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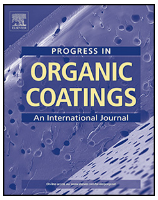

Optimizing polarization efficiency of optically anisotropic films cast from lyotropic chromonic liquid crystals on surface-modified triacetyl cellulose films

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ABSTRACT

Optically anisotropic films by shear coating of a lyotropic chromonic liquid crystal (LCLC) aqueous solution were developed on a triacetyl cellulose (TAC) film instead of a glass substrate. The TAC film surface was treated using a sodium hydroxide (NaOH) solution to increase its surface energy for wetting ability. Although the desired surface energy, which is competitive with glass, was achieved, the TAC film surface became rougher during NaOH hydrolysis, which aggravated the alignment of LCLC aggregates, especially for those with a small length-to-width ratio. To alleviate the surface roughness without compensating the surface energy, further treatment of the NaOH-hydrolyzed TAC film was performed using atmospheric pressure Ar/O_2 plasma. After optimization of the treatment conditions, the combined method could enhance the polarization efficiency (P_{eff}) of the anisotropic film on the TAC substrate from 91.2% to 95.9%, which was nearly equal to that on a glass substrate.

1. Introduction

Recently, many studies have investigated making thin and pliable film polarizers using a coating method to prepare future flexible liquid crystal displays [1–4]. A representative approach is the use a shear coating of a lyotropic chromonic liquid crystal (LCLC) solution, and the prepared coatable polarizers are considered to be potential candidates for replacing conventional iodine complex polarizers [5–10]. The LCLCs used for coatable polarizers have disk-like aromatic central cores with hydrophilic ionic peripheral groups. At appropriate concentrations in a polar solvent, LCLCs form self-organized columnar stacks and exhibit a columnar nematic phase [11–15]. Self-organized columnar stacks are aligned along a particular direction by shear coating and form an anisotropic film after drying. This type of anisotropic film is known as an E-type polarizer.

Because LCLCs are typically used as aqueous solutions, coatable polarizers are easily formed on a glass substrate due to its hydrophilic nature. However, a glass substrate is too rigid for application in a roll-to-roll coating process for flexible devices. Therefore, a flexible plastic film has been proposed as an alternative substrate instead of rigid glass. However, its hydrophobic surface must be modified prior to LCLC aqueous solution coating. The polyvinyl alcohol and TAC used in conventional polarizers can be used for this purpose, and TAC is preferable to polyvinyl alcohol because it has better optical properties, such as low haze, birefringence and depolarization index [16]. However, the TAC film has a surface energy that is too low for use as a substrate in water-based coating.

Representative methods for imparting hydrophilicity to TAC film include the chemical hydrolysis method using an alkali solution treatment and the physical etching method using corona and plasma treatments. Hydrolysis with a NaOH solution is known to be the most effective method for imparting a high surface energy to the TAC film by regenerating hydroxyl groups from acetyl groups [17,18]. However, this treatment is inevitably accompanied by increasing surface roughness. However, low and atmospheric pressure plasma treatments using argon, helium, and oxygen as reactive gases can enhance the surface energy without a significant increase in the surface roughness but they result in a much lower surface energy compared to NaOH hydrolysis [17,19]. In fact, these methods are primarily utilized to improve the adhesion between two different materials, and optical properties, such as transparency and optical anisotropy, have not been an important concern until now.

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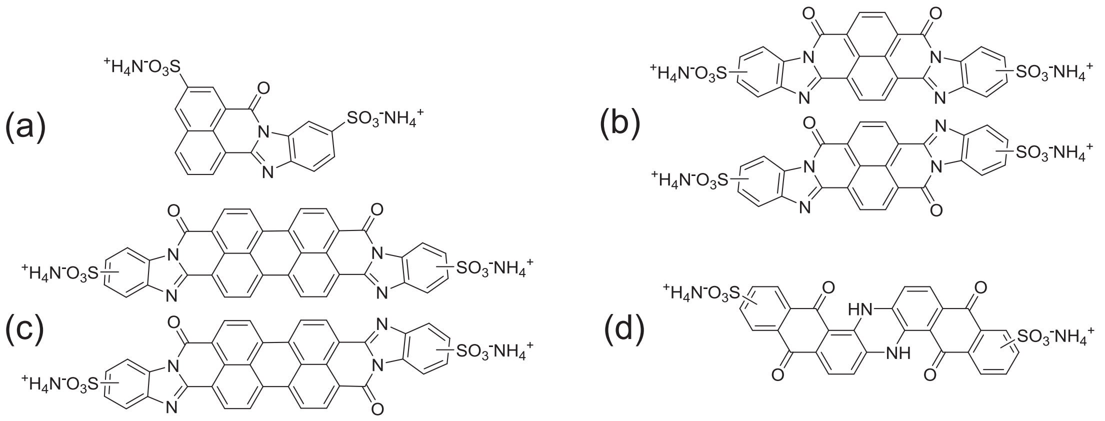

Fig. 1. Chemical structures of lyotropic chromonic liquid crystals: (a) yellow, (b) red, (c) violet, and (d) blue.

In this study, we attempted to develop a surface treatment method that was suitable for preparing optically anisotropic TAC films by coating with a nematic LCLC aqueous solution. The surface energy and topological changes due to surface treatments were analyzed, and their effects on the alignment were interpreted in terms of polarizer efficiency of the fabricated anisotropic films. Based on the results, the factors affecting non-uniformity and misalignment caused by TAC films were investigated and discussed based on the LCLC molecular structure.

2. Experiments

2.1. Materials

The TAC films (60 μm), which have a weight-average molecular weight (M_w) of 130,000, were supplied by SK Innovation (South Korea). Sodium hydroxide from TCI (Japan) was used for preparing the surface hydrolysis solution. Ultrapure water with a specific resistance higher than 18.1 MΩ cm was used for the rinsing and mixing solutions.

Yellow, red, violet, and blue LCLCs, which were used for fabrication of optically anisotropic polarizer films by shear coating, were prepared according to previously reported protocols [20–22], and their chemical structures are shown in Fig. 1.

2.2. Preparation of anisotropic films

Prior to the coating process, the TAC film surfaces were hydrolyzed with a 7% (wt/vol) NaOH aqueous solution at 40 °C by varying the treatment time from 5 to 60 min. After hydrolysis, the TAC films were rinsed with ultrapure water several times, dried at 70 °C for 10 min, and stored in a desiccator prior to use. At least two or more runs were replicated for each set of experiments.

Plasma treatment of TAC films was performed using atmospheric-pressure argon/oxygen plasma generated by the MyPL plasma (AP Plasma, Korea). The MyPL radiofrequency (13.56 MHz) generator produces a filament-free diffuse plasma in argon with a small amount of reactive oxygen. The flow rate of the argon carrier gas was 5 L min^{-1} (5000 sccm), and the flow rate of oxygen was 25 sccm. The dimension and surface power density of MyPL plasma zone were 10 cm × 1 cm and 8 W cm^{-2}, respectively.

Anisotropic films were fabricated by shear coating of the LCLC mixture aqueous solution on glass or TAC substrates using an 8 mm wire wound film applicator rod (#3 wire size, Elcometer) followed by subsequent drying at room temperature to remove the water. The glass substrate was treated with the piranha cleaning solution at room temperature for 30 min, rinsed with distilled water and isopropyl alcohol and dried *in vacuo*. The average film thickness cast from the LCLC solutions was measured by Alpha Step IQ surface profiler.

2.3. Equipment and characterization

The UV–vis light absorbing properties of the LCLCs were measured with UV–vis spectroscopy (Shimadzu spectrometer 1601) using a 1.0×10^{-6} M aqueous solution. The phase behaviors of the LCLCs were monitored by a polarized optical microscope (Nikon LV100POL) equipped with a hot-stage (Mettler Toledo FT-82). The sample was prepared by introducing a LCLC aqueous solution between two glasses that were sealed with epoxy adhesives to prevent concentration changes during the analysis.

The surface polarity change of the TAC substrate due to hydrolysis and plasma treatment was characterized with an OCA 20 system (DataPhysics Instruments GmbH) using the sessile drop method. Fresh single drops of deionized water were dropped onto five different spots on the TAC substrate with a precisely regulated pipette. The contact angle was measured 10 min after drop deposition, and this measurement exhibited an error of less than ±2° at 25 °C.

FTIR-ATR (Perkin Elmer, Spectrum 100) was used to analyze the surface functional groups introduced by surface reaction on the TAC substrate. The FTIR-ATR analysis was performed using a diamond prism with a 45° incident angle.

The surface morphologies of the substrates were examined by AFM (Parksystem XE-100) in tapping mode. The scan size was $1.0 \times 1.0\,\mu\text{m}^2$. The root-mean-square (RMS) roughness (R_q) was calculated from the height variations from a mean surface level, and the peak-to-valley roughness (R_{pv}) was determined by the difference between the highest peak and the lowest valley.

The P_{eff} of the oriented thin films was evaluated by polarized UV–vis spectroscopy (Shimadzu, Spectrometer 1601) using rotating polarizing angles from 0° to 90° with respect to the shear direction of the films. The P_{eff} values were calculated according to the following equation:

$$P_{eff} = \frac{T_0 - T_{90}}{T_0 + T_{90}}$$

where T_0 and T_{90} are the transmittances of a film when it is aligned parallel and perpendicular to the polarizer, respectively.