International Journal of Heat and Mass Transfer 54 (2011) 4135–4142

Contents lists available at ScienceDirect

International Journal of Heat and Mass Transfer

journal homepage: www.elsevier.com/locate/ijhmt

Preliminary investigation of factors determining self-organised structures preparation in polymer layers

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ARTICLE INFO

Article history:
Received 7 June 2010
Accepted 16 March 2011
Available online 7 May 2011

Keywords:
Self-organization
Convection
Evaporation
Process parameters
Polymer solution
Hydroxyethyl cellulose
Molecular weights

ABSTRACT

Factors determining creation of self-organized structures, Bénar–Marangoni cells, during the process of solvent evaporation from the polymer solution and formation of polymer film were studied. Examined parameters were temperature, temperature gradient, rate of drying, height of a liquid layer, area for film preparation, viscosity, molecular weight distribution, etc. A special apparatus, micro condensation drying system, was engineered for this study. As a model system, hydroxyethyl cellulose aqueous solution was used for its excellent film-forming ability and the tendency to self-aggregation. Experimental results, presented in a wide spectrum of self-organized patterns, show the complexity of the problem and the crucial role of molecular weight distribution of the polymer in the fixation of organized structures under highly non-equilibrium conditions.

1. Introduction

Diversity of the surrounding world is transformed by continuously occurring processes of self-organization [1]. These processes are characterized by high complexity, non-linearity and sensitivity to the setting of initial parameters, even of the tiniest detail [2,3]. Thanks to them, new arrangement of matter arises, either in positive or negative meaning [4].

Among the typical examples of self-organized structures, Bénard cells – BMc [5] can be included. They arise as a result of Bénard–Marangoni instability – BM, related to the transport of matter and energy in a layer exposed to a thermal gradient. The leading factor for the creation of BMc is the change of surface tension caused by thermal fluctuations at the phase boundary liquid–gas [6]. The initial part and propagation of this process has been studied over the last hundred years [5–11]. A synoptic summary can be found in the work of Colinet et al. [8] and some other recent works [12–15]. The study of this problem is still relevant, not only for the development of computer techniques and attempts to model the processes [16–20], but also for the need to solve technical challenges where these processes play major role. Examples include protein crystalization [21], Si-wafers drying [22], thermal field-flow fractionation [23,24], thin polymeric film preparation [17,25,26], and others.

Thin polymeric film preparation is the field of our main interest, namely preparation of polymeric films from solution. The creation of BMc in a liquid layer has already been studied, according to the wide spectrum of initial parameters settings [8]. These are (among other): the magnitude of thermal gradient, rate of drying [25,27], thickness of the liquid layer [28], shape of the container with a liquid [13,29] and time [15]. Nevertheless, the creation of organized structures during the evaporation of a solvent from a polymer solution has not been unequivocally explained, so far. There are many non-answered questions, because of the time variability of the system [15,30,31]. Recent experimental works dedicated to such systems dealt with them with respect to the rate of solvent evaporation [25,27] or initiation and fixation of surface corrugation during solvent evaporation [28]. Thus, it is still necessary to study mutual relationships between the range of process and technological parameters, affecting creation and fixation of self-organized pattern in a polymer film prepared from a solution.

A special drying apparatus was engineered, allowing the study of wide spectrum of parameters influencing creation of self-organized structures. Details of the apparatus are given in a previously published paper [32]. In this apparatus, thin polymeric films were prepared from the aqueous solutions of 2-hydroxyethyl cellulose (2-HEC), with a special respect to temperature, temperature gradient, thermal field homogeneity, rate of drying, viscosity, height of the liquid layer, area of the film, molecular weight distribution and substrate cleanliness.

2. Materials and solution preparation

The same conditions for the preparation of polymeric solutions as in the previous study were adopted [32], that means: the aqueous solution of 2-hydroxyethyl cellulose (2-HEC) with

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doi:10.1016/j.ijheatmasstransfer.2011.03.025

Nomenclature

d	thickness of the liquid layer
D	diameter of glass dish
D_f	fractal dimension
dT	temperature gradient between the carrying plate with the sample and the air in the height of 20 mm above this plate
I	intensity value for thresholding
Ma	Marangoni number
MW	average molecular weight (g mol^{-1})
T	temperature
w	mass fraction of polymer in the solution

Greek symbols

γ	surface tension
ΔT	temperature difference between the bottom layer and an open surface
ΔT_c	threshold value of temperature difference for the initiation of the BM-instability
ε	parameter determining transition from symmetric polygonal BM-cells to non-regular
μ	dynamic viscosity
κ	thermal diffusivity

MW = 90,000–1,300,000 g mol^{-1} (Sigma–Aldrich Co.) was used. Dissolution of 2-HEC was performed at constant stirring and the temperature 328 K, during 4 h, in a deionised water. The stock solution was filtered through the S3 glass filter with pore size 15–40 μm and was kept in a sealed (sterile) bottle at the temperature 278 K. Before use, the stock solution was thinned and evacuated, to remove air bubbles. As a substrate, a standard glass Petri dish of a diameter 60–100 mm was used. Cleanliness of the substrate is an essential parameter for obtaining reproducible results. For this reason, the dishes were cleaned with chromsulphuric acid, acetone, ethanol and deionised water, dried and stored.

Onwards, the term Standard Conditions of Film Preparation (SCFP) will be mentioned in the text. These conditions apply to all experiments, except where stated. The SCFP means: Petri dish with a diameter of D = 70 mm as a substrate, initial height of the liquid layer d = 7.1 mm, temperature T = 328 ± 1.1 K, temperature gradient between the heating plate and the air cca 10 mm above the initial liquid level dT = 15 ± 1.1 K, evaporation rate of referential liquid (distilled water) 11.6 ± 0.3 g per 300 min (the rate of 2-HEC film solidification has been expressed in terms of referential liquid evaporation rate, to avoid possible interference to the process of a specific structure formation). The SCFP have been specified after an initial set of experiments, to achieve optimal structures for analysis and digital recording.

3. Film formation and characterization

Polymeric films were solidified in a special apparatus, microcondensation drying system (MCDS), consisting of eight sub-units, each of them working as a condensation dryer. The apparatus has been purposely constructed to minimise negative effect of air dustiness and to allow precise control of temperature, rate of drying, thermal gradient, etc. To protect the sub-units from the outer mechanical effect, the whole system was placed onto anti-vibration tables, four sub-units onto one table. Detailed technical specifications and operating regimes are in detail described in a previously published work [32].

Solidified films were stored in a desiccator and then analysed by and overhead projector 3M, type M2660. Images of the patterns were recorded with a digital still camera. Image analysis was performed in programmes ImageJ 1.3j, Research Services Brand (RSB) of the National Institute of Mental Health, USA and HarFA 5.5.11, Faculty of Chemistry, VUT in Brno, Czech Republic [37,38]. Two ways of image analysis were used to compare obtained structures. For determination of frequency histogram of BM-cells sizes images of manually reconstructed borders were used, whereas for determination of fractal dimension thresholded images were used. Fractal dimension was calculated by box-counting method for certain value of intensity in HarFA software. Detailed information concerning image analysis and its results are included in a supplement to this paper.

Note: figures presented in the text, circular or square, were cut from the images of a circular film, prepared in a glass Petri dish. The shape of figures was chosen intentionally, to illustrate symmetrical or unsymmetrical patterns. Concentric fine lines in the background of some images were caused by an optical lens of the 3M overhead projector.

4. Results and discussion

The creation and fixation of self-organized pattern in the polymeric layer during the solvent evaporation is highly complex process. Not only factors stated in the basic mathematical relation (1) can play significant role.

$$Ma = \frac{(-\partial\gamma/\partial T)\Delta T d}{\kappa\mu}. \quad (1)$$

Here, Ma stands for Marangoni number, determining initiation of the BM-instability, the temperature difference between the bottom layer and an open surface ΔT, the thickness of the liquid layer d, dynamic viscosity μ and the coefficient of thermal diffusivity κ. From the technological point of view, when preparing polymeric films at highly non-equilibrium conditions, it is necessary to count with the range of other factors, discussed later in the text. Each experiment was repeated at least three times, to ensure reproducibility of the results.

The results will be presented according to the increasing value of molecular weight ant the molecular weight distribution of 2-HEC, from the reason of the mutual interconnection of parameters determining creation and fixation of BMc in the polymeric layer.

4.1. Low molecular weight

Generally, temperature is the leading factor, determining the result of the solidification process of 2-HEC films, not temperature gradient, as Fig. 1 might suggest. Dominant role of "absolute" temperature was confirmed by results acquired at constant temperature and varying temperature gradient, Fig. 3. The change in the film structure with rising temperature can be attributed to decreasing viscosity and increasing mobility of polymer coils in the solution. Thus, rearrangement at the BMc boundaries is facilitated leading to creation of characteristic relief.

One of the major concerns is to define the stage of the solidification process, when the structure fixation occurs. With increasing polymer fraction in the solution (increase of viscosity), the possibility of BMc formation decreases, Fig. 2. With respect to these facts, 2-HEC samples with increasing solution viscosity and