NOTE

Spectral Sensitivity of Polycarbonate to Light-Induced Yellowing

Polycarbonates are extensively used in glazing and engineering applications that involve routine exposure of the material to light. Discoloration of the polymer and deterioration of its mechanical properties resulting from light-induced reactions are therefore of practical interest.

Photodegradation of polycarbonates is believed to occur via two concurrent mechanisms: a photo-Fries rearrangement[1,2] and a photooxidative process.[3,4] The former consists of the rearrangement of polycarbonate repeat units to form dihydroxybenzophenones, via a substituted salicylate, and may occur by both a radical and a concerted process.[3] The functional groups associated with the reaction products absorb in the visible region of the spectrum and are believed to impart a yellow color to weathered samples. The oxidative degradation is believed to be a free-radical process involving the formation of hydroperoxides, ketones, and quinones.[4]

In white light, both processes are likely to occur simultaneously. The photo-Fries rearrangement is favored at shorter wavelengths, particularly at <290 nm, forming yellow reaction products. At higher wavelengths (330 nm) and in the presence of air, the oxidative process becomes progressively more significant[5] and a slow destruction of the products formed from photo-Fries reactions occurs.[3,5] These different processes give rise to interesting and complex spectral changes in the polymer weathered in daylight[6] and artificial light.[7]

Wavelength sensitivity of the overall photodegradation of polycarbonate is particularly important because of the complexity of the process. The possible existence of reaction sequences capable of both generating and destroying yellow-colored reaction products should result in a strong dependence of the photoyellowing upon the spectral distribution of the light source. As a preliminary to assessing the potential yellowing discoloration due to exposure to a given source of polychromatic light, it is important to determine the wavelength sensitivity of the material to yellowing under monochromatic radiation. This information, often expressed as an action spectrum[8,9] is also important in the design of stabilizers for control of photodegradation.

Photodegradation of polycarbonates, in general, and wavelength sensitivity to light-induced yellowing, in particular, have received relatively little attention in the research literature. Pryde,[10] working with Lexan films, found the wavelengths <300 nm to induce yellowing, particularly in the presence of oxygen. Mullen and Searle[7] reported the activation spectra for increase in absorbance at specific wavelengths (320, 360, and 400 nm) due to exposure to dispersed light from a xenon source. Maximum effect was found in the region 280–290 nm. In 10 mil-thick extrudates of polycarbonate, the maximum was shifted slightly toward the longer wavelengths.

The photodegradation in polycarbonate often tends to be a surface reaction limited to a depth of about 1 mil from the surface.[11] Highly chromophoric functional groups formed due to surface photoreaction effectively protect the bulk of polymer from degradation.[12]

The present study was undertaken to determine the wavelength sensitivity of commercial polycarbonate sheets, containing a UV absorber, to light-induced yellowing. Particular emphasis was placed on the wavelength interval typical of terrestrial sunlight at unit air mass.

EXPERIMENTAL

Lexan polycarbonate films (GE 8030) were used as received. The irradiation of the samples was carried out at the Okazaki Large Spectrograph Facility (NIBB) in Okazaki, Japan. The equipment and the exposure procedure has been described previously.[8] Essentially, the light from a water-filtered xenon source dispersed using a suitable grating was used. Test samples were exposed to radiation of selected wavelengths isolated from the spectrum. Quartz convex lenses were used to concentrate the light on a small region of the sample. Temperature of the samples under the beams were found to be the same as ambient (25°C).

Yellowness index of the exposed samples was measured using a Macbeth 1500 Colorimeter with an integrating sphere. The specular component of the light was excluded but the ultraviolet portion was included in the measurements. A white ceramic standard tile was used as a backing material. The ASTM yellowness index (ASTM D 1925), YI, was calculated on the basis of the CIE standard illuminant C (CIE = 1931 20 standard observer viewing) and is expressed by[13]

$$YI = [100(1.28\,x - 1.06\,z)/y]$$

where x, y, and z are tristimulus values of the sample with reference to source C. The mean of several YI values measured at different areas of exposed surface was reported as the average YI.

Table I Yellowness Index of Polycarbonate Exposed to Monochromatic Radiation

Wavelength (nm)	Intensity (Photons/sq cm)	Yellowness Index (YI)	Average Change[a] in YI (ΔYI)	ln (ΔYI/Intensity)
Unexposed	0	2.74	0	—
		2.72		
280	5.34×10^{20}	19.48	16.79	—
		19.51		
		19.80		
		19.29		−47.21
300	8.18×10^{20}	7.00	4.27	—
		6.99		−49.00
320	1.18×10^{21}	4.70	1.99	—
		4.73		−50.13
340	1.32×10^{21}	3.03	0.25	—
		2.93		−50.32
400	9.56×10^{20}	2.46	−0.27	—
		2.46		
500	1.87×10^{21}	2.54	−0.37	—
		2.24		
		2.29		

Standard ceramic material had a yellowness index of 2.32. Reproducibility of the measurements is better than ±0.25 yellowness index units.

[a] Change in YI on exposure. Positive values indicate yellowing while negative values show bleaching.

RESULTS AND DISCUSSION

The exposures were carried out at the wavelengths 280, 300, 320, 340, 400, and 500 nm. With a 30 kW xenon source and the present experimental arrangement, it was possible to obtain measurable yellowing within a 7.5 hr period of exposure. An increase in the ASTM yellowness index was obtained in the wavelength region of 280–340 nm. At the two higher wavelengths, the initial yellowness index of the unexposed samples was reduced by a small but significant extent. The data suggest a bleaching of yellow species (possibly present at low levels in the original sample) by exposure to the longer wavelength light. The observation is essentially consistent with the reported data on wavelength-dependent yellowing and bleaching in polycarbonate.

The dependence of yellowing in the wavelength region 280–340 nm is best illustrated by plotting the ln (change in average ASTM yellowness/photons per sq cm) as a function of the wavelength of exposure. Calculation assumes the change in yellowness to be a linear function of the intensity of monochromatic light in the pertinent range of photon fluence rates (see Table I). Although this has not been experimentally demonstrated, it is likely to hold in the relatively short range of intensities (relating to the different wavelengths) dealt with in this study. The plot so obtained, shown in Figure 1, is linear and is described by the equation given below:

$$\ln y = -24.2 - 0.082 \, \lambda \quad r^2 = 0.99$$

The gradient of the plot serves as a quantitative measure of the wavelength sensitivity of this polycarbonate material to light-induced yellowing. Logarithmic dependence indicates the particular sensitivity of yellowing to changes
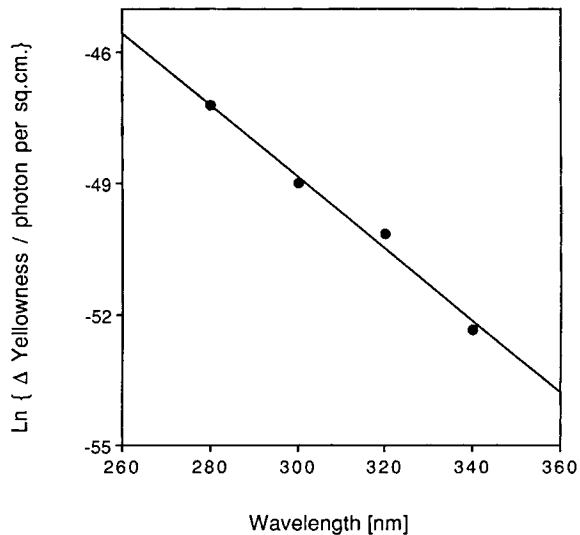

Figure 1 Wavelength sensitivity of Lexan polycarbonate to monochromatic light-induced yellowing.

in wavelength of irradiation. Present results agree qualitatively with the activation spectrum for changes in absorbance of extruded polycarbonate sheets reported by Mullen and Searle.[7] Since the present data (as well as the reported data[7]) were based on the radiation from a xenon source (dispersed), the average yellowness index values in Table I should approximately correspond to the activation spectrum for yellowing. The present data shows maximum yellowness to be associated with 280 nm and the yellowness to drop sharply at longer wavelengths, in qualitative agreement with the previously reported data.[7]

On exposure to a polychromatic source of light such as sunlight, both the yellowing and bleaching reactions occur simultaneously. The yellowing observed on exposure is therefore the net result of the yellowing and bleaching reactions that take place concurrently.

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