

Solution Spinning of Fibers with Oriented Porosity

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SYNOPSIS

The preparation of porous fibers from the quasi-ternary system poly(methyl methacrylate)/poly(ethyl methacrylate)-1-butanol is based on the combination of different liquid-liquid demixing processes that interfere with the vitrification process. Polymer-polymer demixing takes place at high temperature and interferes at lower temperature with polymer-solvent demixing and the vitrification of some of the formed phases. When these processes take place during extrusion, porous "composite" fibers are obtained. They consist of fibrils of poly(methyl methacrylate) coated with poly(ethyl methacrylate), and these fibrils are separated by micrometer-sized channels that extend along the fiber axis. The formation of these fibers is discussed within the framework of the phase behavior of the quasi-ternary system. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Amorphous, porous materials can easily be prepared by cooling a moderately concentrated solution of a noncrystallizable polymer in a poor solvent. This procedure was introduced by Aubert and Clough¹ and Caneba and Soong,² and the mechanism was studied in detail.³⁻⁷ It was shown that these membranlike structures originate from the interference between a liquid-liquid demixing and a vitrification. A multidomain, two-phase situation is generated very quickly during the early stages of the liquid-liquid demixing process. The coalescence of these small domains, however, proceeds much more slowly so that this metastable, multidomain structure can be maintained for a certain time. As the sample is further cooled, vitrification of the concentrated domains freezes this metastable morphology so that porous materials are obtained after elimination of the solvent. Their morphology will be determined by the extent of coalescence at the moment of vitrification and will therefore be controlled largely by the kinetics of coalescence. Important experimental parameters that affect the kinetics of this coalescence are the polymer content of these concentrated

domains, the molecular mass of the polymer, the time and temperature of isothermal annealing before vitrification, and the final cooling conditions.⁶ The use of this demixing-vitrification process during the extrusion of the solution results in the formation of porous fibers with a porosity oriented along the fiber axis.⁸ In this paper this procedure will be applied to the extrusion of solutions of two polymers in one solvent. Solutions of poly(methyl methacrylate) (PMMA) and poly(ethyl methacrylate) (PEMA) in 1-butanol will be used.

EXPERIMENTAL

Materials

Atactic PMMA and atactic PEMA were prepared by radical polymerization.⁹ The number and mass average molar masses of the polymers, determined by gel permeation chromatography, are, respectively, 5×10^4 and 1.2×10^5 for PMMA and 1.1×10^5 and 2.2×10^5 for PEMA. 1-Butanol (supplied by UCB) was used as the solvent (S). The solutions are identified by two parameters: the mass ratio of the solvent-free polymers (PMMA/PEMA), expressed as mass percent (e.g., 70/30, and the overall polymer content, also expressed as mass percent w_2 .

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Extrusion Procedure

The experimental conditions for extrusion were deduced from the temperature-concentration diagram of the system. A mini-twin-screw extruder with a spin hole of 1 mm was used.¹⁰ The different polymer-solvent systems were prepared in the extruder at 85°C and extrusion was performed at this temperature. The extrudate was cooled to room temperature and simultaneously stretched by hand. Most of the solvent evaporated during this treatment and the remainder was eliminated by prolonged drying under vacuum. The samples were cut parallel to the fiber axis and their morphology was investigated by scanning electron microscopy (SEM) (Cambridge Stereoscan 200).

RESULTS

Phase Behavior of the PMMA/PEMA/1-Butanol system

Polymer-Polymer Demixing

PMMA (P1) and PEMA (P2) are not miscible in the melt.¹¹ A complex situation arises when a poor solvent for each of the constituents is added to the blend. The miscibility gap of the latter then extends into the composition triangle and nearly reaches the corner representing the solvent. This type of demixing will be indicated here as polymer-polymer demixing (PP).

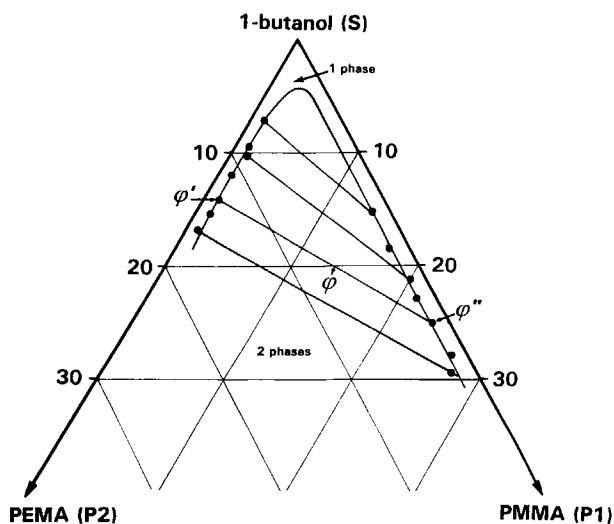


Figure 1 Isothermal composition diagram of the quasi-ternary system PMMA/PEMA/1-butanol at 85°C. ● — ●: tie line.

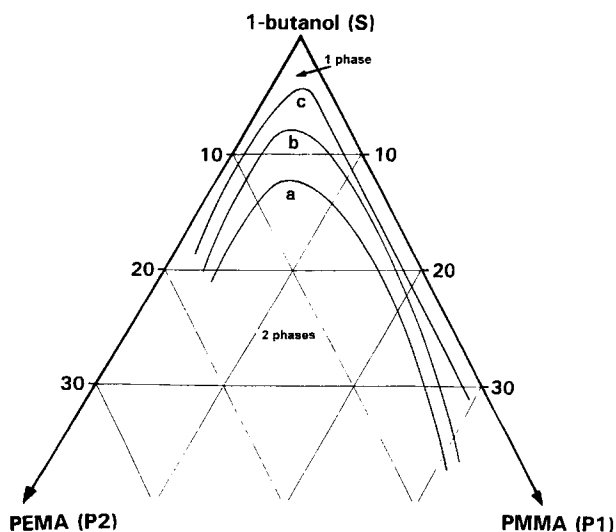


Figure 2 Isothermal composition diagram of the quasi-ternary system PMMA/PEMA/1-butanol at different temperatures: (a) 140°C; (b) 110°C; (c) 85°C.

At high temperatures, far above the Θ -temperatures of the two solvent/polymer systems (SP1 and SP2), the quasi-ternary solution S/P1/P2 separates into two phases that differ in composition and overall concentration. These phases segregate completely within 30 min, even at overall polymer concentrations as high as 30%. The phases can be separated after quenching in liquid nitrogen and breaking the vitrified system along the interface. Analysis of the constituents then allows plotting of the coexisting phase compositions shown in Figure 1, which shows some tie lines. Figure 2 represents the data so collected at three temperatures and demonstrates that the homogeneous concentration region contracts upon a decrease of the temperature, a well-known phenomenon.¹²

Further, Figure 2 shows that the left-hand branch of the PP miscibility gap moves toward the SP2-axis upon a decrease of temperature. A rough estimation indicates that this branch may well almost come to coincide with the SP2-axis at temperatures around 70°C. The right-hand branch, however, appears to show a different behavior, and a small but significant solubility of P2 along the SP1-axis may be expected to exist at relatively low temperatures.

A typical situation is illustrated in Figure 1 for the demixing of a 70/30 P1/P2 solution ($w_2 = 20\%$). At 85°C, this system (ϕ) is separated in the coexisting phases ϕ' and ϕ'' . Phase ϕ' contains most of the PEMA and a small fraction of PMMA, whereas most of the PMMA is found in phase ϕ'' together with a small fraction of PEMA. The two phases can

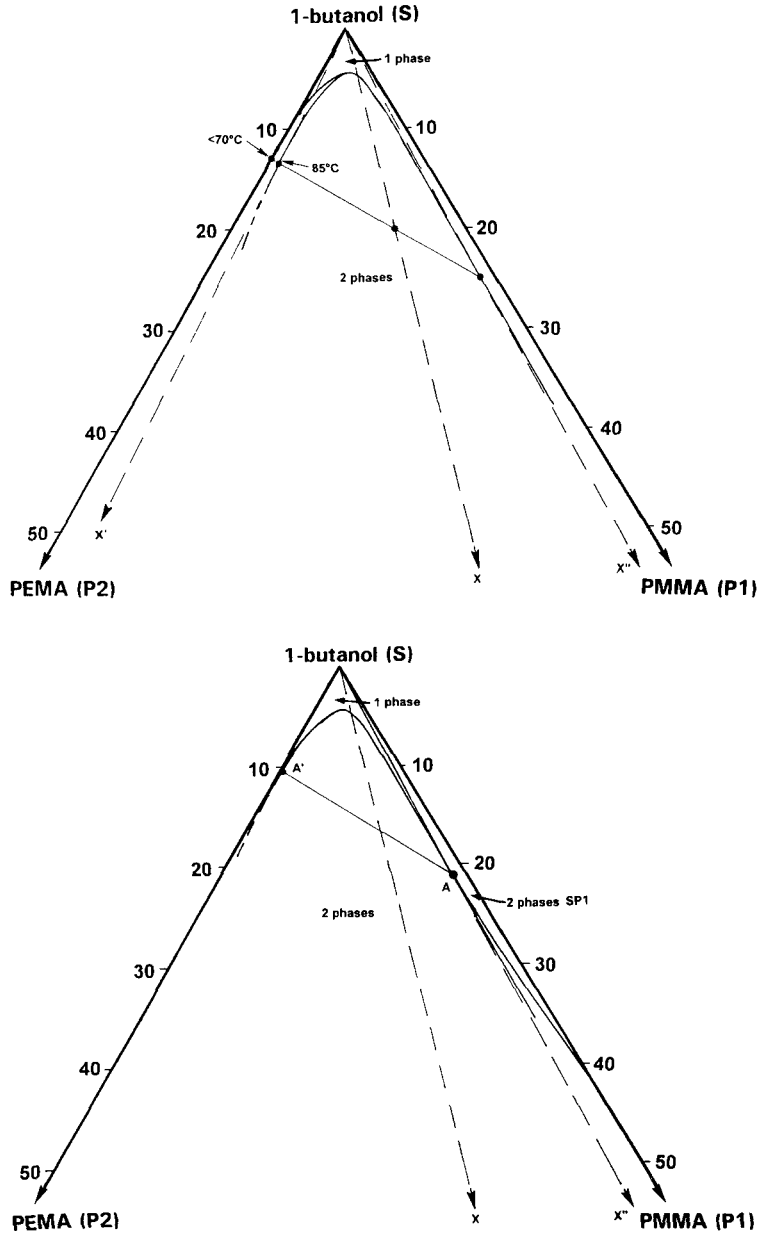


Figure 3 Quasi-ternary phase diagrams for 1-butanol/PMMA/PEMA (S/P1/P2). *SX*, *SX'*, and *SX''*: composition axes for solvent/mixed polymer systems of various [P1/P2] values: (a) Two-phase areas at $T = 85^\circ\text{C}$ (read from Fig. 1) and $T < 70^\circ\text{C}$ (estimated). (b) Coalescence of SP and PP gaps by critical point A, coexistent with phase A'. (c) Formation of a three-phase triangle by the cooling of state (b).

easily be brought into a fine dispersion by mechanical stirring.

Solvent-Polymer Demixing

Cooling below 85°C initiates demixing in each of the two solvent-polymer systems SP1 and SP2, at a temperature below their θ points. The maximum

separation temperatures are 77°C for SP1 and 29°C for SP2. Below 77°C the miscibility gap in SP1 will extend into the composition triangle, as indicated schematically in Figure 3. Figure 3(a) summarizes Figure 2 under the assumption that the orientation of the tie lines does not change appreciably with temperature. In Figure 3(b) the SP1 miscibility gap has entered the composition triangle at $T < 77^\circ\text{C}$

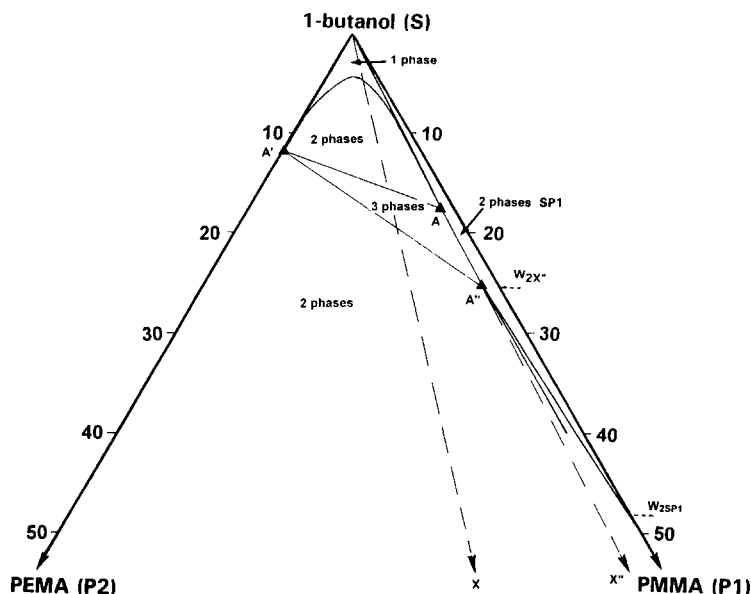


Figure 3 (Continued from the previous page)

and eventually touches the PP gap at A . If the system were strictly ternary, A would constitute a critical phase in equilibrium with another liquid phase (A').¹³ A further decrease in temperature changes tie line $A-A'$ into a three-phase triangle [$A-A'-A''$, Fig. 3(c)]. At the beginning of the development of this triangle, A'' may coincide with or be close to phase ϕ'' .

This classic consideration permits prediction of the phase transitions that may be expected when a 70/30 P1/P2 mixture, dissolved in 1-butanol, is cooled. Its overall composition is plotted on SX where X defines the P1/P2 ratio. At $T = 85^\circ\text{C}$, phases ϕ' and ϕ'' have formed and the composition axis for the P1/P2 mixture in phase ϕ'' is represented by SX'' . Similarly, for phase ϕ' we have SX' , which line practically coincides with $SP2$ at $T < 70^\circ\text{C}$.

Before any SP1 demixing can be observed in system SX'' the temperature must be decreased below 77°C , the maximum separation temperature in SP1. The phase transition would then occur at a smaller overall polymer concentration ($w_{2X''}$) than it does in SP1 (w_{2SP1}), since the separation composition in SP1 is larger at $T < 77^\circ\text{C}$. This behavior has been observed, as demonstrated in Figure 4, which indicates the temperature dependence of the concentrations $w_{2X''}$ and w_{2SP1} . This figure also shows that a similar depression is not found on the SP2 side because of the near coincidence of SX' and $SP2$. In SX' , vitrification of the concentrated P2 phase sets in at -5°C ; this phase will therefore remain liquid at room temperature.

Though the present simple equilibrium treatment may not reflect completely what may happen under the dynamic conditions of scanning calorimetry and extrusion, it is obviously a useful tool in the interpretation of the data presented in this paper. The approach is further justified by the extreme concentration separations and by the vitrification of the concentrated PMMA domains.

This complex problem has been treated more quantitatively,¹⁴ and will be published in future.¹⁵

Morphology

General Observations

Samples with different composition were extruded (Table 1). The extrudate is always transparent when it leaves the extruder head, in spite of the heterogeneous nature of the system. When this extrudate is cooled and stretched, three different situations must be considered; they are indicated in Table 1 as A, B, and C. Most compositions lead to white, porous fibers covered by a closed skin (A); the morphology of some of these fibers will be discussed in the following paragraphs. The formation of the skin is ascribed to the fast evaporation of the solvent at the surface of the extrudate.⁸ The viscosity of two systems was so low that no fibers could be spun (B). Other compositions resulted, after solvent evaporation, in transparent fibers showing no porosity at all (C).

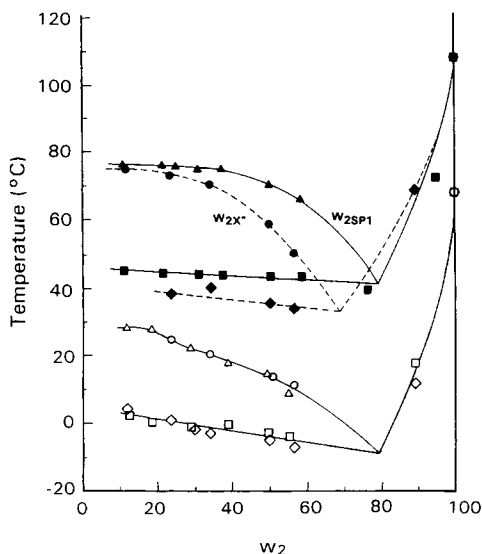


Figure 4 Temperature-concentration diagram: Quasi-binary systems. 1-butanol/PMMA: demixing - w_2 \blacktriangle , T_g - w_2 \blacksquare ; 1-butanol/PEMA: demixing - w_2 \triangle , T_g - w_2 \square . Quasi-ternary system: 70/30 1-butanol/PMMA/PEMA, SP1 demixing - w_2 \bullet , T_g - w_2 \blacklozenge ; SP2 demixing - w_2 \circ , T_g - w_2 \diamond .

Morphologic Observations

The morphology obtained by extrusion of solutions with $w_2 = 30\%$ but with different PMMA/PEMA ratios has been investigated. The SEM pictures are represented in Figure 5.

The extrusion of solutions of 100/0 P1/P2 leads to fibers with a fine, continuous porosity oriented along the fiber axis [Fig. 5(a)]. The addition of PEMA has an important influence on the shape and the size of the pores. Fibers with a similar morphology but a 5-fold larger pore diameter are obtained when 90/10 P1/P2 is used. [Fig. 5(b)]. A much smoother fibrillar morphology is obtained when the relative amount of PEMA is further increased, as illustrated by the fiber morphology obtained by ex-

trusion of 80/20 P1/P2 [Fig. 5(c)] and 70/30 P1/P2 [Fig. 5(d)].

More details about the morphology are obtained when these fibers are subjected to a diethyl ether treatment. At room temperature, diethyl ether is a good solvent for PEMA but a poor solvent for PMMA. Therefore it is possible selectively to extract PEMA and to localize this polymer in the fiber structure. For this purpose, the fiber obtained by the extrusion of 80/20 P1/P2, $w_2 = 30\%$, was cut in two, parallel to the fiber axis, and one part was treated with diethyl ether. Both parts were examined by SEM and the resulting photographs are represented in Figure 6. The untreated fiber has a closed skin and an internal fibrillar morphology. The diethyl ether treatment removes the PEMA phase and leaves the glassy PMMA phase unaltered. Figures 6(a) (not treated) and 6(b) (treated) represent the inside of a fiber, where as Figures 6(c) (not treated) and 6(d) (treated) represent the fiber skin.

This diethyl ether treatment reveals an inside porosity in the fibrils. The same observations can be made for Figures 6(c) and 6(d). The fibrillation brought about by the diethyl ether treatment can be observed clearly with the naked eye.

DISCUSSION

The extrusion of a solution of 100/0 P1/P2 in 1-butanol at 85°C results in a transparent and homogeneous extrudate. Cooling below 85°C, outside the extruder, 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 are formed in a continuous, polymer-rich matrix. The application of a pulling force parallel to the extrusion direction transforms these spherical droplets in elliptical ones. A further increase of the external force will break the walls between the different droplets so that a continuous

Table I Solution Composition and Extrusion Results

Overall Polymer Concentration (%)	PMMA/PEMA				
	100/0	90/10	80/20	70/30	50/50
30	A	A	A	A	B
40	A	A	A	A	B
50	A	A	A	C	C

A = White, porous fibers covered by a closed skin.

B = System viscosity so low that no fibers could be spun.

C = After solvent evaporation, transparent fibers showing no porosity.

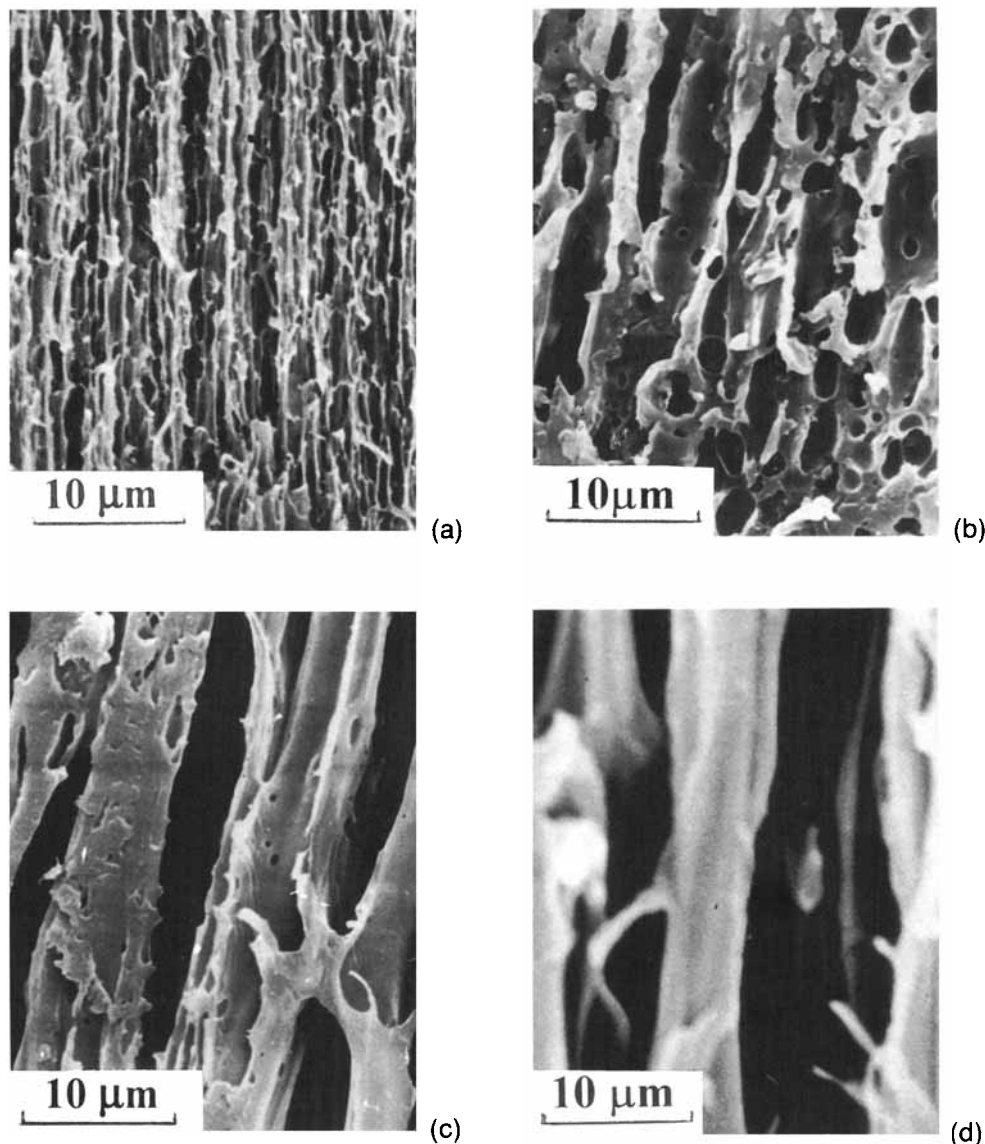


Figure 5 SEM pictures of extruded samples of PMMA/PEMA/1-butanol with different ratios of the two polymers: (a) 100/0, (b) 90/10, (c) 80/20, (d) 70/30. Draw ratios, expressed in percentages, are 100% (a) and 50% (b, c, and d). Stretching direction is vertical and corresponds to the fiber direction.

porosity is realized. When these oriented systems are cooled below their vitrification temperature, the structure is frozen in and the solvent can be evaporated without changing the original morphology.

The situation is more complex when two different polymers are involved and different steps have to be considered. They are represented in Figure 7 of the 80/20 P1/P2 system, $w_2 = 20\%$.

Inside the extruder, at 85°C , the solution is not homogeneous and a multi-domain dispersion of one phase in a continuous matrix of the second phase is realized by continuous movement in the extruder. In the system under discussion, the continuous ma-

trix is a PMMA solution containing a small fraction of PEMA (ϕ'' , step I in Fig. 7) while the dispersed phase consists of droplets of a PEMA solution, containing a small fraction of PMMA (ϕ' , step I in Fig. 7). The heterogeneous extrudate is nevertheless transparent when it leaves the extruder; this absence of opalescence must be ascribed to the small difference in refractive index between the two phases, resulting from the limited difference in refractive index between the two polymers and the presence of a relatively large amount of a common solvent.

As soon as the extrudate leaves the extruder, the dimensions of the dispersed domains increase by co-

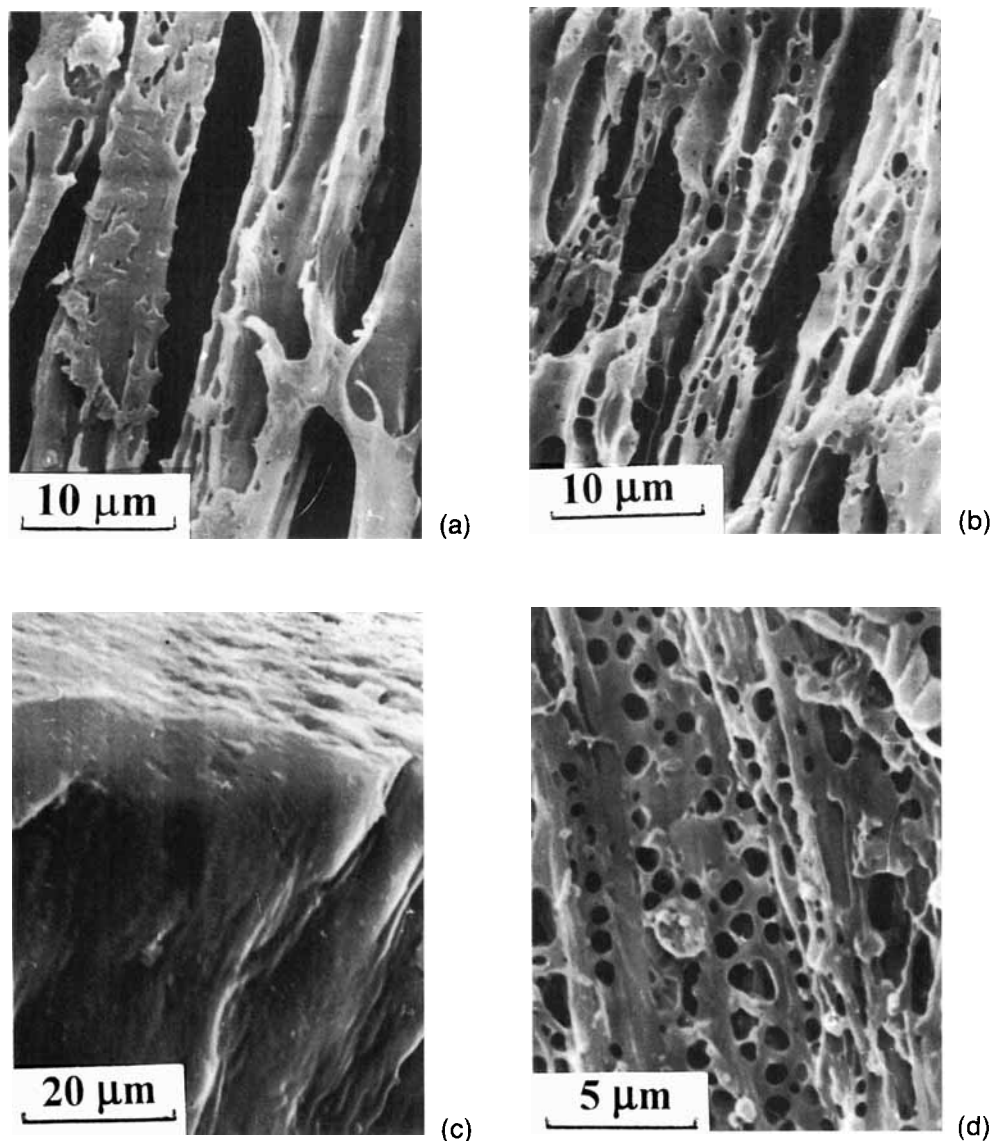


Figure 6 SEM pictures of a fiber obtained with the system PMMA/PEMA 80/20, $w_2 = 30$. (a) and (b) Inside of the fiber; (c) and (d) skin of the fiber. (a) and (c) Before treatment with diethyl ether; (b) and (d) after treatment with diethyl ether. Draw ratio, expressed in percentage, is 50%. Vertical axis corresponds to the fiber length.

alescence and this process will take place in a rather short time when PEMA is present. Therefore, the morphology obtained with PMMA/PEMA is about five times coarser than the one obtained when a PMMA-only solution is extruded under similar conditions. This difference is the consequence of the relatively low polymer concentration in the coexisting phases of the quasi-ternary system.

Cooling below 85°C results in an interference in the PP and SP1 demixing and this leads to a three-phase equilibrium. Two phases will have a different overall concentration but a not-too-different overall composition. They contain mainly PMMA and a

small fraction of PEMA [phases A and A'' of Fig. 3(c)]. This matrix is indicated in Figure 7, step III, as $A + A''$. The third phase [A' of Fig. 3(c)], contains most of the PEMA and almost no PMMA. This phase is indicated as A' in Figure 7, step III. This transition from a two-phase to a three-phase equilibrium is expected to alter the overall phase distribution. But during the short extrusion operation, not much change in the overall macroscopic morphology, already present from the beginning, is to be expected. Therefore the system can still be treated as a macroscopic two-phase, consisting of a matrix (microscopic dispersion of phases A and A'')

containing most of the PMMA, and large, dispersed domains containing most of the PEMA (A'). Demixing will continue on further cooling until the matrix vitrifies around 35°C (step IV, Fig. 7).

During this extrusion, the PEMA-rich phase (A') will be oriented and will form "solution-filled channels" in the vitrifying matrix. This matrix will have a fibrillar morphology because of the presence of these channels. At $T < 29^\circ\text{C}$, demixing will set in inside these channels in A' and this process, as stated earlier, can be treated in a good approximation as a quasi-binary demixing. An equilibrium between a concentrated PEMA/1-butanol solution and almost pure solvent will be established. Vitrification of these channels will take place only at -5°C , so at room temperature these channels are filled with a viscous, demixed solution. When the solvent is evaporated at room temperature, the overall morphology will not be affected because of the presence of the glassy fibrils. The elimination of the solvent from the demixed system that fills the channels between these glassy fibrils (phase A') will result in a deposition of the PEMA-rich phase on the surface of these fibrils, leaving an empty space in between. The solvent will also be eliminated from the glassy domains and a porous fiber will be obtained. The glassy fibrils, composed mainly of PMMA, form the main structure. They have a composite structure because of the occurrence of a three-phase equilibrium; this is revealed by the diethyl ether extraction [Fig. 6(b)]. On top of these fibrils, PEMA is precipitated by the solvent evaporation. A macroscopic white, fibrillar fiber is obtained. The inside morphology is schematically represented in Figure 8.

Conclusions based on an equilibrium discussion cannot be observed in a quantitative manner in the

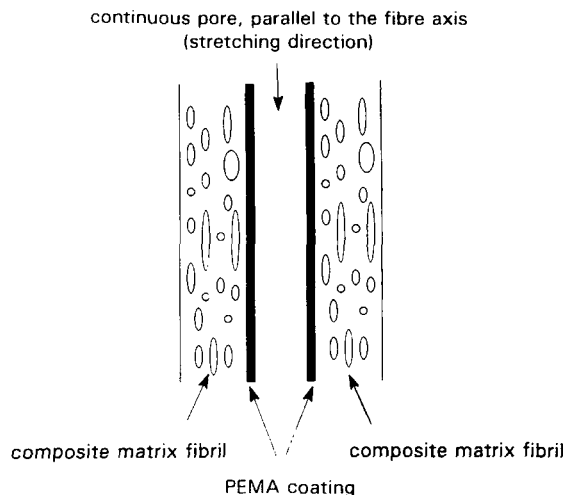


Figure 8 Schematic representation of fiber morphology after solvent evaporation.

experimental observations. The extrusion process proceeds far from equilibrium and the final result seems to originate from a two-phase situation. But the more complex character of the final situation is reflected, for example, in the porous structure of the matrix fibrils after the diethyl ether treatment [Fig. 6(b) and (d)].

CONCLUSIONS

Porous, fibrillar composite fibers with an outside closed skin can be prepared by a single extrusion operation. These fibers consist of porous PMMA fibrils coated with PEMA during the drying process. A minimum amount of PEMA is needed, together

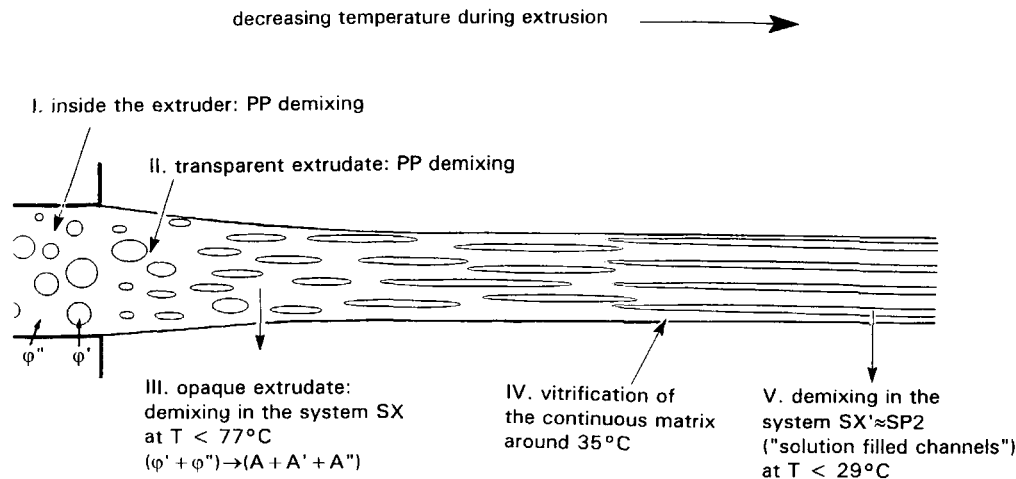


Figure 7 Schematic representation of the extrusion process.

with a not-too-high overall polymer concentration. The process is based on three consecutive liquid-liquid demixing steps, and the interference with a vitrification process. The procedure is completely reversible because it is based on reversible thermal transitions in solution.

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