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STUDIES OF THE FORMATION OF MICROPOROUS POLYMER FILMS IN "BREATH FIGURE" CONDENSATION PROCESSES

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We report studies of the formation of ordered microporous polymer films by the evaporation of polymer solutions following exposure to a humid atmosphere. High-speed microphotographic (HSMP) studies of the formation process reveal that near the surface of the polymer solution, vapor condensation produces near monodisperse water droplets which crystallize to form a close-packed array. Following the evaporation of the solvent, characterization of the solid by Atomic Force Microscopy, confocal microscopy and white light interferometry reveals that the surface of the polymer film features extensive regions of hexagonally close-packed microscopic pores, whose spatial arrangement replicates that of the initial droplet monolayer. Defects recorded by HSMP in the packing of the colloidal monolayer of liquid droplets formed above the surface of the polymer solution are found to correspond to those transferred into the eventual solid film, providing the first direct evidence of the structure templating role of the droplet monolayer.

Keywords: Microporous films; condensation processes; high speed microscopy.

1. Introduction

The term "breath figures" refers to the arrangement of water droplets formed by the condensation of water vapor onto either a cold solid or liquid surface.[1,2] In a humid atmosphere, the cooling associated with the evaporation of a volatile solvent from a polymer solution may be sufficient to initiate and sustain the condensation of water vapor at the solution surface, thereby leading to an array of suspended water droplets. The growing droplets pack, and by a process of rearrangement above the surface of the solution, form a structural "template" consisting of a colloidal monolayer of non-coalescing droplets.[3–5]

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Several workers have mooted that this "template" is ultimately transferred at the surface of, and within, the resulting solid polymer film in the form of ordered arrangements of microscopic pores.[3–7] Whereas solvents containing a concentrated population of droplets ultimately form polydisperse systems by droplet coalescence, certain combinations of polymer and solvent enable droplet coalescence to be suppressed, leading to the formation of porous films with a high degree of monodispersity, in terms of pore size distribution.[5–7] The latter feature lends the polymer films potential application in areas such as tissue culture[8] and controlled drug release[9] while their pore size (typically 0.2–10 μm in diameter) makes them suitable candidates for evaluation as synthetic separation membrane products.

In general, techniques for the production of micropatterned surfaces by the lithographic translation of a pre-existing pattern or "template" onto the surface of an appropriate substrate are well-established.[10–12] However, the development of convenient methods for fabricating large areas of uniform structures at the submicron length scale remains a challenging problem. In addressing this problem, we have studied the "breath figure"-driven templating process described above, stimulated by the potential for a degree of dynamic control over the templating mechanism, and hence of the length scale of the resulting pores.[5]

This is an important aspect of any potential technology in areas such as Tissue Engineering, in which current fabrication methods for the production of synthetic microporous "scaffolds" for tissue growth (i.e. a synthetic extracellular matrix) usually result in irregular pore morphologies.[13–15] The "breath-figure"-driven fabrication technique studied herein represents a possible means by which the characteristic dimensions and morphology of such "scaffolds" may be controlled and significantly improved with monodispersed spherical pores. At present, no satisfactory theory exists to completely explain the formation of the complex pore morphology within the solid polymer scaffolds formed by the breath figure process, and the evidence used to support previous explanations of the process of scaffold formation remain incomplete and (essentially) circumstantial.

The purpose of the present study was to investigate the mechanism of film formation mooted by Srinivasarao *et al.*[5] They envisaged that the ordering of water droplets above the evaporating polymer solution acts as a template. When solvent evaporation is substantially slowed, and the temperature gradient decreases to a level where there is insufficient lubricating gas/vapor flow between the water droplets, the template sinks into the polymer solution, leaving a characteristic packed structure as a remnant imprint on, and within, the eventual solid polymer film.

2. Experimental Details

The polymer solutions used in the present work were monocarboxy-terminated polystyrene (Scientific Polymer Products, USA, $M_w = 50{,}000$), dissolved in carbon disulfide (Sigma Aldrich Chemical Co., UK) in the range of 0.5–5 wt.%.

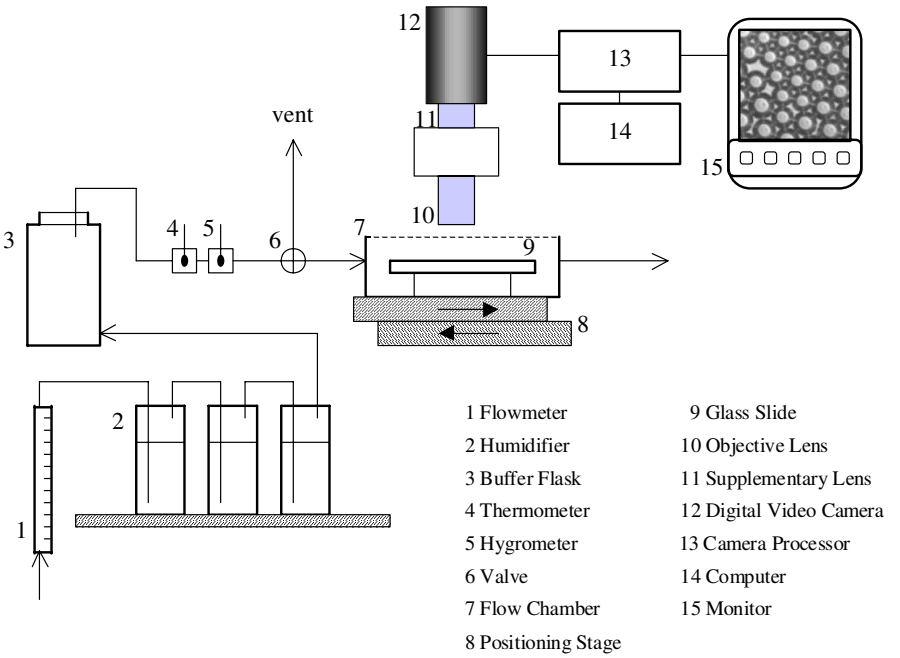

Fig. 1. Experimental arrangement for the formation of microporous polymeric films using the breath figure method. High-speed microphotography was used to record the dynamic process of the growth and rearrangement of the water droplets.

The microporous films were prepared within a flow cell wherein a small quantity of polymer solution was cast onto a glass surface and was subsequently exposed to an airflow of regulated temperature and humidity. As the temperature of the solution dropped due to evaporative cooling, the progressive growth and rearrangement of condensed water droplets at or above the sample surface[5] was observed from the top using a high-speed microphotography (HSMP) system consisting of a video camera attached to a standard microscope incorporating long working distance objective lenses. The camera, a Kodak Ektapro-4540mx system, was connected to a video image processor which facilitated the time-referenced sequential storage of 8-bit monochrome digital images. The system is capable of recording at up to 4500 frames per second (fps) at its maximum resolution of 256×256 pixels. The camera output was also relayed through a video monitor to provide remote observation with simultaneous recording provided by an S-VHS video recorder. The apparatus is illustrated in Fig. 1.

In the present work, standard glass microscope slides were used as the supporting substrate for breath figure formation. The underside of each slide was centrally inscribed with a fine "cross-hair" and placed inside a Perspex flow cell which was attached to a positioning stage. The lid of the flow cell was attached by pressure sensitive adhesive tape and contained an observation window positioned above the

slide. The Perspex flow cell consisted of 26 mm thickness sheets, which were clamped together and cut to a length of 255 mm and a width of 180 mm (these dimensions corresponding to those of the cross flow box). The sheets were screwed together and sealed with silicon prior to being placed horizontally on a router which removed material to a depth of 18 mm from the cell's top surface and 20 mm from all edges. A 30 mm diameter hole was subsequently drilled in the center of the base of the cell such that light could be transmitted to illuminate a sample within the cell. Two microscope slide supports were placed either side of the hole and a transparent acetate sheet was used to cover the cell, the latter being sealed at the edges.

The cell position and microscope focus were adjusted until the "cross-hair" reference was located. Subsequently, the microscope's focal point was raised to a position slightly above the upper surface of the slide. After purging the cell with dry compressed air, a quantity of solution was injected, through the wall of the flow cell, onto the glass slide using a syringe. A source of compressed air was passed, at ambient temperature and known flow rate, through a series of glycerol-water solutions, the relative proportions of which were adjusted to control the humidity of the exiting flow. The humidified air was then directed through a large buffer flask containing glass wool and finally through a gas flowmeter. Immediately after the polymer solution was cast onto the glass slide, the humidified air was diverted through the flow cell and the camera was triggered.

Following the evaporation of the solvent, the residual solid films were inspected using an Atomic Force Microscope (AFM). The AFM used in the present work was a Digital Instruments Dimension 3100 operated through a Nanoscope IV Controller and software (Veeco, US). The principal mode of operation of the AFM in the present work was intermittent contact (tapping) mode. In addition, the solid microporous films were characterized using a white light interferometer (WYCO^{tm} NT2000 Surface Profiler) in VSI mode with a 50× WYCO^{tm} Objective Lens (with 2× software zoom). Further characterization was conducted using a Leica TCS SP2 confocal microscope with N Plan 40× (0.55) dry objective in air.

3. Results and Discussion

Figure 2 shows several (non-successive) images from a HSMP sequence which recorded various stages in the growth and rearrangement of water droplets on the surface of the polymer solution, eventually forming a colloidal monolayer. It has been hypothesized that this colloidal monolayer array acts as a template for the formation of the ordered array of pores in the solid polymer film.[5–8]

In order to test the hypothesis that the colloidal monolayer which assembled at the surface of the solution acts as a template for the formation of the ordered arrays of pores seen in the eventual solid polymer film, it was necessary to exploit the fact that occasional defects occur in the (largely) regular water droplet layer, and to use these defects as "markers" or reference points. This benefits from the fact that in some cases, the stability of the hexagonal packing appeared sufficient

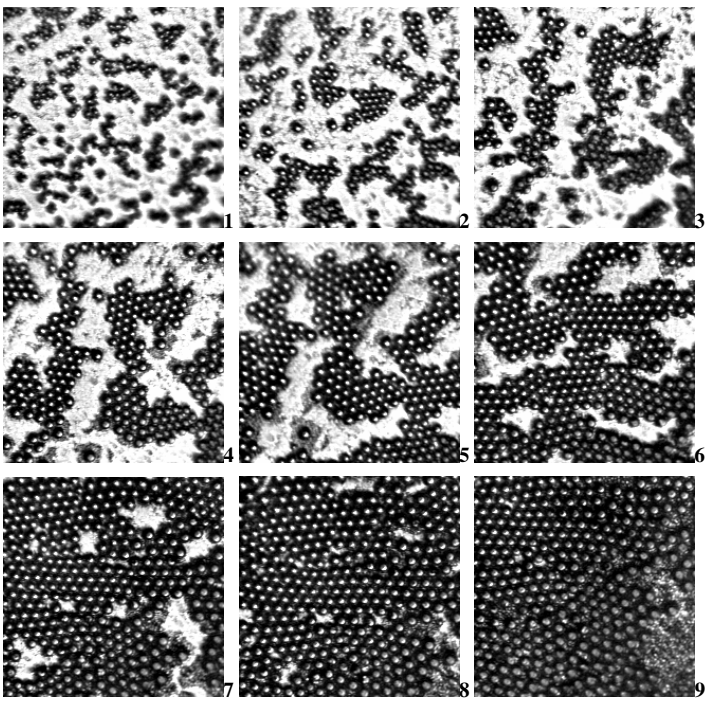

Fig. 2. Optical images by high-speed microphotography showing the water droplet growth and rearrangement at various (non-successive) time intervals. The water droplets in this case are in the range of 1–6 μm in diameter.

to tolerate occasional point defects such as those illustrated in Fig. 3. Clearly, if the template represented by the droplet layer is ultimately transferred into the eventual solid film, then, according to the model proposed by Srinivasarao *et al.*,[5] the accompanying defects should also be transferred as part of this process and, if found on inspection of the solid film at locations corresponding to their origin in the droplet layer, the experiments would confirm the templating ability of the droplet monolayer.

Figure 3 is an optical micrograph taken from the HSMP record. Examples of the occasional defects in the hexagonal packing identified and used in the present study are shown in Fig. 3 as defects A, B and C, respectively.

At the time corresponding to this image the liquid droplets are packing at the surface of the (still fluid) solution. Figure 4 shows the results of an AFM scan of the *same region of the same microporous film in the solid state* (i.e. after complete evaporation of the solvent). The corresponding point defects in both the droplet array and the eventual solid polymer film (Figs. 3 and 4, respectively) have also been marked as A, B and C.

Care was taken in order to ensure that the occurrence of the defects labeled A, B and C was not due to an AFM scanning artefact. In addition, the same physical

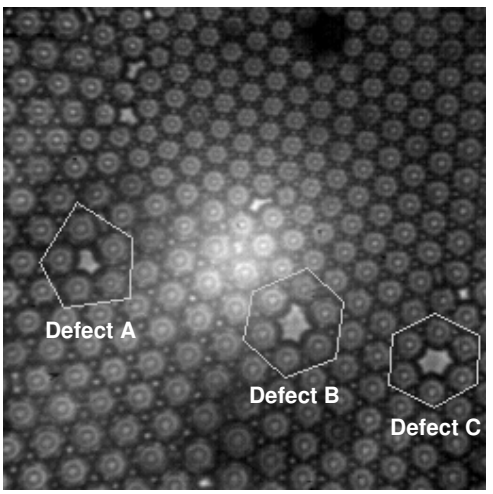

Fig. 3. Optical micrograph from a video sequence identifying three defects in the water droplet structure, identified as defects A, B and C, respectively.

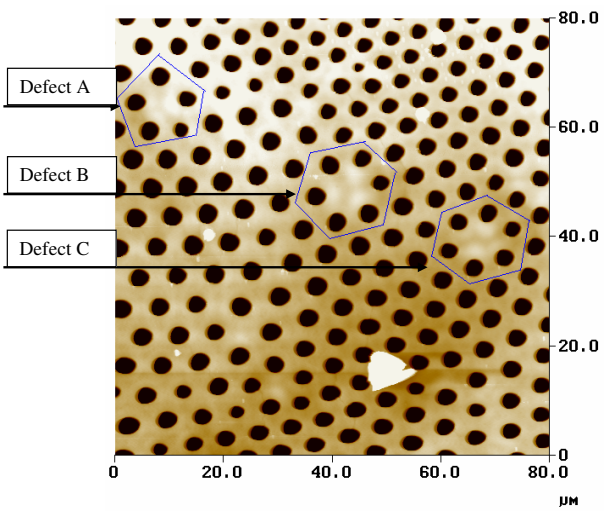

Fig. 4. AFM scan of the same area of the same microporous film as in Fig. 3, in the solid state. The same three defects in the water droplet structure shown as defects A, B and C in Fig. 3 were found to be preserved in the final film and identified as defects A, B and C, respectively in this figure.

films were characterized using two supplementary techniques, namely confocal microscopy and white light interferometry (the results of which are shown in Figs. 5 and 6).

The main finding reported *for the first time* herein is that the structural template represented by the water droplet array is directly transferred into the resulting solid polymer film and, in doing so, maintains the features present in the water

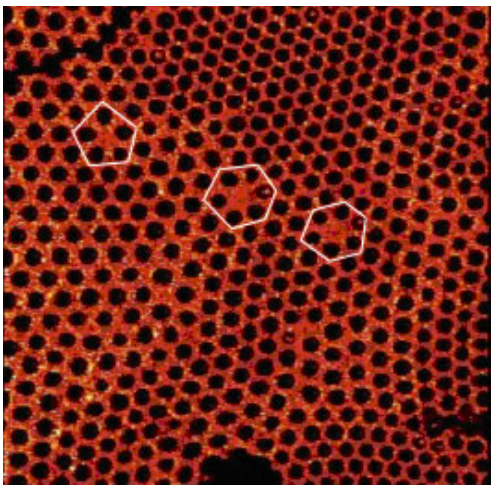

Fig. 5. Confocal microscopy image of the same area of the same microporous film as in Fig. 3, in the solid state. The same three defects in the surface structure of the (solid) polymer film result from the droplet array structure shown in Fig. 3.

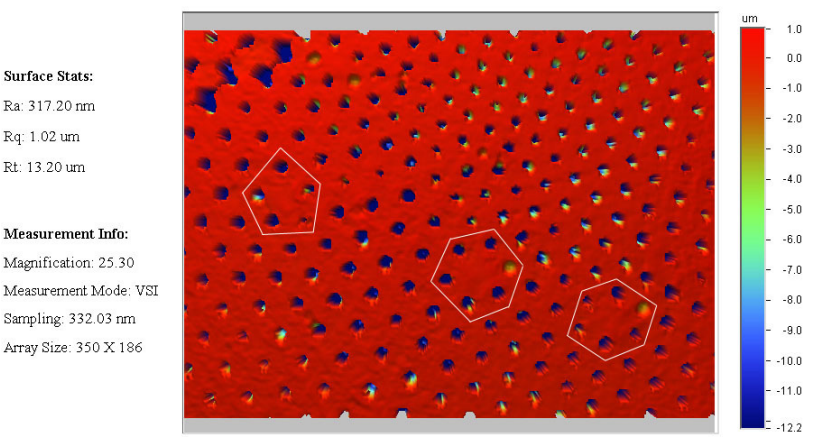

Fig. 6. White light interferometry scan of the same area of the same microporous film as in Fig. 3, in the solid state. The same three defects in the surface structure of the (solid) polymer film result from the droplet array structure shown in Fig. 3.

droplet array. Somewhat surprisingly, this is the first direct (i.e. non-circumstantial) association between the droplet template and pore structure in breath figure work. Previous descriptions of this process have reported that the pores are not formed in the *absence* of moisture.[5–9] The mechanism whereby substantial regions of the water droplet array are transferred into the rapidly evaporating polymer solution is essentially that envisaged by Srinivasarao *et al.*,[5] and the present work provides the first experimental confirmation of their ideas.

In addition, the present finding that the process of transfer of the templating droplet array into the solution (and hence its preservation in the final solid film) may be accomplished without disruption of the features of the array structure has potential technological significance. In so far as the present work demonstrates that a "pattern" of defects originally in the template may be preserved in the solid film, so might another pattern which has been deliberately created (i.e. a pattern "written" by displacing or removing droplets in the templating array).

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