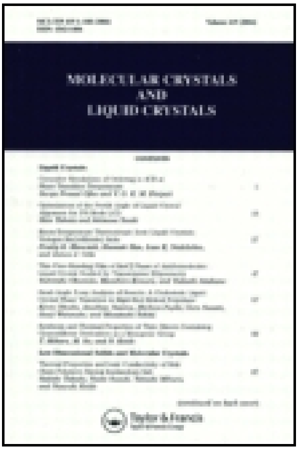

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Liquid Crystal Properties Modulation for High Performance PDLC Films

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PDLC films (Polymer Dispersed Liquid Crystals) can be used in the construction of electrically switchable architectural windows (smart windows). In the last decade many efforts have been devoted in this field by the industries in order to optimize and commercialize a product based on PDLC materials for the building industry. For this application, the main properties that should be controlled in the PDLC film fabrication to obtain a high quality product are the haze and the opacity.

In the present work we show how it is possible to modify the phisical properties of a commercial liquid crystal by adding an isotropic component in order to improve the electro-optical performances of PDLC films containing a given polymer matrix. In particular, a considerable reduction of both normal and off-axis haze can be obtained by properly selecting the chemico-phisical properties of the component added to the liquid crystal mixture.

Keywords: PDLC; haze; opacity; refractive index

INTRODUCTION

The main property of the PDLC films, which are composed of liquid crystal droplets dispersed in a polymer matrix, is the possibility to switch these materials, by applying an electric field, from a scattering field-off state to a transparent field-on state[1],[2]. This property has been largely used in the last years for the construction of electro-optical panels for applications in the building industry[3],[4]. A good product for these applications should have high opacity in the field-off state and high transparency over a wide viewing angle (low haze) in the field-on state.

As it is well known from literature[4],[5], the opacity of the PDLC films is related to the morphology of the liquid crystal droplets and to the birefringence of the liquid crystal used in the formulation. Highly opaque PDLC films can be prepared by properly selecting the process parameters in order to obtain samples with a given morphology. In the case of PDLC films prepared with an UV-curing phase separation method, where the nematic liquid crystal droplets are about spherical with a bipolar distribution of the director[6], it has been found that droplet diameters in the range 2-3μm usually assure a good opacity with the commercial liquid crystals commonly used in PDLC preparation[4]. For a fixed morphology, the opacity is correlated to the liquid crystal birefringence. In this work we have selected the process parameters[7] (UV intensity and curing temperature) in order to have in all PDLC samples droplet diameters in the range above indicated. Thus, the dependence of PDLC characteristics from the morphology can be, in this study, neglected.

Another important parameter which influences the performances of PDLC films for architectural windows is the haze, that is the residual opalescence observed in the presence of the electric field. As it is known[5], in PDLC films it must distinguish between a normal haze and an off-axis haze. The lower is the haze of the PDLC samples (both normal and off-axis), the higher is the quality of the product.

The relation between the refractive indices of the materials (polymer and liquid crystal) and the normal haze, as well as the dependence of the off-axis haze from the liquid crystal birefringence, are well known from literature[3],[4],[8]. Also the influence of the liquid crystal birefringence on the opacity of PDLC films has been largely studied in the past[3],[4]. In practice, it has been found that the lower is the index mismatching between the matrix refractive index and the ordinary refractive index of the liquid crystal (n_m-n_o), the better is the normal haze. In addition, the lower is the birefringence of the liquid crystal, the lower is the off-axis haze of PDLC films.

Thus, the modification of PDLC films normal haze can be accomplished by changing the index mismatching between the liquid crystal ordinary refractive index n_o and the matrix refractive index n_m, while the off-axis haze can be modified by changing the liquid crystal birefringence Δn. The variation of the liquid crystal Δn influences also the opacity of the PDLC films.

One way to produce these modifications is to change the liquid crystal or the polymer in the formulation. This change usually implies a modification in all process parameters. In fact, different liquid crystals have different solubility in the polymer matrix and different UV-absorption. Consequently, the kinetics of phase separation changes dramatically. Also a modification of the polymer matrix usually involves a change in the process parameters and, consequently, needs new experimentation in order to optimize the phase separation.

One important feature that should possess a PDLC formulation for industrial use is the flexibility, that means the possibility to change the electro-optical performances (haze and opacity) of PDLC films without changing the overall materials which should imply a change in the process parameters and, consequently, a modification of the production plant configuration.

In this work we show how it is possible to change some chemico-phisical properties of the liquid crystals, that are the ordinary refractive index and the optical birefringence, in order to improve the haze of the PDLC films, by adding small percentages of an isotropic chemical component to the liquid crystal mixture. The advantage of this method is that in this way it is not necessary to change all process parameters to improve the performances of the films, because the basic materials in the formulation (liquid crystal and polymer) are essentially unchanged.

In order to demonstrate the potentiality of the method introduced in this work, the system selected here shows a considerable mismatching between the matrix and liquid crystal refractive indices. The prepolymers used are NOA65 (Norland) and CN934D60 (Sartomer). The refractive index measured on the matrix used in PDLC preparation is 1.540. This refractive index is strongly influenced by the quantity of liquid crystal dissolved in the matrix[9], wich is about 30% in the system studied here. Consequently, the liquid crystal used in the preparation of PDLC should have an ordinary refractive index in the range 1.525-1.540 to obtain a sample with an acceptable normal haze[4]. The commercial liquid crystals which have the n_o in the range above indicated, usually possess high birefringence ($\Delta n > 0.20$). The basic rules found for the preparation of high performances PDC films[3],[4] indicate that such values of birefringence do not allow the preparation of low-off axis haze PDLC samples.

We have tried in this work to increase the n_o of the liquid crystals, reducing in the mean time the birefringence, by adding to the liquid crystal mixture few percentages of an isotropic material which has a refractive index higher than the ordinary refractive index of the liquid crystal. In this way it should be possible to reduce both the normal and the off-axis haze of PDLC films by decreasing the index mismatching n_m-n_o, through an increase of the liquid crystal n_o, and the Δn of the liquid crystal. The advantage of the method reported in this work is that, by adding some chemical component to the liquid crystal mixture, it is possible to adjust the phisical properties of the commercially available liquid crystals in order to match them to the characteristics of the matrix used in the formulation. The disadvantage is that the introduction of an isotropic component in the liquid crystal mixture decreases its nematic-isotropic transition temperature (Tni). This phenomenon must be taken into account in PDLC preparation because, for architectural applications, the Tni of the final PDLC product should be high enough (usually >70°C).

The component added to the liquid crystal mixture must be chemically compatible with the liquid crystal, because it should remain definitively in the liquid crystal droplets after the phase separation. Thus, it has to be selected by taking into account the chemical composition of the liquid crystal mixture.

In this work we report the results obtained on PDLC films prepared using the liquid crystal TN0623 (Rolic), added with different percentages of diphenilether (DFE by Aldrich). This material is soluble in the liquid crystal examined until more than 15% w/w and has a refractive index n=1.579. The effects of DFE content on the liquid crystal and PDLC properties have been studied.

The method of adding some chemical component to the liquid crystals in order to adjust the properties of the commercially available liquid crystal mixtures to the matrix characteristics and to improve the performances of PDLC films, can be in principle extended to other materials employed in PDLC fabrication.

EXPERIMENTAL

The PDLC samples were prepared with the UV-cureable (UV-PIPS) processing from a solution of acrylic prepolymers and liquid crystal mixture (TN0623 by Rolic). The prepolymers used were the commercial UV-cureable mixtures: NOA65 (Norland) and CN934D60 (Sartomer). The refractive indices of the cured polymers were 1.524 (NOA65) and 1.505 (CN934D60). During the processing of PDLC films, we introduced a small percentage of acrylic acid (n = 1.455) to improve the index-matching of the polymer matrix and liquid crystal refractive indices.

The matrix used in PDLC preparation had the following composition: NOA65=64%, CN934D60=27%, acrylic acid=9%. The refractive index measured on the pure polymer n_p was 1.515.

The PDLC films prepared in this work contained 50% of the matrix and 50% of the liquid crystal mixture. The phisical properties of the liquid crystal selected TN0623 were: n_o=1.507, Δn=0.198, Tni=105°C. The liquid crystal was added of different percentages of diphenilether (DFE by Aldrich, n=1.579) by mixing the solutions for few minutes at a temperature of 50°C. The liquid crystal mixtures obtained were examined with an optic microscopy (Laborlux 12 pol.) equipped with an heating apparatus and with the Differential Scanning Calorimeter (Perkin Elmer DSC7) in order to measure the nematic-isotropic transition temperatures Tni. The refractive indices of the mixtures were measured with an Abbe refractometer (ATAGO 4T). During the processing of PDLC films, a significant quantity of liquid crystal remains dissolved in the matrix, changing its refractive index. This phenomenon has to be taken into account in PDLC preparation because the matrix refractive index n_m, wich influences the normal haze of PDLC, is different than the pure polymer refractive index. This refractive index was measured in our system by mixing the prepolymer with the maximum quantity of liquid crystal wich do not show phase separation after polymerization, and measuring the refractive index of the film cured at the same process conditions utilized in PDLC preparation. This method gave for the matrix an approximate refractive index of 1.540.

The PDLC film samples were prepared between ITO-coated PET films with an in-situ coating and laminating technique, using a specially designed film laboratory coater. The thickness was fixed by using mylar micro-sphere spacers of 15μm. No important influence on the curing process was observed so, all PDLC samples were prepared by curing under a high pressure Mercury UV lamp at a curing temperature of 40°C, UV intensity of 20 mW/cm^2 and

UV energy of $2000 mJ/cm^2$. The haze and opacity of the PDLC films were measured with a Macam LSO-4514 haze-meter instrument, described in a previous work[4]. We chose the 30° as the standard angle for measurements of the off-axis haze. The normal and off-axis haze measurements were made at a voltage of 100 VAC (50Hz sin.wave) well above the threshold voltage of the samples (around 40 VAC).

The opacity was obtained by measuring the off-state transmittance (%Toff). The lower is Toff, the higher is the opacity of the PDLC sample.

RESULTS AND DISCUSSION

In table I the refractive indices of the liquid crystal mixtures obtained by adding different percentages (w/w) of DFE to the liquid crystal TN0623 are reported. The choice of the component DFE is related to the chemico-phisical properties of such material. DFE is chemically compatible with the liquid crystal TN0623, in fact the solutions of DFE in TN0623, observed to the optic microscopy and to the DSC, remain stable for several months.

DFE has a refractive index (n=1.579) higher than the ordinary refractive index of TN0623 mixture (n_o=1.507), consequently it should increase the n_o of the liquid crystal. This increase is necessary to improve the normal haze of the PDLC. In fact, as indicated in the previous section, the matrix used in PDLC formulation has a refractive index of 1.540. Thus, the ordinary refractive index of TN0623 (n_o=1.507) has to be increased to improve the index matching with the matrix and reduce the normal haze of the PDLC samples[4].

DFE is an isotropic material and, consequently, it should have the effect of reducing the optical birefringence when added to the liquid crystal mixture. As it is known[4], the reduction of the liquid crystal birefringence has the effect of improving the off-axis haze and decreasing the opacity of the PDLC films. By properly selecting the percentage of DFE to be added to TN0623, in principle it should be possible to find a range of liquid crystal birefringence which allows the preparation of low off-axis haze PDLC films with an acceptable opacity for the application studied here.

As expected, the data on table I indicate that DFE has the effect of increasing the ordinary refractive index n_o, and decreasing the birefringence Δn of the liquid crystal TN0623.

TABLE I Refractive indices of the liquid crystal mixtures obtained adding different percentages of DFE to the liquid crystal TN0623.

% DFE	n_o	Δn
0	1.507	0.198
5	1.513	0.183
10	1.518	0.167
15	1.523	0.137

In figure 1 we have reported the values of haze at 0° (normal) and 30° (off-axis) measured on PDLC samples containing 50% of the matrix reported in the previous section and 50% of the liquid crystal mixtures reported in table I versus the percentage of DFE present in the liquid crystal mixture.

The plot on figure 1 indicates that the increase of the DFE percentage in the system studied causes a reduction of both normal (0°) and off-axis haze (30°). The reduction of the normal haze is related to the decrease of the index mismatching n_m-n_o between the matrix and the liquid crystal, which is determined by the increase of the n_o due to the DFE loading in the liquid crystal mixture. The decrease of the off-axis haze is explained by the lowering of the liquid crystal Δn due to the increase of the DFE loading.

The reduction of the liquid crystal birefringence causes also a decrease in the opacity of PDLC films, as indicated in figure 2 where the off state transmittance (%Toff) of the PDLC films has been reported versus the DFE loading in the liquid crystal. The increase of % Toff indicates a reduction in the opacity of the films.

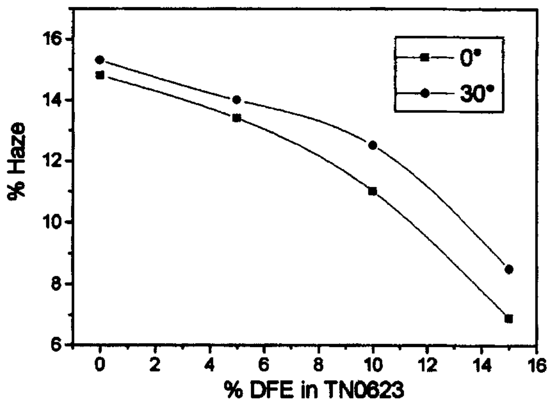

FIGURE 1 Normal (0°) and off-axis (30°) haze of PDLC films versus DFE loading.

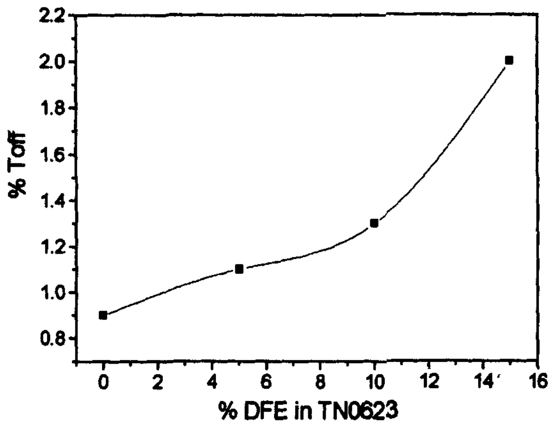

FIGURE 2 Opacity (%Toff) of PDLC films versus DFE loading.

The nematic-isotropic transition temperatures of the liquid crystal mixtures obtained by adding different percentages of DFE to TN0623, as well as the Tni of the PDLC samples containing these mixtures, are reported in table II. The reduction of the Tni in both liquid crystal mixtures and PDLC samples is explained by the introduction of an isotropic material in the liquid crystal eutectic mixture. At the highest concentrations (≥10%), the DFE partially dissolves in the matrix, thus the Tni of the PDLC is higher than the Tni of the corresponding liquid crystal mixture. On the other hand, the quantity of DFE dissolved in the liquid crystal droplets of PDLC increases going from 0 to 15% of DFE, as indicated by the reduction of Tni observable in the samples. Thus, at the highest content of DFE, the reduction of haze and opacity in PDLC samples can be qualitatively explained by considering a progressive increase of DFE in the liquid crystal droplets.

TABLE II Nematic-isotropic transition temperatures of the liquid crystal mixtures (LCs) containing different percentages of DFE dissolved in TN0623 and of the PDLC films prepared using these LCs.

% DFE	Tni LCs (°C)	Tni PDLC (°C)
0	105	95.4
5	87.4	86
10	71.8	75
15	58.7	66.3

It should be remarked here that the results obtained in this work on the haze values are not influenced by the switching voltages, because the haze measurements were carried out at a voltage (100VAC) well higher than the threshold values (about 40V). Thus, although a little change (< 5 volts) in the switching voltages was observed after the introduction of the DFE, due presumibly to a change in the dielectric and/or elastic constants, these phenomena were not treated here, and will be the subject of a future paper.

The method of adding a chemical component, like DFE, to the liquid crystal mixture can be extended to other systems. The materials examined here showed a considerable difference between the matrix and liquid crystal refractive indices, thus it was necessary to introduce a big quantity of DFE to the formulation in order to reduce the normal haze to an acceptable value. Consequently, the reduction of Tni observed in the final product is significant. The selection of this system had the objective to highlight the effects of the method introduced here. In practice, the materials used in PDLC preparation usually do not show a big index mismatching (n_m-n_o ≅ 0.015, which corresponds to a normal haze ≅ 6%). In these systems, our approach allows the reduction of normal haze to values lower than 4% by adding small percentages (<5%) of a proper component, without depressing the Tni of the final product and without changing the overall materials. Further study in this field are in progress at our laboratory.

CONCLUSIONS

The results obtained in this work indicate that it is possible to modify the phisical properties of a commercial liquid crystal by adding some percentages of an isotropic component in order to improve the electro-optical properties of PDLC films. In particular, in the system studied here, the introduction of 15% of DFE in the liquid crystal mixture TN0623 allows the reduction of PDLC normal haze from 15% to less than 7% and the reduction of the off-axis haze from 16% to 9%.

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