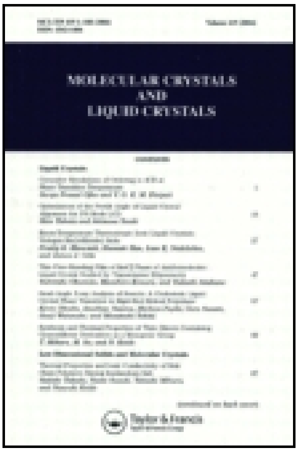

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Mechanical Properties of Polymer/Liquid Crystal Films Elaborated by Electron Beam and UV Radiation

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Mechanical Properties of Polymer/Liquid Crystal Films Elaborated by Electron Beam and UV Radiation

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The thermomechanical properties of electron beam (EB) and ultraviolet (UV) cured TPGDA (tripropyleneglycol diacrylate)/liquid crystal (LC) blends were the subject of static and dynamic analysis. In the glassy region of the LC, a very strong temperature dependence on the polymer storage modulus was found for EB-cured networks in the range of compositions 40–60 weight.-% of LC. Above the LC glass transition temperature (T_g)*, the LC behaves like a plasticizing agent. Below* T_g *of the LC, the LC reinforces the polymer. In the case of the UV-cured system, the effect of plasticizing of the LC remains dominant from −100 to +100°C.*

Keywords Electron beam; glass transition temperature; liquid crystal; mechanical properties; polymer; ultraviolet

1. Introduction

Radiation curing is a widely used technique for applications in thin film coatings, adhesives, paintings etc. [1–7]. Although UV curing is more often used because it does not require any heavy equipment or special care, the electron beam method (EB) has great advantages. EB curing has the advantage of not requiring the presence of a photoinitiator which might be detrimental to Polymer Dispersed Liquid Crystal (PDLC) film performances and to long term ageing. In view of a particular application, the basic formulation can be adapted by the right choice of chemical structures and molecular weights of the polymer precursors, and also by the spatial

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distribution and volume density of the reactive groups. The structure of the obtained polymer network depends also on a large number of other parameters like viscosities and refractive indices of the initiating species, monomer conversion, temperature, etc. In particular, acrylate based compositions are well-known to be versatile materials for radiation curing methods, allowing a good control of processing [5]. The techniques of EB- and UV-curing have been widely used in our laboratory to produce films and composite materials of the PDLC type [8–10]. In a limited concentration range of liquid crystal (LC), these materials consist of micron sized nearly spherical domains filled with low molecular weight LC molecules dispersed in a solid polymer matrix.

In this paper a special emphasis is given to the effect of EB and UV-curing on the mechanical characteristics of films based on tripropyleneglycoldiacrylate (TPGDA). Moreover, the influence of adding LC to the monomer prior to irradiation was investigated in detail. Static and dynamic mechanical measurements were carried out in a wide range of compositions from 0 (pure polymer network) to 80 weight (wt).-% LC.

A large number of nanocomposite and microcomposite polymers have been developed recently [11–18] and many research activities focus particularly on the possibility to obtain a physicochemical reinforcement of the basic polymer. Generally, polymeric composite materials are prepared by introduction of the filler particles to the polymer matrix [11,18,19] where the effects of reinforcement are governed by the chemical nature and surface of the filler-particles, and the polymer/filler interactions. Only few investigations were reported on the preparation of these materials by radiation induced cross-linking polymerization processes of the precursor mixture, including filler particles [17,20,21].

2. Experimental Methods

2.1. *Materials and Film Preparation*

The liquid crystal E7 was purchased from Merck KGaA (Darmstadt, Germany). It is an eutectic mixture exhibiting a nematic-isotropic transition around $T_{NI} = 60°C$. E7 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 (80CB), and 8 wt% 4-cyano-4″-n-pentyl-p-terphenyl (5CT) [22]. The monomer, Tripropyleneglycoldiacrylate (TPGDA), was donated by Cray Valley (France). All materials were used without further purification.

The TPGDA/E7 blends containing x wt.-% of TPGDA and (100-x) wt.-% E7 were homogenized at room temperature. The samples were applied uniformly on glass plates and irradiated either by EB- or by UV curing. 2 wt.-% (with respect to the monomer) Lucirin TPO (BASF) as photoinitiator was added to the initial mixture in the latter case.

2.2. *Electron Beam Curing*

The EB generator is an Electrocurtain Model CB 150 (Energy Sciences Inc.), delivering a high 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 dose values varying between 7.5 and 105 kGy which were achieved using a constant conveyor speed of 0.19 m/s and a beam current between 0.5 and 7 mA. For each composition several samples were prepared to ensure the validity of results. Sample thicknesses of 100 µm were chosen to allow for complete penetration of the electron beam irradiation under the conditions of the experiment.

2.3. *Ultra Violet Curing*

The UV light source used was a Minicure Model MC4-300 (Primarc UV Technology) equipped with a medium pressure mercury arc lamp rated 80 W per cm. The samples were placed on a conveyor belt and exposed to UV light using dose values of 52, 75, 100, 125, and 150 mJ/cm^2, which were obtained by varying the speed of the conveyor belt.

2.4. *Mechanical Measurements*

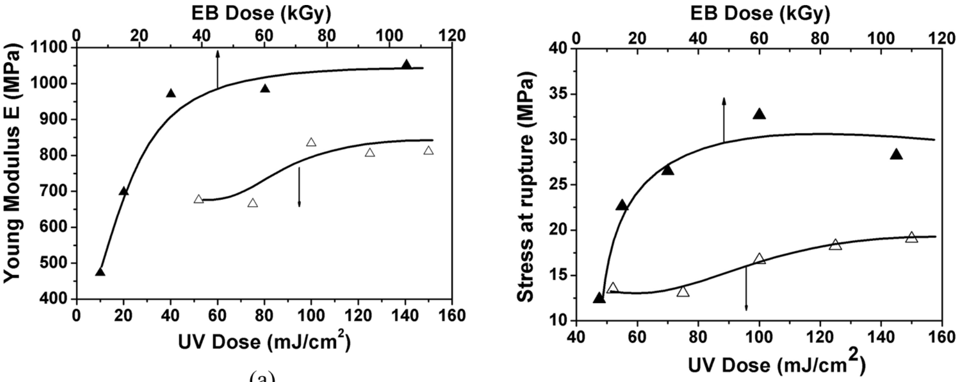
Static properties were analyzed using a mechanical testing machine Instron 6022. The obtained films were characterized by a thickness near 100 µm. Samples of rectangular shapes were cut from these films and the effective sample dimensions were roughly $15 \times 4 \times 0.1$ [mm^3]. Static measurements 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. Young modulus was determined from the slope of the stress/draw ratio curves at zero strain [10]. Five to eight independent measurements were made and the results represent average values.

Dynamic measurements were performed by means of a Rheometrics RMS 800 mechanical 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 temperatures and $\Delta\gamma = 0.05$ at high temperatures 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. The storage and loss tensile moduli (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.

3. Results and Discussion

3.1. *Static Mechanical Measurements*

Figure 1 represents Young moduli (a) and stress at rupture (b) as a function of dose from UV- and EB-cured TPGDA samples, obtained from static mechanical experiments through stress-strain curves [9,10]. Generally, the UV-dose expressed in mJ/cm^2 cannot be easily correlated with the dose from EB-curing, measured in kGy, which means that the results for both methods cannot be presented on the same scaling. However, it can be noticed that an increase of the applied dose results in an increase of the Young modulus [23] for both EB- and UV-cured TPGDA samples.



(a)

(b)

Figure 1. Dependence of the Young modulus (a) and stress at rupture; (b) on the delivered dose for TPGDA films which were exposed to EB and UV irradiation.

In the present case, our interest is essentially focused on the question if constant plateau values could be obtained for the Young moduli and stress at rupture by increasing the radiation dose, for both preparation methods. In the EB-case, Young modulus and stress at rupture increase abruptly with dose and show a plateau. In the UV-case, Young modulus and stress at rupture show also a plateau after a relatively weak increase. Clearly EB treatment yields a highly polymerized and cross-linked polymer network exhibiting a 20% higher mechanical strength than the UV analogue, which shows a lower cross-linking density. Following these results, Dose values of 150mJ/cm^2 and 105 kGy were chosen for UV- and EB-cured samples throughout this work.

Figure 2 shows the evolution of Young modulus and stress at rupture (inset) according to the concentration for the systems elaborated by EB and UV. These data

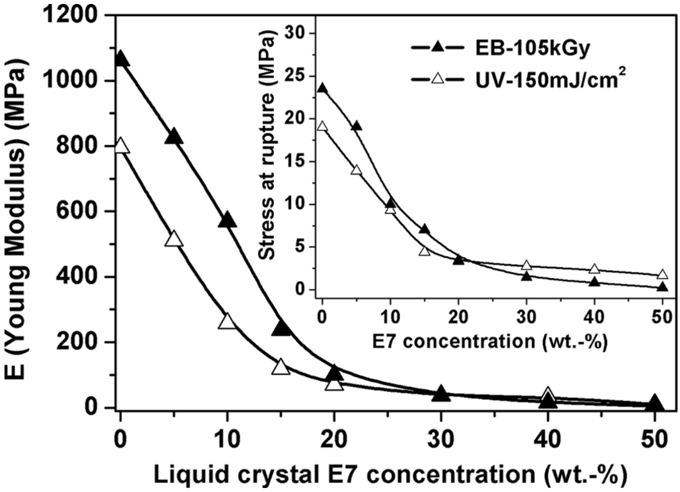


Figure 2. Young modulus versus LC concentration for EB- (105 kGy) and UV- (150 mJ/cm^2) cured TPGDA/E7 systems. The inset shows the dependence of the stress at rupture of these systems on the composition.

are deduced starting from stress-strain curves [9,10] for EB- and UV-curing for various compositions. Note that samples with more than 50 wt.-% LC could not be analyzed experimentally.

Young modulus and stress at rupture fall abruptly with the concentration of E7, up to approximately 20%. EB-cured systems have in this concentration range greater values in module and stress at rupture as UV-systems thus indicating a better rigidity and a better breaking strength. At a LC content of 20 wt.-%, a cross-over phenomenon was observed, indicating lower Young moduli and lower stress at rupture for the EB system at higher LC concentrations.

3.2. *Dynamic Mechanical Measurements*

Figure 3 shows the evolution of T_g (polymer) in the polymer/LC blends deduced from the maxima of *tanδ*. A strong decrease of T_g (polymer) to lower temperatures was observed by increasing the LC content in the films, showing that the low molar mass LC acts as a plasticizer. These results were confirmed recently by Differential Scanning Calorimetry measurements [8].

The insert of Figure 3 represents the rubbery state modulus values obtained from the dynamic mechanical measurements, as a function of LC content. The evolution of these data is quite similar to that of the glass transition temperatures of the polymers in the polymer/LC blends which means that the rubbery state modulus for low LC content corresponding to the EB-cured samples are higher than values from UV-curing. Addition of LC in the composite material induces considerable changes in the mechanical behavior particularly a more flexible network with a lower plateau modulus. This effect is much more pronounced for EB-cured films than for their UV analogues. Interestingly, the results from EB- and UV-cured

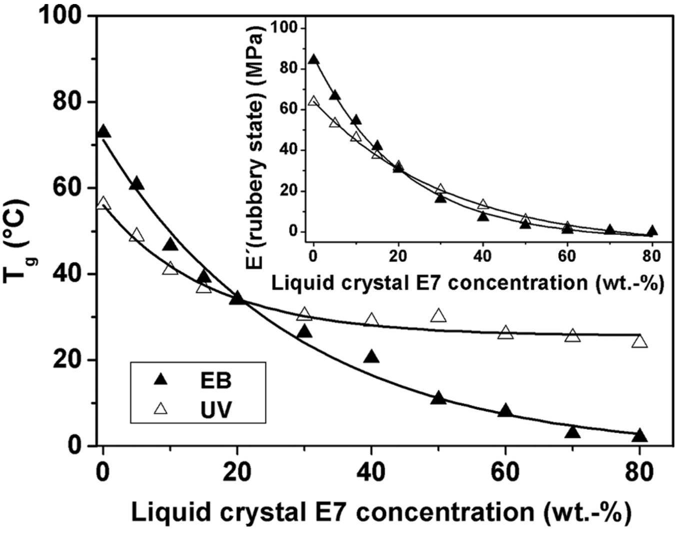


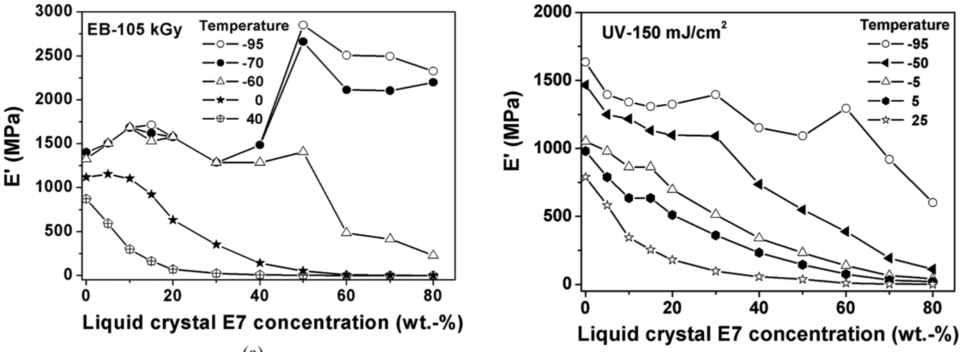
Figure 3. Glass transition temperature versus LC concentration for EB- (105 kGy) and UV- (150 mJ/cm^2) cured TPGDA/E7 systems obtained from corresponding loss and storage tensile moduli. The inset shows the dependence of the rubbery state moduli of these systems on the composition.

samples corresponding to 20 wt.-% E7 overlap nicely. Further increase of LC concentration leads to lower plateau moduli and decreasing polymer T_g values. In particular, UV-cured films with E7 concentrations higher than 20 wt.-% exhibit higher mechanical strength than their EB analogues.

Figure 4 represents the storage moduli from UV- and EB-cured samples as a function of LC concentration for several temperatures in the range from −95°C to 40°C.

The storage moduli of pure UV-cured TPGDA samples strongly depend on temperature in spite of the glassy state of the cross-linked polymer. At $T = -95°C$, a value of $E' = 1650$ MPa was obtained, and at $T = 25°C$, the storage value was evaluated at $E' = 760$ MPa. In the case of EB-cured pure TPGDA, the total range of E' values for all temperatures investigated (−95°C to 40°C) was situated between 850 and 1400 MPa, thus representing much less data dispersion compared to the findings from the UV-system. These results can be explained by the different preparation methods and their consequences on the polymer network structure. Since the UV-irradiation procedure differs from EB-curing by the need of a photoinitiator as starting species, the initial steps of the free radical polymerization process are different. In particular, exposure to UV-light first leads to a decomposition of the photoinitiator which generates radicals, reacting in a second step with the acrylic functions of the monomer. As a result, the photopolymerized system has been elaborated essentially through these reactive functions, and cross-linking generally occurs at the end of the polymerization process via a chain termination reaction [24–26]. EB-curing proceeds without any initiator and the radiation creates radicals not only on the reactive acrylic functions but also randomly on the medium. Cross-linking can thus occur via radical-radical combination or radical attack upon an acrylate group, leading to a chemically highly cross-linked polymer network. It is, therefore, assumed that a more regular structured homogeneous polymeric network was formed during EB-curing, whereas the sample irradiated by exposure to UV light is likely to form a more heterogeneous, less stable network with lower cross-linking density.

Furthermore, the presence of polymer network heterogeneities should be mentioned, which might lead to locally highly cross-linked areas as well as to



(a)

(b)

Figure 4. Storage tensile modulus as a function of LC concentration determined at different temperatures: (a) Moduli from EB-cured TPGDA/E7 films (105 kGy). (b) Results from UV-curing (150mJ/cm^2).

regions, which are loosely cross-linked. It is assumed that such heterogeneities are present particularly in the UV-cured system.

In the case of EB-cured samples (Fig. 4a), for temperatures exceeding $T = -60°C$, storage moduli first show constant plateau values and then decrease monotonously with increasing LC content. This behavior was already found for polymer systems incorporating small molecules, and is known as plasticizing effect [8]. Moreover, the formation of the polymer network depends on the LC concentration in the reactive initial blends: The network elaborated with 60 wt.-% LC represents a much greater distance between two adjacent cross-linking points than the network prepared with 20 wt.-% LC. Such an increase of the distance between cross-linking points leads to an increase of the network elasticity and thus to a decrease of the storage modulus. A dramatic change of the modulus occurs at temperatures below −60°C and particularly for LC concentrations higher than 30 wt.-%. Decreasing temperature leads to a strong enhancement of E' especially in the range of LC concentrations between 50 and 80 wt.-%. For example, at a temperature of −95°C, a storage modulus of $E' = 1300$ MPa was found at 30 wt.-% LC, and a dramatic enhancement yielding $E' = 2800$ MPa was obtained at 50 wt.-% LC. These observations can be explained by the appearance of glassy LC domains below $T = -62°C$, resulting from the phase separated morphology of the sample, which is composed of the polymer network and segregated sub-micron-sized LC domains. The temperature and composition controlled formation of glassy LC domains inside the polymer matrix reinforces the structure and leads to improved mechanical properties.

At LC concentrations below 30 wt.-%, the polymer/LC system does not exhibit a phase separated structure in the whole range of temperatures investigated, thus no reinforcement effect could be observed.

Further increase of the LC content above 50 wt.-% leads to lower storage moduli, since the reinforcement effect becomes less important: Smaller LC domains merge into bigger regions, and as a result, the number of phase separated LC domains decreases. It is known in general, that number density, size, and shape of such reinforcing regions are important parameters for improving the modulus, and not their total volume [27].

In contrast to the results obtained from EB-cured films, Figure 4b shows the observations found for UV-cured samples, which do not represent the same characteristics. Indeed, no enhancement effect on the storage modulus was detected for experiments with varying LC content compared to the pure polymer matrix, even at the lowest temperature measured ($T = -95°C$). At temperatures above −5°C, UV-cured films showed the same behavior when compared to EB-samples. The storage modulus decreases with increasing LC content in the temperature range from $T = 25°C$ to −5°C, due to the plasticizing effect induced by the presence of low molecular weight LC in the polymer matrix. Only in the case of polymer/LC blends with more than 30 wt.-% LC and for temperatures lower than −5°C, a reinforcement effect could be seen, leading to a change of the shape of the decreasing curves. This phenomenon interferes with the plasticizing effect which himself governs the whole mechanical behavior of the UV-cured polymer/LC system. A sort of competition takes place especially for temperatures lower than −50°C, so that the storage modulus increases or remains constant between 20 and 60 wt.-% LC. As for the EB-case, the change of the shape of the curves is due to the glassy LC domains which stabilize the modulus. At LC concentrations above 60 wt.-%, E' decreases continuously since the phase separated LC domains merge together to form bigger objects which no do not furthermore reinforce the structure.

4. Conclusions

Dynamic and static mechanical analysis of in-situ formed cross-linked poly(tripropyleneglycoldiacrylate) matrices are presented. Dilution of the initial mixture with a low molecular weight LC like E7 leads to a significant weakening of the mechanical strength of the obtained cured films. This decrease is essentially due to a plasticizing effect of the LC molecules randomly dispersed in the polymer network. Above 30 wt.-% LC, radiation induced crosslinking polymerization of TPGDA/LC leads to heterogeneous systems consisting of segregated LC domains dispersed in the polymer host. A strong unusual reinforcement of the mechanical modulus was found for EB-cured phase separated TPGDA/E7 films below the LC glass transition temperature. This enhancement effect leads to the conclusion that mechanical properties of these composite systems can be made tunable depending on the dispersion of phase separated LC domains inside the host polymer, and on their glass transition temperature.

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