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Polymer degradation on reflecting metal films:
Fourier transform infrared (FTIR) reflection-absorbance studies

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Abstract

The technique of Fourier transform infrared reflection-absorption (FTIR-RA) spectroscopy has been successfully adapted to studying bulk and interfacially activated photodegradation of several types of polymers on various metallic substrates. The technique enables qualitative and quantitative study of photochemical reaction mechanisms and rates. A Controlled Environmental Exposure Chamber (CEEC), which permits collection of IR-RA spectra of the polymer/metal samples during their exposure to controlled spectral distributions of UV, temperatures, and gas mixtures, was built into the sample compartment of a Nicolet 7199 FTIR spectrophotometer. Surface analysis, gel permeation chromatography (GPC), UV spectroscopy, and UV spectroradiometry were used to complement the FTIR-RA results.

Introduction

Polymers have been proposed or utilized as protective coatings for metallic solar reflectors and photovoltaic devices.¹ Free-standing polymeric films have also been proposed or utilized as components of active or passive solar collectors. The metallic surface layer of composite structures may contain significant concentrations of oxides or salts as a result of deposition of the metal layer or the polymer coating, or subsequent outdoor exposure of the polymer/metal composite.² Knowledge of the mechanisms of photodegradation of bulk polymers and at polymer/metal or polymer/(metal oxide or salt) interfaces is important for assessing the potential durability of technological systems.

Equipment

FTIR-RA spectroscopy was chosen as the primary analytical technique because it is fast, sensitive (particularly to thin organic films on metals), and nondestructive. A Nicolet 7199 dual-beam FTIR with 0.06 cm^{-1} maximum resolution was used. Installation of the CEEC in the front beam of the FTIR permitted the samples to be exposed to simulated environmental conditions, including UV radiation, while IR-RA spectra were collected. A prototype CEEC has been described.^{3,4}; an improved version is sketched in Figure 1. The latter instrument

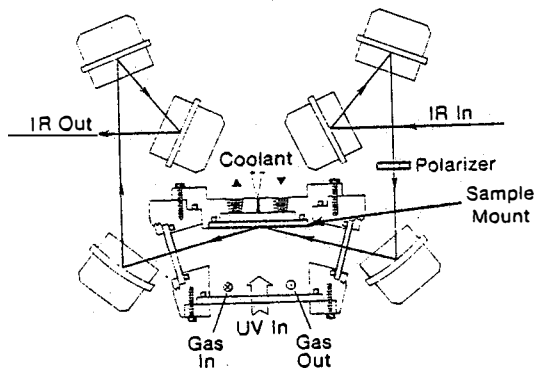


Figure 1. Controlled Environmental Exposure Chamber (CEEC) and IR path incident onto a polymeric coating on a reflecting substrate.

utilizes two off-axis parabolic reflectors to achieve an optical throughput of 75 percent (with the chamber salt windows removed). The reflector focal length was chosen to minimize the area of the IR image at the sample and detector using a software model of the FTIR optical bench. The IR image on the sample is approximately 1 cm x 0.3 cm, and the incidence angle (ϕ) is 77.5°.

The CEEC accepts a collimated UV beam from an Oriol Model 6732 solar simulator with a 1000-W, high-pressure xenon arc lamp. The simulator is equipped with a dichroic reflector that essentially limits the spectral output of the lamp to a band between 240 and 500 nm and greatly reduces the thermal loading of the samples. Dichroic and absorption filters are available to attenuate further the short wavelength portion of this band. The spectral output distributions of the simulator created by using a series of Schott glass absorption filters are presented in Figure 2. The distribution produced by the WG-305 filter is a fair match to the outdoor UV spectrum measured by

Klein and Goldberg⁵ in Panama in December 1975. The simulator intensity is about 16 times the terrestrial irradiance they reported from 310-320 nm. The simulator spectrum for WG-305 filtering is greater than 16 times more intense than their spectrum in the region from 295 to 310 nm. Measured terrestrial UV flux at 295 nm was about 0.025 $\mu\text{W cm}^{-2}\text{nm}^{-1}$, and UV

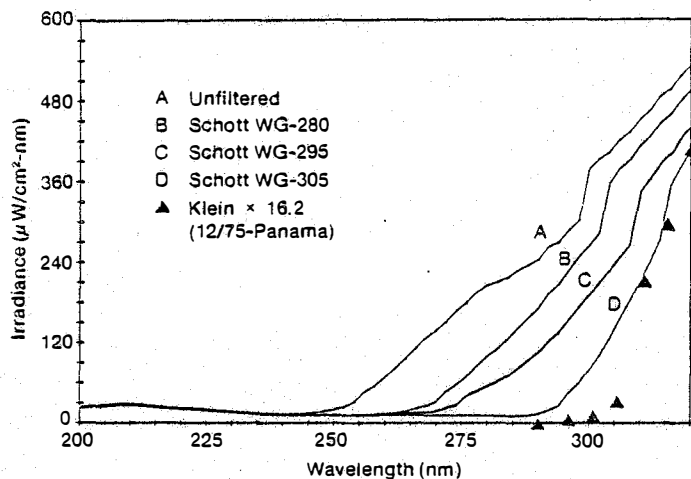


Figure 2. Measured output spectra of an Oriol 6372 solar simulator (high-pressure Xe arc) for various filters, compared to terrestrial (equatorial) UV distribution.⁵

fluxes were detected at wavelengths as short as 290 nm.⁵ UV flux was measured at wavelengths as short as 287 nm in the simulator output spectrum for WG-305 filtering. The non-zero baselines in the simulator spectra are artifacts of stray light in the Gamma Model DR-2 spectroradiometer used to measure these spectra.

To assess the chemical composition of the reflective metallic substrates, a Leybold-Hereaus LHS-10 surface analysis system with capability for AES, XPS, SIMS, ISS, and ion bombardment depth profiling was employed. The molecular weight distribution of the polymeric samples was determined using a Varian Model TSK 5030 liquid chromatograph equipped with a Varian Model TSK 4000H gel permeation column and a Varian Model VUV-10 UV detector with variable wavelength. The thickness of the polymeric films was determined at six points around the periphery of each sample using an Alpha-Step surface profiler.

Samples

The substrates used were float glass, 1.4 x 1 x 0.1 cm. Silver reflective surfaces (100 nm) were prepared by rf/dc sputter deposition onto the cleaned substrates in vacuum. Gold reflectors were prepared by vacuum evaporating silicon 20 nm-thick onto the substrates to promote adhesion, followed by evaporating a 170 nm-thick gold film. Bisphenol-A polycarbonate (BPA-PC) and polymethylmethacrylate (PMMA) films were cast onto these reflectors by dipping from dilute (<1%) tetrahydrofuran (THF) solution. Polyvinylidene fluoride (PVDF) films were cast from dilute cyclopentanone solutions. After annealing in vacuum at 100°C, the polymer film thickness (d) was measured.

Technique

To obtain the IR-RA spectrum of a sample, an uncoated reflector was placed in the CEEC and its spectrum (reference spectrum) was collected and stored. The spectrum of the sample was recorded, divided by the reference spectrum, and converted to absorbance units. Similar IR-RA spectra were generated as the sample was exposed. Subtraction of the original IR-RA spectrum of the sample from those collected subsequently yielded subtraction or difference spectra showing only IR-RA changes.

Quantitative IR-RA

An optical model of the polymer/metal samples was developed to enable quantitative information on polymer functional group depletion and/or reaction product accumulation to be obtained from IR-RA spectra of degrading samples. The model requires knowledge of the optical constants $N = n - ik$ for the polymeric functional groups and reaction products at their fundamental vibrational frequencies, as well as the optical constants of the metallic substrates. Sufficiently accurate optical constants of metals in the IR are generally available in the literature,⁶ but the optical constants must be measured for the polymers. In reference 7, we reported that the optical constants of a thick (3 mm) polymer sheet could be determined from the absorbance of a dilute solution of the polymer, enabling n to be determined using the Kramers-Kronig relationship. For the latter technique, a polarimetric measurement of n_{CD} ⁷ is needed, but this can be done at a single wavelength away from the fundamental frequency. Polarimetrically determined optical constants for BPA-PC are compared with those determined from absorption measurements and a polarimetric n_{CD} in Figure 3. The iterative software for converting the polarized surface reflection spectra of a polymer sheet to n and k as a function of frequency was compiled into a Fortran 77 program compatible with the Nicolet 1180 minicomputer, enabling direct access to the FTIR reflectance spectra used as input data. This program is available through the Nicolet User's Society.

The utility of relatively thick (0.1 - 1.0 μm) polymeric films on metals for studying rapid bulk photoprocesses was discussed in reference 7. Thinner films may be utilized

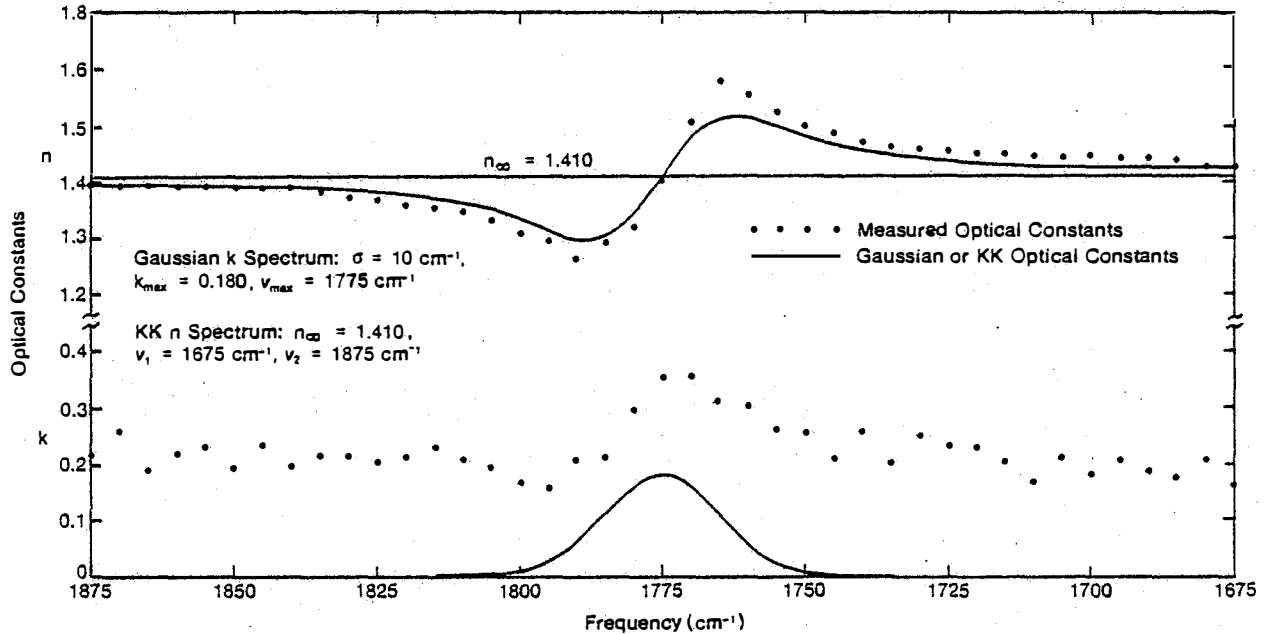


Figure 3. Measured optical constants for the carbonyl absorption band of bisphenol - A polycarbonate, compared with optical constants derived from a Gaussian fit to the k spectrum and Kramers-Kronig integrations of the Gaussian to yield the n spectrum.

to study interfacial reactions. The carbonyl IR-RA band of a 15 nm-thick PMMA film on gold is presented in Figure 4. The spectrum exhibits a S/N of about 30/1, although there is some interference by water vapor at these very low absorption scales. The high IR throughput of the CEEC, achieved by using antireflective-coated salt windows and polarizer, is responsible for the good S/N ratio. Ten thousand scans were made during the 2 h required to collect the data shown in Figure 4. A cooled MCT IR detector was used for collecting data for both the sample and reference spectra.

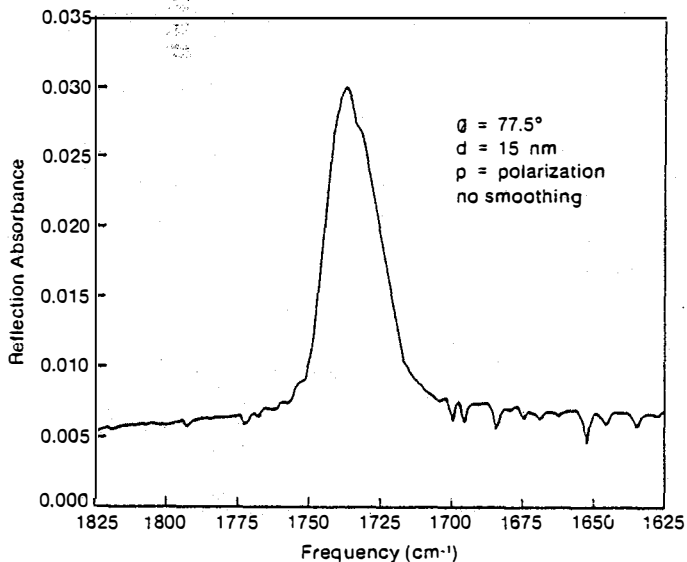


Figure 4. IR-RA spectrum (carbonyl band) of a 15 nm-thick PMMA film on a gold substrate after taking 10⁴ scans of the sample and reference reflector in CEEC.

The optical model of the polymer/metal samples enables the IR-RA spectra of polymer functional groups to be predicted (Figure 5) and enables correlating changes in the measured spectra to changes in the concentration of the functional groups in the polymeric bulk. The current model assumes random functional group orientation, but a model for oriented polymeric films is being developed. Figure 6 is a plot of the concentration of the first product of the photo-Fries rearrangement in two BPA-PC/gold samples as a function of UV exposure time in air at 25°C. The accuracy of the IR-RA concentration measurements was confirmed using UV-RA spectroscopy.⁸ From the initial photodegradation rate, the initial absorption spectrum of the polymeric film, the measured film thickness, and the UV output spectra of the solar simulator (AM-0 spectra not shown in Figure 2), initial quantum yields for this reaction product were calculated. The initial quantum yield of first photo-Fries product for AM-0 filtering was 1.6×10^{-2} , and was 2.3×10^{-2} for no filtering, indicating that the quantum yield of this

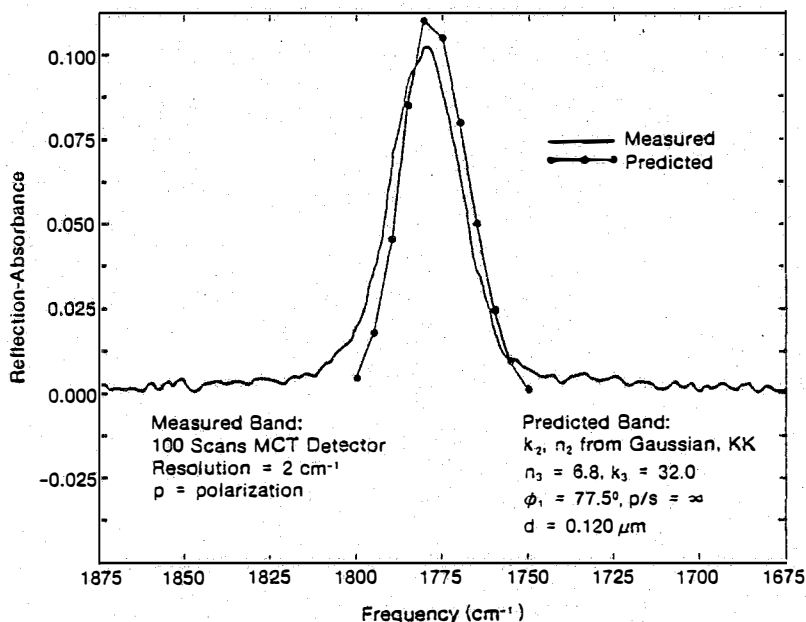


Figure 5. Comparison of calculated and measured IR-RA carbonyl band of a 120 nm-thick BPA-PC film on aluminum substrate.

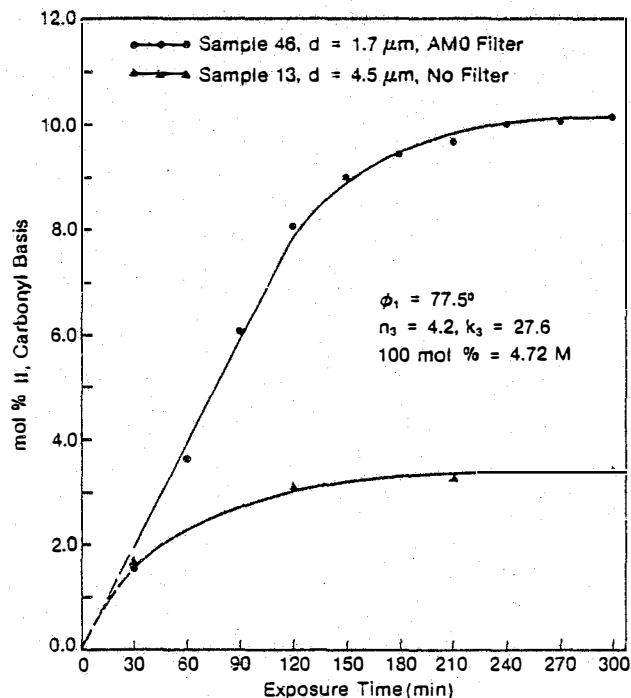


Figure 6. Accumulation of first photo-Fries arrangement product in two BPA-PC/gold samples as a function of exposure time.

rearrangement product increases with decreasing wavelength. Reductions in the thickness of these films of 10-15% were also noted after exposure.

PMMA films of ~ 100 nm thickness were cast onto substrates coated with pure Ag, Au, and Al films. Each sample was exposed in air at 25°C to WG-305, WG-295, WG-280, and unfiltered UV radiation (Figure 2) for 3.75 h each. The sensitivity of the FTIR-CEEC measurements to change in the PMMA carbonyl functional group concentration (fundamental frequency = 1731 cm^{-1}) was about one percent for the 250 scans used to collect the sample spectra. Only when samples were exposed to WG-280 or unfiltered UV were reductions in carbonyl functionality detected. A typical set of PMMA IR-RA spectra, collected before and after exposure of PMMA/gold Sample 67, is shown in Figure 7. The subtraction spectrum generated from these spectra is reproduced in Figure 8 (A), with a subtraction spectrum revealing no change after exposure of the sample to WG-305 filtered UV (B). There was no difference noted in the behavior

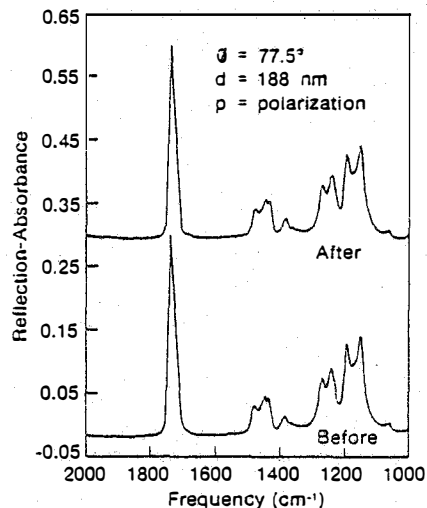


Figure 7. IR-RA spectra of Sample 67 (PMMA/gold) before and after exposure to 3.75 h WG-305, WG-295, WG-280, and unfiltered UV in dry air at 25°C . Upper spectrum displayed above true position for clarity.

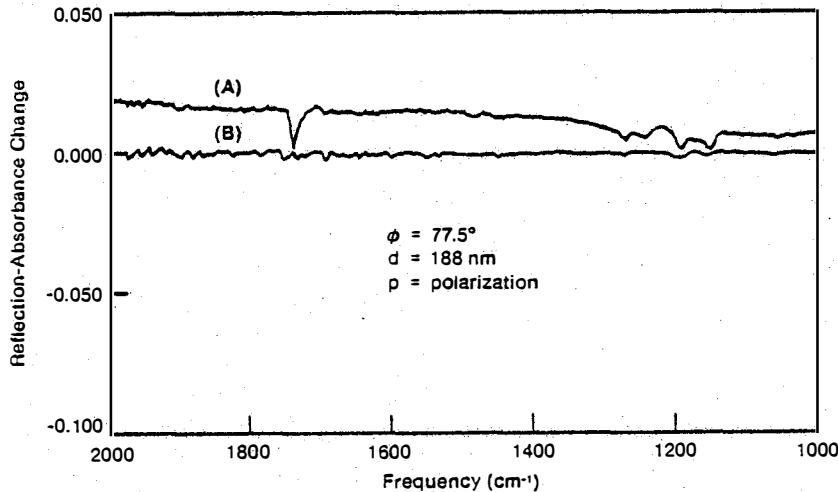


Figure 8. Subtraction spectra generated between IR-RA spectra of Sample 67 (PMMA/gold) collected before and after exposure to WG-305 filtered UV (B) and WG-305, WG-295, WG-280, and unfiltered UV (A) for 3.75 h periods.

UV, contamination of the silver surface can lead to interfacial degradation. Figure 9, Curve C is a subtraction spectrum showing substantial change in the IR-RA spectrum of a PMMA/Ag Sample 74, which was exposed to WG-305-filtered UV for 80 minutes at 25°C in moist air containing 104 ppm NO₂. The sample substrate (evaporated Ag) appeared contaminated (milky yellow-white) before coating with PMMA. UV exposure darkened the sample. The IR-RA spectral changes following exposure of this sample to long-wavelength UV are similar to those observed for PMMA/metal samples exposed to short-wavelength UV (unfiltered or WG-295 filtered). However, Sample 74 exhibited a dramatic loss of IR specularly, as exhibited by the sloping baseline of Curve C. Exposure under identical conditions of two similar PMMA samples (Nos. 73 and 76) which were cast onto silver substrates that appeared clear visually, produced no IR-RA spectral changes, indicating that substrate contamination rather than UV/NO₂/H₂O exposure caused the degradation of Sample 74.

Surface analysis and depth profiling of Sample 74 after exposure and removal of the PMMA film revealed fourteen atomic percent of chloride contamination in a layer extending at least 10 nm into the silver substrate. A contaminated sputtering target was a likely source of AgCl. Similar analysis of Sample 76, which was insensitive to long-wavelength UV, revealed only 1.4 atomic percent chloride contamination. The hypothesis was made that photo-induced decomposition of the silver chloride interfacial layer

of the samples cast on Al, Ag, or Au. Therefore, for a reduction in PMMA carbonyl group concentration greater than 1 percent to be observed in 3.75 hr., UV wavelengths shorter than 260 nm (WG-295 filter cut-off) must be utilized. All of the PMMA absorption bands decreased in intensity under exposure to short wavelength UV, suggesting that the photoproducts are volatile and are carried away by the air flow maintained in the CEEC. In agreement with this hypothesis, GPC analysis of PMMA films solvent-stripped from the substrates showed reductions in weight-average molecular weight and increases in dispersivity for the samples exposed to unfiltered and WG-280-filtered UV.

Although PMMA films cast on pure silver surfaces do not exhibit rapid photodegradation when exposed to WG-305-filtered

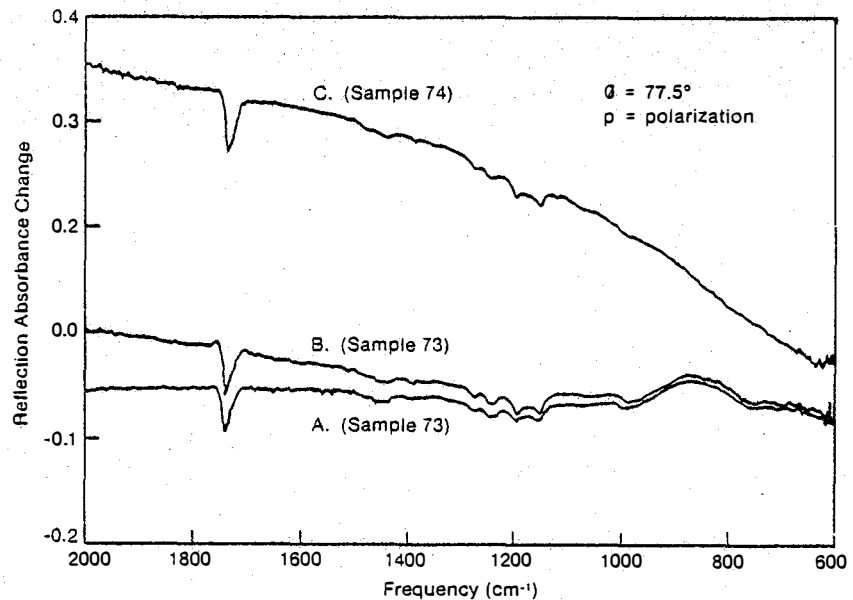
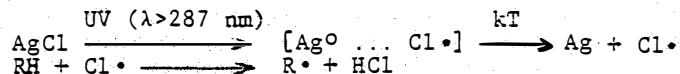


Figure 9. Subtraction spectra: A. Changes in IR-RA of Sample 73 after a 45-min. exposure to Cl₂; B. Changes in IR-RA of Sample 73 after Cl₂ and UV exposure (WG-305 filter); C. Changes in IR-RA of Sample 74 after 80 min. UV exposure (WG-305 filter).

of Sample 74 was responsible for the degradation of the PMMA film. The reaction sequence:



would explain both the degradation of the PMMA film (which itself is insensitive to WG-305-filtered UV) as well as the darkening and loss of IR specularity of Sample 74 (scattering by finely-divided Ag). A similar reaction sequence was proposed by Zaitseva, et al.⁹ to explain the sensitization of PMMA to long-wavelength UV by ferric chlorides. The photo-activity of the silver halides is well-known.

To confirm this hypothesis, Sample 73, which previously exhibited no detectable degradation, was exposed to Cl₂ (92 kPa, 25°C) for 45 minutes. The sample visibly whitened and lost reflectivity, presumably because of AgCl formation and/or Cl₂ attack on the PMMA film.

A subtraction spectrum generated between IR-RA spectra of Sample 73 before and after Cl₂ exposure is given in Figure 9, Curve A. The spectral changes are similar to those reproduced in Curve C for Sample 74, except that specularity was retained and a broad band appeared between 1000 - 750 cm⁻¹ (unassigned). Sample 73 was then exposed to WG-305-filtered UV for 45 minutes in dry air at 25°C. Further losses in PMMA functionality and a decrease in specularity were noted (Curve B). The loss in specularity is similar to that evident in Curve A. Evidently, both the PMMA and Ag were attacked by the Cl₂ to yield volatile fragments and AgCl. Upon UV exposure, the remaining PMMA was further degraded by AgCl. Dispersions of PMMA in solid AgCl exhibited similar spectral changes upon UV exposure. Further experiments, including quantitative assessment of the changes in specific PMMA functional groups, are planned.

The results have important implications for attempts to protect silver surfaces by a polymeric coating, since chlorides are common environmental pollutants¹⁰ and react readily with silver. The polymeric coatings must be chloride-free and must resist permeation by rainwater (containing chlorides) in order to prevent this degradative reaction.

Preliminary results indicate that unoriented, 100 nm-thick films of PVDF on gold substrates are sensitive to WG-305 filtered UV radiation. C-F functionality is lost, but no olefin formation could be detected. Further studies of oriented and unoriented PVDF are planned.

Conclusions

The technique of in-situ FTIR-RA spectroscopy has demonstrated utility in assessing the environmental stability of several different polymers on various metallic substrates. Both bulk and interfacial reactions have been observed, and the capability of obtaining quantitative as well as qualitative information on these reactions has been demonstrated. Coupling the FTIR-RA technique with other analytical methods provides a more detailed understanding of the degradative reactions and confirms the quantitative results obtained.

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