Investigation of liquid crystal dispersion and dielectric relaxation behavior in polymer dispersed liquid crystal composite films

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ABSTRACT

Dispersion dynamics in composites of PMMA-BA and LC E44 were investigated using dielectric relaxation spectroscopy. Morphological studies have shown the homogeneous distribution of LC droplets in the polymer matrix. The outcome was deduced in terms of shape and size of LC droplet, interfacial charge-layer effect, glass transition temperature of composites and miscibility of LC in polymer. The temperature dependent dielectric relaxation spectra have been studied. It was observed that the intensity of Maxwell–Wagner interfacial polarization peak varies with respect to the applied temperature. The high-frequency relaxation process seems to be the Debye-type behavior due to dipolar rotation around the long molecular axis.

1. Introduction

Various studies on phase behavior and physical properties of polymer dispersed liquid crystal (PDLC) composites have been reported [1–5]. PDLCs have found great significance because of their promising use in advanced optical device applications, such as switchable windows, large flexible displays, or paper like displays for e-books [6–9]. In industrial and institutional research, PDLC films are getting more consideration, as liquid crystal (LC) display devices using these films can be switched to an electrically visible state without the use of polarizer and alignment layer on an electrode and also due to various other advantages like low fabrication cost, ease of production and quick electro-optical response [10]. PDLCs are composed of micron-size droplets of LCs dispersed in solid polymer binder and are formed by phase separation of a primarily homogeneous LC–polymer mixture. The composite film is then sandwiched between two conductive Indium-Tin-Oxide (ITO) coated glass substrates with its conducting sides in contact with the composite film. In this study, the LCs and the polymer are dissolved in a common solvent to create a homogeneous phase. As the solvent evaporates, the LC phase starts to separate in the form of droplets and gets set in between the polymer boundaries. The solution induced phase separation (SIPS) technique is the most common method to obtain desired morphology for many technological applications. The phase separation takes place during the solidification of polymer matrix.

Every material has unique electrical properties dependent on its dielectric nature. An analysis of these materials could give an insight into the behavior of molecules with respect to their electric dipole moments and this would enable tailoring of materials to the desired applications. The multidimensional electrical nature of the LC droplets in the PDLC materials can be attributed to the strong dipole moments of the LC, the interfacial charge layers between the droplets and the polymer matrix or among the electrodes of the PDLC cell arising due to the interactions with the applied electric field. When an external electric field is applied to the LC material, the dipole molecules tend to orient themselves along the direction of the field. Due to the structural variation of PDLC films, one can expect an essential difference between the physical properties of these materials and those of pure liquid crystals, especially the dielectric properties. Dielectric relaxation spectroscopy is a very useful technique to investigate the motion of molecules possessing electric dipole moments. Any variation in electric dipole moments is sensitively detected by the dielectric relaxation measurement as a function of the frequency of an applied electric field [11]. Due to conducting impurities and interfacial charge layer effect, dielectric properties of materials are known to respond to the DC conductivity. The interfacial charge layer effect giving rise to polarization is also known as the Maxwell–Wagner effect [12]. This polarization is generally attributed to the migration of charge carriers to the boundaries between components of the heterogeneous system under the influence of an applied electric field [13]. B.R. Jian et al. have studied the electrical properties of the carbon nanotube added liquid crystal system [14]. They have reported that the dielectric permittivity in the low frequency region is due to a number of factors such as electric-double layers, space charge

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polarization and near-electrode dipole polarization. In the PDLC system, LC organization within the droplets is governed primarily by polymer–LC interfacial interactions and LC–LC interactions [15]. The qualitative evaluation of distribution of relaxation time is characterized by the Cole–Cole plot.
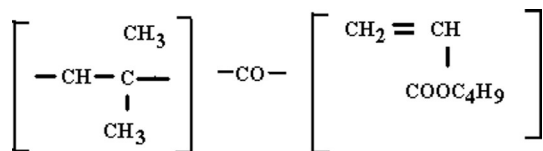
In this experiment, PDLC films have been constructed using nematic LC E44 dispersed in poly(methyl methacrylate-co-butyl acrylate) (PMMABA). The effect of LC concentrations and the morphology on the dielectric properties of the composite films have been investigated.

2. Experimental

2.1. Materials

The nematic mixture consisting of several cyanobiphenyl derivatives E44 (kindly provided by E. Merck, U.K.) was used as the LC material. The polymer used was PMMABA. The physical properties of these constituents are given below.

A. Poly(methyl methacrylate-co-butyl acrylate) (PMMABA)

$$\left[-CH - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - \right] -CO- \left[CH_2 = \underset{COOC_4H_9}{\overset{CH}{\underset{|}{}}} \right]$$

T_g = 90 °C, n_p = 1.4965.
Solubility: In aromatic and chlorinated hydrocarbons.

B. Low molecular weight liquid crystal, E44 (nematic mixture)

$T_{Crystal \to Nematic}(T_{KN})$ = 0 °C, $T_{Nematic \to Isotropic}(T_{NI})$ = 100 °C,
n_o = 1.5284, n_e = 1.7904, Δn = 0.262, $\Delta \varepsilon$ = 17.0.

2.2. Preparation of the PDLC composite films

PDLC films with different compositions (wt/wt.%) of polymer and LC were prepared by the SIPS method [16]. A homogeneous solution of suitable quantity of PMMABA and E44 in chloroform (solvent) was prepared. This solution was subsequently poured on ITO-coated glass substrate at room temperature (25 °C). The glass plate was kept floating on mercury to get a uniformly thick film. Another ITO-coated glass plate was used for sandwiching the PDLC films. A 60 μm thick film spacer of poly(ethylene terephthalate) was used to control the PDLC film thickness. Polymer and LC composite films with 10 to 80% LC (E44) were prepared for this study. However a composite film with LC concentration higher than 80% cannot be stabilized as the reduced proportion of

polymer binder is insufficient to bind the LC droplets effectively. Our previous study shows that the contrast ratio for LC loading less than 60% is very poor [16]. Therefore in the present investigation, the result of 70% and 80% of LC loading in the polymer matrix is reported.

2.3. Morphology

Dispersion of LC droplets in the polymer matrix was viewed under a crossed polarizer with 40× objective using an Olympus Polarizing Optical Microscope (POM) (Olympus, BX-53, Singapore) fitted with a charge coupling device (CCD) camera interfaced with a computer. The morphology of the PDLC composite film was studied using a scanning electron microscope (SEM) (Hitachi, S-3400N). For structural studies, E44 was extracted from the composite film using methanol, which is a non-solvent for PMMABA, and then, these films were dried overnight before they were viewed through the SEM.

2.4. Dielectric characteristics

The dielectric measurements were carried out using a precision impedance analyzer (Wayne Kerr 6500B, UK). The samples were investigated as a function of temperature (24 to 100 °C) and applied frequency (20 Hz to 20 MHz). The area of the ITO coated glass electrode was 4.83 cm^2 and surface resistance was 5.59 Ω cm. The dielectric properties of the composite films were determined from the measurement of capacitance (C_p), dissipation factor (tan δ), phase angle (θ) and impedance (Z), and the relative dielectric constant was calculated using the following formula [17–19].

$$\varepsilon_r = \frac{C_p}{C_0} = \frac{C_p \times D}{A \times \varepsilon_0} \tag{1}$$

Where (ε_r) is the relative dielectric constant/permittivity,

C_p Parallel capacitance,
D   Thickness of composite film,
A   Area of electrode,
ε_0 Free space permittivity (8.854 × 10^{-12} F/m).

2.5. Thermal analysis

The switching from nematic to isotropic (T_{NI}) phase of LC (E44) and the glass transition temperature T_g of the polymer matrix as well as PDLC composites were determined using a Differential Scanning Calorimeter (DSC) (TA Instruments, Waters, INDIA). The scanning rate of the DSC was kept fixed at 10 °C/min, in nitrogen atmosphere.
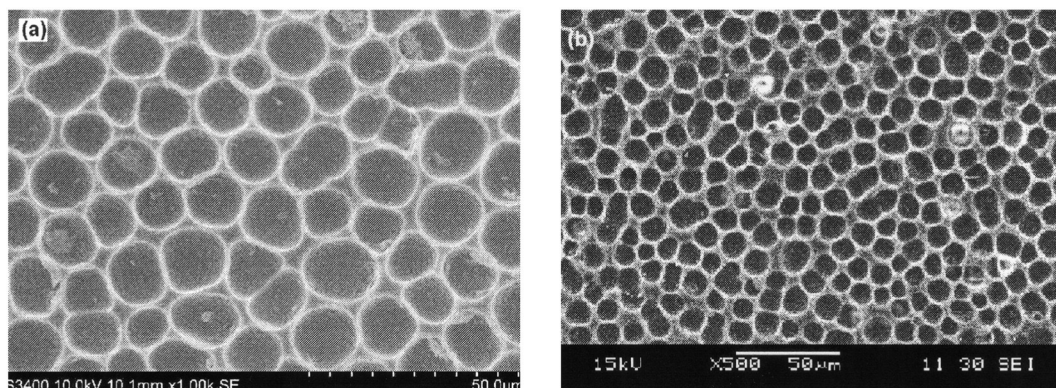

Fig. 1. SEM micrographs of the PMMABA/E44 films: (a) 20/80 and (b) 30/70 wt.%.