE, i.e., the point at which the viscous HIPE becomes an infinite gel-like network. This suggests that the formation of “windows” between neighbouring droplets is indeed due primarily to the volume contraction on conversion of monomer to polymer. Although generally a small effect, this shrinkage is likely to be highly significant in the context of thin monomer films and be maximised at the gel-point.

The surfactant level in the continuous phase is also relevant to the process of formation of the open-cell morphology. Higher concentrations cause thinning of the films separating adjacent droplets, as discussed by Williams et al. [4]. This then facilitates the formation of the “windows” between neighbouring cells during the film contraction process, and explains why Williams and coworker obtained closed-cell PolyHIPE materials at low surfactant levels. In this latter case the films separating adjacent droplets are rather thick.

Conclusions

By following the polymerisation of a styrene/DVB HIPE by cryo-SEM, the point of formation of the open-cellular structure has been identified. This coincides with the polymer gel-point, and implies that the holes between adjacent cells result from contraction of the continuous phase thin films on conversion of monomer to polymer.

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