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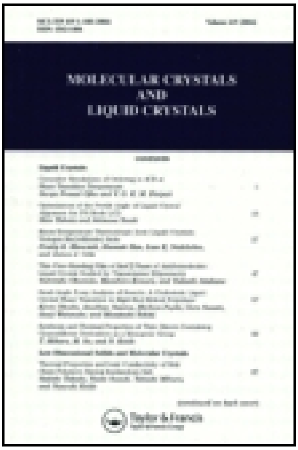

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Morphology and Interface of Liquid Crystal/Polymer Composite System at Nano Scale :A Model Investigation

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Morphology and Interface of Liquid Crystal/Polymer Composite System at Nano Scale : a Model Investigation

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Morphology of the liquid crystal/polymer composite has been investigated at the microscopic level as a model investigation in order to elucidate the nature of microscopic phase separation. It has been observed that the modification of surface interaction between liquid crystal and polymer is different for different system, which is apparent from the nature of phase separation at microscopic scale.

Keywords: Liquid Crystal/ Polymer Composite; Morphology; Nano Scale

Introduction

Dispersion of liquid crystals and polymers forms a broad class of materials composite in which the weight concentration of polymer can range from 80% to down 0.5% depending on the application in view and materials used in the dispersion[1-4]. The structure in equilibrium (***Morphology***) in these class of materials, after reaching the phase separation, has significant influence on electro-optics of the composite. Here, the liquid crystal phase separates either into droplets/domains separated by polymer matrix for high polymer concentration [1,2] or into inter-connected channels for low concentration polymer, a bicontinuous phase [3-5].

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These two types of the composites as mentioned above have one thing in common i.e. the phase separation in these systems takes place at the ***microscopic*** scale. The average physical properties depend on the details of phase separation kinetics on nanoscale in these systems, whereas large area of interface between liquid crystal and polymer governs the optical properties of the composites [6,7]. Research in this light has been focused mainly on the *macroscopic phase behavior* e.g. polymerization kinetics[8,9] and for many reasons, the polymer matrix in the composite has been investigated by various methods, in particular, by electron microscopy[3,9] and confocal microscopy[10,11] depending on the concentration of the polymer in the composite.

Here an understanding of the morphology of the composite in the bulk, and of the interface between two phases at *microscopic level* is quite significant in order to control the properties of the composite for application purposes. However, the direct morphological observation of polymer /liquid crystal composite system at nanoscale resolution is difficult to achieve due to liquid like nature of liquid crystal and glassy or rubber like matrix of polymer in conventional composite system. The achieved resolution until now is 0.2 micron lateral in confocal microscopy. In order to elucidate the microscopic morphology up to 10nm resolution, we have used the polymers and liquid crystal monomer (from Danippon Inc.) for composition. Liquid crystal monomer was used instead of low molar mass liquid crystal in order to freeze the molecular order [12] of liquid crystal in the composite. We have applied atomic force microscopy (AFM) to get images of such samples at high resolution. The AFM was operated in tapping mode where phase of the tapping signal allows to discriminate areas of different surface properties[13-17].

It has been reported that the electro-optical characteristics of the film with liquid crystal as continuous channels are advantageous compared to that of the film with separated domains[18]. The work reported here is motivated to see the microscopic phase separation and the channel structure with different polymers in the composition prepared under same experimental condition.

Experiment

The composite film was prepared by solvent induced phase separation (SIPS) method. The materials used were poly(methyl methacrylate) PMMA,

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Mw = 10,000, Tg = 353K; and poly (diisopropyl fumarate) Pdi-iPF Mw = 150,000, Tg = 500K~decomposition & Liquid Crystal Monomer (Mixture E, UV Curable) Δn = 0.151 $\Delta\varepsilon$ = +0.7 N-I Temp. = 319K.

First to ascertain the nature of phase separation in composite system, polymer and liquid crystal monomer (30:70 wt % ratio) were added along with chloroform (as a solvent) and stirred for 24 hrs to prepare a homogeneous mixture. This mixture was then bar coated on ITO glass using a doctor blade to obtain films of 15-20μm thickness. The films were then allowed to dry for 48 hrs at 301K to achieve equilibrium of phase separation. The composite films prepared on the ITO glass were covered by another ITO coated glass using 10μm glass beads spacers and subsequently, optical microscopic observation was performed. Thick composite films of PMMA/liquid crystal monomer, Pdi-iPF/liquid crystal monomer, (in weight ratio 70:30 with 20wt% chloroform) were prepared respectively, by the above mentioned procedure in a special manner so as to obtain the film of 0.8mm thickness after curing by UV light for 10min at 10mW/cm^2.

For AFM imaging, thick cured films of PMMA/liquid crystal monomer and Pdi-iFF/liquid crystal monomer, were used. The instrument for the AFM imaging was a multimode nanoscope IIIa (Digital Instruments, Santa Barbra , USA). It was opened in the tapping mode with separate electronics for the evaluation of the phase shift between the excitation and responding oscillation of the cantilever. We used TSP cantilevers (Digital Instruments, Santa Barbra, USA). It was operated in the tapping mode with separate electronics for the evaluation of phase shift between the excitation and the responding oscillation of the cantilever. We used TESP cantilevers (Digital Instruments) with spring constants of 17-64N/m and 260-340kHz resonance frequency. The excitation was chosen such, that the signal of free oscillation (free amplitude) reached 1.5V to 2.5V. Two imaging set points were applied: 95% of the free amplitude, referred to as " soft tapping" and "hard tapping" respectively.

Result & Discussion

Figs. 1(a) & (b) are the optical micro-graphs of the polymer and liquid crystal monomer composite films. There seems scattering zones to be quite different from the droplet morphology but are similar to the polymer network morphology in bicontinuous system.

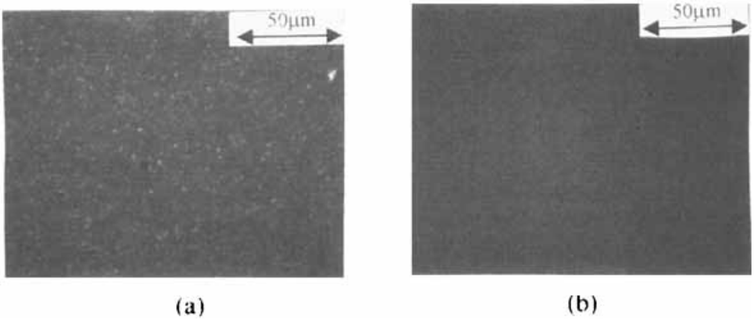

FIGURE 1 Optical micro-graphs of the polymer and liquid crystal monomer (30:70 by weight ratio) composite film under cross Nicole. (a) PMMA/liquid crystal monomers (b) Pdi-ipF/iquid crystal monomers.
(See Color Plate VI at the back of this issue)

AFM images (tapping mode) of the cross sectional surface of the PMMA/LCM composite film are shown in Fig.2. The surface of the composite film exposes bubble shaped clusters partly embedded in a thin interconnected structure. Since cutting the sample produced a rough surface with corrugation up to 1μm in height, the imaged sample areas had to be chosen very carefully in order to minimize tip artifacts. Images were reproducible over time and with different tips. Thus the influence of tip artifacts is minimized. In general, on approaching the sample surface with AFM tip, the interaction between tip and sample changes from attractive to a repulsive regime in close proximity to the surface[19]. The best discrimination between polymer and the liquid crystal in the phase tapping images was obtained with a working set point in the repulsive regime near the transition from the repulsive to the attractive interaction regime. Due to high sample viscosity imaging under the repulsive force regime did not yield clear images. The discrimination between different materials by the tapping phase is based on different interaction between the tip of cantilever and the surface of such materials and a different response of the sample surface to the interaction force. Therefore, the viscoelasticity of the sample material greatly influences the tapping phase. The topography of the sample is represented in Fig. 2(a) height image, while in Fig.2(b) the deviation of the oscillation amplitude from the set point is depicted(amplitude image). Fig.2c shows the material dependent tapping phase contrast. The phase shift between bright and dark is 80 degree. On this image the two material phases can be distinguished clearly, the bright regions corresponds to highly interconnected structure in the amplitude image, the dark ones to the embedded bubble like clusters. The information of scans of different area allowed to assign the bright region in Fig. 2(c) to the cross -linked liquid

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crystal polymer phase where the molecular order aggregation after phase separation state was frozen on curing after phase separation. In the case of Fig.2 PMMA was dispersed in liquid crystal monomers where liquid crystal phase was separated out as contineous channel, i.e. interconnected domains. Since the microscopic phase separation differ from the macroscopic, the surface area fraction of the PMMA to LC is not in accordance with the volume fractions.

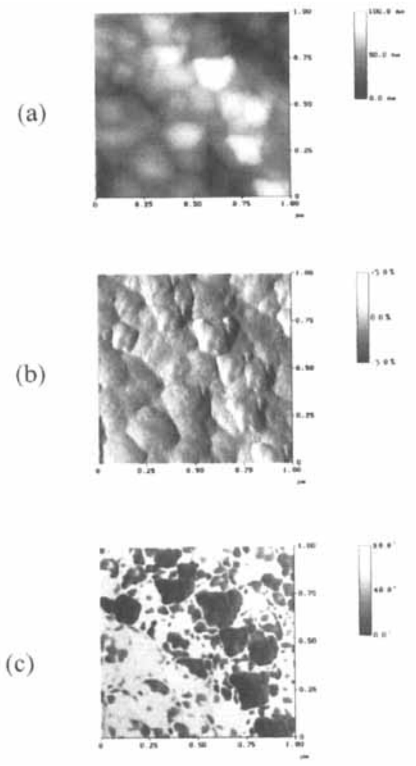

FIGURE 2 AFM image (tapping mode) of the cross sectional surface of the composite film (cured after phase separation, composition PMMA/Liquid crystal monomer 30:70 by weight ratio, (a) height image, (b) amplitude image(deviation of oscillation amplitude from setpoint), (c) phase image(brighter areas =larger phase delay).

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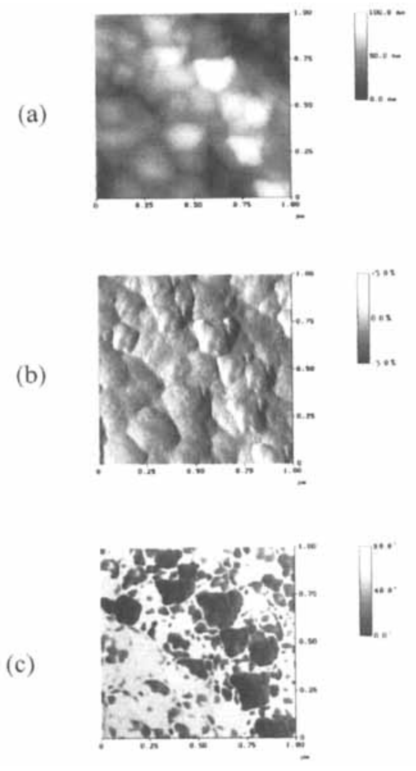
In this figure the ridge like topography induced a shift of the working point of the AFM from the repulsive (upper left part of the images, dividing the images into two be the diagonal given by the ridge in the topography) to the attractive regime(lower right part). In the upper left part of the figure 2(c) (repulsive imaging conditions) it is clearly possible to discriminate two material phases, a cubic like structure (dark regions) embedded in a network like bright background. Under attractive imaging conditions (lower right), cubic like features seem to be covered by a thin film, which only in some parts can be penetrated (or removed) by the AFM tip, thus preventing material contrast in the lower right part of the image.

To compare the nature of the morphology for different polymers in the composition, the Pdi-iPF/ LCM samples were scanned subsequently as shown in Fig. 3 (a) ~ (c). There, dark contrast regions are Pdi-iPF and bright contrast regions are cured liquid crystal monomer phase. The morphology was not like PMMA/LCM sample. The interface between the polymer phase and liquid crystal phase was quite apparent in Pdi-iPF/LCM system as shown in Fig 3(c), taken over the same sample.



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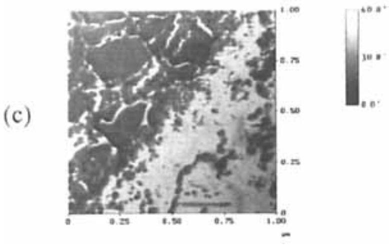

FIGURE 3 AFM image (tapping mode) of the cross sectional surface of the composite film (cured after phase separation, composition Pdi-ipF/liquid crystal monomer 30:70 by weight), (a) height image (b) amplitude image (deviation of oscillation amplitude from setpoint), (c) phase image(brighter areas = larger phase delay).

Conclusion

The phase separation at microscopic scale is different from macroscopic one. For different polymer system, the modification of surface interaction between liquid crystal and polymer is different and hence the properties of electro-optics. In particular, where morphology after phase separation is concerned as a factor to influence the electro-optics, the surface modification at sub-micron level is an important factor.

Acknowledgement

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