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Self-organization in dry photopolymerized acrylate films 2. General experimental description

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Abstract

Viscous acrylate mixtures containing a photoinitiator, deposited as a film on a glass plate, after UV irradiation, show well-organized structures. These structures are observed for films irradiated through a lined mask; the formation of wavy relief on the free surface with the same frequency as that of the mask is obtained. Attention is also focused on the sensitivity of these phenomena to adsorption. For films irradiated over the whole surface and for specific compositions, self-organized structures in the form of waves or even hexagonal cells are observed. This generalizes the previous thermodynamic analysis (Part 1). © 1997 Elsevier Science S.A.

Keywords: Acrylate films; Photopolymerization; Self-organization; Surface structure; UV irradiation

1. Introduction

In the presence of temperature or composition gradients in a liquid layer with an open surface or at a liquid–liquid interface, structures and instabilities can appear. Convective patterns, waves (longitudinal or transverse and with or without oscillations) and even turbulences can be observed. As shown in Part 1 [1], the surface characteristics of the layer have a large influence on the behaviour of the system.

Longitudinal oscillations correspond to a Marangoni effect, resulting from convective deformation. Patterned convection can lead to deformation oscillations and even turbulence can be observed. Therefore the surfactant concentration at the surface may be the relevant variable for longitudinal waves and the surface deviation can sometimes be calculated. As outlined by Velarde and Chu [2], capillary gravity waves can be present with a frequency independent of the bulk film viscosity. The theoretical model of oscillation at the air–liquid interface with transverse and longitudinal waves can be treated by a disturbance equation of harmonic oscillator approach.

For the photopolymerization of acrylate films deposited on a glass plate, typical patterns have been observed and are now described. The aim of this study (Part 2) is to show, outside the two typical cases described in Part 1 [1], the different experimental possibilities offered by dry photopolymerization and to try to connect them with the theoretical models. It will be seen that, even in the case of complete irradiation of a thin polymer sample, dissipative structures can appear. This second part is a generalization of the previous observations with alternative irradiated systems.

2. Experimental details

In all the cases described in the following, relief appears at the polymer surface on irradiation. The sample relief is obtained using a UBM profilometer, giving the profile by moving a red laser probe of wavelength 780 nm along the surface.

Experiments have been performed under different conditions with acrylate films. The first example corresponds to the surface of a thin film which is totally irradiated. In a second example, the polymer film is irradiated through a lined mask, as detailed in Part 1, and the influence of temperature has been screened. The effect of the adsorption of a gaseous species has also been examined. The profile height is sensitive to the temperature and composition, and the shape of the profile can be modified.

2.1. Irradiation over the whole sample

A thin film, 80 μm thick, was deposited on a glass plate as a mixture of acrylates and eosin (photoinitiator). The surface

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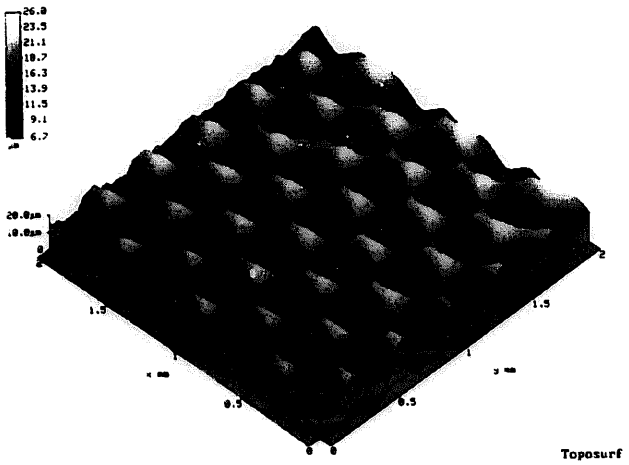

Fig. 1. Cellular self-organization in a completely irradiated acrylate film.

Fig. 2. Wavy profile in a completely irradiated acrylate film.

was then immediately irradiated with a constant luminous flow delivered by a UV lamp. Spontaneously, different types of structure appear. As shown in Fig. 1, hexagonal cells are present, and waves can also appear as shown in Fig. 2. In Fig. 1, hexagonal cells with a size of 100 μm (each side) and a depth of 10 μm are present. In Fig. 2, only waves appear on total irradiation.

2.2. *Irradiation through a lined mask*

According to the experimental conditions described in Part 1, for an acrylate film irradiated with a UV–visible lamp through a lined mask, different kinds of profile can be observed. With a lined mask presenting 20 lines mm^{-1}, the profile at 23 °C is quite sinusoidal; at a temperature of 50 °C, after 15 min of irradiation, modulation is observed as shown in fig. 3 of Part 1. The irradiation times are usually between 1 and 15 min [5].

Further experiments performed with the surface adsorption of gaseous species showed a modification of the relief height. The acrylate film deposited on a glass plate was first exposed for 2 min in an atmosphere equilibrated with an organic vapour having a sufficiently high vapour pressure at ordinary temperature. Irradiation was then performed in the same conditions. The height of the relief increases as shown in Fig. 3 and the lag time at the beginning of the kinetics is longer with acetone adsorbed. In an atmosphere enriched in nitrogen surrounding the acrylate plate, it is observed that the relief is higher than in air and the inhibition time is non-existent, as shown in Fig. 4.

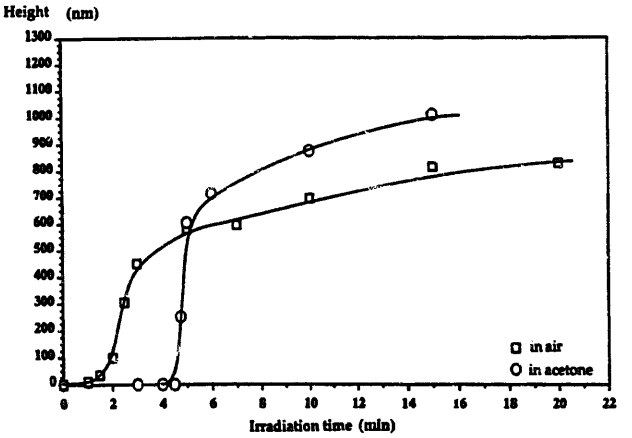

Fig. 3. Relief height variation at the surface of an acrylate film irradiated in air through a 20 lines mm^{-1} mask and in the presence of acetone vapour.

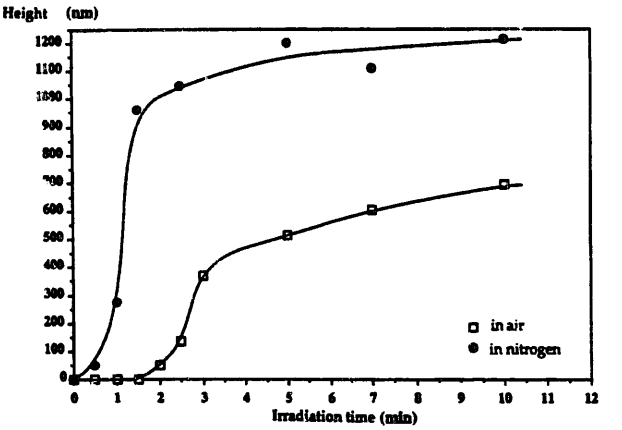

Fig. 4. Relief height variation at the surface of an acrylate film in the presence of nitrogen-enriched air.

These last experiments show the influence of the surface properties on relief formation, all other conditions being identical for the preparation of the acrylate films.

3. Discussion

The complete irradiation of an acrylate film was first examined as given in Section 2.1. The formation of waves and hexagonal cells leads to self-organization at the surface of the film, corresponding to the irreversible thermodynamics of liquid surfaces.

The theoretical approach of liquid surface deformation [1] takes into account the general case of evolution with the observation of different structures: waves, cells and sometimes turbulence. Therefore when the open surface of a liquid layer is excited with thermal or surfactant gradients, convective instabilities can appear. The stress conditions at the liquid surface are determinative for such behaviour. Ripples due to transverse motions have been studied [3] and longitudinal Marangoni-type waves along the surface have been discov-

ered by Lucassen [4]. Therefore the presence of a surfactant monolayer, either by adsorption or by spreading, gives elastic properties. In general, the transverse and longitudinal components appear simultaneously and cannot be separated. The passage from a state of rest to a time-dependent state goes through a so-called thermodynamic bifurcation. The liquid interface is treated as a genuine oscillator, which permits a transition from patterned convection to oscillations and interfacial turbulence to be previewed [2]. Such an evolution appears clearly in the qualitative results obtained for the completely irradiated acrylate film.

Considering the general theoretical approach of Hennenberg et al. [6], detailed in Part 1 of this paper [1], the stability can vary essentially as a function of the bulk and surface properties of the polymer layer. This is also illustrated by the first series of acrylate samples described, where different levels of organization and stability are observed on changing the irradiation conditions.

In the second type of experiment, the results obtained with different adsorbed species show clearly the influence of the surface properties on the kinetics of relief formation. The height increases, as shown in Fig. 3, for experiments performed in an acetone atmosphere [7] in comparison with the basic acrylate mixture in air, and this is in accordance with the model given in Ref. [6] taking into account the influence of the properties of the outer layer of the film.

All these results show the complexity of such thin polymerizable films.

The association of surface properties and unavoidable gradients produces numerous possibilities of behaviour, which can be exploited for information storage in dry photopolymerization. Spatial patterns corresponding to double diffusion in chemical photoreactions have been mentioned [8], but as previewed in theoretical approaches, other evolutions and instabilities can appear. With laser irradiation, some examples of self-organization in optical systems have been reported [9].

The typical examples given here provide a good illustration of the extent of this subject in the field of polymer film photopolymerization.

4. Conclusions

In the field of self-organization, UV–visible photopolymerized films appear to be very rich models for the formation of patterns and waves. Multiple optical applications are associated with these peculiar properties corresponding to refractive index modification.

In the case of photopolymerized acrylate films, dissipative structures with self-organization can appear via total or alternating irradiation in the experimental conditions described above, which illustrates the numerous possibilities of modification in acrylate thin films. Acrylate thin films and their UV–visible photopolymerization are suited to the application of irreversible process thermodynamics. Other polymer films under alternating irradiation can also show similar properties as recently observed in our laboratory.

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