# 고분자량 혼성배열 폴리비닐알코올/염료 복합체 필름의 제조

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# Preparation of High Molecular Weight Atactic Poly(vinyl alcohol)/Dye Complex Film

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## 1. Introduction

Poly(vinyl alcohol) (PVA) obtained by the saponification of poly(vinyl ester) like poly(vinyl acetate) or poly(vinyl pivalate) is a linear semicrystalline polymer, which have been widely used as fibers for clothes and industries, films, membranes, medicines for drug delivery system, and cancer cell-killing embolic materials[1-3]. PVA fibers and films have high tensile and compressive strengths, high tensile modulus, and good abrasion resistance due to its highest crystalline lattice modulus. Especially, PVA film is a second-to-none polarizing material for liquid crystal display.

Recently, high dichroic polarizers are desirable in many industrial applications such as thin-film transistor/liquid crystal displays and high precision optical devices. Conventional polarizers for these applications mostly employ iodine as the dichroic chromophore because polyiodine molecules exhibit much higher dichroism than other dyes[4-5].

Actually, commercial polarizing films were prepared by atactic PVA (a-PVA). PVA/iodine polarizing film is usually laminated on both sides with a polymer film such as cellulose triacetate, acrylic, or urethane polymer for its protection[6]. However, PVA/iodine polarizing film is susceptible to heat and moisture attack. Therefore, in relatively high temperature and/or high humidity conditions, polyiodine molecules are easily deformed and released from the polymer. Recently, much effort has been made to improve the durability of iodine polarizers, but polarizers prepared by dichroic dyes are better from the viewpoint of durability at the moment[7-8].

Especially, azo dye is widely used as a nonlinear optical chromophore, which is semifixed in a In this work, we prepared high molecular weight (HMW) a-PVA/dye polarizing film with high durability. Also, the polarizing efficiency and transmittance of HMW a-PVA/dye film were investigated.

## 2. Experimental

### 2.1. Preparation of PVA/dye film

HMW a-PVA film having a thickness of about 70 ㎛ was prepared by casting HMW a-PVA with number-average degree of polymerization ($P_n$) of 4000/water in a solution of various polymer concentration[9-11]. The homogenized solution was poured into a stainless steel dish and dried under vacuum at 40 °C for about 3 days. The azo dyes (Direct Blue and Red) purchased from Aldrich were used for the dichroic dye. Boric acid (3 wt.%) and $Na_2SO_4$ (0.02-0.05 wt.%) were added to aqueous solutions of the azo dye. Then, PVA film was dipped into azo dye solutions of

various concentrations at predetermined temperature for 1-10 min. The films taken out from the solutions were rinsed with cold water to remove the solution adhered on the film surfaces and dried in a vacuum for 24 h.

**2.2. Drawing of films**

In this work, two drawing methods were used. The films were drawn 5 times in boric acid (3 wt.%) solutions at 40 °C. The stretched films were subsequently dried at 40 °C for 24 h. Also, the films were one step zone-drawn 5 times at 150 °C. Zone drawing was carried out between a pair of narrow-band heaters with dimensions of 7 cm length, 2.5 cm width, and 1 mm thickness and moving at a speed of 5 mm/min. The film having 70 ㎛ thickness, 2.5 cm width, and 10 cm length was drawn under a tension on an Instron model 4201.

**2.3 Determination of efficiency of polarization**

The efficiency of polarization (PE) of HMW a-PVA/dye film was estimated using the Eq. (1).

$$PE\ (\%) = [(T_{//} - T_{\perp})/(T_{//} + T_{\perp})]^{1/2} \times 100 \qquad (1)$$

where $T_{//}$ and $T_{\perp}$ are the transmittances of the film superimposed on each other parallel and perpendicular to the direction of the elongation of the film, respectively.

## 3. Results and discussion

Generally, a dye polarizer suffers from a low degree of dichroism that makes it difficult to use it for applications requiring high contrast imaging. Therefore, an improvement of the dichroic ratio is the most significant task in the study of dye polarizers. In this work, HMW a-PVA/dye polarizing film with high durability was prepared. Fig. 1 shows the photograph of dye polarizer dyed by Direct Blue.

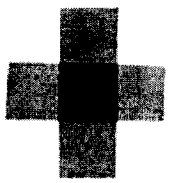

Fig. 1 Photograph of HMW a-PVA/dye polarizing film high durability prepared by soaking in aqueous dye solution (0.3 wt.%) and subsequent drawing (5 times) in aqueous boric acid solution (3 wt.%).

During drawing, the dichroic dyes orient, and consequently, anisotropic absorption of light in the visible wavelength range is generated. This results in the typical characteristics of a polarizer, i.e., two crossed polarizers hardly transmit light whereas two parallel polarizers are highly transparent. Generally, a dye polarizer suffers from a low degree of dichroism that makes it difficult to use it for applications requiring high contrast imaging. Therefore, an improvement of the dichroic ratio is the most significant task in the study of dye polarizers. In this work, HMW a-PVA/dye polarizing film with high durability was prepared.

Effect of dipping time on the transmittance and PE of HMW a-PVA/dye film drawn 5 times is shown in Fig. 2. As increasing dipping time, PE was increased to a very high level. Fig.3 shows

the UV spectrum of PVA/dye polarizer.

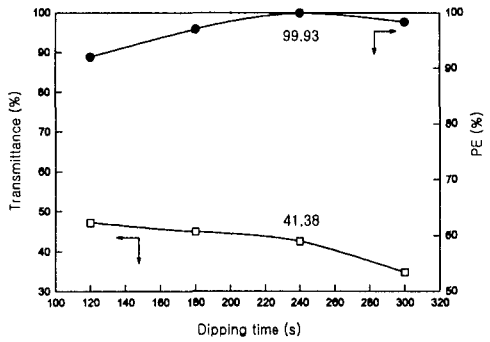


Fig. 2 Effect of dipping time on the transmittance and PE of HMW a-PVA/dye film prepared by soaking in aqueous dye solution (0.3 wt.%) and subsequent drawing in aqueous boric acid solution (3 wt.%).

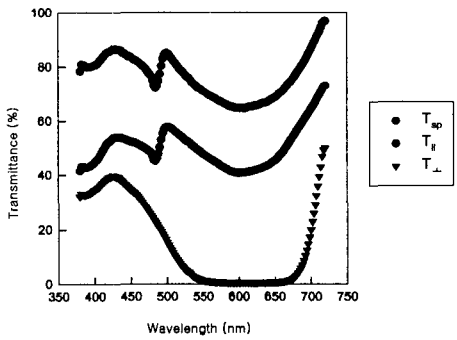


Fig. 3 UV spectrum of PVA/dye polarizer.

## 4. Conclusion

It is very difficult to obtain the PVA/iodine polarizer with high durability. To resolve the defect of a-PVA/iodine polarizing film such as iodine sublimation, in this study, PVA with $P_n$ of 4000/dye polarizer was prepared. PE and transmittance of HMW a-PVA/dye film drawn 5 times were 99.93% and 41.38%, respectively. As increasing dipping time, PE was increased to a very high level (99.93%) and transmittance was decreased.

## 5. References


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