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ChemTech

International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN : 0974-4290
Vol.6, No.3, pp 1836-1839, May-June 2014

ICMCT-2014 [10th – 12th March 2014]
International Conference on Materials and Characterization Techniques

Investigation of dielectric properties of poly(methyl methacrylate)–E7 composite films

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Abstract: Dielectric Relaxation Spectroscopy (DRS) technique provides a potential tool to monitor the phase separations in polymer dispersed liquid crystal (PDLC) films. DRS study is helpful to identify the molecular orientation of the material, which dictates electric and dielectric properties. These properties are also very sensitive to the DC conductivities due to conducting impurities and the interfacial charge layer effect. The existing theories on dielectric behavior in heterogeneous systems can be adapted to the PDLC systems as a result of its phase separated nature. The Maxwell-Wagner (MW) effect due to interfacial charge accumulation between boundaries of LC droplets and surrounding of polymer matrix has been observed. DRS study of a PDLC has been carried out in the frequency range from 20 Hz to 20 MHz and over the temperature range from room temperature to 60°C. In the present investigation Polymer/LC (PMMA/E7, 70 & 80 wt % of E7) composite films were prepared by solution casting method. Composite films having thickness of ~ 60µm were obtained using suitable spacer. Influence of bias voltage at higher temperature on the dielectric parameters has also been investigated. The morphology and the size of the LC droplets in the composite films were observed using microscopic techniques. The measured properties have strong co-relation with the LC droplet size, shape and the morphology.

Key words: - PDLC, Dielectric Relaxation, SIPS and Morphology.

1. Introduction and Experimental

1.1 Introduction

Liquid crystals have attracted attention of scientist and technologist due to its inherent optical and dielectric anisotropic properties. Polymer Dispersed Liquid Crystals (PDLCs) are the composite films in which micron sized liquid crystal (LC) droplets are embedded in a solid polymer matrix prepared by phase separation of initially homogeneous LC-polymer mixture. PDLC films are used in electro-optical devices ranging from light shutters, high resolution displays and projection light valves and switching gratings [1]. To study the dielectric anisotropic properties and reorientational motions of dipoles of LC's, dielectric relaxation spectroscopy (DRS) is a useful method [2]. PDLC is a heterogeneous composite system having LC-polymer interfaces. In the presence of electric field such heterogeneous systems show to space charge polarization; also called as Maxwell-Wagner effect [3].

In the present paper, we prepared PDLC films based on poly (methyl methacrylate) (PMMA) as a host polymer matrix for nematic LC E7. The thermal property, Morphology and dielectric relaxation of PDLC's have been investigated.

1.2 Experimental

The PDLC films were fabricated by solvent-induced phase separation (SIPS) method [4] using host polymer (PMMA) matrix and nematic LC E7 is having nematic to isotropic transition temperature (T_{NI}) 61°C. The film preparation technique is given elsewhere [4]. Composite films with PMMA and E7 in the ratio 20 / 80 and 30 / 70 wt% were prepared. Film thickness was controlled to 60 µm with a poly (ethylene terephthalate) film spacer. The morphology of the PDLC composite film was studied using a scanning electron microscope (SEM). The dielectric measurements were carried out using a precision impedance analyzer. Glass transition temperature of films was observed using Differential Scanning Calorimeter (DSC).

2 Results and Discussion

2.1 Morphology

The dielectric properties of the PDLC films and device performance depend on the morphology LC droplets in the polymer matrix. Morphology of LC droplets depends on many factors, such as the types of polymer and LC used, their anchoring at the boundary, composition and elastic properties, and film forming technique [1]. Figure 1 (a and b) shows the SEM micrographs of the PMMA/E7 composite films (20/80 & 30/70 wt/wt %), obtained after extracting E7 with methanol as described elsewhere [5].

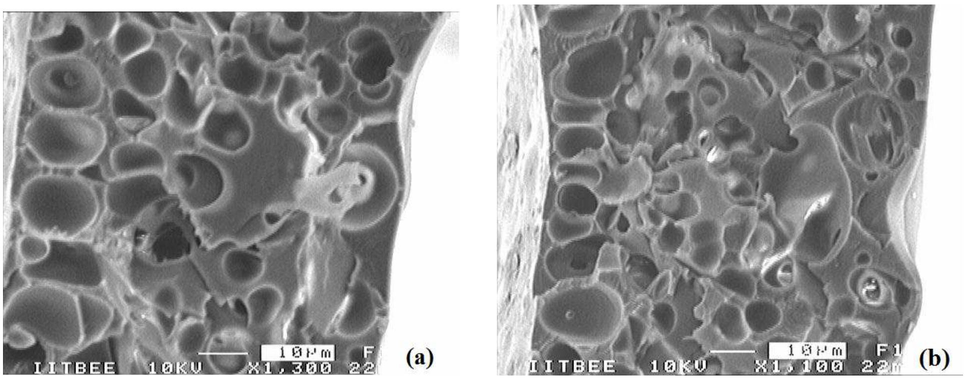

Figure 1 SEM micrographs of PDLC composite films: (a) 20/80 and (b) 30/70 wt %

A polymer network in which the phase separated LC domains is seen in SEM micrographs. Bigger droplet morphology with uniform distribution and size was observed in case of 20/80 composite film; Thus 20/80 composite films show better morphology.

2.2 Thermal Study

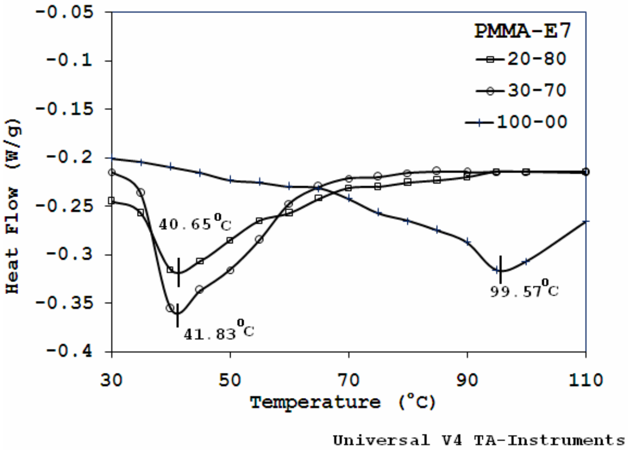

Figure 2. DSC thermograms of PMMA / E7 composite films

DSC results in Figure 2. Show single T_g at 99.57°c for each composition PMMA. It decreased on addition of LC to ~ 41 °C for both the composite films. The decrease in T_g of PMMA/E7 composite film indicates limited miscibility between the two phases.

2.3 Dielectric Relaxation Study

Figure 3(a) the increase in the relative permittivity up to 40 °C temperature is most likely due to molecular reorientation, raised by the applied temperature. But at the higher temperature, thermal agitation becomes more dominant over intermolecular interaction which produces randomization of dipoles [2, 5], results in decreasing trend of ε_r at higher temperature.

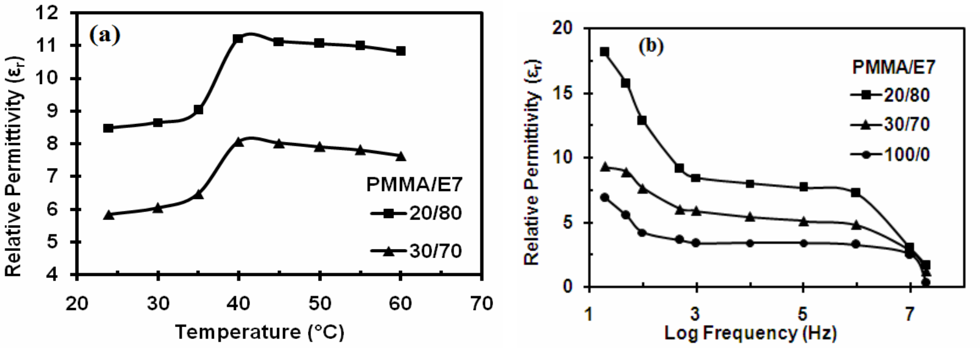

Figure 3. Relative permittivity (ε_r) versus (a) temperature and (b) log frequency of PMMA/E7 composite films.

In Figure 3(b), the higher values of ε_r at low frequency for both the concentrations are attributed to space charge polarization; also known as Maxwell-Wagner effect in heterogeneous system. However, at high frequencies molecules have less time to tune with an applied field, results in decrease in the dielectric permittivity to a minimum value [5].

2.4 Modeling of dielectric relaxation spectra

The space charge polarization is referred to the migration of charge carriers to the interfaces of the heterogeneous system under the effect of applied electric field [2]. In order to understand the characteristics of dielectric relaxation, the data is fitted in different models [6]. In mathematical terms, $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ are the real and imaginary parts of the complex relative permittivity $\{\varepsilon^*(\omega)\}$ and is given by.

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) = \varepsilon'_\infty + \frac{\varepsilon'_s - \varepsilon'_\infty}{1+\omega^2\tau^2} - \frac{(\varepsilon'_s - \varepsilon'_\infty)\omega\tau}{1+\omega^2\tau^2} \quad (1)$$

The real part ε' increases up to a certain temperature and then it decreases for the higher temperature (graphs not shown here). The maximum value of the real part of relative permittivity for 20/80 and 30/70 composite films was observed at 40 °C. The maximum value was observed exactly where thermal agitation starts. Similarly, the frequency dependence of the imaginary part (ε'') of the relative permittivity was studied at different temperature. It also shows similar trend to that of real part; showing maximum value at 40 °C for both the composite films. Therefore we can conclude that, at glass transition temperature, thermal agitation becomes more dominant and anisotropic molecules change their orientation.

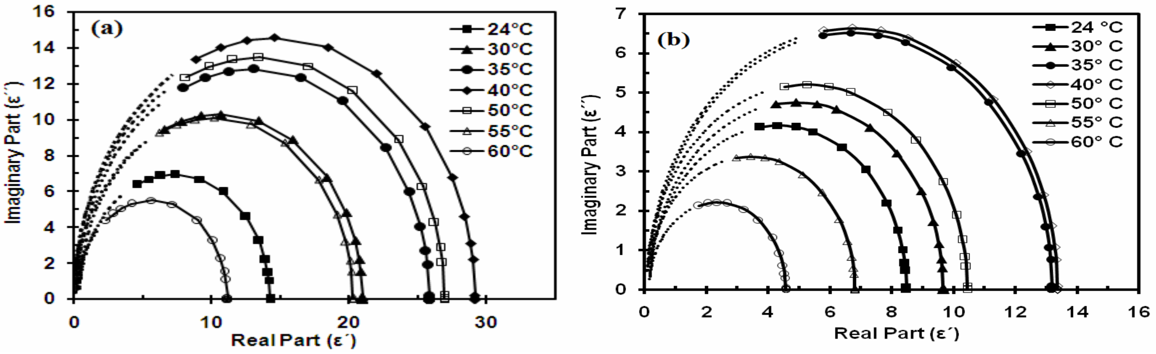

Figure 4. Cole-Cole plots for the PMMA/E7 composites for (a) 20/80 and (b) 30/70 wt/wt %.

The effect of distribution of relaxation time is illustrated by Cole Cole plot [7, 8]. Figure 4 (a and b) shows complex relative permittivity plots of imaginary part versus real part at different temperatures. From these plots, it is observed that the centre of the semicircle lie on ε' axis and the value of $\alpha = 0$, clearly indicating that it is a Debye type of mono-dispersive relaxation behavior because of the dipolar rotation around the long molecular axis of LC molecule.

2.5 Conclusion

DRS properties of PMMA / E7 composite films have been evaluated. SEM study indicates that 20/80 composite films reveals better morphology. We can alter the dielectric properties of composite films by controlling LC loading. The incorporation of LCs in the polymer matrix demonstrates improved dielectric properties. PDLC film with 80 wt % E7 shows better dielectric properties as compared to 70 wt% concentration. Relaxation study reveal single relaxation peak at higher frequency which indicate the Debye type behaviour.

3. References

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