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A STATIC AND DYNAMIC STUDY OF THE MECHANICAL PROPERTIES OF ELECTRON BEAM CURED PDLC FILMS

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This paper reports a study of static and dynamic mechanical properties of electron beam (EB) cured polymer dispersed liquid crystals. These systems consist of micron-sized droplets dispersed in a solid polymer matrix. They are prepared according to the polymerization induced phase separation process initiated by exposure to electron radiation. A difunctional monomer Tripropylene Glycol Diacrylate in short TPGDA is used with the eutectic liquid crystal mixture E7 having a nematic to isotropic transition temperature at 60°C. Strong effects are found on Young modulus and rubbery state modulus in terms of the EB dose and the liquid crystal concentration. As the concentration of small molecules increases, these mechanical parameters drop significantly together with the glass transition temperature T_g of the polymer showing a plasticizing effect. The results for T_g are confirmed by DSC thermograms in terms of liquid crystal concentration and EB dose.

Keywords: electron beam curing; glass transition; mechanical moduli; plasticizer; polymer dispersed liquid crystal

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INTRODUCTION

Polymer Dispersed Liquid Crystals (PDLCs) are composite materials made of micron sized droplets filled with liquid crystal (LC) molecules dispersed in a solid polymer matrix. They are the subject of intensive studies because of fundamental interest and potential applications. Their unique optical and electro-optical properties make them suitable for applications in various technological fields such a display devices, smart windows and communications [1,2].

Recently, we performed systematic studies of various systems in order to characterize their physical properties based on different techniques. An attempt was made to evaluate the major parameters influencing their physical behaviour and performance in practical applications. Essentially, the aim is to identify the molecular species (i.e., polymer and LC) and the method of preparation to reach the optimal conditions for film performance [3,4]. The present work is a contribution along these lines focusing on the static and dynamic mechanical properties of PDLC films. Films made according to the polymerization Induced Phase Separation (PIPS) process under Electron Beam (EB) curing of Tripropyleneglycodiacrylate (TPGDA)/E7 are considered [5–7]. Variations of the parameters describing the mechanical strength of polymer networks with the EB dose and concentration of the low molecular weight LC E7 are investigated.

EXPERIMENTAL PART

Materials

The liquid crystal E7 was purchased from Merck Eurolab (Darmstadt, Germany). It is an eutectic mixture exhibiting a nematic-isotropic transition at $T_{NI} = 60^{\circ}C$. It is made of 51 weight percent (wt%) 4-cyano-4′-*n*-pentyl-biphenyl (5CB), 25 wt% 4-cyano-4′-*n*-heptyl-biphenyl (7CB), 16 wt% 4-cyano-4′-*n*-octyloxy-biphenyl (8OCB), and 8 wt% 4-cyano-4″-*n*-pentyl-p-terphenyl (5CT) [8]. The monomer Tripropylene-glycoldiacrylate (TPGDA) was donated by Cray Valley (France).

Film Preparation

TPGDA was used as received and without further purification. The TPGDA/E7 blends containing x weight-percent (wt-%) of TPGDA and (100-x) wt-% E7 were stirred at room temperature until they became homogeneous. The samples were applied uniformly on glass plates and irradiated

under a fixed EB dose. The obtained films were characterized by a thickness near 100 μm.

Electron Beam Curing

The EB generator is an Electrocurtain Model CB 150 (Energy Sciences Inc.), delivering a voltage of 175 kV. The samples prepared according to the above procedure were placed on a tray which went under the irradiation source on a conveyor belt in a nitrogen atmosphere. Samples were exposed to doses by setting the beam current and the conveyor speed. For example, a dose of 105 kGy can be achieved using a beam current of $I = 7$ mA and a conveyor speed of 0.19 m/s. For each composition, several samples were prepared to ensure the validity of results. Sample thicknesses of 100 μm were chosen to allow for the complete penetration of the electron beam under the conditions of the experiments. Beyond 100 μm, the electron beam shows a steep gradient and the sample exposure gets poorer. Throughout the systematic studies we performed in our laboratory for a variety of EB-cured PDLCs based mainly on polyacrylate/LC systems, we found no evidence of damage caused by the electron beam under conditions similar to those of the present work.

Mechanical Measurements

Static properties were analyzed using a mechanical testing machine Instron 6022. Samples of rectangular shape were cut from the films and the effective sample dimensions were roughly $15 \times 4 \times 0.1$ [mm^3]. Measurements were performed at room temperature (20°C) at a constant rate of 1 mm/min. The stress vs. draw ratio λ was recorded where λ is the ratio of the final length l to the initial length l_0 prior to the application of stress. Duplicate films were used to check the reproducibility of the results. Similar results were found within the elastic deformation range at small strains up to draw ratios of ca. 1.02. Five to eight independent measurements were made and the results represent averaged values. Young modulus was determined from the slope of the stress/draw ratio curves at zero strain [7].

Dynamic measurements were performed by means of a Rheometrics RMS 800 mechanic spectrometer. Rectangular samples of effective dimensions $20 \times 4 \times 0.1$ [mm^3] were cut from the prepared films. Uniaxial tensile deformation was applied under the condition of a controlled deformation amplitude which was changed with temperature between $\Delta\gamma = 0.0001$ at low T and $\Delta\gamma = 0.05$ at high T but remaining in the range of a linear viscoelastic response. A special set-up designed for the investigated films was used and the experiments were performed under dry nitrogen atmosphere.

Curves representing the storage tensile and loss moduli (E' and E'') versus T were obtained for several compositions. E' and E'' were measured at a constant deformation frequency of 10 rad/s and a heating rate of 2°C/min starting from $T = -100$°C up to the temperature where the rubbery state plateau modulus was detected.

RESULTS AND DISCUSSION

For shortness, only a small selection of results are represented here to identify the general trends observed in the mechanical analysis. A typical plot of E' versus T is given in Figure 1 obtained on TPGDA/E7 systems at increasing dilution with E7. Distinction between T_g's of the network and the LC clearly indicate a phase separation and coexistence of two distinct phases. The large drop in the glass transition temperature of the polymer shows that the low molar mass LC acts as a plasticiser. The high plateau corresponds to the glassy state at low temperatures accompanied by a softening range of temperature while at higher temperatures, the plateau characterizing the rubbery state is reached. The transition between

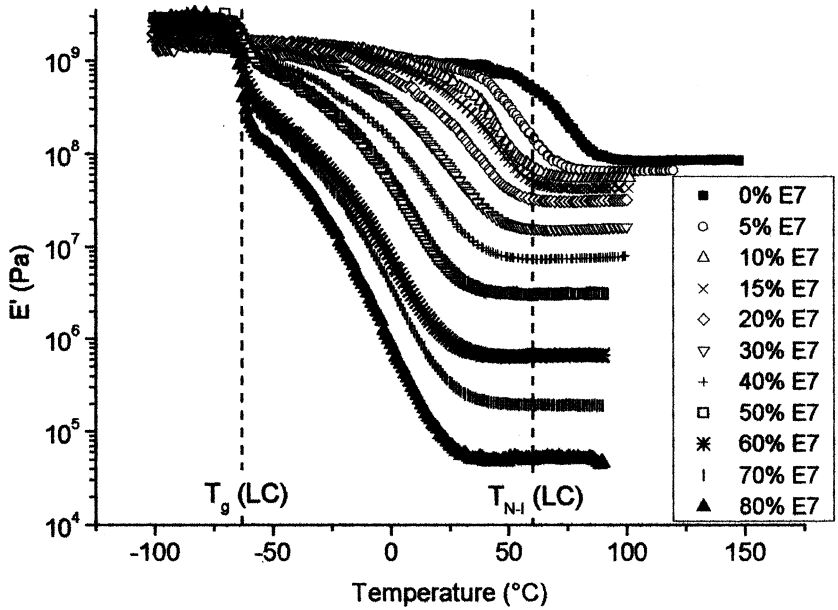

FIGURE 1 The storage tensile modulus E' versus temperature for TPGDA/E7 systems at several LC concentrations as indicated on the figure. The vertical dashed lines designate the glass and nematic to isotropic transitions of pure LC.

the glassy and rubbery states is accompanied with a maximum in the imaginary part of the modulus (E''). Addition of LC in the composite material induces considerable changes in the mechanical behavior. Whereas the glassy plateau of E' remains nearly independent of composition, the rubbery plateau emerging above 75°C drops by nearly four orders of magnitude when the LC concentration goes from zero (pure polymer) to 80 wt-% E7. Initially, the rubbery plateau drops smoothly until 20 wt-%LC followed by a more rapid decrease as the concentration of LC exceeds 20 wt-%. At the same time the glass transition shifts considerably to lower temperatures and becomes much broader. All samples show good elastic recovery after deformation and behave as elastomers in the whole temperature range. The cross-linking density of the network decreases as the precursor mixture is diluted with the LC and the molecular weight of strands between cross-links increases. The consequence of this is a more flexible network with a lower plateau modulus. Poor mechanical response of a system with a high LC content cannot be attributed only to low cross-linking density and the presence of topological defects. Thermal and morphology changes with larger droplets of ordered LC molecules should also have a certain influence on mechanical properties. Figure 2 shows the effects of LC concentration on Young modulus E and rubbery state modulus E''. Both quantities decay sharply with the concentration

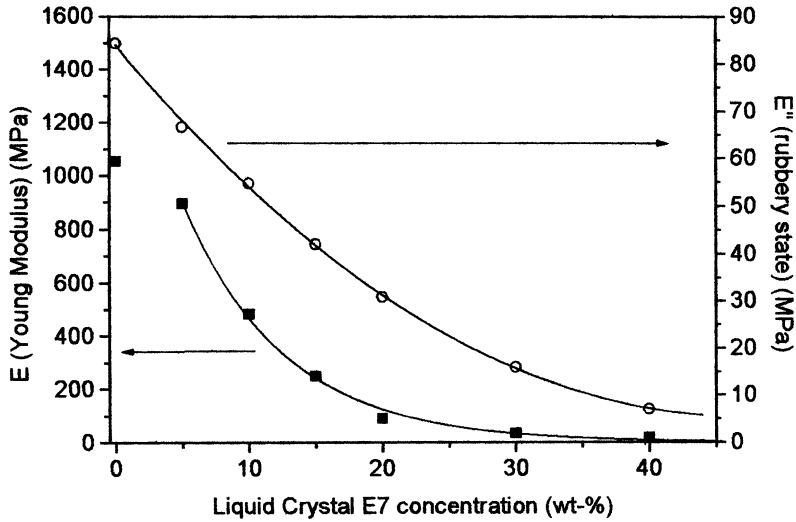

FIGURE 2 Young modulus E (left hand side axis, filled squares) and rubbery state modulus E'' (right hand side axis, open circles) versus E7 concentration for TPGDA/E7 systems prepared under PIPS and EB curing mechanisms.

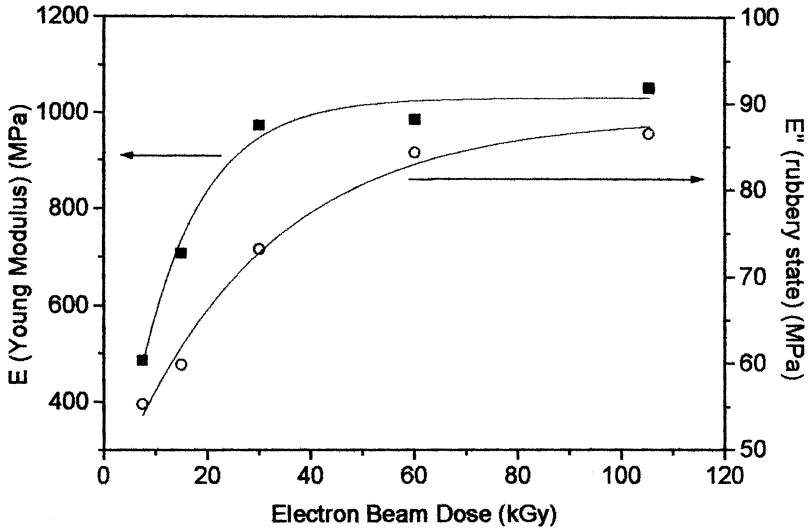

FIGURE 3 Young modulus E (left hand side axis, filled squares) and rubbery state modulus E'' (right hand side axis, open circles) versus EB dose for the TPGDA (60wt-%)/E7 (40wt-%) system.

of LC indicating a substantial reduction of the mechanical strength of the film.

Mechanical and elastic properties of cross-linked polymer networks depend on the conditions of preparation. The dose of radiation curing controls to some extent the network architecture and elasticity. To illustrate this effect, we plot in Figure 3 typical results showing the Young modulus and rubbery state modulus versus the EB-dose. Mechanical moduli increase sharply with the radiation dose which is expected since the cross-linking density of the film goes up with the dose.

CONCLUSIONS

Static and dynamic mechanical properties of TPGDA/E7 films prepared according to a PIPS process under EB curing are investigated. At high radiation doses, these films exhibit a rubbery plateau with a high modulus reminiscent of dense polymer cross-linking. Addition of a low molecular weight LC leads to a drop in the mechanical strength of the film. The glass transition temperature also drops since small molecules act as plastisizer. This effect remains significant even if the EB dose is relatively high. It is worth nothing that the samples did not undergo any damage when exposed to the electron beam throughout the range of doses applied in the present

work. Further investigations along the same lines involving other systems are being pursued and we hope to report additional mechanical data and their interpretation in the near future.

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