

Cut-Out Filter for Ultraviolet Radiation from Poly(Vinyl Alcohol)

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ABSTRACT: The effects of ultraviolet (UV) radiation and thermal annealing on the optical and mechanical properties of polyvinyl alcohol (PVA) were studied. Pure PVA samples were prepared by casting technique. Xenon arc lamp was used to irradiate the sample. The irradiated PVA sample was heated at 150°C for 2 h. The optical and mechanical properties of original, irradiated, and irradiated and then heated samples were measured. The irradiated and then heated sample showed lower transmission in the wavelength range from 190 to 320 nm and the transmission was higher in the visible region than the original and irradiated samples. The stress–strain measurements were performed. Modulus of elasticity of the double-treated sample was approximately four times higher than that of original sample. The obtained results show the possibility of using this sample as cut-out filter for UV radiation. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1295–1299, 2002; DOI 10.1002/app.10486

Key words: UV–Vis spectroscopy; infrared spectroscopy; radiation; stress; strain

INTRODUCTION

Polyvinyl alcohol (PVA) is one of the most important polymeric materials, because it has many optical uses which result from its lack of color, its clarity, and its high transmission.^{1–9}

The optical uses of PVA are concerned with the retardation, polarization, and filtration of light, and with photography and related imaging fields. Filters can be prepared for visible and ultraviolet radiation from combinations of dyes or ultraviolet (UV) absorbers with PVA. Near-infrared band-pass filters and polarizers may be based on polyvinylene.⁵

UV filters may be prepared by imbibitions in aqueous dye baths of water-soluble UV absorbers such as a sulfonated hydroxybenzophenone.⁵

Some light filters based on PVA cut-out ultraviolet and infrared radiation and transmitted the visible part of the spectrum.¹⁰ These filters contain a polyindamine in PVA, formed by the oxidation of aniline and various aniline derivatives. Hoffman¹¹ described a green filter of this type, which is green, absorbs between 750 and 1000 nm and below 400 nm, and transmits 30% of 500-nm light. A similar filter¹² based on PVA containing cupric chloride absorbs below 430 nm and from 760 to 1300 nm and transmits 80% of 550-nm light.

Gamma radiation effects on the thermal degradation of PVA were reported.¹³ They explained the variation of absorption spectra due to radiation induced events, which contributes to the formation of conjugated structure.

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Many problems appeared to be due to the use of additive such as antioxidant and photostabilizers of low molecular weight, which may evaporate during the molding and extrusion processes and also may migrate from the plastics during the storage.

This article is devoted to study the effect of UV irradiation and thermal treatment on the optical and mechanical properties, aiming for PVA with low transmission in UV region and high mechanical properties.

EXPERIMENTAL

PVA of molecular weight of 17,000 g/mol (BDH, England) was used as a basic polymeric material in this work. PVA solution was prepared by dissolving PVA in bidistilled water. PVA was maintained in water for 24 h at room temperature to swell. The mixture was then warmed up to 60°C and stirred, using a magnetic stirrer, thoroughly for 4 h until the polymer became completely soluble. The solution was poured into flat glass-plate dishes. Homogeneous films were obtained after drying in an air oven for 48 h at 40°C. The thickness of the produced films was 0.16 mm. The films were divided into three parts, sample (a) original, and samples (b and c) were irradiated with Xenon arc lamp for 5 min at 400 W. Sample (c) after irradiation was heated at 150°C for 2 h.

The optical absorption and transmission measurements of (a, b, and c) samples were measured by using the Jasco V-570 spectrophotometer (Japan) in a range from 190 to 900 nm.

Fourier transform infrared spectrometer (Jasco FT/IR-420) was used to measure the infrared spectra of the samples (a), (b), and (c) in a range of 4000–400 cm^{-1} .

The samples used in mechanical measurements were strips with dimensions of 20, 2, and 0.67 mm. The stress–strain measurements were performed by using a mechanical test machine (Ametek), in which a force gauge (Hunter Spring Accu Force II, 0.01N resolution) is attached. The readings were automatically recorded through a microprocessor as a function of time. A locally devised motor with a microswitch system was attached to the test machine to control the strain rate. The strain rate throughout the experiment was 0.04 cm/s. Characteristic stress–strain curve was repeated at least three times to ensure the reproducibility.

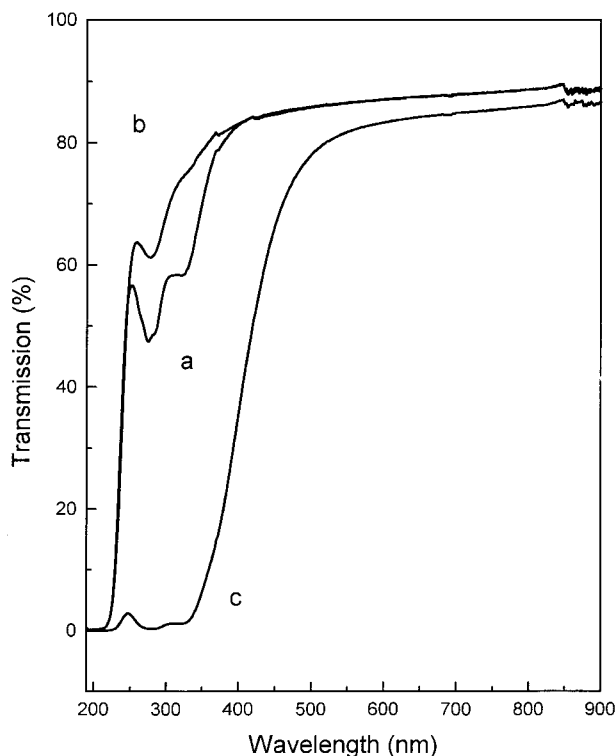


Figure 1 Transmission spectra of PVA samples (a) original, (b) UV irradiated, and (c) UV irradiated and then heated at 150°C for 2 h.

RESULTS AND DISCUSSION

Figure 1 shows the transmission spectra for original PVA sample (a), irradiated sample (b), and irradiated and then heated sample (c). One can observe a nearly zero transmission in the UV range of 190–330 nm for sample (c). At a longer wavelength, the transmission increases gradually until it reaches ~40% at ~430 nm, after which it tends to slow increase in the visible region. This indicates a total cut-off in the wavelength range of 190–330 nm (UV region).

UV–Visible Spectra

Most applications of absorption spectroscopy to organic compounds are based upon transition for (n) or (π) electrons to the (π^*) excited state because the energies required for these processes bring the absorption peaks into an experimentally convenient spectral region (200–700 nm). Both transitions require the presence of an unsaturated functional group to provide the (π) orbital,¹⁴ which is already present in the samples under investigation.

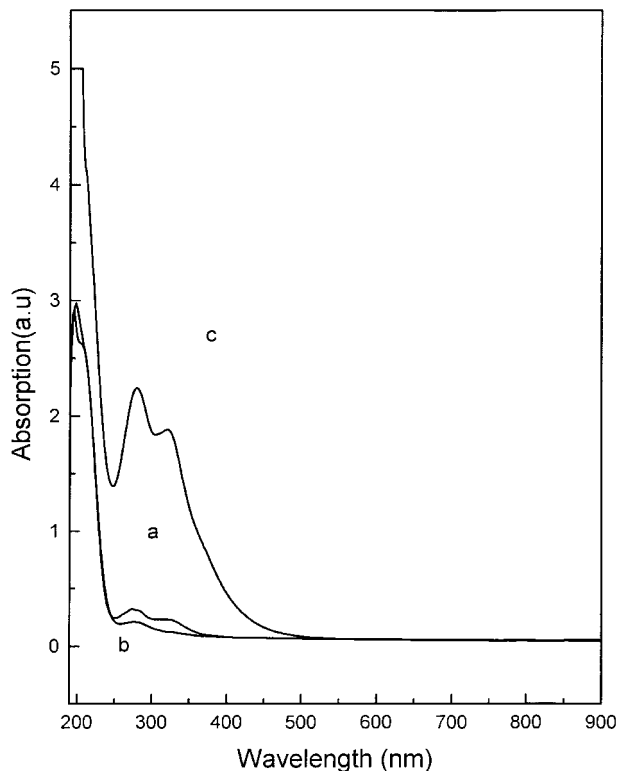


Figure 2 Absorption spectra of PVA samples (a) original, (b) UV irradiated, and (c) UV irradiated and then heated at 150°C for 2 h.

Figure 2 shows the absorption spectra for the three samples (a, b, and c) and Table I contains the analyses for these spectra.

The band at 200 nm is a strong one for all the samples and may be assigned as $n \rightarrow \pi^*$ transition because of the presence of C=O group; meanwhile, there are two bands at 275 and 325 nm

Table I The Analyzed Data of UV Spectra for PVA Samples a, b, and c, Respectively

| Significant Samples | Bands (nm) | Absorption (au) | Assignment |
|---------------------|------------|-----------------|-------------------------|
| a | 200 (s) | 3 | $n \rightarrow \pi^*$ |
| | 275 (w) | 0.4 | $\pi \rightarrow \pi^*$ |
| | 325 (w) | 0.2 | $\pi \rightarrow \pi^*$ |
| b | 200 (s) | 3 | $n \rightarrow \pi^*$ |
| | 275 (w) | 0.2 | $\pi \rightarrow \pi^*$ |
| | 325 (w) | 0 | |
| c | 200 (s) | 5 | $n \rightarrow \pi^*$ |
| | 275 (s) | 2.4 | $\pi \rightarrow \pi^*$ |
| | 325 (sh) | 2 | $\pi \rightarrow \pi^*$ |

s, strong; sh, shoulder; w, weak.

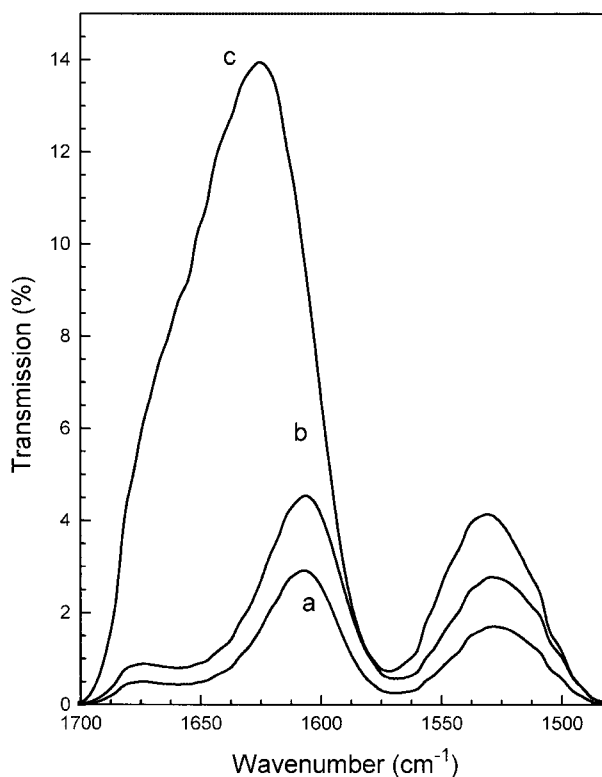


Figure 3 FTIR spectra of PVA samples (a) original, (b) UV irradiated, and (c) UV irradiated and then heated at 150°C for 2 h.

assigned as $\pi \rightarrow \pi^*$ and the bands described as weak, strong, and shoulder for (a), (b), and (c) samples, respectively, may be due to the presence of a different conjugated system.¹⁴ The absorption intensity of sample (c) was found to be higher than the absorption intensity of samples (a) and (b), respectively; the reason may be due to breaking of some intra- and or interhydrogen bonds,¹⁵ which leave the electrons in n , π free and can be moved easily from n to π^* or from π to π^* , or isomerization ring formation, and/or additional reaction of other chemicals.^{16,17}

Infrared Spectra

Figure 3 shows the plots of infrared transmission spectra for samples (a), (b), and (c), in the spectral range 1700–1480 cm^{-1} . The significant IR data of the samples are listed in Table II.

The observed features can be summarized as follows. The band centered at 3600 cm^{-1} , which is present in all samples as a medium or strong broadband, may be due to the stretching vibration of the O—H bond, which was affected by intra-

Table II The Significant IR Data PVA Samples a, b, and c, Respectively

| Significant Samples | $\nu_{\text{O-H}}$ (cm^{-1}) | $\nu_{\text{C=O}}$ (cm^{-1}) | $\nu_{\text{C=C}}$ (cm^{-1}) |
|---------------------|---|---|---|
| a | 3600 (broad, s) | 1605 (m) | 1529 (m) |
| b | 3600 (broad, m) | 1605 (m) | 1529 (m) |
| c | 3600 (broad, m) | 1625 (s) | 1529 (m) |

s, strong; m, medium.

and/or interhydrogen bond, which plays an important role for aggregation of many chains of polymer molecules.^{18–21}

The stretching vibration bands which appear at (1605), (1605), (1625, 1675 cm^{-1}) for (a), (b), and (c) samples, respectively, were assigned as $\nu_{\text{C=O}}$. The frequency values of this band indicate that the C=O group enters as a coordinate site to the hydrogen bond system (for C=O whose $\nu_{\text{C=O}} = 1700 \text{ cm}^{-1}$). The tendency of this behavior decreases for sample (c), which may be due to the breaking of the hydrogen bond and/or the radiation and heating-induced structure changes on the polymer chains as well as the generated small molecular product.¹³

$\nu_{\text{C=O}}$, which appeared at 1529 cm^{-1} for all the samples, indicated that irradiation and thermal annealing were not affected on the C=C moiety.¹⁵

Mechanical Properties

Also, the stress–strain behaviors are shown in Figure 4. Table III summarizes the mechanical properties, Young's modulus Y , strength σ , and strain at break ϵ_b for the three samples (a), (b), and (c).

In general, the irradiation at low doses increases crosslinking. This is reflected in an increase of Young's modulus. It is noticed that sample (c), which was first irradiated and then heated, has the largest values of Y , σ , and ϵ_b . This information indicates higher crosslinking and formation of more conjugated bonds of longer length. The mechanical data confirm that obtained from the optical measurements.

CONCLUSIONS

The effects of UV light and thermal treatment on the PVA sample were studied. The results indicated that by using UV light irradiation could

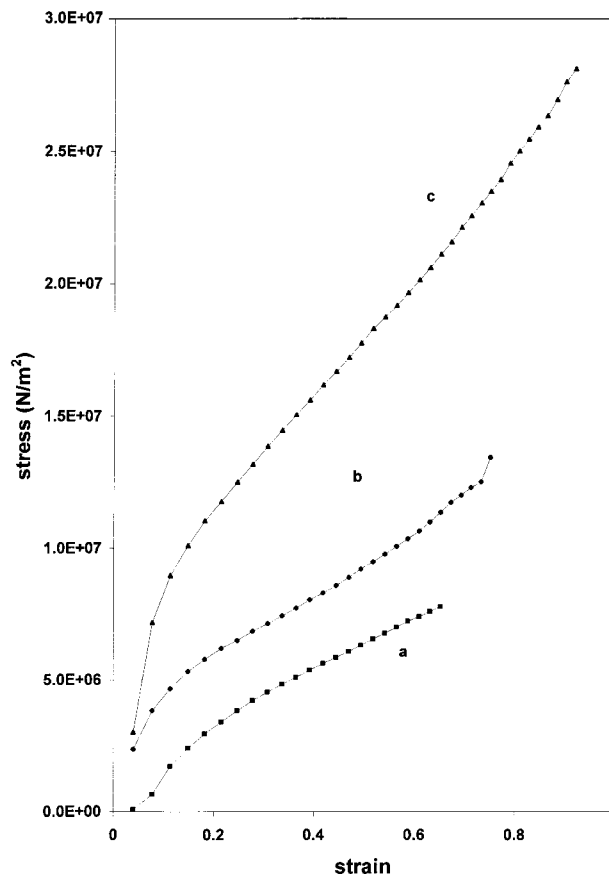


Figure 4 Stress–strain behavior for of PVA samples (a) original, (b) UV irradiated, and (c) UV irradiated and then heated at 150°C for 2 h.

remove the absorption peak at 275 nm for the sample irradiated and the absorption intensity of sample (c) was found to be higher than the absorption intensity of samples (a) and (b), respectively; the reason may be due to the breaking of some intra- and/or interhydrogen bonds,¹⁵ which leave the electrons in n , π free and can be moved easily from n to π^* or from π to π^* so that the absorption intensity increased and the transmission decreased in the range of 190–330 nm.

Table III The Mechanical Properties PVA Samples a, b, and c, Respectively

| Samples | $Y \times 10^{-7}$ (N/m^2) | $\sigma \times 10^{-7}$ (N/m^2) | ϵ_b |
|---------|---------------------------------------|--|--------------|
| a | 2.00 | 0.80 | 0.63 |
| b | 3.00 | 1.30 | 0.73 |
| c | 8.00 | 2.80 | 0.9 |

With respect to the mechanical properties of sample (b), Young's modulus increased by 1.5 times and the strain at break increased approximately one time in comparison with the original sample. This may be attributed to the effect of radiation, which induced chemical reactions of vinyl polymers, including crosslinking, chain scission, small molecular elimination, and internal or terminal double-bond formation.

For sample (c), the Young modulus was increased four times and the strain at break was increased by approximately 1.5 times in comparison with original sample.

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