Color change of an iodinated poly(vinyl alcohol) film by physical deformation

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ABSTRACT: The color change of an iodinated poly(vinyl alcohol) (PVA) film caused by physical deformation was investigated in this study. The color of a PVA film soaked in an aqueous potassium iodide (KI)/I_2 solution was light yellow, but it turned light blue when the film was physically deformed. The ultraviolet–visible absorption spectrum of the iodinated PVA film extended uniaxially in air was measured at various extension levels. Without deformation, the film showed UV absorption bands at 210, 290, and 360 nm. However, under deformation, the film showed new visible light absorption bands at 440 and 620 nm. From the UV–vis absorption spectra of several iodinated solutions, we found that the absorption wavelength of iodine was affected by the cohesive energy of the solvents. The KI/I_2 diethyl ether solution showed an absorption band at 460 nm, and this provided a clue to understanding the color change of the PVA–iodine complexes caused by physical deformation. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43036.

INTRODUCTION

When polymers such as starch,[1–4] nylon 6,[5] cellulose derivatives,[6–8] protein fiber complexes,[9,10] and poly(vinyl alcohol) (PVA)[11–15] are complexed with iodine, they show unique colors. These complexes involve highly sensitive color change reactions and have been used to indicate the endpoint of iodine titration.

PVA–iodine complexes involve one of the most important color change reactions because they are widely used for making polarizer films in liquid-crystalline displays[16,17] and for antiseptics in medicine.[18] These colored complexes have long been studied since the blue color development of aqueous PVA solutions with iodine was studied by Staudinger et al.[12] and Herrmann et al.,[11] who first synthesized PVA. Because the color change reaction of iodinated PVA films has attracted much attention, lots of researchers have conducted studies on the phenomenon from various points of views. Some researchers have studied PVA in the solution state, and some have studied PVA in the bulk state (film[19] and fiber[20]). Many studies were summarized by Pritchard and Akintola[21] and Moulay.[22] Miyasaka et al.[23] surveyed the structure and properties of I_2–PVA complexes. In these studies, researchers reported that the formation of the PVA–iodine complex was enhanced by increases in the concentrations of PVA and iodine and by the additions of boric acid[24] and o-telluric acid[25] in aqueous solution. They also found that complex formation in the PVA films was enhanced in dilute

solution[24] or in the vapor of iodine.[26] Complex formation controls the stereoregularity of PVA films[27,28] and results in the main UV absorption bands at λ_{max} values of 226, 290, 360, and 620 nm (where λ_{max} is wavelength of maximum absorption); these were assigned to the mono-iodine ion (I^-), tri-iodine ion (symmetric I_3^-, and asymmetric I_3^-), and penta-iodine ion (I_5^-), respectively.[29] The tacticity and molecular weight of PVA affected the durability of the I_2–PVA complex in warm and humid conditions (relative humidity = 80% and temperature = 323.15 K).[17]

The mechanism of complex formation[30,31] is similar to the creation of polarizer films, which are prepared by soaking in an iodinated solution with subsequent drawing to cause a high degree of uniaxial orientation. To produce a high-efficiency polarizer, it is important to understand how to control the absorption of long wavelengths in visible light by polyiodide. However, PVA–iodine interactions and complex formation mechanisms have not been clearly elucidated yet because of other reactions due to several iodine species in the surroundings.

In this study, we investigated the complex induced by the drawing of a PVA film in dilute molecular iodine (I_2) and potassium iodide (KI) solutions by ultraviolet–visible (UV–vis) spectroscopy, attenuated total reflectance (ATR)–Fourier transform infrared (FTIR) spectroscopy, and water-absorption ratio and contact angle measurements. The purpose of this study was to understand the color change reaction of PVA–iodine complexes

Table I. Basic Properties of the PVA Film Used in This Study

	Unit	Average	Standard
Transparency	%	91.1	0.08
Average thickness	μm	73.6	0.43
Tensile strength (MD)	MPa	88.9	1.89
Tensile strength (TD)	MPa	99.1	1.6
Softening temperature	°C	67.2	0.14

MD = machine direction; TD = transverse direction.

caused by physical deformation and determine the control factors that improve polarizer efficiency.

EXPERIMENTAL

Materials

A PVA film with a thickness of 73.6 μm was purchased from Kuraray Co., Ltd. (Japan). The film was more than 99.9%hydrolyzed with a number-average degree of polymerization of 2400. The basic properties of the film are listed in Table I. Iodine and potassium iodine were commercially supplied by GodoShigen Sangyo Co., Ltd., Japan. Before it was soaked in the I_2/KI solutions, the PVA film used in this study was soaked for 5 min in deionized water and dried for 24 h(water content = 3.95%) in a thermostatically controlled room (294.15 K, relative humidity = 55%) to prevent side effects of additives.

Deionized water and other solvents with various polarity indices (PIs) from 0 to 4 were used, as listed in Table II. All of the solvents were extrapure grades and were used without further purification.

Preparation of an Aqueous Iodine Solution and Extension of the Iodinated PVA Film

An aqueous iodine solution with a concentration of 4×10^{-3} mol/L was prepared by the mixture of a KI/I_2 mixture (43:1 molar ratio) with water and stirring for 24 h at room temperature. An iodine solution with a concentration of 4×10^{-3} mol/L was also prepared by the mixture of a KI/I_2 mixture (43:1 molar ratio) with diethyl ether (DEE). The experiments were conducted in the absence of boric acid to prevent any structural hindrance, which might have been caused by the interaction between boric acid and PVA. The pretreated PVA film was soaked in the KI/I_2 aqueous solution at 294.15 K for 5 min to

Table II. Solvents Used in This Experiment

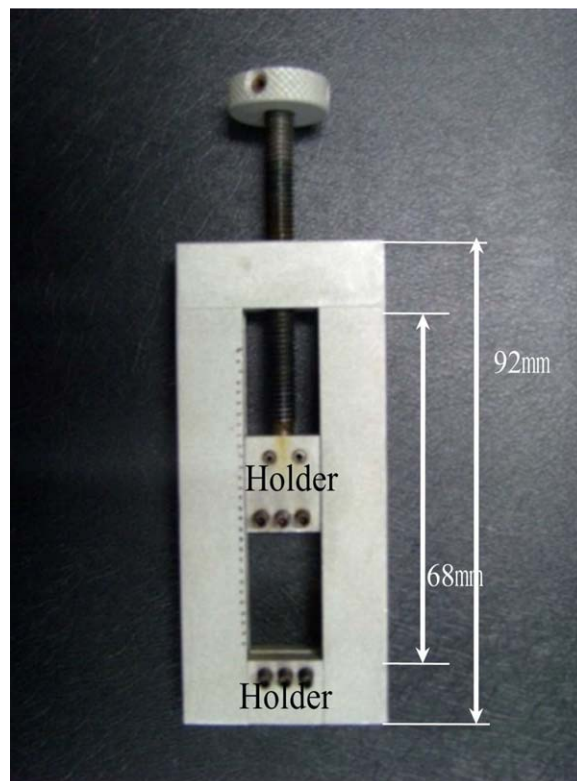| PI	Solvent	Solubility in water (%)	Maker
0	Hexane	0.001	Junsei
0	Heptane	0.0003	Junsei
0.2	Cyclohexane	0.01	Sigma-Aldrich
2.5	Xylene	0.018	Samchun
2.7	Benzene	0.18	Samchun
2.8	DEE	6.89	Sigma-Aldrich
3.1	Dichloromethane	1.6	Deajung
4	n-Propanol	100	Deajung
9	Pure water	100	—

Figure 1. Image of the apparatus for uniaxial extension and UV absorption analysis. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

make the film sample named 5m-PVA. On the other hand, the pretreated PVA film was soaked first in water at 294.15 K for 5 min and then soaked again in the KI/I_2 DEE solution at 294.15 K for 10 s to make the film sample named DEE–PVA. The soaked PVA films were wiped off with absorbent paper to measure their optical properties. The dimensions of the PVA film for drawing were 5 mm $\times$ 15 mm $\times$ 73.6 μm. The 5m-PVA film was extended in a thermostatically controlled room at 294.15 K with a relative humidity of 55% with the apparatus shown in Figure 1 in air. The draw ratio [(Final length − Initial length) $\times$ 100/Initial length] measured by length change was changed to 400%.

Measurements

A UV–vis spectrophotometer (Jasco V 550) was used to obtain the UV absorption spectra of the iodinated PVA film (5m-PVA) at various uniaxial strains of 0, 100, 200, and 400%, and each solution was composed of an organic solvent and KI/I_2 mixture (2×10^{-4} mol/L).

An IR spectrophotometer (Agilent Cary 600) was used to obtain the IR transmittance spectra of DEE and the I_2/KI DEE solution at a concentration of 2×10^{-4} mol/L. IR transmittance was measured in ATR mode.

The water-absorption ratios of the iodinated PVA films at various soaking times of 10–240 s in deionized water before and after 400% strain were measured in a thermostatically controlled chamber (294.15 K/55%). The soaked PVA film was weighed first after the superficial water was wiped off with absorbent
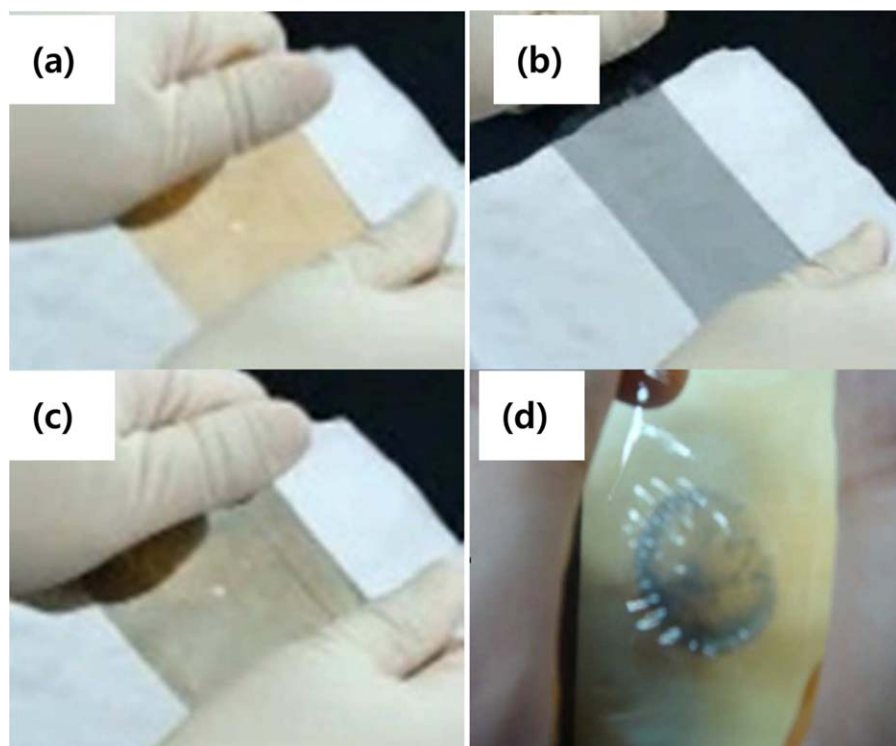
Figure 2. Images of the iodinated PVA film (a) before extension, (b) during extension, (c) after the removal of extensional stress, and (d) after compression. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

paper (this weight was designated as W_s) and then weighed again after it was hand-drawn by 400% and the superficial water was wiped off (this weight was designated as W_d).

The contact angle on the 5m-PVA film surface before and after 400% strain was measured by a Phoenix 300 Touch instrument (Surface Electro Optics). A water droplet was made by the sessile drop technique at 294.15 K and a relative humidity of 55%. The volume of the droplet was controlled to 3 μL, and the measurement time was fixed at 3 s after the droplet fell onto the 5m-PVA film surface.

RESULTS AND DISCUSSION

Color Change Reaction of the Iodinated PVA Films during Physical Deformation

Figure 2 shows the color change of the iodinated PVA film caused by physical deformation. The color of the iodinated PVA film was light yellow at the beginning [Figure 2(a)], but it turned light blue during uniaxial extension [Figure 2(b)] because of the formation of PVA–iodine complexes. The 5m-PVA film was extensible over 400% strain. After the stress was removed [Figure 2(c)], the film was restored almost to the original state, which was similar to a rubbery material, but it still showed a subtle light blue color. The 5m-PVA film also turned light blue when it was compressed by hydrodynamic compressor at 600 psi [Figure 2(d)]; this indicated the formation of the same PVA–iodine complexes. The compressed film was not restored to the original state because the compressional strain was bigger than its yielding strain.

Effects of Film Extension on the UV–vis Absorption Spectra of the Iodinated PVA Film

UV–vis absorption spectra of the iodinated PVA film were obtained to investigate the color change of the film during extensional deformation. The UV–vis absorption spectra of the 5m-PVA film at various strains of 0, 100, 200, and 400% are shown in Figure 3. The thicknesses of the strained films were 74.4 (0%), 36.7 (100%), 30.8 (200%), and 23.7 μm (400%). The iodinated PVA film at 400% strain showed five absorption bands at λ_{max} values of 220, 290, 360, 440, and 620 nm with
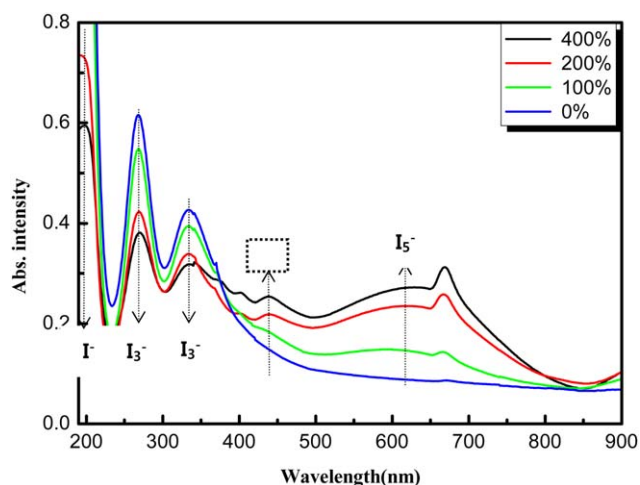

Figure 3. UV–vis absorption (Abs.) spectra of the 5m-PVA film at various strain levels. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

maximum absorbances of 0.6, 0.38, 0.32, 0.25, and 0.28, respectively. As the strain increased, the maximum absorbances of the bands at 220, 290, and 360 nm decreased, whereas those of the bands at 440 and 620 nm increased. At 0% strain, the iodinated PVA film was yellow because the absorption intensity around 380–480 nm (the blue band) was higher than that around 480–780 nm (the red band). However, with increasing strain, the absorption intensity around the red band increased significantly compared to the blue band; this changed the color of the film from light yellow to light blue.

The oxidation states of the I atom range from I (VII) to I (-I) and include the intermediate states of I (V), I (III), and I (I). Even though only the −1 oxidation state exist in iodide salts and polymer–iodine complexes, the energy level can easily be altered, depending on the conditions. Many researchers have reported that the absorption bands at 220, 290, 360, and 620 nm should be assigned to I^-, I_3^-, I_3^-, and I_5^-, respectively.[32–37] Deplano et al.[38] classified I_3^- adducts into two types: (1) I−I_2 adducts, which have a linear asymmetric geometry with one strong I–I bond and one weak I·I bond, and (2) a covalent I–I–I complex with a linear symmetric geometry with two equivalent I–I bonds. It has been reported that the bands of I_5^- ($\lambda_{max} = 620$ nm)[23] could not be found in the solution state without a polymer matrix, such as a starch,[39] cellulose derivatives,[40] a protein–fiber complex,[41] or PVA.[42] So, there is still little information about the formation conditions for these bands. Unlike the I_5^- band ($\lambda_{max} = 620$ nm), the 440-nm band was observed in the solution state.[43] So, knowing the conditions of PVA–iodine complex formation is important for understanding the formation mechanism of the complex and, consequently, for producing an efficient polarizer with high performance at visible wavelengths.

Formation Conditions of the 440-nm Band

I_2/KI solutions with one of the weak polar organic solvents of PI ranging from 0 to 3.1 showed maximum absorption bands at three different wavelengths, as shown in Figure 4(a). The solubility of nonpolar I_2 without KI was very low in the PI range from 4 (n-propanol) to 7.2 (dimethyl sulfoxide). So, the most I_2 was observed as the I_3^- form ($\lambda_{max} = 290$ and 360 nm) in the polar solvents in our study. However, the solubility of polar KI was very low in weak polar solvents, whereas that of nonpolar I_2 was high. The three maximum absorption wavelengths (λ_{max}) were 460, 500, and 520 nm. It has been reported that absorption bands at 500 nm[44] and 520 nm[45] were attributed to electronic transition in I_2. It has been reported that the band at 460 nm was due to hydrated I_2, but the absorption of covalently bonded electrons of I_2 usually appears at 196 nm,[24] which is in the far-UV region. The absorption at 460 nm appeared and disappeared with deformation, as shown in Figures 2 and 3. So, we considered that the 460-nm band was due to a type of iodine electron, not to covalently bonded electrons.

The UV–vis absorption spectra of the PVA film dipped in a KI solution showed almost the same absorption characteristics at both 0 and 400% strain levels, as shown in Figure 4(b); this indicated that the 460- and 620-nm bands were not due to a type of KI electron. The result supports the fact that the
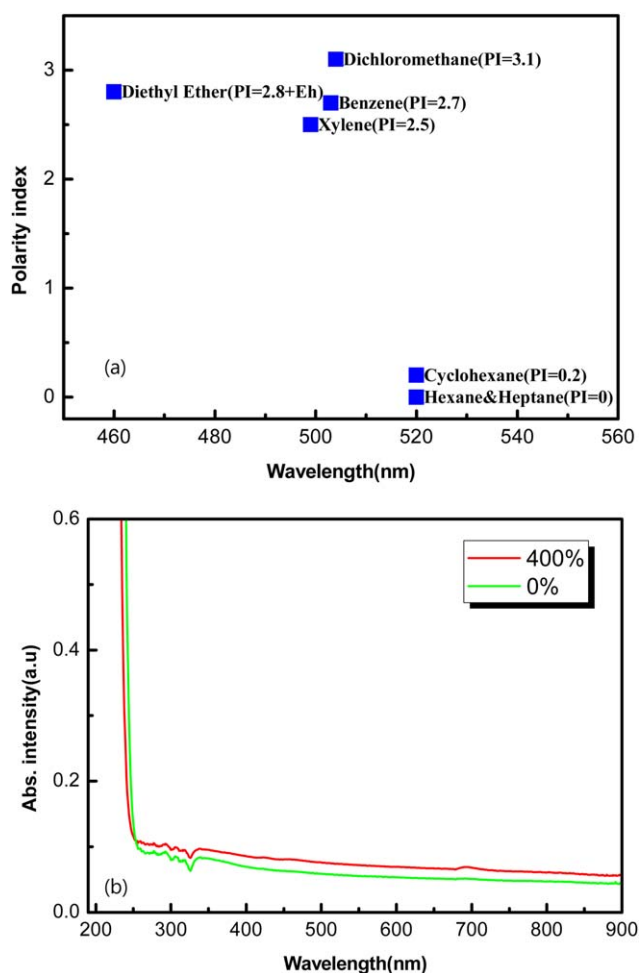

Figure 4. (a) Maximum absorption wavelengths of various I_2/KI solutions and (b) UV–vis absorption spectra of the KI PVA films at 0 and 400% strain levels. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

460-nm band was due to a type of iodine electron. Therefore, we considered that electrons in the I_2 molecules existed in the three energy bands of λ_{max} of 460, 500, and 520 nm.

PI of DEE (PI = 2.8) was lower than that of dichloromethane (PI = 3.1), but the electronegative oxygen atom in DEE that had hydrogen-bonding-like interaction (E_h) affected the energy band of electrons in the I_2 complexes. This explained why the DEE solution showed the 460-nm band.

Figure 5 shows the UV–vis absorption spectra of KI/I_2 solutions with one of the weak polar solvents, with PI ranging from 0 to 4. The absorption intensity order at 360 nm was 1-Propanol (PI = 4) > DEE (PI = 2.8&E_h) > Dichloromethane (PI = 3.1) > Cyclohexane (PI = 0.2). The absorption intensity for I^-·I–I decreased, but that for I–I·I–I increased; this indicated that I^-·I–I ($\lambda_{max} = 360$ nm) was turned into I–I·I–I ($\lambda_{max} = 460$, 500, and 520 nm). The nonpolar I–I induced a dipole as its electrons were attracted or repelled by a polar solvent. The attractive interaction, called the *Debye force*, between the permanent dipole and an induced dipole of a nonpolar I–I molecule increased as the whole polarity level, including E_h, of the solvent increased.[46]
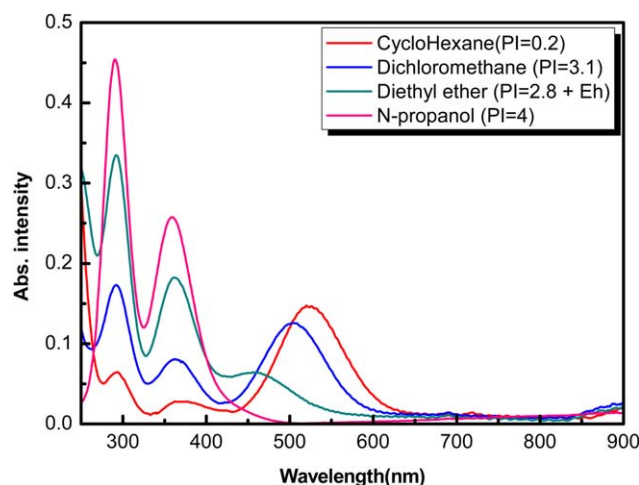
Figure 5. UV–vis absorption spectra of various iodinated solutions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The wavelength for the absorption band of I_2 molecules decreased in the following order: Cyclohexane (PI = 0.2, λ_{max} = 520 nm) > Dichloromethane (PI = 3.1, λ_{max} = 500 nm) > DEE (PI = 2.8&E_h, λ_{max} = 460 nm) > 1-Propanol (PI = 4, λ_{max} = 360 nm). As the whole polarity level of the solvent decreased, the energy band gap of I_2 molecules decreased; this indicated that the Debye force between the polar KI and nonpolar I_2 decreased, and only van der Waals forces between the nonpolar I_2 molecules existed.[47,48] The weak polar solvent and solvated KI formed intermolecular interactions with both the ground and excited states of I_2 but was stronger with the excited state in a weak polar environment.[49–51] In the DEE solution (PI = 2.8 and E_h), which had a chemical structure similar to that of the extended PVA chains, the absorption wavelengths occurred at λ_{max} values of 290 nm (I_3^-), 360 nm (I_3^-), and 460 nm. The absorption band at 460 nm, which came from interactions between I^- and I–I, was observed between I_3^- (360 nm) and I_2 (500 nm).

Figure 6 shows the ATR–FTIR transmittance spectra of DEE and the I_2/KI DEE solution. We observed that there was no transmittance change with the addition of I_2/KI in DEE, except in the C—O stretching band. This indicated that bond cleavage or formation did not occur with the addition of I_2/KI in DEE. The redshift (1132 → 1119 cm^{-1}) of the C—O stretching peak was considered to be due to affluent electrons in C—O groups by electron-donating groups, such as $I^- \cdot I_2$; this resulted in the easy stretching of C—O groups.[52] Although the solubility of KI in weak polar organic solvents was very low, we observed I_3^- in the DEE solution, as shown in Figure 5. So, we considered that $H^{\delta+}$ atoms induced by electronegative $O^{\delta-}$ atoms formed a more stable $C_4H_9O^{\delta-}H^{\delta+} \cdot I^- \cdot I_2$ complex, which showed a broad absorption band at a λ_{max} value of 460 nm. Consequently, the following reaction occurred in the solution:

$$C_4H_9O^{\delta-}H^{\delta+} \cdot I_3^- \leftrightarrows C_4H_9O^{\delta-}H^{\delta+} \cdot I^- \cdot I_2 \text{ (complex)}$$
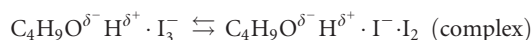
Figure 7 shows the UV–vis absorption spectra of the DEE KI/I_2 solution (KI/I_2 DEE), the PVA film just taken out of I_2 DEE (DEE–PVA), and the 400% extended DEE–PVA. All of the samples showed 290- and 360-nm bands; however, the 460-nm band, which was observed in KI/I_2 DEE, was not observed in
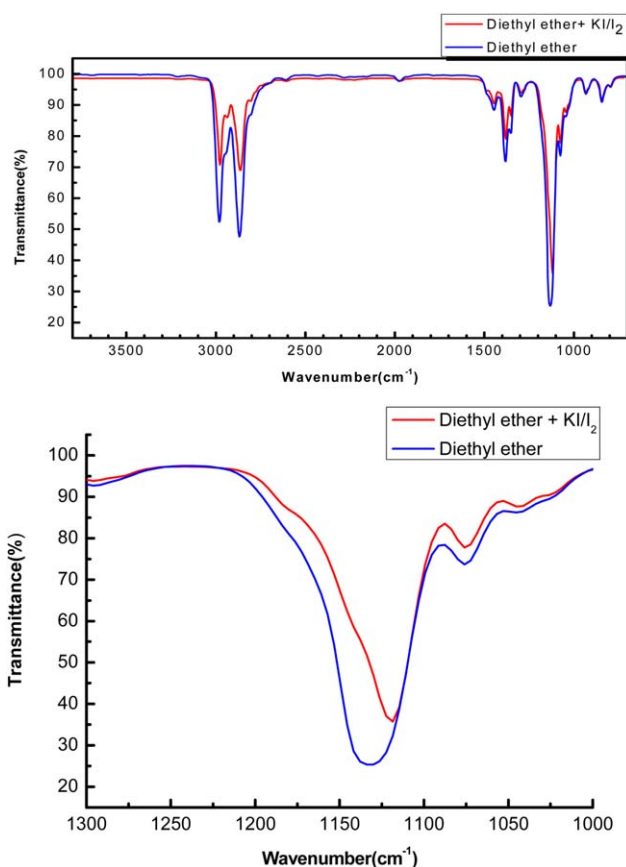

Figure 6. ATR–FTIR transmittance spectra of the DEE and I_2/KI DEE solution. The bottom shows an enlargement of the spectrum for 1300–1000 cm^{-1}. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the PVA film that had just been taken out of KI/I_2 DEE (DEE–PVA). This indicated that the 460-nm band, unlike the 290- and 360-nm bands, was due not only to the whole polarity level but also to interactions between the DEE solution and I_3^-. This supported the conclusion that the 460-nm band was caused by complexes such as $C_4H_9O^{\delta-}H^{\delta+} \cdot I^- \cdot I_2$. It was noteworthy that the PVA film taken out of I_2 DEE (DEE–PVA) also showed the 460-nm band when extended by 400%; this resulted from iodine–PVA complexes formed by the extension. We also elucidated that both the 440-nm band of the 400% extended 5m-PVA film and the 460-nm band of the 400% extended DEE–PVA film were formed by the extension, and the difference between the absorption bands was considered to be due to the difference in intramolecular interactions.[53]

We considered that the 440- and 460-nm bands of the extended PVA film were due to iodine–PVA complexes formed between the $\sim O^{\delta-}H^{\delta+}$ group and I_3^- in the extended PVA film as follows:

$$\sim O^{\delta-}H^{\delta+} + I_3^- \leftrightarrows \sim O^{\delta-}H^{\delta+} \cdot I^- \cdot I_2 \text{ (complex)}$$
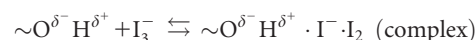
Effects of Film Extension on the Water Content and Polarity Change of the Iodinated PVA Film

Figure 8 shows the water-absorption ratios of the PVA films with soaking time in deionized water for the unextended and
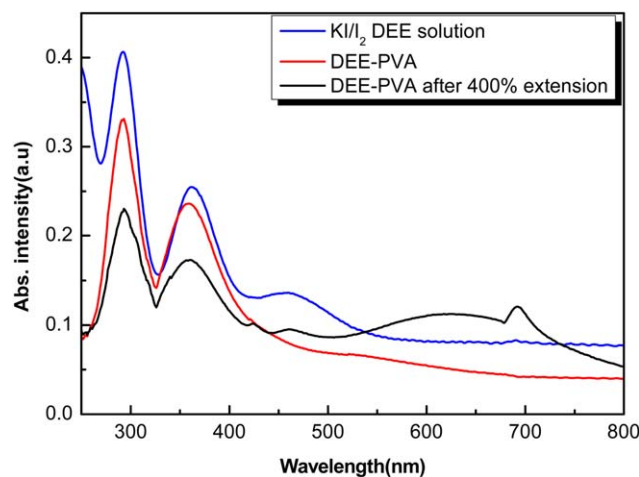
Figure 7. UV–vis absorption spectra of KI/I$_2$ DEE and PVA film just taken out of KI/I$_2$ DEE (DEE–PVA) and extended 400% (DEE–PVA after 400% extension). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

400% extended PVA films. The equilibrium water-absorption ratio (W_{eq}) of the swollen film was calculated by the following equation[54]:

$$W_{eq} = (W_s - W_d) \times 100 / W_d \qquad (1)$$

A dramatic loss in water content occurred during the extension. As a result, the whole polarity level of the swollen PVA film would be dominated by the PVA matrix itself and the main solvent for I2 and KI would be also changed from water (PI = 9) to PVA matrix. In industrial applications, it has been considered that visible light absorption of a polarizer film, which improves the polarizer efficiency, will be controlled by the whole polarity level of the PVA matrix and water content in the PVA film.

To obtain direct proof of polarity change during extension, the water contact angle of the iodinated PVA film was measured before and after extension, as shown in Figure 9. The water contact angle on the iodinated PVA film surface was 24.5°
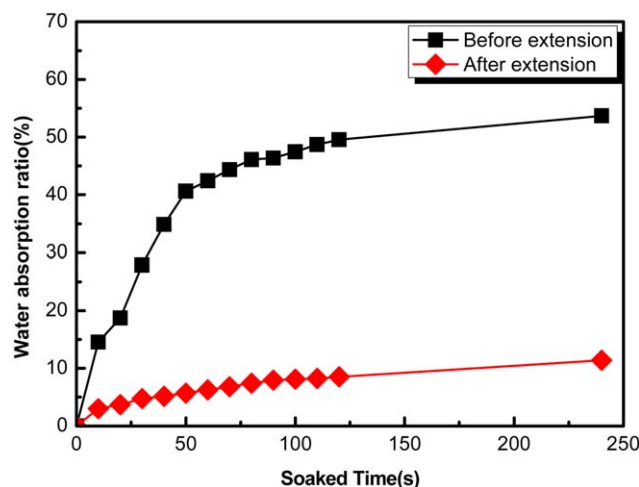

a) Before extension   b) After 400% extension

Figure 9. Water droplets placed on the iodinated PVA film surfaces (a) before extension (contact angle = 24.5°) and (b) after 400% extension (contact angle = 39.9°).

before extension, but it increased to 39.9° after 400% extension. The hydrophilicity of the PVA film decreased considerably as it was extended 400%.

Effect of Controlling the Drying Time

UV–vis absorption spectra of the 400% extended 5m-PVA film containing boric acid were prepared to investigate the effects of the drying time on the intermolecular interaction energy change. The UV–vis absorption spectra of the PVA film at various drying times of 10, 20, 30, 40, 50, and 60 s at 353.15 K in a thermostatically controlled chamber are shown in Figure 10. The absorbance bands at 480 and 620 nm increased with drying time; this indicated that the polarizer efficiency in visible light could be controlled by changes in the intermolecular interaction energy. We considered that I$_5^-$ (λ_{max} = 620 nm) was developed by aggregation of $\sim O^{\delta-} H^{\delta+} \cdot I^- \cdot I_2$ and I$_2$ in the extended and dried PVA films as follows:

$$\sim O^{\delta-} H^{\delta+} \cdot I^- \cdot I_2 + I_2 \rightleftharpoons \sim O^{\delta-} H^{\delta+} \cdot I^- \cdot I_2 \cdot I_2$$

CONCLUSIONS

The 440- and 460-nm absorption bands of the PVA–iodine complex, which were assigned to $\sim O^{\delta-} H^{\delta+} \cdot I^- \cdot I_2$, were observed when the iodinated PVA film was extended over 200%. Various solvents with PIs from 0 to 4 were tested to study the formation conditions of the 460-nm band and the driving force of the color change caused by physical deformation. As the whole polarity

Figure 8. Water-absorption ratios of the PVA films with the soaking time for the unextended and extended PVA films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
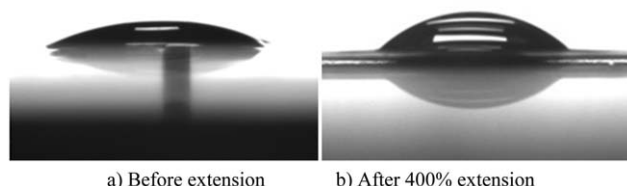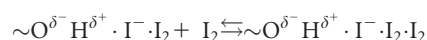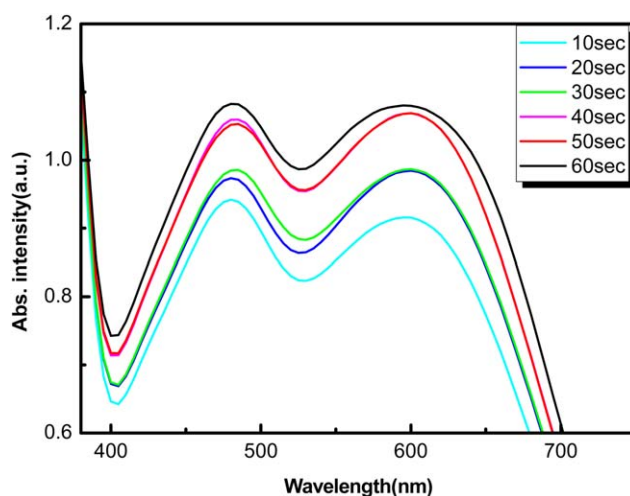

Figure 10. UV–vis absorption spectra of the 5m-PVA film at various dry times. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

level of the solvent decreased, the energy band gap of I_2 molecules decreased; this indicated that the Debye forces between polar KI and nonpolar I_2 decreased and only van der Waals forces between the nonpolar I_2 molecules existed. We found that the 460-nm band of DEE, which was assigned to the $C_4H_9O^{\delta-}H^{\delta+}\,I^-\,I_2$ complex, was produced by the whole polarity level change of the solvents and electron donating–accepting between the $\sim O^{\delta-}H^{\delta+}$ group and I_3^-. The dramatic loss in water content of the 5m-PVA film by extension led to the whole polarity level change of the film. The absorbance peaks at 480 and 620 nm increased with drying time; this indicated that the polarizer efficiency in visible light could be controlled by changes in the intermolecular interaction energy. The PVA matrix acted as a medium of the whole polarity level change and as an enhancement site of I_5^- by aggregation of $\sim O^{\delta-}H^{\delta+}\cdot I^-\cdot I_2$ and I_2.

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