Effects of solution thickness on dissipative structures and surface patterns in solvent casting

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Novel dissipative structures can be formed in the course of solvent casting using ternary solutions consisting of phenolic resin / methanol / water with specific compositions. The morphology of the dissipative structure varies according to the solution thickness and its composition. Rings observed in the dissipative structure exhibit a distinct size dependence on the initial solution thickness. As the initial solution thickness (d_0) is increased, the average number of rings per unit area (n) decreases, that is, the average ring size increases with increasing solution thickness. Further, the dissipative structure also forms uneven surface patterns with a bicontinuous nature in the final thermosetting films. The surface morphology exhibits good periodicity in the surface roughness measurement and can be characterized in terms of periodicity (S_m) and average height (R_z), where the periodicity increases in proportion to the solution thickness. In accordance with the dissipative structure, the surface pattern also varies with solution thickness. The average height of unevenness also increases with increasing solution thickness although it is saturated in thicker samples. Thus, the scale of unevenness in the surface pattern as well as that of its constituents in the dissipative structure can be controlled by changing the initial solution thickness.

Key words: pattern formation, dissipative structure, phase separation, solvent cast, phenolic resin

1.INTRODUCTION

Pattern formations developed in both liquid and gas layers by thermal convection have been given experimental and theoretical consideration over the last century [1~3]. The thermal instability needed for the thermal convection can be achieved in the solvent casting without external heating or cooling, since the heat of evaporation is able to cool the upper surface in the solution layer. Solvent casting is seen as an important technique in industries, which involve printing, coating, films and membrane formation.

In the previous paper, we reported a new type of pattern formation prepared using a ternary solution with the components, phenolic resin / methanol / water [4,5]. This pattern formation exhibited both a dissipative structure, observed in the early stages of solvent casting, and an uneven surface pattern, obtained in the resulting coating film. It was shown that the former consists mainly of small, distorted rings, while the latter exhibits a homogeneous, uneven pattern with a bicontinuous nature. The formation of the dissipative structure is most probably attributed to the phase separation induced in the vicinity of the convection cell formation during solvent casting. Subsequently the dissipative structure turns into the uneven surface pattern. The appearances of the dissipative structures and resultant surface patterns are heavily dependent on the nature of the solution composition. As shown in Fig.1 both are only observed in the solutions with specific compositions which contain sufficient non-solvent (i.e. water). It has also been reported that both morphologies can vary depending on the thickness of the solution.

Here, we intend to determine how the dissipative structure and the resultant surface pattern change with relation to the solution thickness. We will investigate what part the initial solution thickness plays and how it effects the various features of the dissipative structure such as number and size of the constitutional rings. We also aim to define the relationship between the solution thickness and certain features of the surface pattern such as the periodicity and the unevenness in the height of the surface roughness measurement.

2. EXPERIMENTAL

The preparation of the ternary solution and the solvent casting procedure are performed according to the method described previously [4]. Firstly, homogeneous solutions are prepared by mixing the following three components, (i) polymer: resole-type phenolic resin (formaldehyde / phenol = 1.18, catalyst = 1 wt % of NH_3 against polymer, Mw=1690), (ii) solvent: CH_3OH and (iii) non-solvent: distilled H_2O, with stirring at 23 °C. This ternary system was selected because it exhibits a distinct, reversible phase separation (clouding point) with adequate water content, with only small temperature changes (ca.1°C) [5]. The polymer concentration / CH_3OH ratio in the solution is fixed at either 20wt% (Solution B) or 30wt% (Solution C), while the H_2O % / polymer ratio in the solution is fixed at 30 or 35wt%. Then the solutions used here are designated as B30 and C35 in accordance with the respective polymer and water content. The clouding point of C35 is ca.3 °C and that of B30 is not observed until 0 °C. For the purpose of this study, the solution is kept uniform at

this stage of the experiment so that no turbidity or precipitation occurs. The composition range in which dissipative structure and subsequent surface pattern were obtained is shown in Fig.1.

Next, the solution is poured onto a clean glass slide ($26 \times 76 \times 1.8$ mm), placed on a microscope stage, and then solvent casting is performed under standard atmospheric conditions (temp.= 23 °C, relative humidity = 45%). The solution volume (V_0) ranges from 0.15ml to 1.2ml. The initial solution thickness is calculated by dividing V_0 by the surface area of the substrate. The changes in morphology are observed using an optical microscope (Nikon, Optiphot-pol). After solvent casting for 3 hours, the sample is dried at 70 °C and 100 °C (1 hour each) and then finally heated at 180 °C for 2 hours in an air oven to ensure thermosetting of the phenolic resin. The surface characteristics and morphology of the coating films are measured using a surface roughness apparatus (Tokyo Seimitu, Surfcom 550AD) and optical microscopy. The morphological change (the number and the size of constituents) in the dissipative structure is evaluated with the aid of photographs.
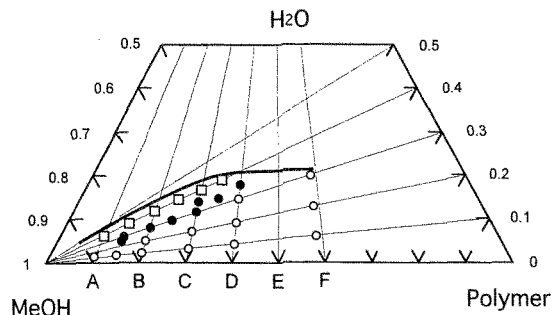
H2O

Fig.1 Relationship between solution composition and pattern formation in a phenolic resin / methanol / Water system. Casting temp.= 20°C, RH=45%, Initial solution thickness = 200µm, Solid line = Cloud point; Surface pattern (○: flat, ●: bicontinuous, □: rough). Dissipative structure is only observed in ●.

3.RESULTS AND DISCISSION

3.1 Effect of solution thickness on dissipative structure

Fig.2 shows the dissipative structures for three different quantities of solution C35, (a) 1.2 ml, (b) 0.4ml and (c) 0.15 ml, obtained using optical microscopy. The initial solution thickness of each sample is (a) 607, (b) 202 and (c) 76 µm, respectively. In all experiments, the dissipative structure appears during the course of solvent casting. Fig.2(a) ~ (c) are observed approximately (a)10min., (b)3.5min. and (c)1.5min. from the start of solvent casting. The solution thickness corresponding to Fig.2(a)~(c) is estimated at about 70% of the initial solution thickness, that is (a) 430µm, (b) 140µm and (c) 50µm, by the simultaneous weight change measurement. The polymer concentration in Fig.2 is about 37wt% (cf. 26wt% for the initial solution).

The main constituents of these structures are ring-like patterns, where each individual ring has a uniquely twisted form. A few string-like patterns with a non-looping shape are also observed in the dissipative structures. We believe that these rings and strings are the polymer aggregations because they form regions of polymer rich (mountain) in the final coating film. Also it

is considered that rings may consist of fine polymer particles which appeared by the phase separation in each convection cell. Such fine particles can be observed by light scattering measurements if a solution with high water content is used [5]. The most distinguished morphological changes caused by the solution thickness are the number of rings per unit area and the actual size
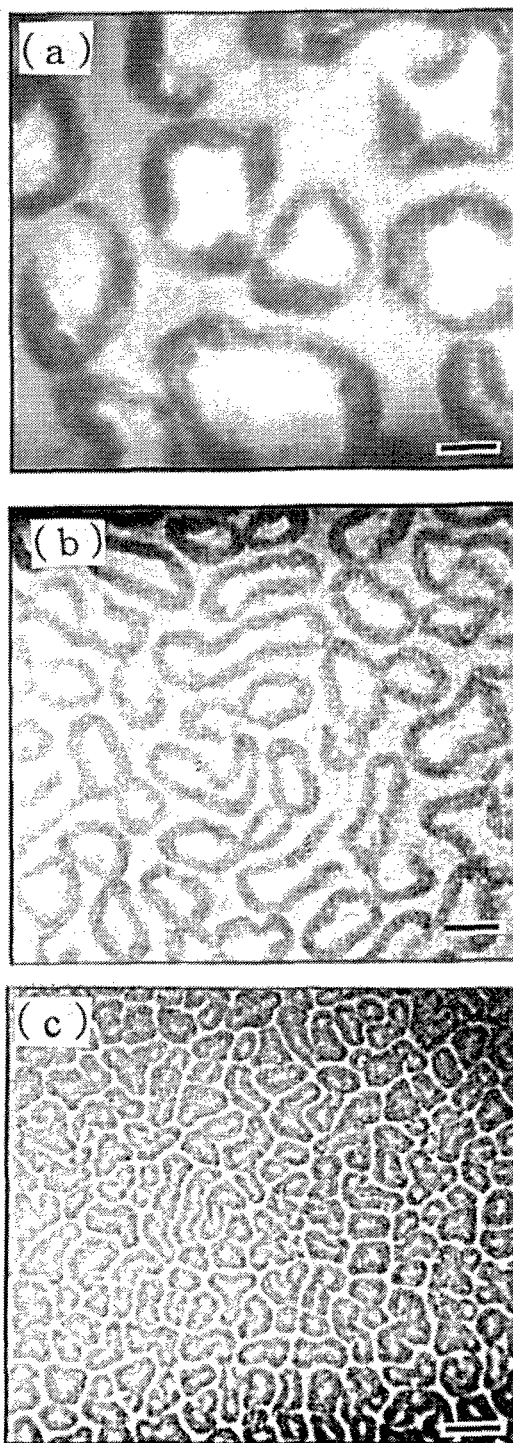

Fig. 2 Effects of solution thickness on the dissipative structures formed during solvent casting: Solution C35. Initial solution thickness (µm) = 607(a) , 202(b) , 76(c). Each scale bar represents 300µm.

of the rings.

Fig.3 shows the effect of solution thickness on the average ring number per unit surface area. It is found that the average number of rings n increases as the initial solution thickness d_0 decreases. In particular, n shows a steep rise when the solution thickness is small. Further, we estimated the average ring size r from n, where r = $(S)^{1/2}$. Here, the average surface area S denotes the area assigned to one ring (S = S(total surface area) / n). The variation of r with respect to the initial solution thickness is also shown in Fig.3. The ring size r increases monotonically with increasing solution thickness. These results suggest that the ring formation mechanism is strongly influenced by the solution thickness. Since it is well known that the size of thermal convection pattern is determined by the layer thickness of fluid [6], by analogy with this we can consider the most possible mechanism to be the interplay between thermal convection and phase separation near the upper surface.
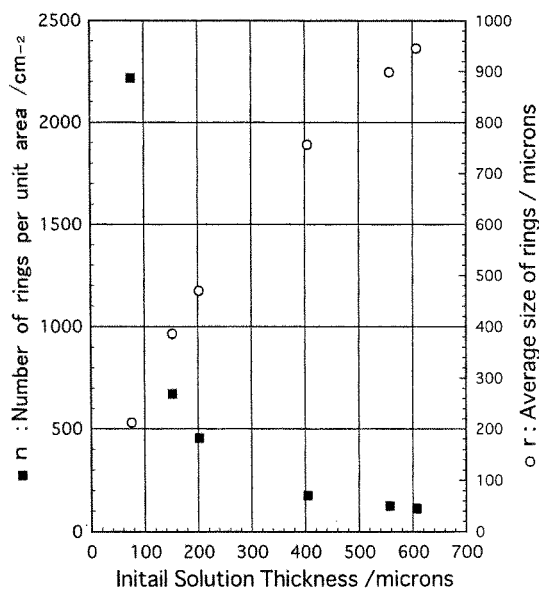

Fig.3 Initial solution thickness dependence of the average number of rings per unit area n and the average ring size r in the dissipative structures: r={(total surface area)/n}$^{1/2}$. Solution C35.

3.2 Effect of solution thickness on the surface morphology in the resulting coating film

In the previous work we found that the appearance of dissipative structures does affect the overall surface morphology in the final coating film [4]. The dissipative structure is observed to be stable only for a short time (~1 min.). Then the ring collapses into a more distorted form probably because the thermal convection becomes difficult due to the increase of the solution viscosity. At the same time the collapsed rings move and collide with each other to form the resulting uneven surface pattern. Thus, when dissipative structures were observed in the solvent casting, the surface of the resulting coating film was not flat but exhibited an uneven pattern with a bicontinuous nature, and vice versa. Such large morphological change is caused by small difference in the solution composition like C20 (smooth flat surface)

and C35 (uneven surface pattern).

In addition to the solution composition, the solution thickness also has an effect on the surface morphology of the final coating film. Fig 4 shows the surface morphologies observed by optical microscopy when the solution thickness is varied in the same manner as Fig.3. Here, the morphology consists of polymer rich regions ("mountains": dark areas in photo.) and polymer poor regions ("valleys": bright areas in photo.) with bicontinuous nature. It is apparent in Fig.4 that the surface morphology shows a strong dependence on the
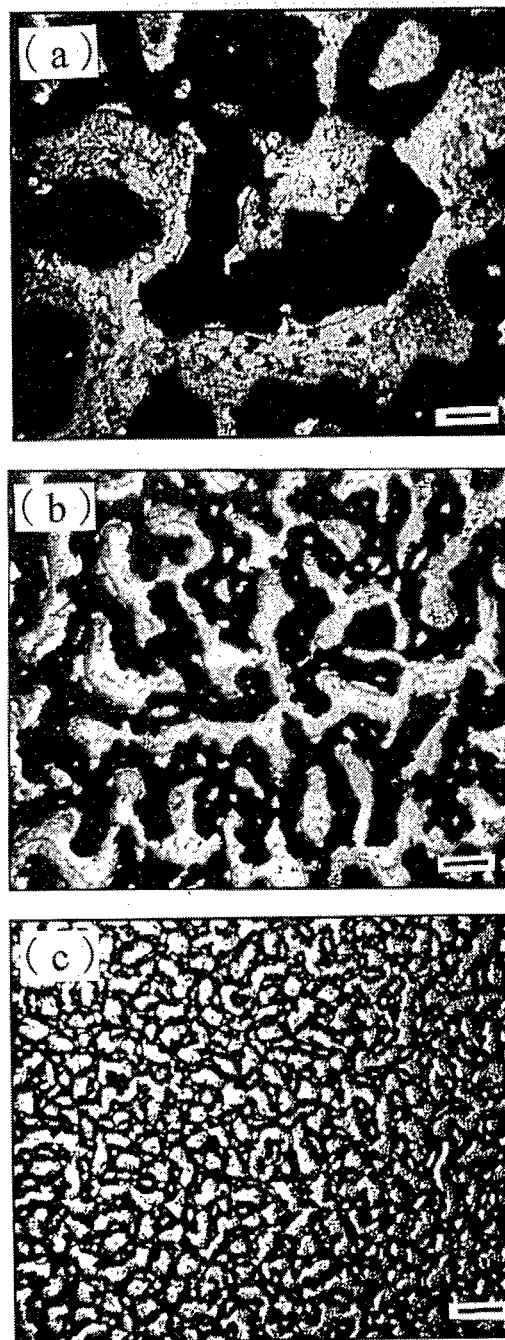

Fig.4 Effects of the initial solution thickness on the uneven surface pattern in the final coating films: Solution C35. Initial Solution Thickness (μm) = 607 (a), 202 (b), 76 (c). Each scale bar represents 300μm.

solution thickness. The characteristic size of surface pattern decreases with a decrease in the initial solution thickness d_0. This is coincident with the fact that the size of the constituent in dissipative structure decreases with decreasing solution thickness, as above. The characteristic sizes in Fig.4(a)~(c) are consistent with those in Fig.2(a)~(c), respectively. This is due to the same transformation mechanism from the dissipative structure to the bicontinuous surface pattern in each solution. Thus, the effect of solution thickness is also a decisive factor for the appearance of the final surface morphology. The scale and the regularity of the surface patterns can be evaluated using the surface roughness measurement scanned in an arbitrary direction. The characteristics of an uneven surface pattern can be expressed quantitatively in terms of the ten points-averaged height (R_z) between top and bottom and the periodicity (S_m: mean value between mountains or valleys) of unevenness.

Fig.5 shows the surface roughness measurements for coating films having uneven patterns, prepared using solution B30 with different quantities ranging from 0.2 to 1.2 ml. All samples possess homogeneous unevenness throughout the sample and exhibit regularity in height and periodicity in the horizontal direction. The solution thickness dependence of R_z and S_m is shown in Fig.6. S_m increases almost proportionally to an increase in solution thickness, while R_z increases with solution thickness in the thinner regions, but becomes saturated ca. $R_z = 15$ μm. Thus, it becomes clear that the surface pattern in the final coating film can be varied depending on the solution thickness, so that the periodicity and the height of unevenness in the thinner regions can be controlled.

4. CONCLUSION

The effects of solution thickness on the morphologies of dissipative structures formed during the course of solvent casting, and on the uneven surface patterns formed in the final coating films, have been investigated. The following results have been revealed.
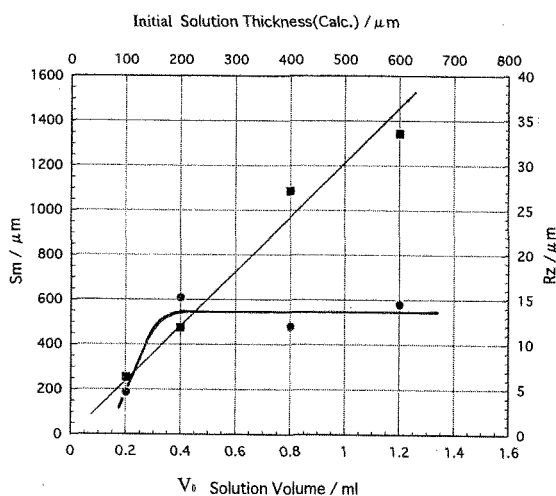
(1) As for the effect on dissipative structure, the number of constituent rings n per unit surface area increases with a decrease in the initial solution thickness d_0 and, as a result, the average ring size increases with respect to d_0.
(2) As for the effect on uneven surface patterns, the characteristic sizes in the pattern vary with d_0. The relationship between d_0 and the periodicity S_m is almost proportional. The average uneven height, R_z, increases with respect to d_0, and rapidly becomes saturated.

The results from these findings, combined with the general knowledge regarding the solution thickness dependence on thermal convection, confirms that the formation associated with the dissipative structure is related to the convection phenomena, a phenomenon similarly dependent on solution thickness. Also, it should be noted that the average ring sizes are 2~4 times of the solution thickness at the time when the rings are observed. This indicates that the ring size is comparable to the size of thermal convection.
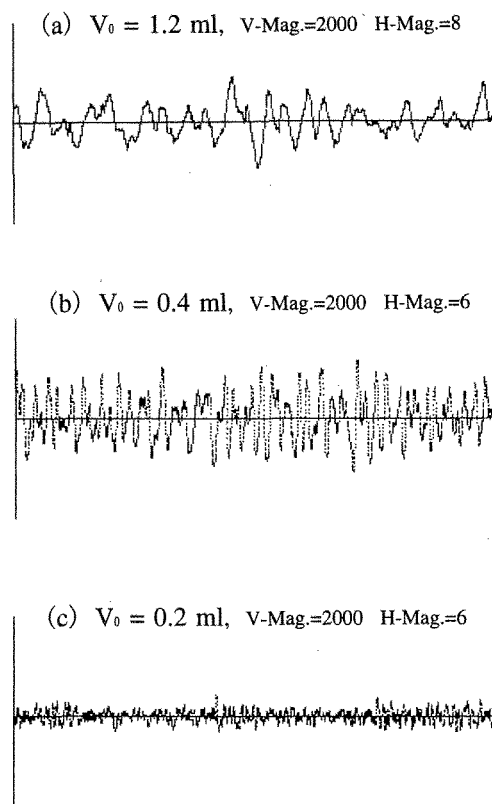
(a) $V_0 = 1.2$ ml, V-Mag.=2000 H-Mag.=8

(b) $V_0 = 0.4$ ml, V-Mag.=2000 H-Mag.=6

(c) $V_0 = 0.2$ ml, V-Mag.=2000 H-Mag.=6

Fig.5 Roughness measurements for coating films with patterns of a bicontinuous nature with differing degrees of unevenness. Solution B30.

Initial Solution Thickness(Calc.) / μm

V₀ Solution Volume / ml

Fig.6 Relationship between initial solution volume V_0 (solution thickness) and roughness in the final coating film: periodicity (S_m, ■) and ten-points averaged height (R_z, ●). Solution B30.

References
[1] H.Bénard, Ann.Chim.Phys., 23, 62 (1901).
[2] Lord Rayleigh, Phil.Mag., 32, 529 (1916)
[3] M.C.Cross, P.C.Hohenberg, Rev. Mod. Phys., 65, 851(1993)
[4] K.Haraguchi, to be submitted.
[5] K.Haraguchi, Polym. Prep. Jpn., 49, 2460(2000)
[6] E.L.Koschmieder, "Bénard Cells and Taylor Vortices", Cambridge University Press, New York (1993)