The Use of FT-IR Reflection-Absorbance Spectroscopy to Study Photochemical Degradation of Polymeric Coatings on Mirrors

J. Webb
P. Schissel
A. W. Czanderna
D. M. Smith
A. R. Chughtai

Solar Energy Research Institute

A Division of Midwest Research Institute

1617 Cole Boulevard
Golden, Colorado 80401

DISCLAIMER

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

THE USE OF FT-IR REFLECTION-ABSORBANCE SPECTROSCOPY TO STUDY PHOTOCHEMICAL DEGRADATION OF POLYMERIC COATINGS ON MIRRORS

John Day Webb, Paul Schissel, A. W. Czanderna
Solar Energy Research Institute
1617 Cole Boulevard
Golden, CO 80401

D. M. Smith and A. R. Chughtai
University of Denver
Department of Chemistry
Denver CO 80208

ABSTRACT

A technique is presented for in situ study of degradative changes in polymeric coatings on metallic substrates. The technique uses a controlled environment chamber in conjunction with a Fourier-transform infrared (FT-IR) spectrophotometer. The chamber design permits collection of IR reflection-absorbance spectra from a sample undergoing exposure to controlled ultraviolet (UV) radiation, gas mixtures, and temperatures. Initial data presented confirm the ability of the technique to provide information regarding the bulk photochemistry of bisphenol-A polycarbonate coatings on gold and aluminum substrates. Refinements of this technique should allow a detailed kinetic study of degradative reactions at the polymer/metal interface.

INTRODUCTION

An understanding of photodegradative reactions of polymers and the extent to which these reactions are influenced by the presence of a polymer/metal (oxide) interface is important for using polymers in solar energy conversion systems. For example, a polymer used to encapsulate a photovoltaic device may be in contact with a semiconductor, grid metallization, interconnections, antireflection coating, and cover plate. Polymers are used in a similar way to protect mirror surfaces from exposure to sources of environmental degradation such as atmospheric gases, moisture, and abrasive particles, with the object of maintaining a constant solar reflectance of the composite for over 20 years. To protect the substrate in all cases, the bulk properties of the polymer must be stable with respect to UV radiation, temperature, moisture, and atmospheric gases. However, the polymeric coating may actually contribute to an accelerated degradation of the protected materials if degradative or catalyzed interfacial reactions change the desirable properties of the polymer. It is known that the thermally induced oxidative degradation of certain polymers is accelerated when they are placed in contact with copper(oxide) surfaces (1). What is not known is whether similar catalytic effects result when the polymer is in contact with silver, aluminum, or other metallic (oxide) surfaces.

Realistic studies of the bulk and interfacial degradation of polymers for solar applications must be concerned with the effects of UV radiation, temperature, temperature cycling, atmospheric gases, and other degradative parameters. The experimental method should be sensitive to small chemical changes in the samples studied, preferably in the configuration in which they will actually be used. The results obtained should be reproducible and be comparable to those obtained by outdoor exposures. Finally, the analytical technique should not itself contribute to sample deterioration, and should be rapid compared to the degradation events being observed.

We have chosen reflection-absorbance spectroscopy to obtain analytical information on samples of polymer/metal multilayer stacks subjected to degradative factors. The method is sensitive and nondestructive, and permits continual examination of the polymer/metal composite during exposure to several degradative parameters (UV, T, ΔT, gases). The apparatus allows simultaneous control of UV intensity, UV energy distribution, temperature, and gases surrounding a particular sample.

The primary purpose of this communication is to summarize the capabilities of the apparatus described in detail elsewhere (2). Data representative of initial studies undertaken to determine an appropriate UV energy distribution are also referenced (2,3). The data demonstrate the feasibility of collecting infrared spectra on a sample undergoing exposure to UV and a flow of gases while maintaining control of sample temperature. This capability represents an improvement over previously reported methods (4), which depend upon removing the sample from the spectrophotometer for irradiation with a resultant loss of control over the sample temperature, environment, and orientation. Preservation of sample orientation is particularly important if spectroscopic accuracy is to be maintained in the external reflection experiment.

EXPERIMENTAL APPARATUS

The spectrophotometer used in our studies is a Nicolet Model 7199 Fourier-transform instrument initially equipped with a deuterated triglycine sulfate (DTGS) detector. To expedite data collection, a mercury cadmium telluride (MCT) detector was substituted for the DTGS unit. During data collection, 100 scans of the Michaelson interferometer at 2 cm^{-1} resolution are routinely utilized. The data collection time was 7 minutes for the DTGS detector but is only 2 minutes using the MCT unit.

A controlled-environmental chamber was designed to fit the Nicolet spectrophotometer by using a software model of its optical components. A schematic diagram of the chamber and the symmetrical infrared optics is shown in Fig. 1. The off-axis paraboloids at either side of the chamber were designed for a 75° angle of incidence to minimize spot size on the sample and on the detector. This angle was chosen to optimize the sensitivity to absorbing species near the polymer-metal interface (5,6) within the spatial constraints imposed by the spectrophotometer sampling compartment. Radiation from a xenon arc lamp, which is filtered to yield various UV energy distributions, is incident on the sample through quartz windows in the spectrophotometer cover

and chamber. The sample may be subjected to a metered flow of blended gases or a vacuum by using the ports at the top of the chamber. The IR radiation may be passed through KRS-5 windows while maintaining these ambient conditions. During irradiation, the sample temperature is controlled · by water that is circulated in thermal contact with the rear of the sample. The samples used to date consist of glass/metal reflectors coated with polymeric films via solvent evaporation or metallized polymeric films.

RESULTS

After establishing a flow of reagent-grade air blend in the environmental chamber and purging the FT-IR compartment with dry air, a spectrum of each sample was taken before irradiation. For each sample, this initial spectrum was subtracted from a series of spectra collected at 30-minute intervals during irradiation to yield a series of absorbance-difference spectra indicative of changes in the polymer functionalities.

In one example, the differences observed in the infrared spectra, Fig. 2, are shown for three similar samples after five hours' exposure to three different UV energy distributions. The subtraction results obtained from spectra collected five hours after the start of irradiation are presented here for clarity, although changes were prominently visible after the first 30 minutes of exposure. The samples consisted of polycarbonate films of 2- to 3- μm thickness on gold substrates. The UV distributions showed significant reductions in intensity at 325, 300, and 250 nm, respectively, as produced by filtering. Inspection of the upper spectrum reveals that little change is produced in the polymeric film by radiation with wavelengths longer than 325 nm. Exposure to UV with wavelengths down to 300 nm produced considerable change, and further decrease in UV wavelength to 250 nm appears to have changed the mechanisms as well as rates of photodegradation. Evidence for chain scission and photorearrangement can be obtained from analysis of the lower two spectra. The variations in baseline slope at frequencies between the major reflection-absorbance bands for the two samples exposed to UV radiation with wavelengths shorter than 325 nm may be explained in terms of degradative optical distortions of the films. Each sample exhibited an average reduction of 10% in thickness following exposure.

Figure 3 shows the reflection-absorbance spectra of a 25-μm, aluminized polycarbonate film before and after irradiation with UV light wavelengths longer than 300 nm, with the result of a digital subtraction between the two spectra plotted beneath. A sharp (5 cm^{-1}) absorbance band at 2338 cm^{-1} is indicative of the buildup of rotationally restricted CO_2 in the polymer. This signal decreases slowly upon cessation of UV illumination corresponding to diffusion of CO_2 out of the polymer, and if gas flow through the environmental test chamber is stopped, signals corresponding to gas phase CO_2 increase. These observations are obtained more easily in situ, compared to previously reported methods (4) which require removal of the sample from the spectrophotometer.

The differences in sensitivity to spectral changes exhibited between the spectral subtraction results for the 2- to 3- μm films (Fig. 2) and for the

3

25-μm film (Fig. 3) are interesting to observe. Since two of these samples were irradiated under similar conditions, the subtraction spectra might have a similar appearance. Similarities indeed exist for the bands above 2800 cm-1 which in transmittance spectroscopy correspond to weakly absorbing species. However, the CO_2 band prominently visible in Fig. 3 can only be seen in an expanded plot of Fig. 2. This is more easily explained by a uniform buildup of CO_2 throughout both films than by possible catalytic activity of the aluminum substrate. We expect the thicker film would contain more CO_2 and thus would exhibit stronger absorption. Since both films were optically thick, it is likely that the difference spectra presented in Figs. 2 and 3 predominately represent bulk rather than interfacial changes in the polymer structure.

Another discrepancy between the two spectra is visible in the region associated with the strong carbonyl absorption centered at about 1775 cm^{-1}. The reduction in carbonyl absorption visible in Fig. 3 is much less than that visible in the difference spectrum of the thinner film displayed as the central trace in Fig. 2. This observation confirms the conclusion reached by Greenler (5) and Allara (7) that reflection-absorbance band heights do not exhibit a linear relation to film thickness. Predictive work based on thin film/reflector optics that is in progress at SERI indicates that sensitivity to changing concentrations of strong IR absorbers for polycarbonate films that are more than 1-μm thick will be low in the IR reflection-absorbance mode. Despite evidence for degradation-related production of CO_2, optical calculations can predict the lack of sensitivity to reduced carbonyl functionality exhibited in Fig. 3. A similar analysis predicts that the appearance of an additional band at 1790 cm^{-1} (to yield an apparent split of the carbonyl peak) results from the anomalous dispersion. Allara (7) reported splitting of the carbonyl reflection-absorption band of thick polymethylmethacrylate films, and verified the role of dispersion effects in producing this split. Use of thinner films and polarized IR incident radiation should provide information that is less biased by dispersion effects and has a more linear relation to concentration changes.

CONCLUSIONS

In situ measurement of IR reflection-absorbance spectra from polymeric films on metallic substrates demonstrably yields valuable information about the bulk photochemistry of polymers intended for outdoor use. Refinements of this technique are now in progress and should allow a detailed study of degradative interfacial reactions between thin polymeric coatings and metallic substrates. Using optical models of the IR reflection-absorbance experiment will permit quantification of experimental results and determination of kinetic variables for the reactions.

ACKNOWLEDGMENT

REFERENCES

(1) H. H. G. Jellinek, H. Kachi, A. W. Czanderna, and A. Miller, J. Polymer Sci., 17, 1493 (1979), and references therein.

(2) John Day Webb, Paul Schissel, A. W. Czanderna, D. M. Smith, A. R. Chughtai, Appl. Spectros., 35, 6 (1981), p. 598.

(3) John Day Webb, Paul Schissel, A. W. Czanderna, A. R. Chughtai, and D. M. Smith, Proc. of SPIE, 289 (1981), p. 190.

(4) S. C. Lin, B. J. Bulkin, and E. M. Pearce, J. Polymer Sci: Polymer Chem. Ed., 17, 3121 (1979).

(5) R. G. Greenler, J. Chem. Phys., 44, 310 (1966); 50, 1963 (1969).

(6) D. L. Allara, Characterization of Metal and Polymer Surfaces, L. H. Lee, Ed., Academic Press, Inc., N.Y., V. 2 (1977), p. 193.

(7) D. L. Allara, A. Baca, and C. A. Pryde, Macromolecules, 11, 6 (1978), p. 1215.
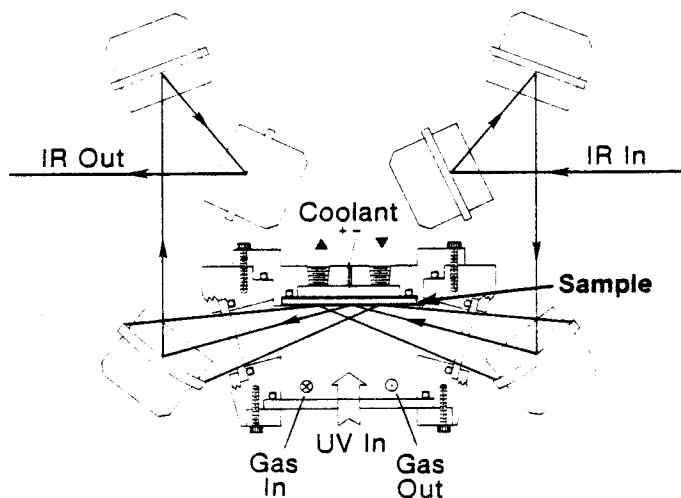
Figure 1. Environmental Test Chamber and Optics

Wave Number
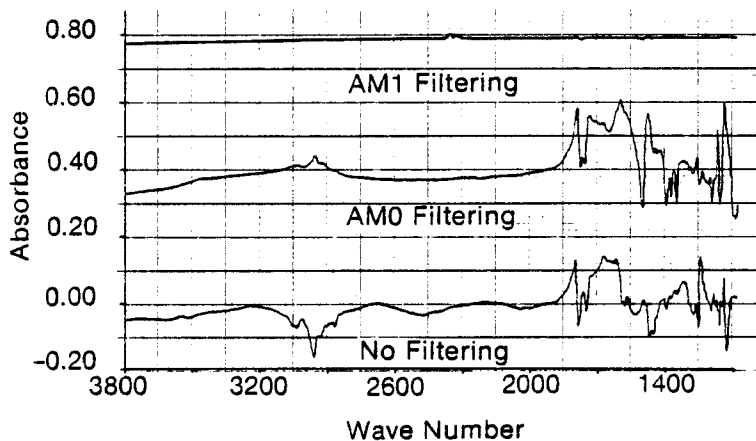
Figure 2. Subtraction Spectra Collected from Three Polycarbonate/Gold Samples, Following Five Hours' Exposure to Ultraviolet Radiations at Various Energy Distributions (Energy Distributions Generated by Filtering the Simulator Output Beam)
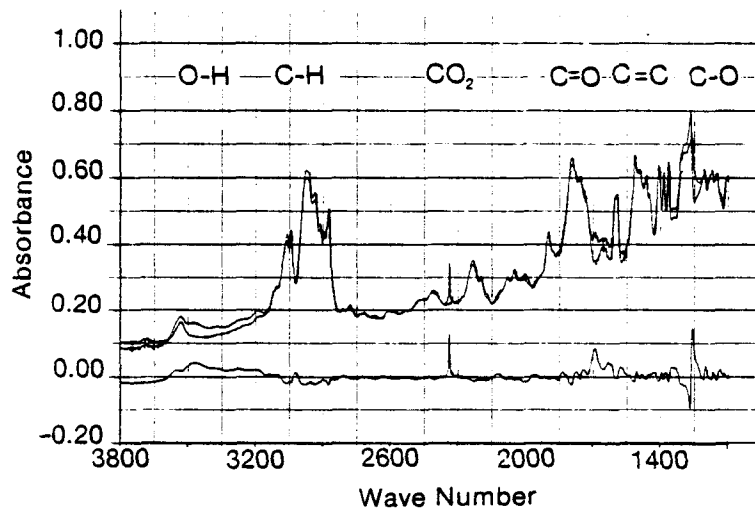
Figure 3.   Spectra of Polycarbonate/Aluminum Film Taken Before
and After Five Hours of Simulated Solar Irradiation,
with Results of Subtraction of the Two Spectra Showing
Functional Group Changes