polymer communications

Two-dimensional undulation pattern on free surface of polymer film cast from solution

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Non-linear pattern formation in polymer systems has been studied. We present the undulation pattern observed on the free surface of a polymer film cast from solution, for poly(styrene-*ran*-butadiene) random copolymer and for mixtures of polystyrene and dioctylphthalate. The undulation pattern was similar to a hexagonal cellular pattern observed for low viscous fluid produced by Rayleigh–Bénard convection. It was considered that steady-state convective flows occur in a polymer solution with relatively low viscosity, which is induced by solvent evaporation in the earlier stage of casting. Inhomogeneity of the polymer concentration attributed to the convection was considered to play an important role in the pattern formation.

(Keywords: pattern formation; Rayleigh–Bénard convection; hexagonal pattern; surface pattern; undulation pattern; hydrodynamic instability; non-linear phenomena; polymer cast film)

Introduction

Rayleigh–Bénard convection creates various kinds of two-dimensional pattern in horizontal layers of fluid heated from below[1]. Patterns and their formation in the fluid layer, in which the temperature of the bottom is sinusoidally modulated, have been intensively studied both experimentally and theoretically for fluids with low viscosity[2–4]. The pattern formation is discussed in terms of the Rayleigh number, R. For relatively small values of R, there is only conduction and no convection in the fluid layer. With increasing the value of R beyond a critical value, R_c, convection is induced and a steady-state hexagonal cellular pattern is first observed. Transition from hexagons to rolls is then observed with further increase in the value of R. In viscous fluids containing polymers, convective flow is not expected due to the high viscosity; however, this does not necessarily mean that pattern formation by convection in these polymer systems is impossible. This study concerns non-linear pattern formation prompted by convection in casting polymer solution.

We start with a dilute solution and concentrate the solution by gradually evaporating the solvent. When the upper layer becomes heavier than the lower layer of the solution during solvent evaporation, convective flow occurs and inhomogeneity of concentration is induced by the flow. When the solution becomes viscous, the convection is damped down and eventually terminates. During successive evaporation of the solvent, homogenization of the concentration fluctuation induced by the convection competes with an increase of the solution viscosity. If the latter overcomes the former, the inhomogeneity of concentration results in undulation of the free surface of the as-cast polymer film.

We have actually observed convective flows in the casting toluene solution of poly(styrene-*ran*-butadiene) random copolymer (SBR) with about 5 wt% polymer concentration at 50°C. The flows were visualized by dispersing a small amount of aluminium powder in the solution. A two-dimensional undulation pattern of the free surface of the as-cast SBR film was obtained, which is very similar to the hexagonal flow pattern produced by Rayleigh–Bénard convection.

Pattern formation in the polymer system has to be studied in terms of the Rayleigh number as for the low viscosity fluid. However, it is difficult to determine the change in the value of R during casting. Therefore, in this communication we present a qualitative discussion of the formation of the undulation pattern in terms of the convective flows and glass transition temperature, T_g. For the purpose of this study two kinds of polymer were used: SBR, and polystyrene (PS) mixed with dioctylphthalate (DOP) as plasticizer. The T_g of SBR is lower than that of PS. For the mixtures of PS and DOP, T_g can be lowered by increasing the fraction of DOP.

Experimental

The SBR used in this study was produced by Japan Synthetic Rubber Company (sample code 0202). The content of styrene segments was found to be 46% by i.r. characterization. Contents of *cis*-1,4, *trans*-1,4 and 1,2-butadiene segments were also characterized by i.r. (Morero method) and found to be 21, 27 and 6%, respectively. The number- and weight-average molecular weights (M_n and M_w) are 1.5×10^5 and 4.7×10^5, respectively. These values are PS equivalent determined by g.p.c. The PS specimen used (Aldrich Chemical Company) had M_n and M_w values of 1.2×10^5 and 2.2×10^5, respectively, as determined by g.p.c.

The SBR specimen was dissolved in toluene to make approximately 5 wt% SBR solution. The PS and DOP were mixed at given weight ratios of x to $100 - x$, as indicated in the sample name of PS/DOP ($x/100 - x$). The PS/DOP mixtures were also dissolved in toluene to make approximately 5 wt% solutions. Then the solution was poured into a Petri dish (diameter 12 cm). In order

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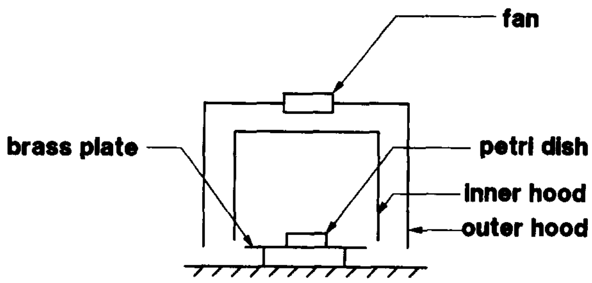

Figure 1 Experimental set up for preparation of cast films

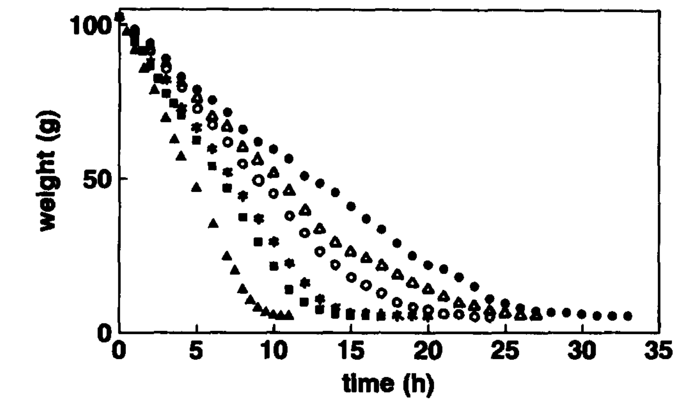

Figure 2 Change of weight with time for SBR-0202/toluene solution at various values of voltage applied to the fan: ●, 0 V; △, 100 V; ○, 125 V; ∗, 150 V; ■, 175 V; ▲, 200 V

to control the rate of evaporation of the solvent, the container shown schematically in *Figure 1* was used, made of acrylic resin. The Petri dish was put on a horizontal brass plate in the container. The temperature of the brass plate was kept at 50°C. The temperature of a free surface of the casting solution was not measured, but is likely to be below 50°C throughout the casting because of the endotherm of solvent evaporation. As discussed below, the temperature difference between the free surface and the bottom layer of the solution plays an important role in pattern formation.

The rate of evaporation was controlled by operating a fan attached to the centre of the ceiling of the outer hood. The change in weight of a solution of SBR-0202 in toluene with time was plotted in *Figure 2*, where the initial weight was about 103 g. It is clear that the solution weight decreased linearly with time until reaching about 8 g, at which point the concentration of the solution was about 65 wt%. Thus the rate of evaporation could be roughly controlled by voltage applied to the fan before the solution weight reached about 8 g. However, it was impossible to control the rate of evaporation at the higher concentration.

Results

In order to show the two-dimensional undulation pattern of an as-cast film, a photograph was taken of the image transmitted through the as-cast film. The undulation pattern of the free surface is shown in *Figure 3* for the as-cast film of SBR without operating the fan. It should be noted that no systematic change in the pattern was seen when the solvent evaporation rate was varied by means of the fan. The black and white regions correspond to raised and dented surfaces, respectively. The black (raised) region forms a mesh all over the surface. Although the contrast between black and white regions is not sufficient, this pattern looks similar to the hexagonal cellular pattern observed for the low viscosity fluid produced by Rayleigh–Bénard convection[1–3].

The undulation pattern of the free surface is presented in *Figure 4* for the as-cast film of PS/DOP mixtures without operating the fan. Although bright and dark regions were ambiguous for both PS and PS/DOP (80/20), it can be seen that the dark regions form a mesh on the surface. These patterns are similar to the case of SBR and may also correspond to the hexagonal cellular pattern produced by Rayleigh–Bénard convection. For the PS/DOP (20/80) mixture, the hexagons are more distinct over a wide area of the surface, except for a marginal region as compared to the PS/DOP (80/20) mixture or the SBR. Here the cell edge is clearly seen. It is suggested that the plasticizer DOP made it easier for the polymer to form a convective flow pattern on the as-cast film, even though the polymer itself has a high T_g. Thus the undulation pattern was more easily observed by lowering the T_g of the as-cast specimen either through random copolymerization or by adding plasticizer.

Discussion

Let us discuss the mechanism of pattern formation prompted by convection. Since the temperature of the free surface of the casting solution is lowered by the solvent evaporation, the specific gravity of the upper layer is greater than that of the lower layer. In addition to the temperature difference, a specific gravity difference is also induced by the difference in concentration between the upper and lower layers. Since the specific gravity of SBR-0202 ($\sim$0.90) is larger than that of toluene (0.868), the specific gravity of the SBR-0202/toluene solution increases with an increase in polymer concentration. Thus the upper layer becomes heavier than the lower layer. These apparent effects prompt the convective flows (density currents) which cause inhomogeneity of the concentration in the horizontal direction of the solution,

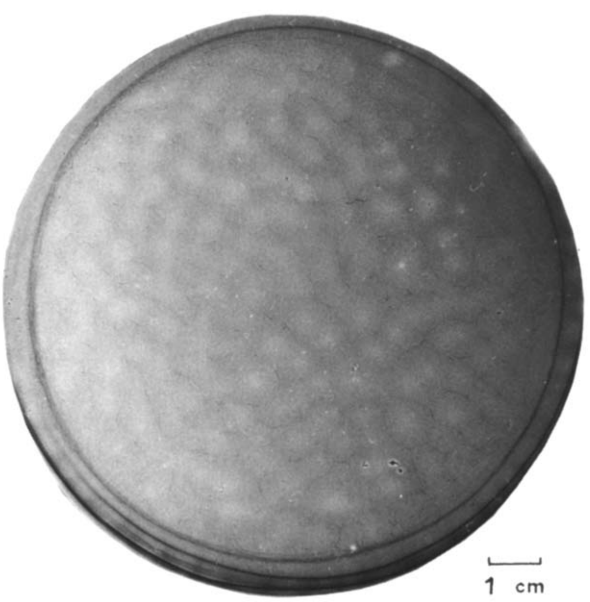

Figure 3 Two-dimensional undulation pattern of a free surface of the SBR film cast from toluene solution

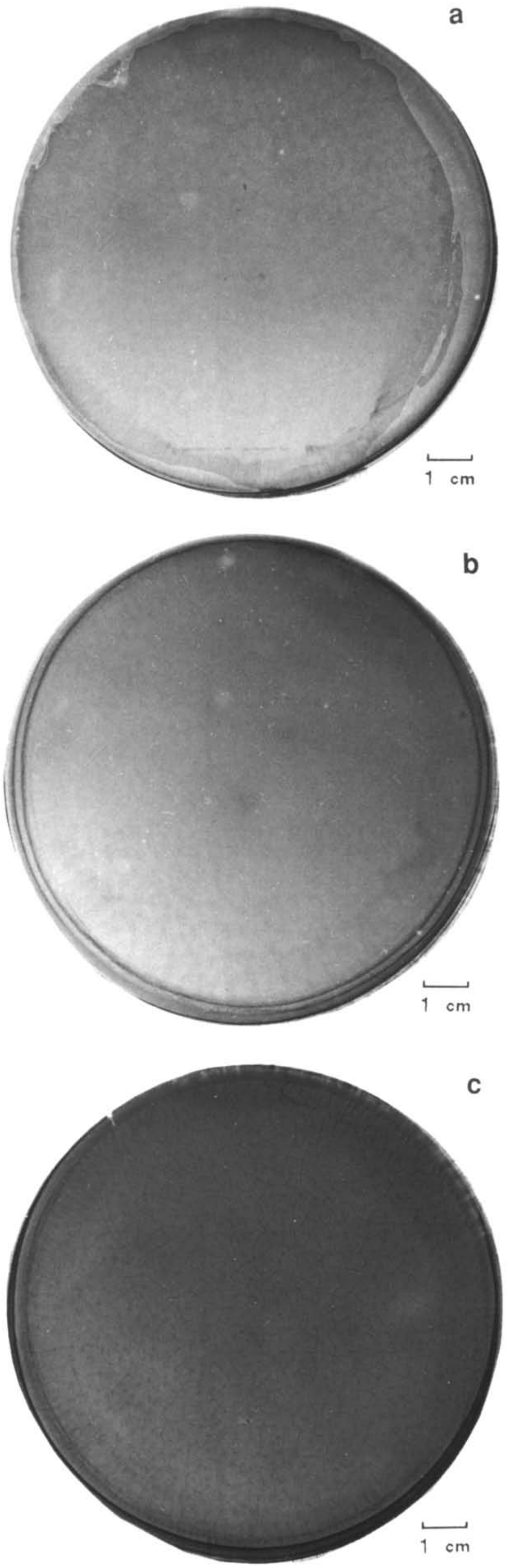

Figure 4 Two-dimensional undulation patterns of free surfaces of the PS/DOP mixtures cast from toluene solutions for (a), 100/0, (b) 80/20 and (c) 20/80 mixtures

especially near the free surface. We have actually observed convective flows in the casting toluene solution of SBR at 50°C with about 5 wt% polymer concentration. The flows were visualized by dispersing a small amount of aluminium powder in the solution.

As the solution becomes more concentrated, the convection is gradually damped down and eventually terminates due to the high viscosity of the solution. Although the density current is discontinued, diffusion of the polymer may occur in order to homogenize the concentration gradient produced by the convection. The polymer diffusion is, however, suppressed by an increase of the solution viscosity. When the solution becomes sufficiently viscous to prevent polymer diffusion before complete homogenization of the concentration, the inhomogeneity of the polymer concentration is frozen in. Finally the undulation pattern is formed on the free surface of the as-cast polymer film corresponding to the frozen inhomogeneity of the concentration. In accordance with this scheme, the observed dented (black) and raised (bright) parts of the free surface can be attributed to upward flows with lower concentration and downward flows with higher concentration, respectively. The scheme described above is only speculation and experiments to confirm this scheme are now underway.

At present, it is difficult to say whether the temperature difference or the concentration difference is effective in driving the convection. However, the casting temperature is essential to the pattern formation. According to the scheme, an important element in pattern formation is the time between the discontinuation of convection and solidification of the specimen. If the time is not long enough to homogenize the fluctuation of the polymer concentration, the undulation pattern eventually appears. The time becomes shorter when the rate of evaporation is higher at the later stage of casting after convection has ceased. If the rate of evaporation can be controlled at the later stage, it will be possible to observe a systematic change in the pattern. Let us assume that convection continues until the solution viscosity reaches a given constant value under a given evaporation rate. Then the time is expected to become shorter as the casting temperature becomes higher because of the lowering of solution viscosity. It is noted here that the casting temperature also affects the rate of evaporation. The combined effect of the higher evaporation rate and the lower solution viscosity at the higher casting temperature explains why the undulation pattern is manifest for the film cast at 50°C rather than at room temperature. The correlation of pattern formation with T_g of the as-cast specimen can be understood by the effect of viscosity lowering with a decrease of T_g.

Finally we discuss the results of PS/DOP solutions. The results show that the pattern becomes obvious by adding DOP. The specific gravity difference between DOP (0.988) and toluene is much larger than that between PS ($\sim$0.94 in the rubbery state) and toluene. Therefore, adding DOP not only reduces the viscosity of the solution of PS/DOP/toluene, but also enhances the driving force of the convection. These combined effects prompt pattern formation through reduction of the time discussed above.

In this communication we have presented the preliminary results for pattern formation on the free surface of as-cast polymer film; however, more experimental evidence is necessary. It has been shown that it is extremely important to control the rate of evaporation at higher concentration rather than at lower concentration of the casting solution. However, the similarity of the two-dimensional undulation pattern observed here to the hexagonal flow pattern produced by Rayleigh–Bénard convection strongly indicates that other kinds of pattern can occur on the free surface of the polymer cast film.

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