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Dielectric relaxation and electro-optical switching behavior of nematic liquid crystal dispersed in poly(methyl methacrylate)

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ABSTRACT

Polymer dispersed liquid crystal composite films were prepared from poly(methyl methacrylate) and nematic liquid crystal E44 by solvent induced phase separation method. In the present investigation we report effect of liquid crystal concentration on the electro-optical and dielectric properties of the composite films. The results were interpreted in terms of phase separation of liquid crystal and polymer, shape and size of liquid crystal droplet, interfacial charge layer effect, liquid crystal loading and miscibility of liquid crystal in the polymer matrix. The miscibility between two phases at interface was investigated by employing Fourier-Transform Infrared Spectroscopy and differential scanning calorimetry. Morphological study showed that liquid crystal phase is embedded in a spongy poly(methyl methacrylate) matrix and homogeneous distribution increased with increasing E44 content. Electro optical behavior of these composite films under the condition of an externally applied AC electric field (0–200 Vp-p, 50–1000 Hz) and wide range of temperature was determined using He–Ne laser (wave length 632.8 nm) as a light source. It was found that Poly(methyl methacrylate)/E44 (30/70) wt.% composite has more significant properties than the other concentrations. The performance of all composites showed variations with respect to applied voltage as well as temperatures. Dielectric measurement of polymer dispersed liquid crystals has been carried out in the frequency range from 20 Hz to 20 MHz and over the temperature range from 24 °C to 100 °C. The Maxwell–Wagner effect due to interfacial charge accumulation between boundaries of liquid crystal droplets and surrounding of polymer matrix has been observed.

1. Introduction

Due to the increasing importance of liquid crystals (LC) in science, technology, industry and medical applications, it has received considerable attention from many scientists in the past few decades. LC's have found applications in electro-optical materials because their anisotropic molecular order can be controlled by external electric field. Polymer dispersed liquid crystal (PDLC) films have acquired greater importance since these materials are used in electro-optical devices ranging from light shutters, high resolution displays, projection light valves and switching gratings [1–7]. The property of liquid crystals that cause the director to respond to an applied electric field is the basis for most of the applications. The polymer matrix being self-supporting and mechanically stable, eliminates the use of polarizers and/or optical elements and alignment layers for the modulation of incident light, gives PDLCs an advantage over other liquid crystal technologies. Every material has a unique set of electrical characteristics that are dependent on their dielectric properties. Accurate measurement of these properties can provide valuable information about the behavior of molecules possessing electric dipole moments to properly incorporate that material into its intended application with improved performances [8]. PDLC's are composed of two nonmiscible components, liquid crystal droplet and a polymer [9]. PDLC composite films are a new class of materials, which consist of micron-sized droplets of liquid crystals dispersed in polymer binder. The composite film is sandwiched between conductive indium–tin–oxide (ITO) coated glass substrates with its conducting sides facing inwards in contact with the composite film. This resulting assembly is very much responsive to electric field and thermal gradient [10,11]. In OFF-state mode a PDLC film strongly scatters light and becomes opaque, but in the influence of sufficient electric field i.e. in ON-state LC director reorients within the microdroplets and the film appears clear transparent. Various methods such as solvent induced phase separation (SIPS), polymerization-induced phase separation (PIPS), thermally induced phase separation (TIPS) and encapsulation are being used to prepare PDLC composite films [12]. In this study, we have used the SIPS method where the LC's and the polymer are dissolved in a common solvent to

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create a single phase. As the solvent evaporation takes place, the LC phase starts to separate in the form of droplets and gets embedded between polymer walls.

Dielectric relaxation spectroscopy (DRS) is a useful technique for the investigation of liquid crystals which enables the dielectric anisotropic properties, the reorientational motions of dipoles and the conduction behavior of extrinsic ions in the material. This technique gives drastically to the overall characterization of spongy materials in general, and analysis of condensed matter confined to porous media in particular [13,14]. The main purpose of DRS is to examine the distribution of relaxation times as well as changes in the phase and the glass transition temperatures. The complex electrical nature of the LC droplets dispersed in polymer matrix arises as a result of the strong dipole moments of the LC along with interfacial charge layers between the droplets and the polymer matrix when subjected to an applied electric field. The study of dielectric property can be used to detect these electric complexities over a wide temperature and frequency range, and is also very sensitive to the DC conductivities due to conducting impurities and the interfacial charge layer effect. The existing theories on dielectric behavior in these kinds of heterogeneous systems can be adapted to the PDLC systems as a result of its phase separated nature [15]. The Maxwell–Wagner (MW) effect due to charge accumulation between boundaries of LC droplets and surrounding of polymer matrix has been observed by J. Liu et al. [16]. This effect may be useful to enable the electrical applications of such PDLC composite.

In this study, few PDLC films were fabricated using nematic LC E44 dispersed in poly(methyl methacrylate) (PMMA). The effect of various LC concentrations and the morphology on the dielectric properties of the composite films has been investigated. Furthermore, hysteresis behavior was studied as a function of voltage and the comparative results of those composite films have been discussed in terms to correlate dielectric and electro-optical properties.

2. Experimental

2.1. Materials

The nematic mixture consisting of several cynobiphenyls derivatives E44 (kindly provided by E. Merck, Darmastadt, Germany) was used as a LC material. The polymer used was PMMA. The physical properties of these constituents are given below.

a. Poly(methyl methacrylate) (PMMA)
   $T_g = 95$ °C, $M_N = 26912$, $M_W = 82264$, $n_p = 1.4985$.
   Solubility: In aromatic and chlorinated hydrocarbons.
b. Low molecular weight liquid crystal, E44 (nematic mixture)
   $T_{Crystal \rightarrow Nematic}$ $(T_{KN}) = 0$ °C, $T_{Nematic \rightarrow Isotropic}$ $(T_{NI}) = 100$ °C,
   $n_0 = 1.5284$, $n_e = 1.7904$, $\Delta n = 0.262$, $\Delta\varepsilon = 17.0$.

2.2. Preparation of the PDLC composite films

In this study, PDLC films with different compositions (wt/wt.%) of polymer and LC were prepared by SIPS method [17]. We prepared the homogeneous solution of an appropriate amount of PMMA and E44 in chloroform (solvent), this solution was then poured on ITO-coated glass as a 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. Film thickness was controlled with a poly(ethylene terephthalate) film spacer 60 μm thick. Polymer and LC composite films with 10 to 80% LC (E44) were prepared for the study. However we could not prepare a composite film LC more than 80% as polymer binder seems to be insufficient to hold LC droplets. Similar observations were seen for other type of liquid crystals viz. E8, E7 [18,19].

2.3. Morphology

The morphology of the PDLC composite film was studied using a scanning electron microscope (SEM) (Hitachi, S-3400N). For structural studies, E44 was first extracted from the composite film using methanol, which is non-solvent for PMMA, and then, these films were dried overnight in a vacuum oven before they were viewed by a scanning electron microscope. Dispersion of LC droplets in the polymer matrix and observation in the presence of an applied electric field was viewed under crossed polarizer at a magnification of 50× through Olympus Polarizing Optical microscope (POM) (Olympus, BX-53, Singapore) fitted with charge coupling device (CCD) camera interfaced with computer.

2.4. Electro-optical measurements

The electro-optical properties of PDLC films were studied in terms of transmission changes under the influence of electric field. A collimated beam of He–Ne laser of 10 mW power with 632.8 nm wavelength (photochemical Inc. Canada; Model 10SP) was used as an incident light source. This laser equipped system was fitted on an optical bench with a photodiode detector. An AC field was applied with the help of conducting ITO coated glass plates. The applied field was driven by a square wave voltage with frequency variation from 50 Hz to 1 kHz, and it was found that 200 Hz was the optimum frequency. The applied voltage was increased and decreased between 0 V and 200 V to obtain scan up and scan down cycle for measuring hysteresis phenomenon. The temperature was controlled by PT 100 resistor, which was in direct contact with sample. Temperature was monitored between 25 °C and 50 °C with an accuracy of ±0.1 °C. The graphs were plotted using the average of three sets of readings and subsequently the variation is reported in terms of an error bar in the figures. The detail of experimental setup for electro-optical measurement is given elsewhere [18,19].

2.5. Dielectric characteristics

The dielectric measurements were carried out using a precision impedance analyzer (Wayne Kerr 6500B, 20 Hz–20 MHz, 0–40 DCV, UK). The samples were tested as a function of frequency and temperature. The samples were heated up to 100 °C with the accuracy of ±0.1 °C by using Electrotech Temperature Control system. The area and surface resistance of the ITO coated glass electrode were 4.83 cm^2 and 5.59 Ωcm respectively. The dielectric properties of the composite film were evaluated from the measurement of capacitance (Cp), dissipation factor (tan δ), phase angle (θ) and impedance (Z). The relative dielectric constant was obtained from the measurement of the parallel capacitance using the following formula [14,20];

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

where (ε_r) is relative dielectric constant/permittivity, (C_p) is parallel capacitance, (D) is thickness of composite film, (A) is area of electrode and (ε_0) is free space permittivity and its value is 8.854×10^{-12} F/m.

2.6. FT-IR Measurement

The relation between the phase – mixing at polymer – LC interface was studied by employing Fourier Transform Infrared (FT-IR) spectrometer (Perkin Elmer Paragon 500, USA) at a resolution of 4 cm^{-1}.

2.7. Thermal analysis

The phase transition from nematic to isotropic state of T_{NI} LC (E44) and the glass transition temperature T_g of the polymer matrix