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DIFFERENTIAL SCANNING PHOTOMETRY (DSP): A NON-DESTRUCTIVE APPROACH TO STUDY THE MORPHOLOGY IN PDLC FILMS

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Abstract We present a new non-destructive and direct analytical method to study the morphology in PDLC films. This method, referred to as Differential Scanning Photometry (DSP), is based on continuous monitoring of the differential optical transmission as a function of applied voltage. Here, the preliminary experimental results of DSP analysis, are compared with the informations obtained by Scanning Electron Microscopy (SEM), on a set of UV-cured PDLC samples where morphology was changed via variation of the liquid crystal content. Although the present DSP morphological analysis is based on the available theoretical models, their correlation with SEM morphology is straight forward. Further analytical improvements of DSP method for quantitative analysis of PDLC morphology is in progress at our laboratory.

INTRODUCTION

PDLC systems are thin films consisting of a dispersion of liquid crystal micro-droplets in a continuous solid phase of polymer matrix. Application of an electric field on a thin layer of PDLC sandwitched between two transparent electrodes results in a change from translucency (off-state) to transparency (on-state).

PDLC films are prepared by either micro-encapsulation or phase separation approaches, where the LC micro-droplets are formed before or during (in-situ) polymer curing, respectively. While formation of LC micro-droplet morphology with encapsulation is rather straight forward, it is more complicated with the phase separation approach, due to the contribution of the curing kinetics parameters. In either case, the morphological properties, such as micro-droplet sizes, number density and polydispersity, are responsible for the electro-optical phenomena, such as switching voltages, transparency/opacity (contrast ratio), response times, hysterises, etc. in PDLC films.

With the three known phase separation methods; i.e., Polymerization Induced Phase Separation - PIPS, Solvent Induced Phase Separation - SIPS and Thermally Induced Phase Separation - TIPS [1 2 3], it is possible to establish and control the micro-droplet

morphology, i.e., dimension, number density and dispersity, via appropriate selection of material processing. Consequently, the control and knowledge of PDLC morphology is essential for the understanding and improvement of the electro-optical behavior of PDLC films.

Conventionally, the analysis of morphology in PDLC is carried out by SEM,[4] which is a very precise analytical approach, yet costly, time consuming and destructive. The DSP approach has been developed on the basis of the need for a simple and non-destructive method to provide quick knowledge of morphology during the industrial-scale processing and fabrication of PDLC films.

DSP METHOD

The development of DSP method is based on a simple continuous monitoring of the "differential transmittance" of a PDLC sample as a function of small increments of the applied voltage. This choice arises from the premise that in the region between the "threshold voltage" and "saturation voltage", the slope of the conventional "integral transmittance-voltage" curve is sensitive to micro-droplet dimension. In fact, because of interactions at the droplet boundaries, there is a strict correlation between the droplet sizes and their orientation voltage of nematic director within the droplets. In this case a "differential transmittance-voltage" plot would be descriptive of the kind of morphology in the sample. In particular, in a series of PDLC samples with the same formulation (i.e., PIPS, SIPS or TIPS) and sample thickness, but with different morphology (obtained by variation in their curing and phase separation conditions), the DSP method is not only able to differentiate between various morphologies, but also is capable of distinguishing the presence of poly-dispersity in the samples[5].

In its present state of development, the DSP method is limited to a qualitative differentiation of the morphologies in similar group (i.e., all UV-cureable, thermoset, etc.) of the PDLC samples. In another words, the morphological information, such as micro-droplet dimensions, numbers and size distributions, can be only presented in arbitrary units proportional to their actual quantitative values. Otherwise, this technique is potentially more advantageous than SEM, because of its non-destructive, rapid and economic capabilities in analysis of the PDLC morphology.

Although with some strong assumptions, the DSP procedure of Transmittance vs Voltage data analysis is strictly connected to the available theoretical model. The correlation between the electro-optical properties i.e., transmittance and applied voltage, and morphology in a PDLC film, had been theoretically described in the literature by the following relationships: [6, 7]

$$T = \frac{I_t}{I_o} = F\, e^{-N \sigma t} \qquad (1)$$

$$V = \frac{K t}{D} \qquad (2)$$

where T is the percent of light transmittance in the absence of the electric field; I_o is the intensity of the incident light; I_t is the intensity of transmitted light; F is the transmittance of the support (metallized glass or PET film); N is the number of LC micro-droplets per unit volume; σ is the light scattering probability (which depends on the refractive index of the materials, wavelength of the light and dimensions of micro-droplets); t is the PDLC layer thickness; V is the voltage which is applied to the PDLC sample; K is a constant dependent on the dielectric constants of LC and electrical properties of the matrix, and D is the average dimensions of the LC micro-droplets.

Based on equation (1) and (2), it is clear that a gradual increasing of the voltage applied to the PDLC sample results in an increasing of the transmittance, due to the gradual orientation of the liquid crystal droplets, from the biggest to the smallest.

This is the reason, as it will be seen in the experimental results, that by just differentiating the transmittance vs. voltage curves, a strong correlation with the PDLC morphology is observed.

In order to make these correlations more evident, the experimental transmittance vs. voltage curves, was elaborated according to the following criteria, that, although based on very drastic assumptions from a theoretical point of view, allows an easier understanding of the results.

In equation (1), N is the total number of liquid crystal micro-droplets and assuming that n(D) is the number of micro-droplets between D and D+dD (including the micro-droplet size distribution function), it can be represented by the following relation:

$$N = \int_{D_{min}}^{D_{max}} n(D)\, dD$$

According to equation (2), we will assume that application of a voltage V, will result into a complete orientation of nematic phase in micro-droplets larger than $D_v = K\ t\ V^{-1}$. In this case, from equation (1) the value of light transmission at a constant voltage could be written as:

$$T(D_v) = F\ e^{-N_v \sigma t} \tag{3}$$

where

$$N_v = \int_{D_{min}}^{D_v} n(D)dD \tag{4}$$

The droplets larger than D_v do not contribute to light scattering because they are already oriented with the applied voltage. In equation (3), $T(D_v)$ can be extracted from transmission-voltage experimental points, which was reported in terms of transmittance vs voltage^{-1} [$T(V^{-1})$] and then linearly interpolated.

In the limit that polydispersity in the PDLC morphology is very small, it is possible to demonstrate that the micro-droplet size distribution n(D) is proportional to:

$$\frac{-1}{T(D_v)} \frac{dT(D_v)}{dD_v} \tag{5}$$

From assumptions made previously the DSP curves obtained using equation (5), have only an indicative value and the n(D) vs. D plots that will be reported later on, are just representative of the micro-droplet size distribution (so we will report them in arbitrary units - a.u.).

Furthermore, we must take into account that the validity of the criteria adopted is very limited in the case of high polydispersity in the PDLC morphology.

This type of plots will be utilized to elaborate the experimental electro-optical results, and to correlate with the morphological data obtained from SEM.

EXPERIMENTAL

Sample preparation

The proposed method in this study has been experimentally verified with many classes of PDLC samples prepared by the PIPS method.

As an example, in this work, the results with the DSP method are compared with the ones from SEM micrographs on a class of PDLC films prepared with the UV-cureable

(UV-PIPS) processing, in which the micro-droplet morphology was changed via variation of the liquid crystal content in the formulation.

The PDLC samples having different morphologies were prepared by a UV radiation induced polymerization in homogeneous mixtures of polyurethane NOA65 prepolymer (Norland) and TNO403 nematic liquid crystal (Rolic). The concentration (in weight percent) of TNO403 with respect to NOA65 in these formulations were 30%, 40%, 45%, 50%, 60% and 70%.

The PDLC samples were prepared between the ITO-coated PET films by an in-situ coating and laminating technique utilizing a lab-coater. The uniform spacings of the film was accomplished by the use of micro-sphere mylar spacers of 15 μm. All PDLC samples were prepared at a temperature of 30 °C and under the same processing conditions with a UV intensity of I=20 mW/cm^2 and a UV radiation energy of E=2000 mJ/cm^2.

Transmittance vs. voltage measurements

A block diagram of the photometric system for the electro-optical measurements is shown in Fig. 1. The system consists of an electronic network of data acquisition capable of scanning the transmittance from a minimum to a maximum voltage with small incremental steps. For this class of PDLC samples, the voltage scan was made from 0 to 64 Volts (sin. wave - 1 kHz) with a step of 50 mV (1280 transmittance readings in total).

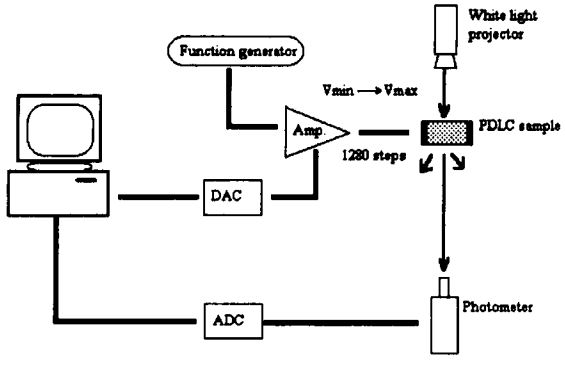

Figure 1 Block diagram of photometric system for the scanning transmittance vs. voltage measurements.

Scanning Electron Microscopy (SEM)

A cross-section of the PDLC samples was observed with a scanning electron microscope (JEOL - JSM 6300) with fracture analysis approach. On the SEM images of the PDLC samples the number and the diameter of each micro-droplet was measured. From these analyses the average diameter and the number density of LC droplets were extracted.

RESULTS AND DISCUSSION

SEM Analysis

In fig. 2 and 3 we show the SEM micrographs and the results of the image analysis of the PDLC samples with various concentrations of liquid crystal.

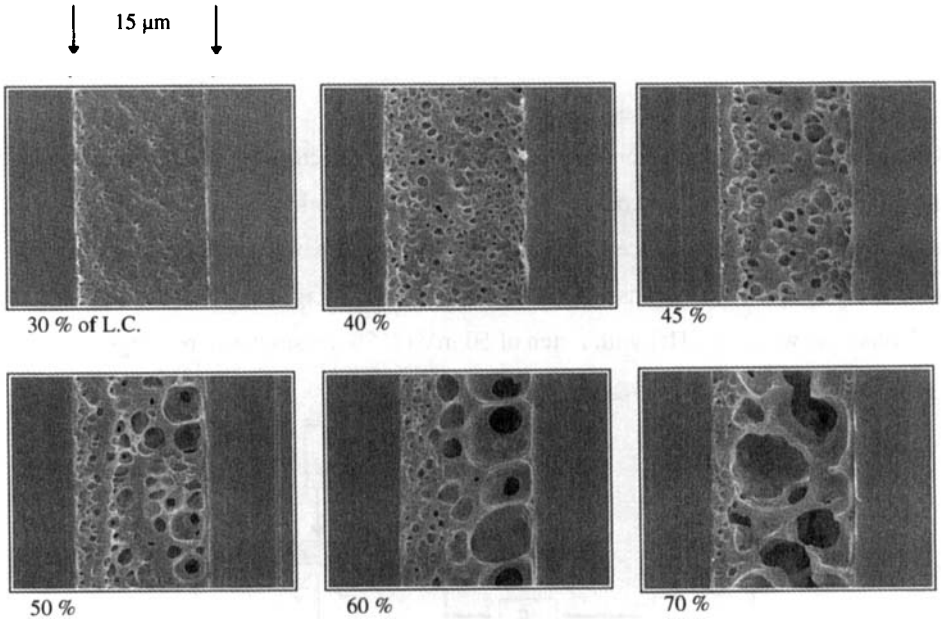

FIGURE 2 SEM micrographs of sections of PDLC films from 30 to 70 % of liquid crystal content.

The main conclusion that can be obtained out from these data can be summarized as follows:

(a) the droplet size increases with the liquid crystal content in the formulation;

(b) the droplet number density shows an increase within 30 to 40 % of liquid crystal content, then it decreases with droplet size growth;

(c) when the content of liquid crystal is more than 50 % a droplet size polydispersity is observed between the left (directly exposed to UV rays) and right edge of the micrographs. A plausible explanation of this effect is the absorption of the liquid crystal at wavelenghts of curing which cause a different rate of UV radiation along the film thickness.

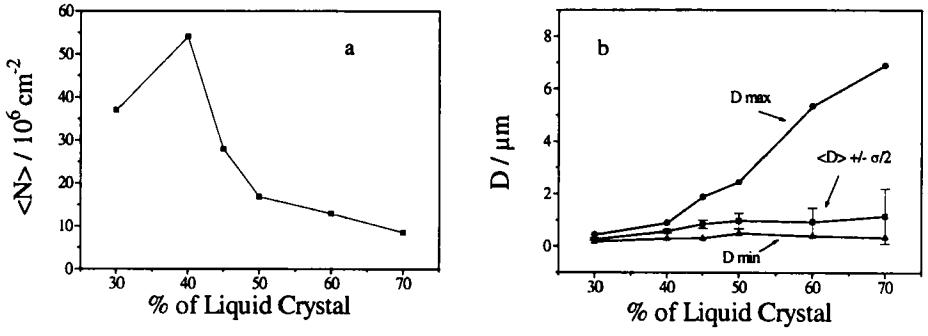

FIGURE 3 Effect of the liquid crystal concentration on number density (a) and their average diameters (b) of micro-droplets.

DSP Analysis

In fig. 4 and 5 the transmittance vs voltage curves and their differential curves are shown. In these differential curves, it can be observed that while the droplet size increases (increasing the liquid crystal content in the formulation), a different position of the voltage peak occurs at lower voltages.

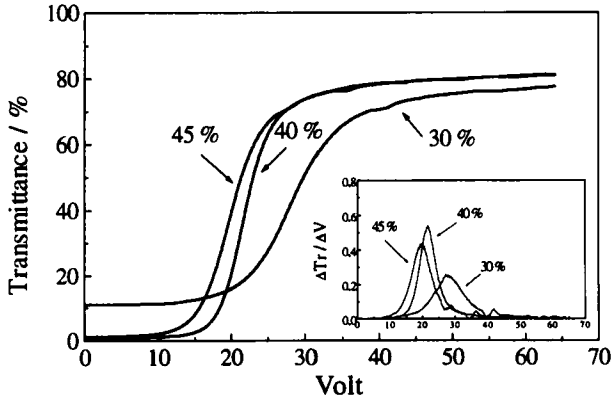

FIGURE 4 Transmittance vs voltage curves on PDLC samples from 30 to 45 % of liquid crystal content with their differential curves.

This is due to the increase of the polymer / liquid crystal surface interactions: for the same liquid crystal volume, higher are the droplet diameters, the lower is the total droplet surface and the lower the voltage needed to align the liquid crystal within the droplets. This behavior was described by the Lavrentovich model in eq. (2). In addition, we observe also a broadening in these differential curves corresponding to the appearance of poly-dispersity in the PDLC samples.

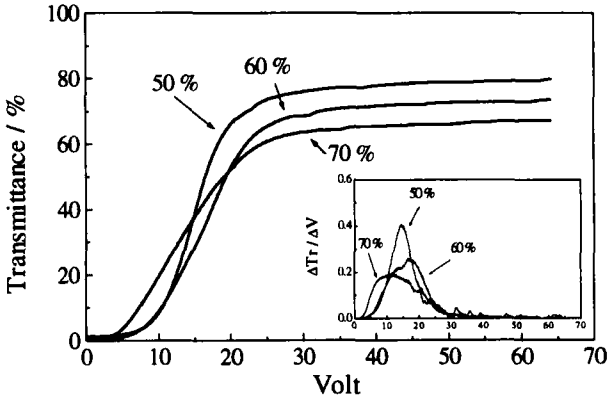

FIGURE 5 Transmittance vs voltage curves on PDLC samples from 50 to 70 % of liquid crystal content with their differential curves.

In fig. 6 we report the previous differential curves according to the DSP method. Taking into account that these curves were extracted from a simple transmittance vs. voltages measurements, the agreement with the SEM data in fig. 3 is impressive.

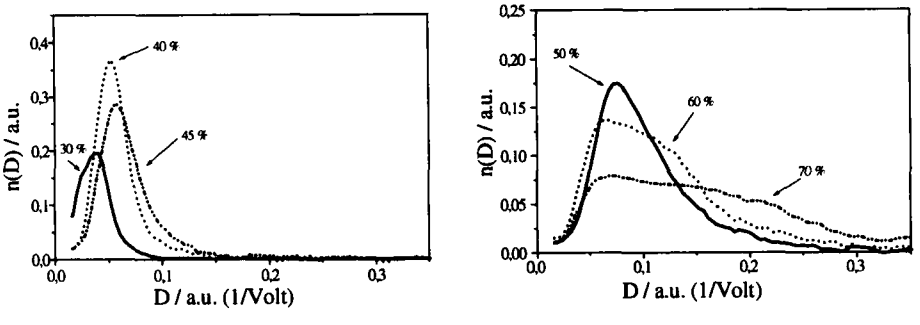

FIGURE 6 Transmittance vs voltage differential curves according the DSP method on PDLC samples from 30 to 70 % of liquid crystal content.

Although qualitative, the information that can be obtained from DSP analysis (i.e., the plot obtained from eq. (5) and represented in fig. 6) are quite similar to those from SEM. Respectively:

(a) the droplet dimension (position of DSP peaks) increases on increasing the liquid crystal content;

(b) the number of droplets (height of the DSP peaks) increases between 30 to 40% of liquid crystal content. Then it decreases with droplet size growth;

(c) when the amount of liquid crystal is more than 50 % a droplet polydispersity is observed. This is evident from the dispersion of the curves and their broadening towards wider droplet sizes.

CONCLUSIONS

We have presented a new approach for studying the morphology in PDLC films, based on the differential measurements of transmittance as a function of the applied voltage.

In its present state of development, this method, referred to as DSP, is not only able to differentiate between various morphologies, but also is capable of distinguishing the presence of poly-dispersity in PDLC samples.

As an example, the efficiency of this approach was illustrated by comparing its results with the SEM image analysis, on a class of UV-cured PDLC sample where the morphology was changed via variation of the liquid crystal content. Detailed analysis of this DSP method will be published later.

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