

Inhibition of Photoinitiated Degradation of Polycarbonate by Cerium(III) Overcoating

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Synopsis

Photodownconversion of UV radiation incident on a polymeric substrate, polycarbonate, into visible and IR region is effected by coating the substrate with cerous chloride (CeCl_3)/poly(vinyl alcohol) complex whereby photolytic degradation of the substrate is significantly inhibited. Thus it appears that cerous ion coating serves as an effective UV screener. The testing method consists of exposing the coated and naked substrate films to a medium intensity UV source with a cutoff filter below 280 nm for different intervals and determining their optical transmission characteristics. Some of the cerous ion coated films were further overcoated with polyvinyl acetate in order to prevent ion leaching by water. The final product retains the visible and IR transmittance of untreated polycarbonate film, and when the optimum composition of CeCl_3 in poly(vinyl alcohol) is coated, its transmission spectrum is barely changed even after 24 hr of UV irradiation. The object is to develop inexpensive solar glazing materials which can last up to 20 years without deterioration of their optical and mechanical properties upon solar irradiation.

INTRODUCTION

Polymeric substrates as the glazing material for solar collectors are gaining wide currency in recent years.¹ One principal drawback in the use of organic polymers as the glazings resides in their susceptibility to photodegradation² whereby solar transmittance of the glazings is reduced with attendant deterioration of mechanical properties upon exposure to solar radiation. These characteristics of polymer glazings render them less attractive despite their low cost of initial installation compared to the inorganic glass glazings.

Chemistry for the decreasing of solar transmittance is simple enough. As the ultraviolet component of solar radiation induces photo-oxidative chain reaction in any carbon backboned polymers,³ there results increasing concentration of chromophoric moieties, mainly the carbonyl group of aldehydes, ketones and carboxylic acids, giving rise to yellowing of the glazing panels. This phenomenon, long known for hydrocarbons,⁴ is referred to as "solarization" in the solar energy literature.

To the extent that the solar spectrum incident on the earth's surface peaks at about 500 nm and has high- and low-energy cutoffs at 300 nm and 2.5 μm , respectively and that the near ultraviolet (UV) portion of 300–400 nm comprises about 8% of the total radiant energy,^{5,6} we must devise ways to deal with the chemical effect of the near UV component as long as we require low cost glazings

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for the solar collectors. This paper addresses the problem of how to inhibit the photo-oxidative degradation effect. Conventionally we have three different methods to effect the inhibition. These include screeners, quenchers, and scavengers.^{7,8} Screeners simply act as a radiation shield for the substrate thus preventing the solarization. In this instance, there normally attends a substantial reduction in the optical transmittance in the visible and near IR since the most efficacious of them is carbon black or certain classes of organic dyes.^{9,10} The former of course interferes with solar transmittance and the latter suffers from the additional problems of toxicity, expense and photodegradation. Absorbers are organic molecules that have high absorptivity in the 300–400 nm range, hence act as the uv radiation sink provided their absorptivity exceeds that of the polymer matrix by a few orders of magnitude. Salicylic ester derivatives, benzotriazoles and *o*-hydroxybenzophenones are the examples of such absorbers. Compatibility with polymer matrix, photolytic and thermal stability of the absorbers however restrict their widespread uses although their effect on optical transmittance of polymer matrix is less serious as contrasted to the screeners. Quenchers interact principally with the photoexcited reaction centers and some fraction of the original quencher is able to regenerate back to the initial state but they are known to modify the optical and mechanical properties of the polymer substrate because of the large concentration required to be effective. Thus it is known that Ni(II) chelates (e.g., Ferro Am I, Cyasorb 1084, etc.) act as effective singlet and triplet quenchers but they invariably impart color to the substrate.^{11,12} Scavengers, e.g., trialkyl phenols,¹³ on the other hand, interact with the fully initiated free radicals derived from the photoexcited chromophores thus preventing the oxidative chain mechanism, however they lose the efficacy as the kinetic chain length is shortened. In the last two cases, dosage saturation results by necessity as the solarization process proceeds because the inhibition mechanisms require chemical reactions involving quenchers and scavengers. Hence, once these are exhausted the photo-oxidative degradation of the substrates proceeds without inhibition. These three models are schematically summarized in Figure 1.

Our method is novel because it departs conceptually from these three methods by optical recycling of the screener and downconversion of UV energy. It is derived from the unique optical property of lanthanide ions. In particular, the first allowed electronic transition of cerium(III) 4*f* ion entails the promotion of one of the active electrons into the 5*d* configuration which is generally a vacuum UV transition.¹⁴ However if the 4*f* configurations are dispersed in solution, it

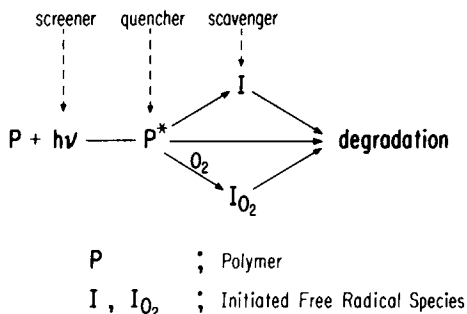


Fig. 1. Schematic description of polymer photodegradation and its inhibition.

is found that the $5d$ states shift to lower energy and broaden considerably into wide bands. The depression in energy is substantial and is found to depend on the strength of the static field generated by the ionic near neighbors. If these interactions are strong enough, the $5d$ transitions may be shifted into the visible. The states also are broadened by ion-coordination interactions which in turn lead to Stoke's shifts in the relaxation of the excited state. This is simply due to the difference in the ground and excited states orbitals leading to differences in the binding equilibrium point (coordination diagram). Ce(III) is a particularly simple example of this inasmuch as only a single $4f$ electron is involved; the energy level scheme consists of a ${}^2F_{5/2,7/2}$ low-lying doublet (J states) and the allowed band of higher configurations of $5d$ and $6s$ states. Because they are well shielded, the doublets are not affected by the ion surroundings; and they fall normally in the far infrared, thus no visible transitions are expected from this ion. Under some appropriate coordination, the absorptive $5d$ band of cerium(III) having the oscillator strength of near unity may be located at an energy range of interest since the energy gaps encountered by the photoexcited $4f$ electron are large, nonradiative transitions are known to play a minor role in relaxing these states. Cerium(III) thus presents us with an ideal candidate for a near uv screening Stoke's downconversion if appropriately coordinated.

This is precisely how we accomplish the inhibition of photo-oxidative degradation of bisphenol-A polycarbonate by first coordinating cerium(III) ions by poly(vinyl alcohol) and coating them over the polycarbonate substrate.

EXPERIMENTAL

Materials

Lexan, a trademark of General Electric, is the polycarbonate of bisphenol-A and was obtained in sheet form (0.03 in. thick) from Central Plastics (Madison, WI). $\text{CeCl}_3 \cdot x\text{H}_2\text{O}$ was obtained from Alfa Products (Danvers, MA). The cerium content was specified as 99.9% with respect to the other lanthanides. Poly(vinyl alcohol) and poly(vinyl acetate) were obtained from Aldrich Chemical Co. (Milwaukee, WI). The poly(vinyl alcohol) was 88% hydrolyzed with an average molecular weight of 10,000. All other chemicals employed were of reagent grade or better.

Apparatus

A 450 W mercury vapor lamp (Conrad-Hanovia) was employed in accelerated photodegradation experiments. The lamp, power supply, and reflector were obtained from Ace Glass Inc. (Vineland, NJ). The spectrofluorometer was a Farrand MK II from Farrand Optical Company Valhalla, NY. The UV-visible transmission spectra were obtained on a Cary 118 double beam spectrophotometer from Varian. A Beckman model 3500 millivoltmeter was used for potentiometric measurements.

Analysis of CeCl_3

The commercial CeCl_3 contained an unknown amount of hydration water. The water content as specified by the manufacturer was 37.6%. In addition the CeCl_3 contained a small amount of insoluble material, probably Ce_2O_3 . This amounted to ca. 0.2% by weight of the $\text{CeCl}_3 \cdot x\text{H}_2\text{O}$ as determined gravimetrically. After filtering to remove the insoluble material, the CeCl_3 content was determined very precisely by a modification of the method of Tomicek.¹⁵ The method involves the potentiometric titration of Ce(III) in 50% potassium carbonate solution with potassium ferricyanide under a nitrogen atmosphere. The particular lot analyzed contained $64.57\% \pm 0.06\%$ CeCl_3 , the balance being water.

Coating of Lexan

Casting solutions were prepared in deionized water containing 10% by weight of poly(vinyl alcohol) and varying amounts of CeCl_3 (from 0.01 to 5 gram of CeCl_3 per gram of polymer). Enough solution to prepare a film of 100 to 150 μm thick was applied with a transfer pipet to squares of the 8 mm (0.03 in.) thick Lexan. Each sample of Lexan was 6.5 cm^2 (1 in.^2) in area. The solutions were filtered through a 0.22 μm Millipore filter to remove insoluble material before coating. A gentle stream of purified N_2 was passed over the films to speed the evaporation of the solvent. The resulting films were transparent and free from bubbles and cracks. Some samples were overcoated with poly(vinyl acetate) to protect the poly(vinyl alcohol) coating from moisture. This was accomplished by casting a 100–150 μm thick film from a 10% by weight poly(vinyl acetate) solution in ethyl acetate.

Accelerated Photodegradation

Various samples were irradiated with the 450 W Hg vapor lamp at a distance of 10 cm from the reflector. Only natural convection of the air in the irradiation chamber was used to cool the samples. A beaker of water placed 10 cm from the lamp reached a temperature of 50°C after 5 hr of irradiation. In some photodegradation experiments, the short wave (<300 nm) UV radiation was filtered out by a 3 mm thick piece of Pyrex (Corning glass No. 7740).

RESULTS

Figure 2 presents the excitation and emission fluorescence spectrum of a casting solution which was used to coat Lexan with a protective film of CeCl_3 dispersed in poly(vinyl alcohol). The solution is 10% by weight of poly(vinyl alcohol) and contains 50 mg of CeCl_3 per gram of polymer. The relative fluorescence intensity is shown on the ordinate and is uncorrected for variations in lamp intensity and photomultiplier sensitivity with wavelength. The observed fluorescence signal arises from Ce(III), the residual signal from poly(vinyl alcohol) fluorescence and scattering and the Raman scattering from water being minimal at this concentration of Ce(III).

Figure 3 contains the UV-visible transmittance spectra of poly(vinyl alcohol) coated Lexan containing varying amounts of CeCl_3 . The spectra were obtained after 24 hr irradiation in the UV lamp after which all of the films were visibly

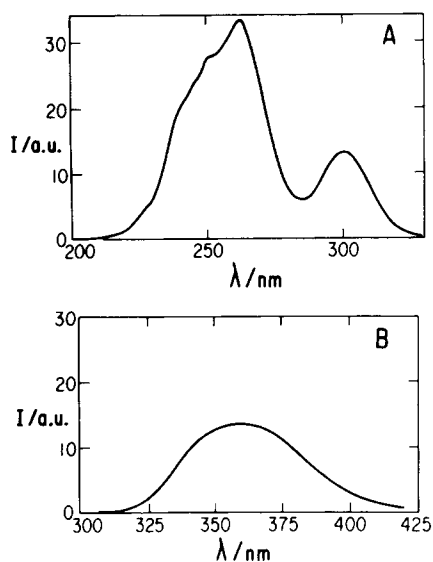


Fig. 2. Fluorescence spectra of CeCl_3 /poly(vinyl alcohol) coating solution. [1 g of poly(vinyl alcohol) and 50 mg CeCl_3 made up to 10 ml with H_2O .] (A) Excitation spectrum, $\lambda_{\text{em}} = 355$ nm; (B) emission spectrum, $\lambda_{\text{ex}} = 300$ nm.

yellow. All spectra were obtained with air in the reference beam, and are referenced to nonirradiated poly(vinyl alcohol) coated Lexan by adjusting the instrumental response to give a 100% T reading at 500 nm with this blank sample in the sample beam. The transmittance readings in the wavelength region from 500 to 350 nm were obtained with the tungsten-halogen lamp, while the region shorter than 350 nm employed the deuterium lamp. Note that spectrum B in Figure 3 was obtained on a sample prepared by casting a film from 1 ml of the solution whose fluorescence spectrum is shown in Figure 2 onto Lexan, followed by irradiation.

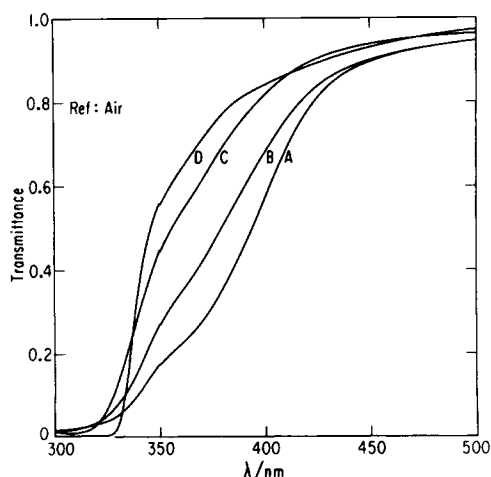


Fig. 3. Transmittance spectra of CeCl_3 /poly(vinyl alcohol) coated Lexan sheets after 24 hr of irradiation. (A) 0.1 g poly(vinyl alcohol) on Lexan; (B) 0.005 g CeCl_3 in 0.1 g poly(vinyl alcohol); (C) 0.010 g CeCl_3 in 0.1 g poly(vinyl alcohol); (D) 0.050 g CeCl_3 in 0.1 g poly(vinyl alcohol).

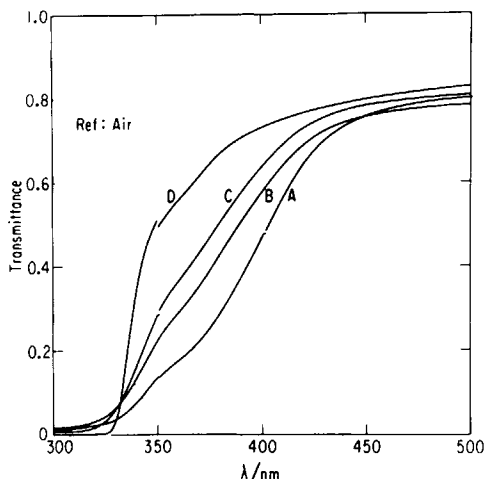


Fig. 4. Transmittance spectra of CeCl_3 /poly(vinyl alcohol) coated Lexan sheets sealed with a poly(vinyl acetate) overcoat after 20 hrs of UV irradiation. (A) 0.1 g poly(vinyl alcohol); (B) 0.005 g CeCl_3 in 0.1 g poly(vinyl alcohol); (C) 0.010 g CeCl_3 in 0.1 g poly(vinyl alcohol); (D) 0.050 g CeCl_3 in 0.1 g poly(vinyl alcohol).

Figure 4 presents UV-visible transmittance spectra of irradiated, coated samples nearly identical to those in Figure 2, except that each of the four samples was coated with 100 mg of poly(vinyl acetate) in a film approximately $125 \mu\text{m}$ thick. The irradiation time was 20 hr instead of 24 hr. In Figure 4 the four spectra are referenced not to a nonirradiated cerium free sample as in Figure 3, but to air. This was done by adjusting the instrumental response to read 100% T with air in both the sample and reference beams. As previously all spectra were recorded with air in the reference beam. Thus Figure 4 shows the decrease in transmittance relative to air due to the 30 mil thick Lexan, the $150 \mu\text{m}$ Ce(III) /poly(vinyl alcohol) coating, and the $150 \mu\text{m}$ thick poly(vinyl acetate) overcoating. Figure 5 shows the UV-visible spectra of the samples under the same conditions as in Figure 3 with unirradiated Lexan as the reference.

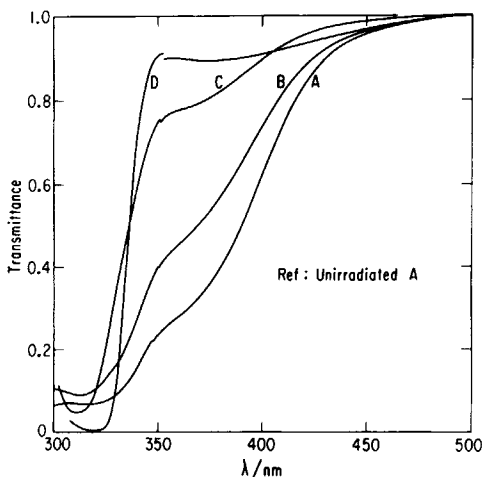


Fig. 5. Same as Figure 3 with unirradiated Lexan as the reference.

DISCUSSION

Figure 2 demonstrates that the fluorescence of Ce(III) is unaffected by the poly(vinyl alcohol) with excitation maxima at 263 and 300 nm and a single emission maximum at 360 nm when the excitation monochromator is set to pass radiation from 225 to 320 nm. This implies that the most energetic region of the terrestrial solar spectrum will be downconverted to less energetic wavelengths. The ideal way to utilize this downconversion for the inhibition of solarization is to coat a thin layer of cerium(III) on the surface of the substrate to be protected from photodegradation. This coating scheme is superior to incorporation of the cerium in the bulk of the Lexan because less cerium(III) will be needed, and the properties which make Lexan ideal for solar collector applications will be undiminished.

Ideally, cerium(III) could be incorporated directly into a thin layer of polycarbonate and directly cast onto a sheet of Lexan but CeCl_3 (and other cerium salts) is insoluble in all the common solvents for polycarbonate. (The suspected carcinogen 1,4-dioxane will dissolve CeCl_3 and polycarbonate but its use was rejected because of safety considerations.) The alternative was to use a carrier matrix with a large affinity for cerium salts, which could then be cast onto the polycarbonate sheet. Poly(vinyl alcohol) was chosen as the carrier matrix because it offers a number of advantages. It is inexpensive and shows excellent stability towards UV photodegradation. It can be easily cast from solution and its solubility can be modified by controlling the degree of hydrolysis of the original poly(vinyl acetate). Most importantly it can coordinate a very large amount of CeCl_3 , up to 5 g CeCl_3 to 1 g of poly(vinyl alcohol), without any apparent change in the optical properties of the resulting film.

Poly(vinyl alcohol) suffers from the two major disadvantages in the application proposed. First, it is water soluble and therefore must be protected from dissolution by rain. Second, poly(vinyl alcohol) is incompatible with polycarbonate. After the film has completely dried, it can be removed from the Lexan very easily. Both of these problems can be solved by sealing the cerium containing poly(vinyl alcohol) film onto Lexan with an overcoat of poly(vinyl acetate). The sealant coat is formed by casting poly(vinyl acetate) from an ethyl acetate solution over a film of cerium containing poly(vinyl alcohol). Ethyl acetate swells the Lexan resulting in an opaque border around the edge of the poly(vinyl alcohol) film. It does not attack the Lexan under the poly(vinyl alcohol) film leaving a transparent window.

The poly(vinyl acetate) is quite effective in preventing water from dissolving the cerium chloride. A one square inch sample prepared as outlined above was stirred in a beaker of distilled water for seven days after which time the water was analyzed for Ce(III) by spectrofluorometry. The detection limit of the method was shown to be 0.3 ng of CeCl_3 per milliliter or 300 parts per trillion, yet no cerium was observed implying that less than $1.6 \times 10^{-5}\%$ of the originally added cerium had diffused through the sealant layer. Extrapolating this figure to one year gives a diffusion rate of 0.001% of added CeCl_3 per year! The poly(vinyl acetate) sealant layer also makes it impossible to remove the CeCl_3 -poly(vinyl alcohol) coat without destroying the sample.

In order to achieve photodegradation of the coated samples in a reasonable time and at an acceptable cost, a compromise was needed. The medium pressure mercury lamp was chosen because its intense lines longer than 300 nm could be

easily isolated using borosilicate glass as an optical filter. This arrangement essentially eliminated radiation shorter than 280 nm which is very damaging to the coated samples. Of course none of this high-energy radiation reaches the earth's surface because of the filtering effects of the atmosphere. It was found that 15 to 25 hr illumination of polycarbonate at a distance of 10 cm from the discharge tube under a 2 mm thick borosilicate glass sheet gave substantial yellowing as the UV-visible transmittance spectrum of exposed Lexan in Figure 5 shows.

Figure 3 shows that the addition of CeCl_3 is protecting the coated samples. Sample D, which contains the most CeCl_3 , is most resistant to photodegradation, while even sample B with a small amount of CeCl_3 is significantly better than the poly(vinyl alcohol) blank. Also note the reversal in the transmittance with cerium content at 310 nm where cerium(III) is absorbing strongly. Figure 4 shows that the degree of protection also follows the CeCl_3 content when the poly(vinyl acetate) sealant coat is added. In both cases the 50 mg of CeCl_3 per 100 mg of poly(vinyl alcohol) is far from the maximum amount of CeCl_3 which can be added, and even greater resistance to yellowing would be expected with larger amounts of CeCl_3 , and work is proceeding along these lines. Furthermore the effects of coating thickness and degree of hydrolysis of the poly(vinyl alcohol) remain to be investigated.

CONCLUSIONS

The feasibility of protecting Lexan from yellowing in the presence of uv radiation from 300 to 400 nm by coating CeCl_3 in a thin layer on the surface has been demonstrated. This protection arises from the downconversion of radiation from 300 to 320 nm to less damaging radiation in the ultraviolet and blue. Furthermore this CeCl_3 coat has been shown to be unaffected by water indicating it may retain its uv screening properties in the environment. Work is proceeding on scaling up the coating process as well as performing more realistic weathering tests. The application of this coating scheme to other polymers is also being investigated.

We should point out here that our accelerated testing scheme with use of a high intensity mercury arc lamp (with a cutoff filter below 300 nm) provides a reasonably fast method to screen efficacious cerium(III) overcoatings, but ultimately we must subject these coated films to out-door solar exposure testing. Only by such a testing, can we examine the direct weathering characteristics and optical property changes of these films for the solar glazings use. Thus such testings are now in progress at various locations.

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