Microelectronic Engineering 103 (2013) 42–48

Contents lists available at SciVerse ScienceDirect

Microelectronic Engineering

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

Structure control of lattice-patterned liquid crystals–polymer composites prepared by polarization-selective UV-curing through the addition of a fluorinated acrylate monomer

Shi-Joon Sung [a], Eun-Ae Jung [a], Kyoseung Sim [a], Dae-Hwan Kim [a,*], Kuk Young Cho [b]

[a] *Daegu Gyeongbuk Institute of Science and Technology (DGIST), 50-1 Sang-ri, Hyeonpung-myeon, Dalseong-gun, Daegu 711-873, Republic of Korea*
[b] *Division of Advanced Materials Engineering, Kongju National University, 275 Budae-dong, Cheonan, Chungnam 331-717, Republic of Korea*

ARTICLE INFO

Article history:
Received 10 April 2012
Received in revised form 3 August 2012
Accepted 15 September 2012
Available online 16 October 2012

Keywords:
Liquid crystal–polymer composite
Photo-induced phase separation
Patterned polymer walls
Fluorinated acrylate
Polarization-selective UV curing

ABSTRACT

The formation of lattice-patterned liquid crystal (LC)–polymer composites by polarization-selective ultraviolet (UV) curing of prepolymers containing cinnamate functional groups is known to be an effective method for controlling the interfacial properties between LC and polymer walls. However, due to the good miscibility of cinnamate functional groups with LC, phase separation between LC and prepolymers is insufficient, and challenges remain with regard to control of the phase separation structure. In this work, we focused on improving the phase separation behavior between LC and a prepolymer containing a photoreactive cinnamate oligomer by introducing a fluorinated acrylate monomer. The results showed that the larger difference in the solubility parameter between the fluorinated acrylate and LC improved the phase separation behavior between the LC and prepolymer, resulting in the fabrication of a more accurate and clear lattice structure of polymer walls. In addition, the introduction of a fluorinated acrylate monomer was found to slightly influence the control of the interaction between LC and polymer walls; this was verified by the decrease in driving voltage of LC–polymer composites. By using the fluorinated acrylate monomer as a component of prepolymers, control of the lattice structure and interfacial properties of polymer walls formed by polarization-selective UV curing becomes possible.

1. Introduction

Various types of liquid crystal (LC)–polymer composites have been widely studied for a broad range of applications, such as displays, shutters, and membranes [1–6]. In particular, flexible displays based on LC–polymer composites have been extensively studied and widely used for display applications because of their higher mechanical stability [7]. From many types of LC–polymer composites, micro-wall structure of LC–polymer composite is one of the most promising fabrication methods for flexible display devices [8–15]. In this structure, LC molecules are isolated in pixels surrounded by inter-pixel vertical micro-scale polymer walls. In order to fabricate polymer walls within the gap between substrates, a mixed solution of LC and Ultraviolet (UV)-curable prepolymers is inserted into the gap. UV light is then irradiated on the selective regions to form polymer walls by crosslinking the prepolymers and the monomer concentration is reduced by the UV-induced photo-polymerization of prepolymers. In the process of photo-polymerization, monomer diffusion occurs for maintaining the equilibrium in mixed solution and LCs are repelled from the UV-irradiated regions. Finally, the solid polymer walls are formed in the UV-irradiated regions and the LCs are isolated between the polymer walls.

Lattice-patterned LC–polymer composite shows not only good mechanical stability but also nearly the same optical behavior as that of the normal LC mode. However, lattice-patterned LC–polymer composite has many boundary regions between LC and polymer walls, and thus the movement of the LC molecules at the boundary regions is considerably disturbed by the interaction between the LC molecules and the polymer walls. Therefore, in the process of operating LC–polymer composite devices, the driving voltage of LC molecules surrounded by polymer walls would be much higher than normal LC devices due to the hindered movement of LC molecules, which is an important issue for the electro-optical performance of flexible display devices.

In order to utilize LC–polymer composites as flexible display devices, the electro-optical performance of LC–polymer composites needs to be improved, and control of the interaction between the LC and polymer domains is an important factor for obtaining better electro-optical performance. In our previous work, polarization-selective ultraviolet curing of prepolymers containing a cinnamate oligomer, which is well known for its polarization-selective photo-dimerization reaction, was proposed to control the orientation of

---

* Corresponding author. Tel.: +82 53 785 3720; fax: +82 53 785 3739.
E-mail address: monolith@dgist.ac.kr (D.-H. Kim).

0167-9317/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.mee.2012.09.010

LC molecules near the polymer walls [16,17]. Polarized ultraviolet (UV) irradiation on prepolymers containing a cinnamate oligomer was found to be effective in improving the electro-optical performance of lattice-patterned LC–polymer composites. However, when using a cinnamate oligomer as a prepolymer, difficulty in controlling the micro-wall structure still remains, and the polymer wall thickness becomes larger than the pattern of the photomask. According to the increase of polymer wall thickness, aperture ratio of LC device decreases and this induces a decrease of brightness and an increase of power consumption of the LC devices. Due to the good miscibility of a cinnamate oligomer with LC, it is difficult to control the phase separation structure between LC and prepolymers containing a cinnamate oligomer. In order to improve the phase separation structure between LC and prepolymers containing a cinnamate oligomer, the miscibility between LC and prepolymers must be controlled separately.

In this study, we have tried to control the micro-wall structure and electro-optical performance of lattice-patterned LC–polymer composites independently by using multi-component prepolymers. The strategy for applying the polarization-selective UV-curing of a cinnamate oligomer to the fabrication of lattice-patterned LC–polymer composites without the deterioration of the micro-wall structure was suggested. In order to control the phase separation behavior between LC and prepolymers, a fluorinated acrylate monomer was used for a constituent for prepolymers containing a cinnamate oligomer. Miscibility between LC and prepolymers was theoretically estimated by comparing the difference of solubility parameter between of each constituent for prepolymers and LC. The miscibility between LC and prepolymers was found to be correlated with the micro-wall structure of LC–polymer composites. By adjusting the composition of a fluorinated acrylate monomer in prepolymers, it was possible to control the polymer wall structure. Moreover, in spite of adding a fluorinated acrylate monomer, it was possible to control the interfacial properties between LC and polymer walls by using polarized-UV irradiation. Polarization-selective UV-curing of multi-component prepolymers was still effective for the control of electro-optical properties of lattice-patterned LC–polymer composites.

2. Materials and methods

2.1. Materials

The cinnamate oligomer of polyethylene glycol-dicinnamate (PEG-diCi) was synthesized by using a PEG of molecular weight 600 (Aldrich Co.) and cinnamoyl chloride (Aldrich Co.), in reference to the results of our previous study [17]. In order to investigate the effects the addition of a fluorinated acrylate monomer on the lattice-patterned LC–polymer composites containing a cinnamate oligomer, pentafluorpropyl acrylate (PFA, Aldrich) was used as a monomer together with ethylhexyl acrylate (EHA, Aldrich). For preparation of the prepolymers, ternary-component prepolymers were prepared by blending the PEG-diCi, EHA, and PFA with a photoinitiator (Darocur 4265, Aldrich) and crosslinker (polyethyleneglycol diacrylate, PEGDA, Aldrich). The detailed chemical compositions of the ternary-component prepolymers are summarized in Table 1.

2.2. Fabrication of lattice-patterned LC–polymer composites

The effect of prepolymer composition on the phase separation behavior between LC and prepolymers was investigated by preparing lattice-patterned LC–polymer composites using the ternary-component prepolymers. LC cells were prepared by using two ITO glass slides coated with polyimide that was rubbed on; between them, the LC mixture (E7, Merck, 50 wt.%) and prepolymer (50 wt.%) were injected by capillary effect at 100 °C, which is above the LC–prepolymer mixture's clearing temperature. In order to form a lattice structure of LC–polymer composites, LC cells were maintained at 100 °C, and they were irradiated with UV light for 800 s through a photomask having $300 \times 300\ \mu m^2$ dark square patterns with 30 μm spacing. 350 W high pressure mercury lamp was used for an UV irradiation system and the intensity of UV light at 365 nm was maintained at 10 mW/cm^2. In order to induce an anisotropic photoreaction of cinnamate functional groups, a UV linear polarizer (20LP-UV, Newport) was used for UV irradiation. Fig. 1 illustrates the fabrication process of lattice-patterned LC–polymer composites via photo-induced phase separation of the LC–prepolymer mixtures.

2.3. Characterization of lattice-patterned LC–polymer composites

For the investigation of microscopic phase separation structure of lattice-patterned LC–polymer composites, polarized optical microscope (ECLIPSE LV100D, Nikon) was used. In order to investigate the interfacial properties between LC and polymer walls of lattice-patterned LC–polymer composites, the driving voltage of LC molecules surrounded by polymer walls was measured by using an electro-optic measurement system. For the comparison of surface properties of polymer walls, water contact angle of UV-cured prepolymer thin films was measured at a temperature of 23 ± 1 °C using the sessile drop method with contact angle measurement system (Pheonix300, Surface & Electro-Optics Co.).

3. Results and discussion

The photo-induced phase separation procedure is based on the phase separation between the miscible monomers and LC during the curing reaction of monomers; this results in the formation of domains of wall structure made up of photocured monomers and domains of LC. In our previous report, it was shown that the selection of the monomer and polarization-selective curing of the monomer significantly influence the orientation of the LC molecules near polymer walls after phase-separated structure formation [17]. However, precise control of the wall thickness from the pattern width of the photomask as well as the alignment of LC near the wall is important to obtain the necessary image quality of the cells in the display. Incorporation of the photodimerizable PEG-diCi in prepolymer composition produced well-aligned LC molecules near the polymer walls, leading to improved display quality due to the similar chemical structure of the cinnamate functional group with LC molecules. However, this also affects the formation of the wall structure integrity. In order to control the phase separation with the aim of improving the polymer wall formation and obtaining good display quality near the wall structure, a monomer containing fluorine molecules was introduced to the LC–prepolymer composition.

It is important to investigate miscibility between the LC and photoreactive monomer to predict the phase separation of the resulting components after photocuring. Miscibility between LC and prepolymers can be measured by the solubility parameter δ of the molecules; this parameter is normally expressed as the square root of the cohesive energy density (E_c) [18,19].

$$\delta = E_c^{0.5}$$

Cohesive energy density can be calculated from the group contribution theory that E_c of a molecule can be obtained by summing the E_c values of all the groups that compose the molecule [20]. The miscibility between LC and prepolymers can be estimated through the difference in their solubility parameters; if the difference is