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Ferroelectric Liquid Crystal-Polymer Composites: A Novel Display Material

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Liquid crystals constitute an important class of display materials used in liquid crystal display (LCD) devices. Although, these materials were discovered over a century back (1988), but they gained importance about mid 1970's when used in seven segment display devices like digital watches, calculators *etc*. Since then, the subject became a household name considering the market potential and varied use in consumer electronics. At present, LCD's constitute about 68% market share in display industry starting from small seven segments to high definition projection displays. Behind this technological development, liquid crystalline materials play a very important role. In this talk, we shall discuss the work being carried out in our research group at TIET in this subject. We will also deliberate on the development of ferroelectric liquid crystal-composite materials and physics behind the LCD technology.

Key Words: Polymer dispersed ferroelectric liquid crystal, Polymerization induced phase separation, Polysiloxanes, Ferroelectric liquid crystal, Spontaneous polarization, Polymer viscosity, Alignment.

INTRODUCTION

De Gennes[1] first contemplated that liquid crystal–polymer gels can form composite materials and shall exhibit interesting electro-optic properties. This idea generated considerable interest in these materials and in mid-1980s, polymer dispersed liquid crystals (PDLCs) attracted significant attention among various scientific groups[2,3]. The PDLC displays are simple to make, flexible, have a minimal fabrication cost, high brightness and small switching time[4,5]. These materials were found to be of great interest for light control devices like optical shutters, switchable windows, thermo-optic and electro-optic switches, memories, gas flow sensors, optical sensors, and optical gratings[5-8] *etc*. These composite materials present a polymer film with liquid crystal droplets dispersed therein. A large variety of structures are possible depending on concentration, viscosity, nature and properties of both polymer and the liquid crystal. PDLC films can be broadly prepared by four different techniques; however, one of most widely employed method is the polymerization induced phase separation (PIPS)[9-11]. The polymerization is induced through the application of heat or UV irradiation depending on the type of initiator. Variations in the phase separation process can lead to different morphologies, which have profound effects on the electro-optic characteristics of the PDLC films.

The dispersion of ferroelectric liquid crystals in a polymer matrix also gives rise to several interesting electro-optic effects. These composites are known as polymer dispersed ferroelectric liquid crystal (PDFLCs). PDFLC have been demonstrated to be at least three orders of magnitude faster than nematic-based displays commonly used in portable computers. The switching field of PDFLC films depends on a variety of factors amongst which film morphology plays a crucial role[12–14], which is strongly dependent on composition, curing parameter, nature, kind of polymer, viscosity of the polymer, structure of the polymer, and also the mutual solubility of ferroelectric liquid crystal (FLC) and prepolymer[15–17]. These materials exhibit unique linear and nonlinear optical properties, which are expected to find use in liquid crystal displays (LCDs).

It has also been reported that the contrast ratio and viewing angle of ferroelectric liquid crystal devices are superior to all other LC displays. It has also been reported that the performance of a PDFLC device relies on the uniformity of alignment of the liquid crystal molecules in the device. Therefore, in the present work, an attempt has been made to study the behaviour of ferroelectric LC droplets dispersed in flexible polymer matrices synthesized in our laboratory[15,16]. Efforts were also made to study the influence of polymer viscosity, electric field, temperature and also the alignment of liquid crystal droplets in PDFLC composite films on film morphology and the electro-optic properties and also to understand the structure-property correlation of the complex system that require precise morphological and processing control. Advance experimental and theoretical studies on the dichroic polymer dispersed liquid crystal materials are in evolution to explore the physical parameters for the opto-electrical device and displays using ferro-electric liquid crystal composites system.

EXPERIMENTAL

The polysiloxane dispersed ferroelectric liquid crystal (PDFLC) composite films were prepared using ferroelectric liquid crystal mixture (ZLI –3654) exhibiting SmC* phase between -30°C and 62°C and poly dimethyl siloxanes of different viscosity grades by solvent induced phase separation followed by the polymer induced phase separation techniques[3]. The poly dimethyl siloxane and FLC mixture (ZLI-3654) in 1:1 wt/wt ratio were mixed in an appropriate amount of the solvent diethyl ether. The solvent was evaporated after ensuring the proper mixing of the material and the homogenous PDFLC mixture was cross-linked using the room temperature vulcanizer in 0.2% ratio. Some other PDFLC samples have been prepared in a fixed 30:70 wt/wt ratio with

Norland polymers and FLC mixture ZLI–3654. The aligned PDFLC composite films were prepared by pre-treating the indium tin oxide (ITO) coated glass substrates by spin coating with the polyamide (nylon 6,6) solution at 1400 rotations per minute speed and then the coated substrates were heated under vacuum to remove the traces of the solvent and to get a uniform film coating on the glass substrates. The treated glass substrates were then rubbed uni-directionally using nylon cloth to induce the planar alignment. The method of polysiloxane synthesis and sample preparation is discussed elsewhere[17].

In order to ensure proper mixing, this homogenous mixture was heated to isotropic temperature in a vacuum oven and simultaneously shaken rapidly. A thin sample cell consisting of two indium tin oxide (ITO) coated glass substrates were used. The cell gap was controlled by a mylar spacer of thickness 10µm. The mixture was then filled between two ITO coated glass substrates by capillary action after heating the material to its isotropic temperature. The sample cells were sealed by optical adhesive and exposed to UV light (intensity *ca.* 2 mW/cm^2) for about an hour at room temperature. The sample was placed in a programmable temperature controller coupled to hot stage (Model TP 94 and THMS 600) and then cooled down to room temperature @ 0.1°C per min. Uniform dispersion of ferroelectric LC droplets in the polymer matrix were viewed under crossed polarizers at a magnification of 10X through Olympus polarizing microscope (Model BX-51P) fitted with charge coupling device (CCD) camera and interfaced with computer. The opto-electric responses were studied when an electric field was applied to the sample using a function generator (Philips FG -8002) and detected using photo- multiplier tube (Model RCA 931-A). The data was acquired in the computer interfaced with digital storage Oscilloscope (Tektronix Model TDS 2024). Spontaneous polarization studies were carried out using polarization current technique[18].

RESULTS AND DISCUSSION

Droplet morphology

The optical textures of PDFLC (ZLI-3654) composite films using polysiloxanes of different viscosity grades were observed under cross polarizers using Olympus polarizing microscope (model BX51P; Japan). As observed in Table 1, the liquid crystal droplet size is smaller in PDFLC systems of lower viscosity and increases as the viscosity increases. This increase may be due to the difficulty in the droplet formation in high viscous polymer matrix because of the strong surface forces exerted by it. Liquid crystal droplet size increases by increasing the polymer viscosity. The droplets appear uniformLy dispersed in polymer matrix only in the low viscous polymers. This may be due to the partial solubility and better mutual interaction of polymer-LC systems for low molecular weight polymers.

TABLE 1
EFFECT OF THE POLYMER VISCOSITY ON DROPLET SIZE OF PDFLC COMPOSITE FILMS

Intrinsic viscosity (dl/g)	Average droplet size (μm)
0.06	3-5
0.08	17
0.11	27
0.13	40
0.15	50

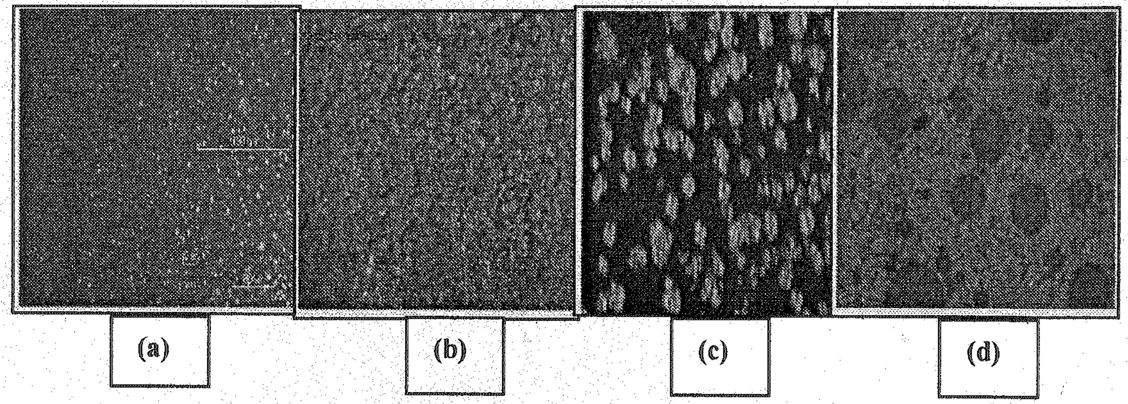

Fig. 1. Polarizing microscopic textures of PDFLC unaligned composite films at polymer intrinsic viscosity (a) 0.06 dl/g, (b) 0.08 dl/g, (c) 0.11 dl/g and (d) 0.15 dl/g

Droplet size was also controlled by the polymer-curing rate. As polymer viscosity decreases, the dispersion as well as distribution of the curing mixture (tetraethoxy silane and dibutyl tin dilaurate) in the polymer increases resulting to the higher crosslinking density (tight network formation). Therefore, the liquid crystal molecules distribute in the free volume of uniform network leading to the small and uniform droplets. At high viscosity, the uniform distribution and mixing of the curing mixture is difficult causing the non-uniform and bigger droplets. The predicted network morphology of the system is shown in Fig. 2.

Spontaneous polarization

Ferroelectricity in liquid crystals is a specific property of smectic C* liquid crystal phase. They exhibit spontaneous polarization in the absence of the electric field due to molecular asymmetry, which makes them ideal for use in fast electro-optic switching display devices. The spontaneous polarization (P_s) gives information about the internal structure of the mesophase and also

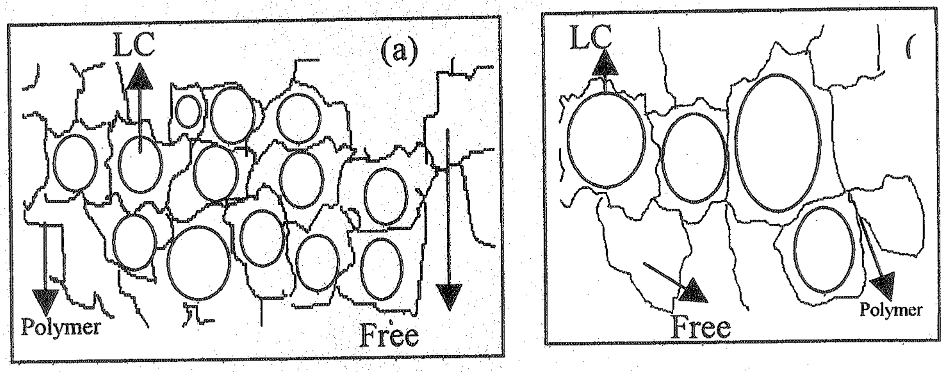

Fig. 2. Predicted network structure of crosslinked polysiloxane systems (a) polysiloxane of low viscosity (b) polysiloxane of high viscosity

about the quality of the phase separation since it is directly correlated to the fraction of switching molecules. Polarization switching responses were measured using field reversal technique. Spontaneous polarization (P_s) of the unaligned and aligned PDFLC composite films was calculated using polysiloxanes and NOA polymers of different viscosity.

We observed that with the increase in the polymer viscosity, the spontaneous polarization decreases irrespective of the nature of the alignment. It has also been observed that in all the polymer systems, the spontaneous polarization of aligned polysiloxane dispersed ferroelectric liquid crystal composite films is higher than that of the unaligned PDFLC composite systems.

The spontaneous polarization of aligned PDFLC films prepared by a polysiloxane of intrinsic viscosity 0.06 dl/g is found to be 21.28 nC/cm^2. Spontaneous polarization value rises to 27.28 nC/cm^2 after surface treatment using polyimide. The same trend is observed in all the PDFLC systems prepared by different viscosity grades. This may be due to the orientation of the liquid crystal droplets along a particular direction and the induction of the planar alignment in pre-treated ITO coated glass substrates.

The spontaneous polarization for UV cured PDFLC composite films at room temperature in presence of an electric field (100V_{pk-pk}) were also measured. Our results indicate that the PDFLC sample of lower polymer viscosity (NOA-73) shows higher P_s (*ca.* 10.60 nC/cm^2) than the sample with higher polymer viscosity (NOA-68) [P_s *ca.* 6.45 nC/cm^2] whereas the pure ferroelectric liquid crystal mixture (ZLI-3654) has a P_s (*ca.* 23 nC/cm^2) at 30° C. Thus the polymer viscosity affects P_s and lowers it by about 50% in low viscosity polymer matrix and about 30% in high viscosity polymer matrix. Over the whole temperature range studied, we found that polarization decreases but at the same time flexibility in the composite films has enhanced.

Conclusions

Polysiloxanes were synthesized and characterized for the preparation of polymer-dispersed ferroelectric liquid crystal films. The electro-optic responses of aligned PDFLC composite films are better than that of the unaligned composites in both polysiloxane and Norland based system. The spontaneous polarization decreases with increase in the polymer viscosity irrespective of the nature of alignment. Polysiloxane-dispersed liquid crystals have low T_g, greater flexibility, and mechanical properties compared to conventional polymers. This makes Polysiloxane-dispersed ferroelectric liquid crystals ideally suited to electro optic applications in several display technologies.

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