Polymer Vol. 37 No. 11, pp. 2201–2204, 1996
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0032-3861/96/$15.00 + 0.00

Possibility of porosity control in nylon-6/nylon-6,6 blend membranes

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(Received 3 August 1995; revised 8 September 1995)

Nylon-6 (N6)/nylon-6,6 (N66) blend membranes were prepared from N6/N66 blend solutions in calcium chloride–methanol mixture of the concentrates in order to investigate the possibility of porosity control. During the pore formation process, which took place at 10 and 20°C by adding water onto the blend solution surface in a cylindrical glass bottle, a four-phase structure of solid, gel 1, gel 2 and solution (in order from the top) was observed clearly. With increasing the ratio of N66 in solution, the semitransparent grey colour of gel 2 hardly changed, but the colour of gel 1 changed gradually from semitransparent grey to white. In the boundary region between gel 1 and gel 2, microphase separation between N6 and N66 was predicted. The macroscopic pores in membranes prepared at 10 and 20°C were almost spherical and with increasing the ratio of N66, the pore size decreased abruptly between blend ratios of N6 and N66, 1 : 0 and 2 : 1, and then gradually approached that of N66. when the humidity in the concentration conditions was increased from ~35 to ~80% r.h. at 20°C, the pore size increased by about 46% in diameter. Copyright © 1996 Elsevier Science Ltd.

(Keywords: blend membrane; phase inversion; porosity control)

INTRODUCTION

For the preparation of polymer blend membranes by phase inversion[1,2], the selection of the common solvent and the non-solvent pore former for polymers is very important. For nylon-6 (N6) and nylon-6,6 (N66), calcium chloride–methanol mixture is an appropriate common solvent for preparing blend membranes[3]. Recently, for concentrated N6 and N66 solutions in this mixture in a cylindrical glass bottle, the appearance of a three-phase structure of solid, gel and solution (in order from the top) has been observed after adding water onto the solution surface[4,5]. Pores were formed in membranes as the end product of the structural development by the migration of water of a non-solvent pore former[4,5]. The pore size was made as small as the concentration of N6 or N66 in a casting solution was high and decreased with decreasing the preparation temperature. However, in the structural development for N6/N66 blend solutions by the same manner, a four-phase structure of solid, gel 1, gel 2 and solution was observed[6]. In this paper, for N6/N66 blend solutions, the mechanism of pore formation and the possibility of porosity control are investigated through the observation of blend effects on phase inversions by adding water. In particular, the appearance of a two-phase gel structure (gel 1 and gel 2) was related to microphase separation between N6 and N66, because the gradual colour change of gel 1 with the ratio of N66 in solution corresponded to the change from transparency to turbidity by phase separation observed for polystyrene–poly(vinyl methyl ether) mixture during the heating process[7]; however, it should be noted that the dominant factor of phase separation is the amount of added water for the former and the temperature for the latter[7].

EXPERIMENTAL

Preparation of membranes

N6/N66 blend membranes were prepared from the mixture of N6 and N66 solutions[3] with the composition of 6.67 g N6 or N66/20 g $CaCl_2$/100 ml CH_3OH. The volume ratios of blends of N6 and N66 solutions are 2 : 1, 1 : 1 and 1 : 2. First the blend solution (30 ml), mixed using a stirrer, was concentrated naturally by leaving it in a cylindrical glass bottle (30 mm diameter) open to the incubator atmosphere of 10 and 20°C under low humidity (~35% r.h.) or ambient conditions (~20°C and ~80% r.h.) until a skin formed on the solution surface (about a week). The skin was almost transparent in the former atmosphere and semitransparent in the latter one. Then after putting the bottle in an incubator controlled at a constant temperature (10 or 20°C), water was added onto the surface skin. In the pore formation process after adding water, gelation and solidification behaviours and two-phase gel structure composed of gel 1 and gel 2 were observed. The interfaces between solution and gel 2, gel 2 and gel 1, and gel 1 and solution shifted downwards at very slow rates, 0.2–0.3 mm h^{-1} at 20°C, respectively[4]. The membranes prepared by these processes were washed with water and then dried under ambient conditions before being photographed.

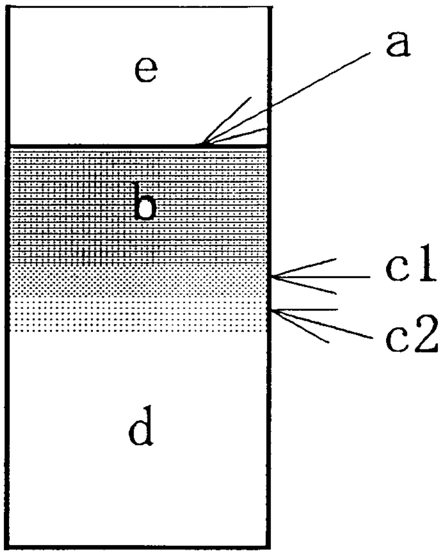

Figure 1 Schematic diagram of pore formation process for N6/N66 blend solutions: (a) surface skin, (b) solid, (cl) gel 1, (c2) gel 2, (d) solution and (e) water

Photography

The porous morphology of membranes and the gelation behaviours were photographed by a camera with a bellows focusing attachment or TV camera. The images by TV camera were contrasted by the operation tool of image analysis. By the image procedure, the cut pores on the cross-section were imaged sterically as if they were inside the membrane.

RESULTS AND DISCUSSION

Pore formation

The pore formation is started by adding water onto the surface skin of a solution. For N6/N66 blend solutions at 10 and 20°C, a four-phase structure of solid, gel 1, gel 2 and solution (in order from the top) was observed. *Figure 1* shows a schematic diagram of the pore formation process for N6/N66 blend solution. *Figures 2A–2E* show the actual photographs of pore formation at 20°C and 1 day after adding water for N6/N66 blend solutions, N6 and N66 solutions concentrated naturally in ambient conditions (~20°C and ~80% r.h.). In the boundary region between gel 1 and gel 2, the microphase separation between N6 and N66 and the subsequent solidification of N66 at an earlier stage than N6 could be predicted, because (1) for N6 or N66 solution, only one gel was observed, (2) with increasing the ratio of N66 solution, the colour of gel 1 changed from semi-transparent grey to white, but the transparent grey of gel 2 indicated little change, and (3) for all blend

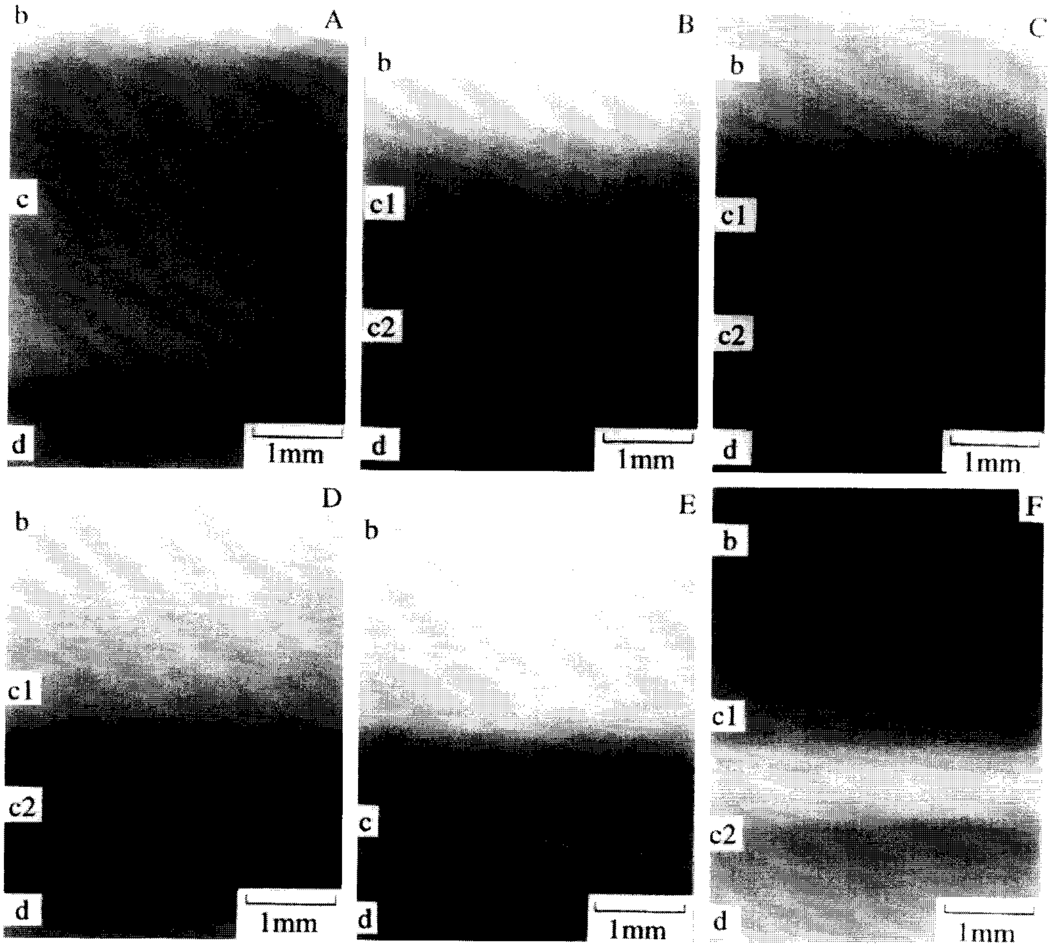

Figure 2 Photograph of pore formation process at 20°C and 1 day after adding water for N6/N66 blend solutions concentrated naturally in ambient atmosphere of ~20°C and ~80% r.h. (A–E), and the incubator atmosphere of 20°C and ~35% r.h. (F). Blend ratio of N6 and N66: (A) 1 : 0, (B and F) 2 : 1, (C) 1 : 1, (D) 1 : 2 and (E) 0 : 1. Photographs were taken by TV camera for A–E and by a camera with a bellows focusing attachment for F

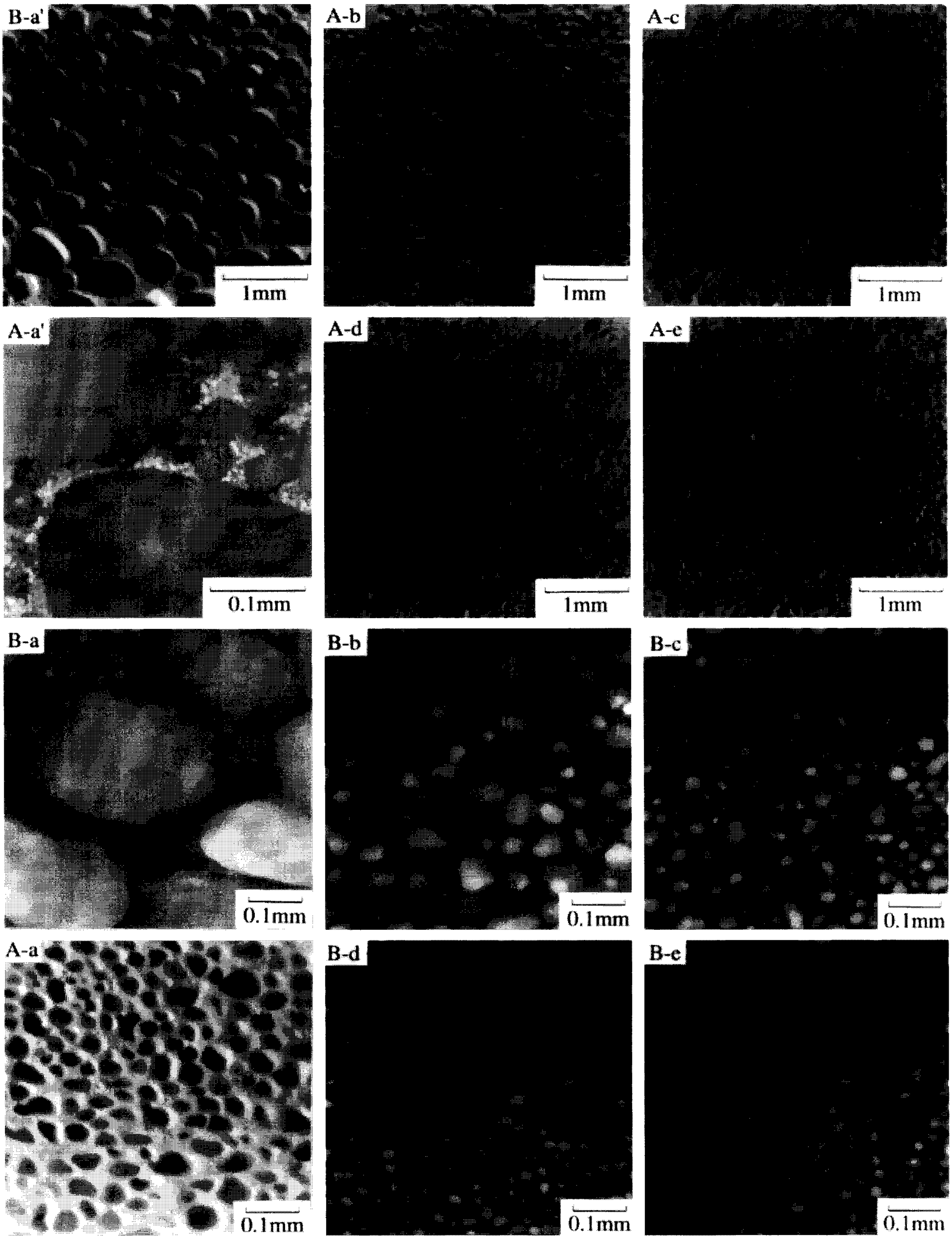

Figure 3 Morphology of vertical sections in the centre parts for N6/N66 blend membranes prepared at 20°C (A) and 10°C (B). Blend ratio of N6 and N66: (a) 1 : 0, (b) 2 : 1, (c) 1 : 1, (d) 1 : 2 and (e) 0 : 1. Photographs were taken by a camera with a bellows focusing attachment for A series and a' of B series, and by a TV camera installed in an optical microscope for B series and a' of A series

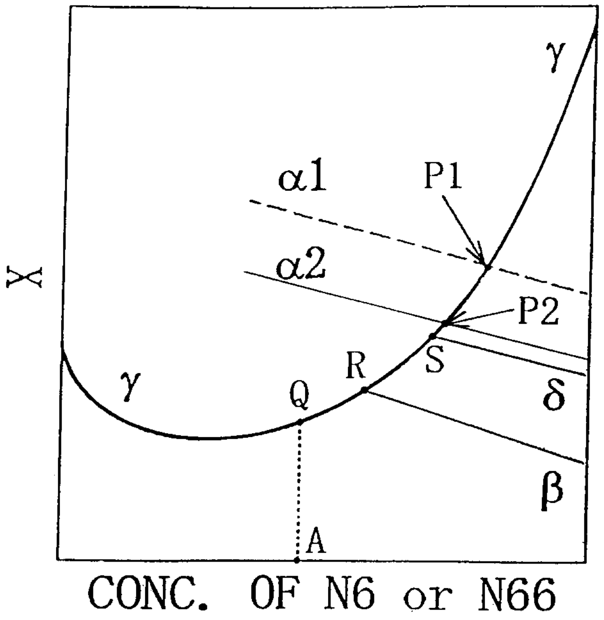

Figure 4 Schematic relationship between the concentration of N6 or N66 in a calcium chloride–methanol mixture and the amount of additional water per unit volume, X, needed for solidification ($\alpha 1$ for N6 and $\alpha 2$ for N66), sol–gel inversion (β), phase separation (γ), and microphase separation between N6 and N66 (δ) at a horizontal cross-section point. The dotted line is the supplementary one which shows the patch of X from points A to Q

solutions, the thickness of gel 2 (1.8–2.2 mm) was only a little larger than 1.8 mm for N66 and smaller than 4.2 mm for N6, and for gel 1 it was about 0.8 mm. Whereas, for all blend solutions concentrated in the incubator atmosphere at 20°C and ~35% r.h., the same tendency as described in (1), (2) and (3) was obtained, though the thickness of gel 2 (~0.8 mm) was less than that (1.8–2.2 mm) of the above case and the thickness of gel 1 was 0.7 mm (0.8 mm in the above case). The thickness of the gel phase for N6 and N66 was 3.0 mm and 0.7 mm, respectively[6]. *Figure 2F* shows the actual photograph of pore formation of 20°C and 1 day after adding water for N6/N66 blend solution (blend ratio 2 : 1) concentrated at 20°C under ~35% r.h.

Figure 3 shows the morphology of a vertical section in the centre parts for membranes prepared at 10 and 20°C after concentration at 10 or 20°C under ~35% r.h. The pores were spherical and with increasing the ratio of N66, the pore size decreased abruptly between blend ratios of N6 and N66, 1 : 0 and 2 : 1, and then gradually approached that of N66. In the matrix parts between pores, smaller pores were observed, as shown in *Figure 3A-a′*. The lower parts of a membrane have larger pores. This result could be attributed to the decrease of the concentration of N6 in the solution phase (d in *Figure 1*) with the progress of gelation and solidification[8]. Increasing the humidity in the concentration conditions from ~35 to ~80% r.h. at 20°C, the pore size increased by an average of 46.2% in diameter.

Schematic process of pore formation

In *Figure 4*, the amounts of additional water per unit volume, X, needed for solidification ($\alpha 1$ for N6 and $\alpha 2$ for N66), sol–gel inversion (β), phase separation (γ) and microphase separation between N6 and N66 (δ) at a horizontal cross-section point, are shown schematically as functions of the concentration of N6 or N66 in calcium chloride–methanol mixture, respectively. The schematic process of pore formation in *Figure 4* is as follows. First, water is added onto the concentrated solution with a surface skin at point A. Water diffuses into the solution through the surface skin. Here, let us focus on the inversion behaviours in a very small constant volume of a horizontal cross-section point at a fixed site of the glass bottle.

For a solution at point A, the increase of water into the phase separation region over point Q on the curve γ results in liquid–liquid phase separation. The concentration in all of N6 and N66 in the polymer-rich phase increases with increasing the amount of water. At point R, the polymer-rich phase is gelled. With increasing water, the separated gel phase increases the polymer concentration along the curve γ, accompanying pore growth. At point S, microphase separation occurs between N6 and N66 and then soon at point P2, N66 is solidified earlier than N6. At that time, pore growth should be strongly restricted by solidification of N66, from the results described in (1), (2) and (3). Finally, at point P1, the gel phase of N6 is solidified. This scheme is predicted on the basis of the observation of the pore size, the thickness and colour change in gel 1 and gel 2 as functions of blend ratio.

ACKNOWLEDGEMENTS

The author wishes to thank Gunma University Foundation for Science and Technology for the support of paying travelling expenses to participate in the Rolduc Polymer Meeting (May 1995, Kerkrade, The Netherlands) for the presentation of this work.

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