

Gel spinning of porous poly(methyl methacrylate) fibres

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Solutions of poly(methyl methacrylate) in 1-butanol demix on cooling. By solution extrusion, fibres are produced which have an oriented porosity. The relation between this morphology, the phase diagram and the extrusion procedure is discussed.

(Keywords: poly(methyl methacrylate); 1-butanol; phase separation)

Introduction

Porous, membrane-like polymer materials can be prepared easily by cooling a moderately concentrated solution of a polymer in a poor solvent. This process was developed for solutions of crystalline polymers by Castro¹ and extended to solutions of amorphous polymers by Aubert and Clough² and Caneba and Soong³. The mechanism of this process of structure formation has been studied in detail⁴⁻⁷. The poor quality of the solvent induces a liquid-liquid demixing on cooling and this demixing results in the formation of two phases of different composition. The equilibrium situation is a macroscopic two-layer structure. This equilibrium is difficult to reach when polymers are involved because of the high viscosity, and is only obtained at very low polymer concentration. At sufficiently high polymer concentrations, the multidomain structure is retained for a long time and the two-layer, equilibrium situation will not be realized in most cases. The coalescence of the initially formed, nanometre-sized domains proceeds slowly, and the multidomain structure is frozen in by a vitrification process⁸. Porous materials are obtained after solvent elimination. Their morphology is controlled mainly by coalescence, and consequently it depends strongly on the experimental conditions such as cooling rate, annealing conditions, overall polymer concentration and molar mass of the polymer⁸. The processing of these demixing solutions by extrusion and the resulting supramolecular morphology are discussed in this paper. Solutions of poly(methyl methacrylate) (PMMA) in 1-butanol were used.

Experimental

Atactic PMMA was prepared by radical polymerization⁹. The number and mass average molar mass of the polymer, determined by gel permeation chromatography, are 1.2×10^5 and 3×10^5 , respectively. 1-Butanol (UCB) was used as the solvent. The polymer concentration

is expressed as mass fraction, w_2 . A concentration of $w_2=0.25$ was always used. The morphology was investigated by scanning electron microscopy (SEM; Cambridge Stereoscan 200). The solutions were extruded using a Berstorff twin screw extruder.

Results and discussion

Phase behaviour of the system PMMA/1-butanol. The experimental conditions were deduced from the temperature-concentration diagram of the system. This behaviour is discussed in detail in a previous paper⁷ and is illustrated in Figure 1 for a PMMA sample with almost the same average molar mass and molar mass distribution as the one used in this work. Cooling of a solution with $w_2=0.25$ results in liquid-liquid demixing with the

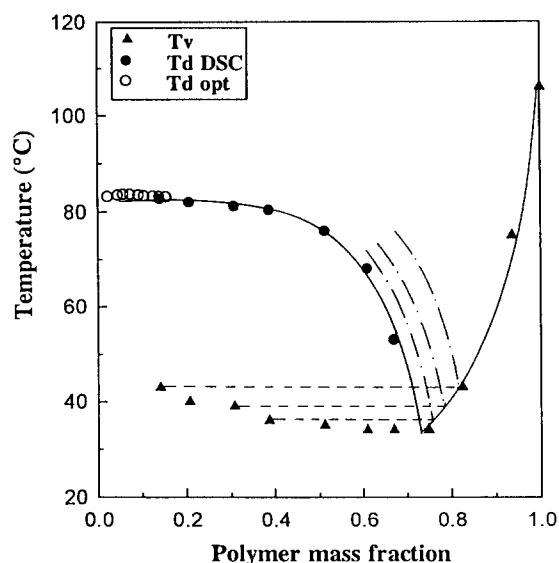


Figure 1 Phase behaviour of the system PMMA-1-butanol ($M_n=1.4 \times 10^5$; $M_w=3.8 \times 10^5$). ○, Liquid-liquid demixing, optical observations; ●, liquid-liquid demixing, calorimetric observations; ▲, glass transition

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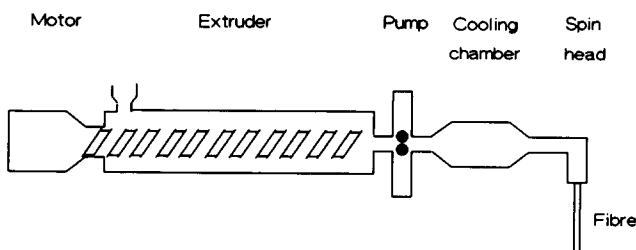


Figure 2 Schematic representation of the extrusion equipment

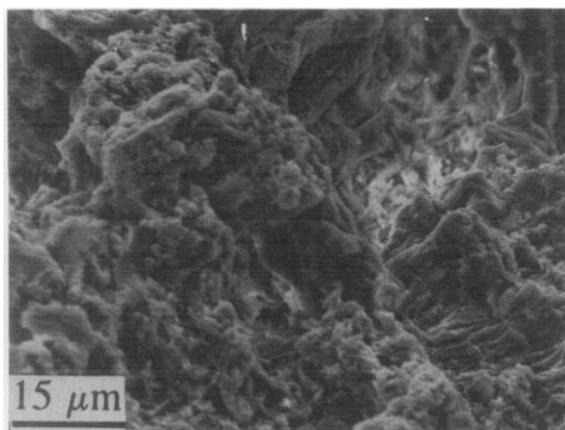


Figure 3 SEM picture of the porous material obtained by extrusion at 65°C of a PMMA/1-butanol solution with $w_2=0.25$

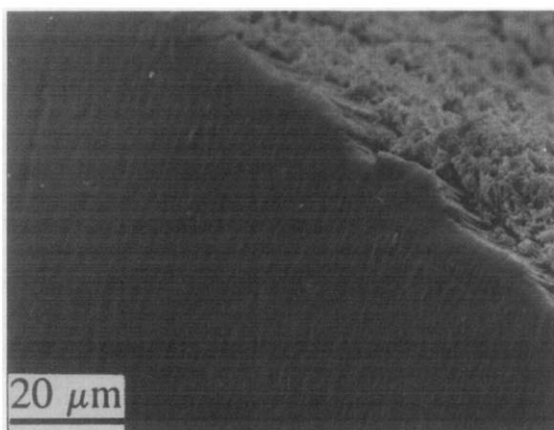


Figure 4 SEM picture of the closed skin of the porous material obtained by extrusion at 85°C of a PMMA/1-butanol solution with $w_2=0.25$

formation of a multidomain, two-phase system. When the temperature is further lowered to the glass transition of the polymer rich phase, vitrification of these domains takes place. Due to the polydispersity of the PMMA sample, the demixing curve differs from the binodal. Therefore, the T_d value beneath the demixing curve increases with decreasing polymer content⁷. After elimination of the solvent, a porous, glassy material is obtained. The final morphology of this porous system, such as the size and shape of the pores and the structure of the glassy interconnecting phase, can be monitored by the experimental conditions. The demixing of a solution with $w_2=0.25$ sets in at around 80°C (T_d). Vitrification of the concentrated domains takes place at around 40°C (T_v).

Extrusion procedure. A schematic representation of the experimental set-up is given in Figure 2. It consists of a twin screw extruder combined with a pump, a cooling chamber and a spinhead (the dimension of the spin hole is 1 mm). A solution of PMMA in 1-butanol was homogenized in the extruder at 100°C, above the demixing temperature. This homogeneous solution was pumped through the cooling chamber into the spinhead at a pumping rate of 150 g min⁻¹. The cooling chamber and the spinhead were kept at the same temperature, T_{ex} , below 100°C. The solution cools to room temperature when it leaves the spinhead and vitrification of the concentrated domains sets in at around 40°C. The extrudate was manually stretched during this cooling process. Once the extrusion was complete and the sample brought to room temperature, the solvent was exchanged for isopropanol. The samples were cut parallel to the extrusion direction and examined by SEM.

Morphological observations. Extrusion was performed at two different temperatures, one above and the other below the demixing temperature of 80°C. This extrusion temperature was controlled by the temperature of the cooling chamber and the spinhead.

(i) **Extrusion at $T_{ex} < 80^\circ\text{C}$.** Extrusion was performed below the demixing temperature at 65°C. For this purpose the cooling chamber and the spinhead were maintained at this temperature by a thermostat. Liquid-liquid demixing has already set in inside the cooling chamber and the spinhead and therefore a demixed system is forced through the spinhead. An opaque extrudate is obtained and the result is a porous material that does not show any orientation. The corresponding SEM picture is presented in Figure 3.

(ii) **Extrusion at $T_{ex} > 80^\circ\text{C}$.** Extrusion above the demixing temperature is realized by keeping the cooling chamber and spinhead at 85°C. A homogeneous, transparent extrudate is obtained. The outside of this extrudate is quickly covered by a closed skin. This is ascribed to the evaporation of the solvent at the surface of the extrudate (Figure 4). Cooling below 80°C, outside the spinhead, induces liquid-liquid demixing and the formation of a multidomain, two-phase system. In the absence of any outside force, spherical droplets of almost pure solvent will be formed in a continuous, polymer-rich matrix^{7,8}. The die swelling of the solution induces a deformation of these spherical domains perpendicular to the extrusion direction (Figure 5a). The spherical droplets are elongated perpendicular to the fibre axis. The application of a pulling force parallel to the extrusion direction will counteract and almost suppress this die swelling (Figure 5b). The pores at the inside of the fibre are spherical while the pores at the outside are elongated parallel to the fibre axis. The deformation at the outside of the extrudate may be the consequence of the formation of the closed rigid skin and the increase in flow rate. On leaving the spinhead, the flow rate at the edge of the extrudate increases from almost zero to its maximal value. A further increase of the pulling force narrows the extrudate and results in the formation of more elongated pores (Figure 5c). The difference in morphology between the inside and outside pores is negligible. Consequently, the increase in pulling force induces an equal deformation throughout the fibre. The application of a very high degree of deformation breaks the walls between adjacent pores and a continuous porosity is realized in the

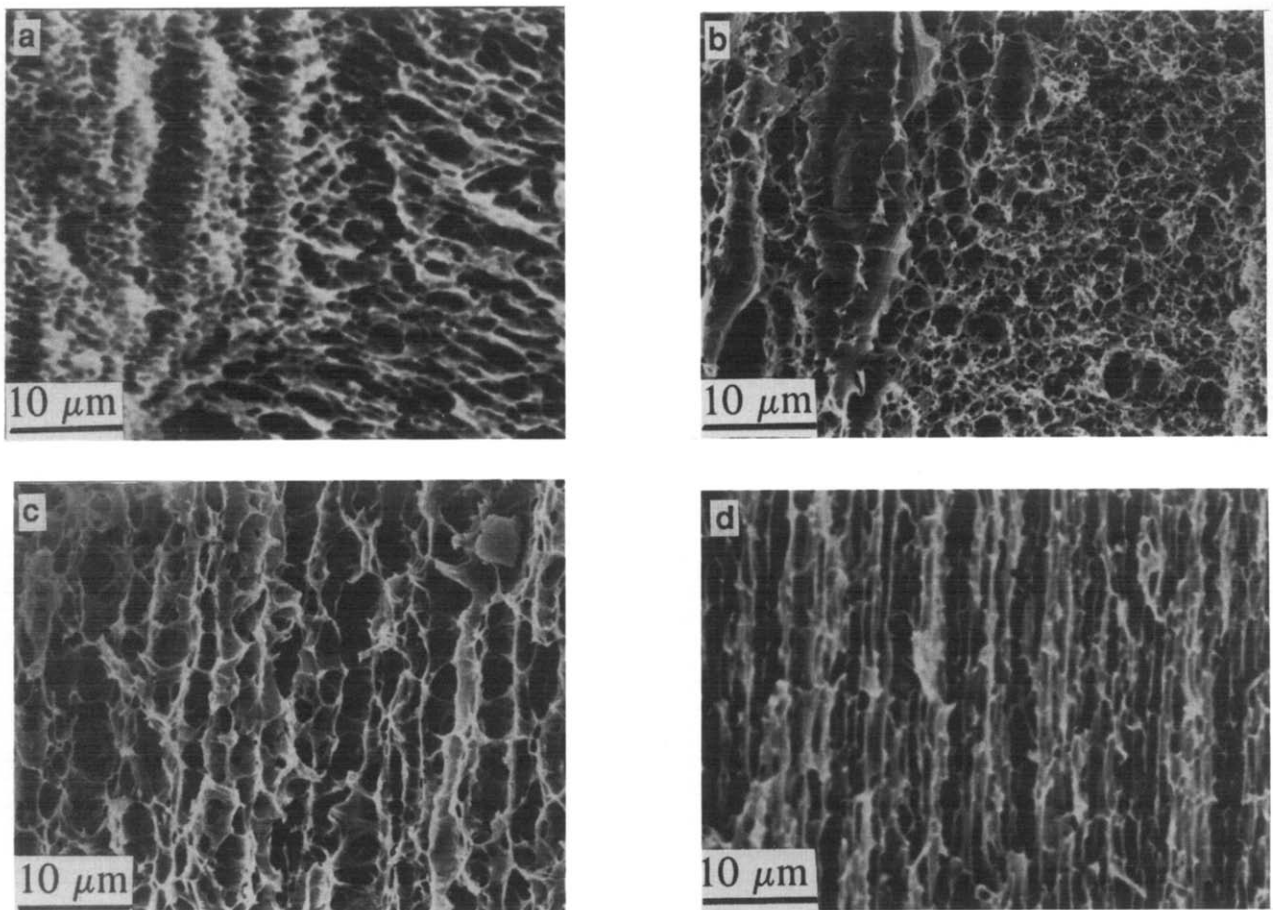


Figure 5 SEM pictures of the porous material obtained by extrusion at 85°C of PMMA/1-butanol solutions with $w_2 = 0.25$. The vertical axis of the pictures corresponds to the extrusion direction. The left-hand part of each picture corresponds to the outer area of the fibre whereas the right-hand part corresponds to the area close to the centre of the fibre. The degree of orientation increases from (a) to (d). The draw ratio expressed in percentage: (a) 0%, (b) 10%, (c) 30% and (d) 100%.

direction of extrusion (*Figure 5d*). A thin fibre, covered with a closed film and containing pores which extend over the complete length of the fibre, is obtained.

Conclusions

Porous PMMA fibres with their porosity oriented along the fibre axis and a closed outside skin can be prepared by a solution-extrusion process. This specific morphology is not unique to PMMA solutions but can be realized by the correct combination of a liquid-liquid demixing in a polymer solution, a vitrification process and the necessary stretching of the extrudate. Only one solvent is needed, the structure is induced by a simple cooling operation and the process is completely reversible.

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