

Intrinsic UV Reflection and Fluorescence Studies for Water Sorption in Polycarbonate, Polyurethane and Poly(Ethylene Terephthalate) Films

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Abstract: Intrinsic UV reflection and fluorescence behaviors of polycarbonate, polyurethane and poly(ethylene terephthalate) films were investigated in order to characterize the interaction of water in these films. During water sorption process, UV reflection spectra of polycarbonate and polyurethane films showed little peak position changes. Fluorescence emission spectra of polycarbonate films showed red spectral shifts from 332 nm with water immersion time. This red-shifted peak could be due to phenyl-2-phenoxybenzoate, which is one of the major thermal degradation products in polycarbonate. Fluorescence peaks of polyurethane films appeared at two different positions and the ratio of these peak intensities increased with increasing immersion time. In the case of PET films, the UV reflection spectrum showed the peak intensity around 340 nm to change in response to water sorption. The fluorescence near 388 nm probably due to ground state dimer exhibited sensitivity with water sorption, when excited at 340 nm.

Keywords: UV reflection, Fluorescence, Emission, Water sorption, Polymer film

Introduction

Water sorption of polymeric materials can change the physical and mechanical properties, such as glass transition temperature and modulus [1]. Therefore, sorption behavior in various polymer films has been intensely investigated due to their theoretical and practical significance. Water sorption can be characterized by using various techniques such as UV-Vis [2,3], fluorescence [4], NIR [5], NMR [6], and dielectric [7] method. Especially, UV-vis and fluorescence spectra is very sensitive to water sorption due to the interaction of water with polar groups in polymers. In our previous studies [2], water uptake in epoxy cured with diamino diphenyl sulfone (DDS) was monitored using UV reflection and fluorescence spectroscopy. In UV reflection spectra, there was a progressive shift to a longer wavelength upon exposure to water due to water's H-bonding to SO₂ group of DDS. By spectral deconvolution, the fraction of H-bonded DDS through SO₂ with water was estimated. Also, in polyimides, UV reflection spectra showed a sensitive red shift upon water uptake [3].

The objective of this paper is to show that it is experimentally possible to characterize the interaction of water in various polymers using UV reflection and fluorescence spectroscopy. The water sorption behaviors of polycarbonate, polyurethane and poly(ethylene terephthalate) films are investigated by UV reflection and fluorescence spectroscopy. To perform an in-situ monitoring, UV reflection technique by using fiber-optic accessory has been used.

Experimental

Sample Preparation

Polycarbonate film was obtained from Bayer Company. Polyurethane contains methylene-4,4'-diphenyl diisocyanate (MDI) based polyether with small amount of UV stabilizer, antioxidant and additives. Poly(ethylene terephthalate) (PET) films as well as polyurethane films were obtained from SK Chemical, Korea.

Moisture Absorption Measurements

Polycarbonate, polyurethane and PET film were cut into 1.5 in. square pieces and immersed in a sealed deionized water flask. At specific time intervals, the films were removed from the water and quickly dried with a paper towel, and the weight was measured with a Mettler AE 200 balance.

UV Reflection and Fluorescence Measurements

After measuring the weight, UV reflection and fluorescence emission spectra were taken on a Perkin-Elmer Lambda 6 UV/Visible Spectrophotometer and a Perkin-Elmer LS-50B luminescence spectrometer, respectively. To perform an in-situ monitoring, the samples were immersed in water at room temperature and UV reflectance spectra were obtained at different immersion times using a bifurcated fiber-optic probe [2(b)]. For fluorescence in-situ monitoring, fluorescence spectra were obtained with each sample placed diagonally in a cuvette.

Results and Discussion

Polycarbonate

Figure 1 shows the gain in weight due to water absorption

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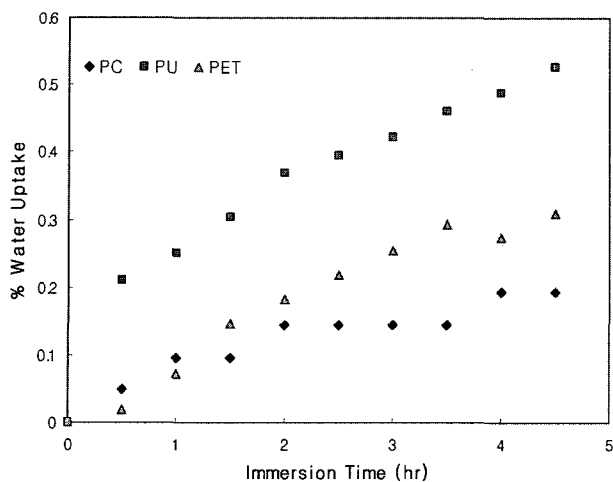


Figure 1. Percentage water uptake of polycarbonate, polyurethane and poly(ethylene terephthalate) films as a function of water immersion time at room temperature.

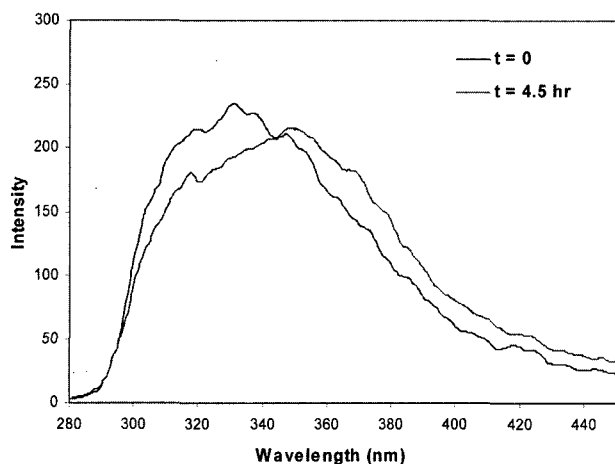


Figure 2. Fluorescence emission spectra of polycarbonate films when excited at 260 nm as a function of water immersion time.

as a function of immersion time for polycarbonate, polyurethane and poly(ethylene terephthalate) films. It shows that polycarbonate absorbs very small amount of water, about 0.2 wt% after 4 hrs.

UV reflection spectra of polycarbonate film show little position changes. Figure 2 shows the in-situ fluorescence emission spectra of polycarbonate film when excited at 260 nm as a function of water immersion time. Interestingly, the emission peak around 332 nm is progressively red shifted to around 350 nm after 4.5 hr water immersion and the peak intensities decrease with increasing immersion time. Plot of peak positions as a function of % water uptake is presented in Figure 3, which shows a good sensitivity to water sorption, after 0.15 % water uptake.

According to Rofus *et al.* [8], the thermal degradation products of polycarbonate formed during extrusion process seem to account for the distinct structured fluorescence spectra.

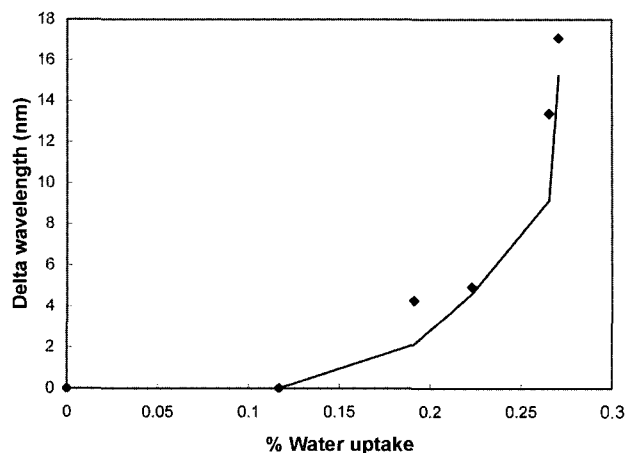


Figure 3. Emission spectral shift as a function of % water uptake in polycarbonate films.

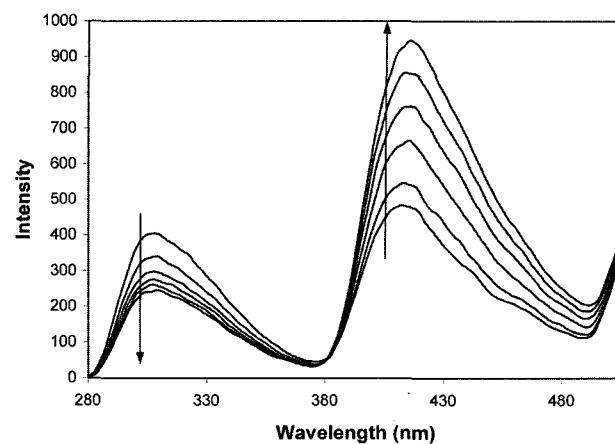


Figure 4. Fluorescence emission spectra of polyurethane films with water immersion time when excited at 260 nm. The arrow at 308 nm shows the increasing immersion time ($t=0, 30, 90, 150, 210,$ and 270 minutes) from the top. The arrow at 413 nm shows the increasing time from the bottom.

They identified phenyl-2-phenoxybenzoate and dibenzofuran as two major contributors for the fluorescence spectrum in the polycarbonate films. Dibenzofuran and phenyl-2-phenoxybenzoate show their maximum peaks at 318 nm and 336 nm, respectively. Therefore, the peak around 332 nm observed in our experiments, which might be due to phenyl-2-phenoxybenzoate appears to be sensitive to water sorption, even though water uptake of polycarbonate film is a very small amount, below 0.25 %.

Polyurethane

During the water uptake process (Figure 1), UV reflection of polyurethane film shows increasing % reflectance but peak positions show little change. In Figure 4, the emission spectra of polyurethane film by exciting at 260 nm are shown as a function of water immersion time, where two main

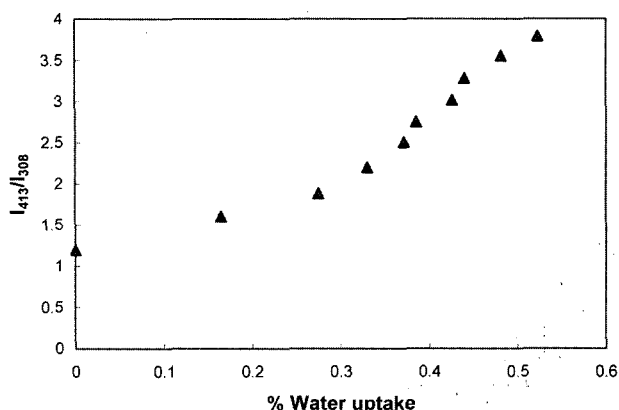


Figure 5. Emission intensity ratio (413 nm/308 nm) as a function of % water uptake in polyurethane films.

peaks are observed at 308 nm and 413 nm. The peak at 308 nm can be assigned as MDI urethane [9]. The peak at 413 nm may be due to aging, since no fluorescence was observed above 400 nm in fresh polyurethane sample, while it appeared at 413 nm after two weeks.

In Figure 4, a progressive decrease in intensity for peak at 308 nm and an increase in intensity for peak at 413 nm with water immersion time are observed. The ratio of those two peak intensities is plotted as a function of % water uptake in Figure 5, showing sensitivity to water uptake.

Poly(ethylene terephthalate)

Figure 1 shows the %water gain of PET as a function of water immersion time. The UV reflection spectra of PET film shows the gradual increases in % reflectance in the main peak around 260 nm with increasing immersion time in Figure 6. Especially, the intensity of peak around 340 nm which may be due to ground state dimer [11] appears to be sensitive to water sorption.

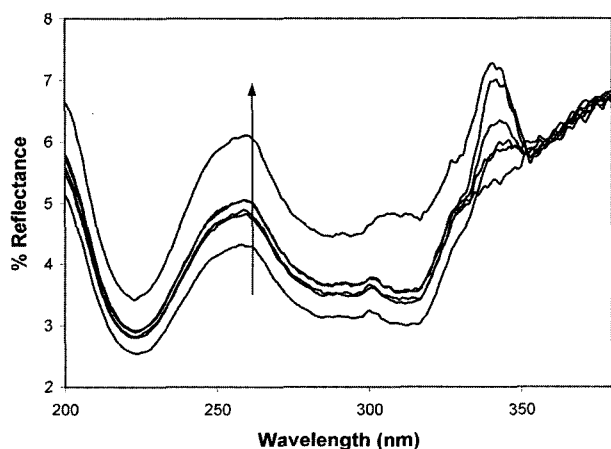


Figure 6. UV reflection spectra of PET films as a function of water immersion time. The arrow shows the increasing immersion time ($t=0, 60, 120, 180, 240,$ and 270 minutes) from the bottom.

PET has a fluorescent phenylene moiety in the main chain showing its fluorescence peak at 330-340 nm in fluid solution. However, the intrinsic luminescence of PET films has been less well characterized. The emission at longer wavelengths was first reported by Phillips and Schug [10], who suggested that an emission at 370 nm originates from either the triplet state or a tightly bound excimer. Allen and McKellar [11] attributed the fluorescence with a peak at 392 nm to the ground state dimer. The existence of the ground state dimer has been established by several authors [12]; the ground state dimer of PET films shows the fluorescence and absorption at 390 nm and 340 nm, respectively.

In our work, when excited at 260 nm, PET fluorescence does not show much change with water uptake. However, when excited at 340 nm as shown in Figure 7, two emission peaks at 368 nm and 388 nm decrease in intensity with increasing % water uptake as shown in Figure 8. The peak at 388 nm probably due to the ground state dimer shows some sensitivity to water uptake.

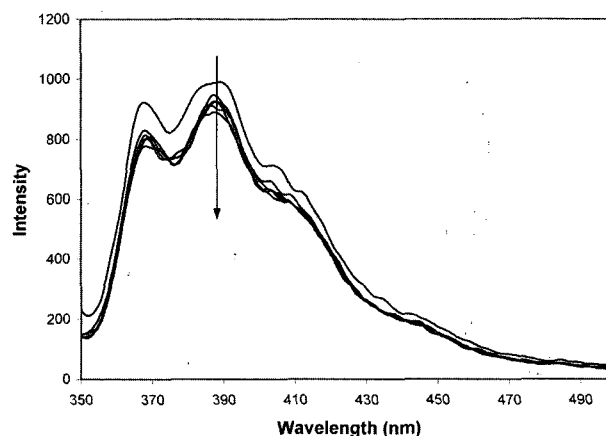


Figure 7. Fluorescence emission spectra of PET films when excited at 340 nm as a function of water immersion time. The arrow shows the increasing immersion time ($t=0, 60, 120, 180, 240$ and 270 minutes) from the top.

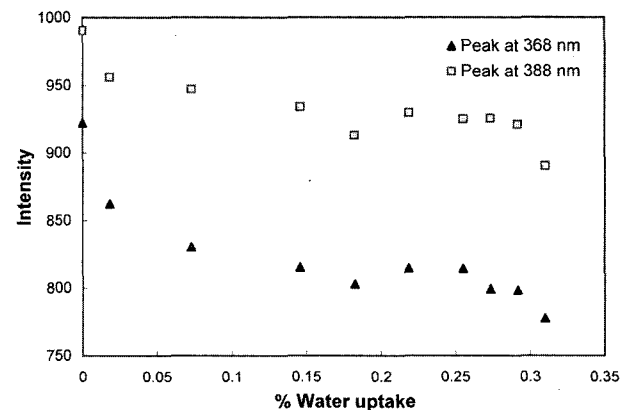


Figure 8. Emission intensities at 368 nm and 388 nm as a function of % water uptake in PET films.

Conclusions

In this study, water uptake in polycarbonate, polyurethane and PET films have been investigated using UV reflection and fluorescence spectroscopy. During water sorption process, UV reflection spectrum of polycarbonate and polyurethane films showed little peak position changes. In the case of PET films, the UV reflection spectrum showed the peak around 340 nm, which is sensitive to water sorption.

Fluorescence emission spectra of polycarbonate films showed red spectral shifts from 332 nm with water immersion time. This red-shifted peak could be due to phenyl-2-phenoxybenzoate, which is one of the major thermal degradation products in polycarbonate. Fluorescence peaks of polyurethane films appeared at two different positions and the ratio of these peak intensities increased with increasing immersion time. PET films exhibited its ground state dimer fluorescence, which showed sensitivity with water sorption.

Through this study, we have demonstrated the sensitivity of UV reflection and fluorescence spectroscopy for water sorption, which was more accurately monitored in situ by using a bifurcated fiber-optic attachment.

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