EFFECTS OF RELATIVE HUMIDITY ON PHOTODEGRADATION OF ACRYLIC MELAMINE COATINGS; A QUANTITATIVE STUDY

by

T. Nguyen, J.W. Martin, E. Byrd and N. Embree
Building and Fire Research Laboratory
National Institute of Standards and Technology
Gaithersburg, MD 20899 USA

NIST CENTENNIAL

NIST
National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

EFFECTS OF RELATIVE HUMIDITY ON PHOTODEGRADATION OF ACRYLIC MELAMINE COATINGS: A QUANTITATIVE STUDY

T. Nguyen, J. W. Martin, E. Byrd, and N. Embree

National Institute of Standards and Technology, Gaithersburg, MD 20899

Introduction

This study is part of an effort to generate experimental data for validating a reliability-theory approach to predict the service life of polymeric coatings (1). This approach is based on the effective dosage model, relating damage by radiation dosage absorbed in the coating through the quantum yield. These parameters depend not only on physical and chemical properties of the material but also strongly on environmental factors, such as moisture and temperature. To provide data for validating the effective dosage model, the effects of over 200 different combinations of exposure conditions of ultraviolet light, temperature, and relative humidity on the photodegradation of coatings have been investigated. In a previous publication, we have presented the methodology to measure and calculate the absorbed dosage and apparent quantum yield over a wide range of exposure conditions using FTIR and UV visible spectroscopies (2). Factors critical to the accuracy and reproducibility of these quantities include UV-visible absorption characteristics of the coatings, degradation products, infrared and UV-visible spectra processing, and reproducibility of UV-visible and FTIR spectrometers. The effects of relative humidity (RH) on the apparent quantum efficiency and the magnitudes and rates of photodegradation and moisture-enhanced photolysis of a partially-methylated melamine acrylic coating are presented in this paper. Partially-methylated melamine acrylic coating was one of the materials chosen for study.

Experimental

A model acrylic melamine coating consisting of a mixture of a hydroxy-terminated acrylic polymer and a partially-methylated amine resin was used. The ratio of acrylic resin to melamine crosslinking agent was, by mass, 70:30. Coatings were applied to CaF_2 substrates by spin coating. The films were then cured at 130 °C for 20 min; all coated samples were well cured. The coating thickness was $10 \mu m \pm 2 \mu m$ and was uniform over the entire coated surface.

Complete details of the instrumentation used in this study are described elsewhere (2). Briefly, the experimental setup consisted of solar simulators, exposure cells, and various controlling systems and instruments. Coated CaF_2 samples were placed in an exposure cell, which consisted of 12 windows corresponding to the 12 exposure conditions. Ten of the windows contained narrow bandwidth filters covering radiation from 290 nm to 525 nm, one was completely covered, and one was left open without a filter (designated as "full UV"). A quartz disk was placed directly underneath the filter and above the coated CaF_2 plate. Each cell contained an inlet and an outlet to allow air with the desired temperature and RH to circulate in the space between the quartz disc and the coated-CaF_2 plate. Temperature and humidity sensors connected to each cell and to a computer were used to control temperature and RH in each cell.

Nominal RHs of <<1% (dry), 20%, 40%, 70% and 90% at nominal temperatures of 30 °C, 40 °C 50 °C and 60 °C and 12 different UV conditions were selected. The relative humidity in each cell was provided by a specially-designed RH generator, which controlled RHs in the 0% - 90% range to within ±3% by controlling the ratio of dry air and moisture-saturated air. The temperature in each cell was maintained within ± 2° C of the desired value. The radiation source was supplied by two 1000 W xenon arc solar simulators, which provided infrared-free, near ambient temperature (24 °C) radiation of wavelengths between 275 nm and 800 nm. A UV-visible spectrometer equipped with a fiber-optics sensor and connected to a robotic controlling system was used to measure the irradiance at each of the 12 windows.

UV-visible and IR absorbance spectra of the coating as a function of exposure were recorded by UV-visible and FTIR spectrometers using an automated sampler. The automated sampling device allowed unattended, efficient, and quick recording of the UV and IR absorbance spectra of the coating specimens at all locations. At each specified time interval, the coated CaF_2 plate was removed from the exposure cell, fitted into a demountable ring on the automated sampler, and UV and IR spectra were collected. UV-visible spectra were recorded from 190 nm to 820 nm with a resolution of 2 nm at 2s

per scan. FTIR spectra were the average of 128 scans, which were recorded a resolution of 4 cm⁻¹ using a liquid nitrogen-cooled MCT detector and a purge air. Data on irradiance and coating UV absorption were employed calculate the absorbed dosage in the coating.

A computer program was written to estimate absorbed dosage, damage and quantum yield using inputs provided by UV-visible and FT measurements. The apparent quantum yield in this study is expressed as change in FTIR intensity per unit thickness per amount of radiation absorb in the coating. If FTIR intensity for the degradation is expressed absorbance (A), thickness in meter (m), and radiation absorbed by the coat in Joules (J), the apparent quantum yield is expressed in $A m^{-1} J^{-1}$. Absorpti coefficients of relevant IR bands are being measured to convert IR absorbar units into functional group concentration. Only the results on the effects of I on photodegradation in the full UV at 50 °C are presented in this paper.

Results and Discussion

FTIR difference spectra (spectrum of exposed specimen-spectrum specimen before exposure) of the acrylic melamine coatings after exposure 2040 h under different RHs in "full UV"/50 °C condition are displayed Figure 1. Decreases in FTIR intensity were observed in the 2750 cm⁻¹-30 cm⁻¹ and 1600-1000 cm⁻¹ regions and increases in intensity occurred in 3100 cm⁻¹-3400 cm⁻¹ region. Several new bands appeared, including those 1760 cm⁻¹ (anhydride C=O), 1670 cm⁻¹ (amide C=O), and 1630 cm⁻¹ (prim NH). The bands associated with the acrylic resin, e.g., 1730 cm⁻¹ (C=O) a 1175 cm⁻¹ (ester C-O), which were essentially unaltered in the absence of I light even at high RH (3), also changed substantially with UV exposure. 7 formation of amines and various carbonyl-containing compounds observed the dry/UV condition are in good agreement with a photolysis pathw proposed recently for acrylic melamine coatings (4).

Figure 2 depicts FTIR intensity changes with exposure time for the 10 cm⁻¹ (chain scission) and 1670 cm⁻¹ (oxidation) bands of the coating at f RHs under the UV/50 °C condition. Both the rate and magnitude of th degradation modes increased with increasing RH. The total intensity chang a particular RH was due to four different degradation processes: post cur (PC) reactions, dark hydrolysis due to the RH (H), photolysis (P) a moisture-enhanced photolysis (MEP). Experiments were conducted so t these processes were measured individually. In this way, the effects of RH the rate and magnitude of each of these processes of a partially-methyla melamine acrylic coating could be quantified. Selective data are presentec Table 1 and Figure 3. More complete results are given elsewhere (3)

Table 1. Effects of RH on Total Degradation (T) and Moisture-enhance Photolysis (MEP) Rates for several Functional Groups of the Coating Exposed to UV/50 °C. (Rates, dA/dt, are Measured from the Initial Slop of, e.g., the Curves Given in Figure 2)

Wave No. (cm⁻¹)	0 % RH		19.2 % RH		72.7 % RH		90.8%	
	T	MEP	T	MEP	T	MEP	T	M
1085	0.86	-	1.86	0.70	3.52	1.24	4.45	1
1175	0.46	-	0.53	0.25	1.14	0.70	1.64	1
1670	0.95	-	2.16	0.80	3.94	1.55	4.97	2

Since the degradation due to PC was very small, the total rate value at 0% RH condition represents the rate of photolysis of the coating. Obviou both the rates and extents of the total degradation were larger than the sun those of the PC, P and H combined. This difference [(T- (H+P+PC)] is ter here as moisture-enhanced photolysis because the enhancement is caused the moisture present in the film. Formaldehyde released during hydrol) which acts as a sensitizer, is believed to be responsible for the enhancer (3). Both the magnitudes and rates of moisture-enhanced chain sciss oxidation, and ester side chain cleavage increased with increasing However, the rates of the chain scission enhancement at all RHs observe this study are smaller that those reported previously (5,6).

The apparent quantum yield was determined from the initial portio the slope of the IR intensity (damage)/absorbed dosage curves show Figures 4a and 4b for chain scission and oxidation, respectively. A fou order polynomial function was used to fit the damage/dosage curve to ob the quantum yield values. The presence of moisture appeared to incr

apparent chain scission quantum yield, from 0.30 x 10⁻⁶ A m⁻¹ J⁻¹ ±
at dry/UV to 0.37 X 10⁻⁶ A m⁻¹J⁻¹ at 90 %RH/UV condition.
little effect of RH >19 %RH on the quantum yield was observed.
quantum efficiency due to moisture has also been observed for
... photolysis at room and elevated temperatures (7).

CONCLUSIONS

200 different combinations of exposure conditions of relative
... temperature, and UV light have been investigated to validate the
prediction model of polymeric coatings based on the effective
model. The effects of RH on the photodegradation and quantum yield
... partially-methylated melamine acrylic coating exposed to 50 °C and "full
... reported. The total degradation consisted of four different processes:
... reactions, dark hydrolysis, photolysis, and moisture-enhanced
... The effects of RH on each process were quantified, which showed
presence of moisture accelerated the photo-oxidation, chain scission,
... side chain cleavage of the coating. Not only the rate of this
... but also those of the total degradation and dark hydrolysis
with increasing RH. Also, moisture appeared to increase the
quantum efficiency of acrylic melamine coatings.

References

Martin, J. W., Saunders, S. C., Floyd, F. L., and Wineburg, J. P.,
Methodologies for Predicting the Service Life of Coatings, Federation
Series on Coatings Technology, Federation of Societies for Coatings
Technology, PA, 1996.

Martin, J.W, Nguyen, T., Byrd, E., Embree, N., and Dickens, B.,
Relating Laboratory and Outdoor Exposures of Coatings: I. Estimation of
Absorbed Photolytic Dosage and Quantum Yield, to be Submitted to
Polym. Deg. and Stab.

Martin, J.W, Nguyen, T., Byrd, E., Embree, N., Relating Laboratory
and Outdoor Exposures of Coatings: II. Effects of Relative Humidity on
Photodegradation and Quantum Yield of Acrylic Melamine Coatings, to be
submitted to Polym. Deg. and Stab.

Lemaire, J., in D. Bauer and J.W. Martin, Eds, Service Life Prediction of
Organic Coatings, A Systematic Approach, ACS Symposium Series 722,
American Chemical Society, Washington, DC, 1999, p. 246.

Bauer, D.R. and Mielewski, D.F., Polym. Deg. Stab., 1993, 40, 349.

Gerlock, J.L., Anal. Chem., 1983, 54, 1529.

Gupta, A. Rembaum, A., and Moacanin, J., Macromol., 1978, 11, 1285.

Figure 2. Chain scission (1085 cm⁻¹ band) (a) and oxidation (1670 cm⁻¹ band) (b) as a function of time for a partially-methylated melamine acrylic coating exposed to different relative humidities under "full UV"/50 °C condition.

Figure 3: FTIR intensity changes for post curing (PC), photolysis (P), hydrolysis (H), and moisture-enhanced photolysis (MEP) for chain scission (a) and oxidation (b) of a partially-methylated melamine acrylic coating exposed to different relative humidities under "full UV"/50 °C condition (data taken at 14d).
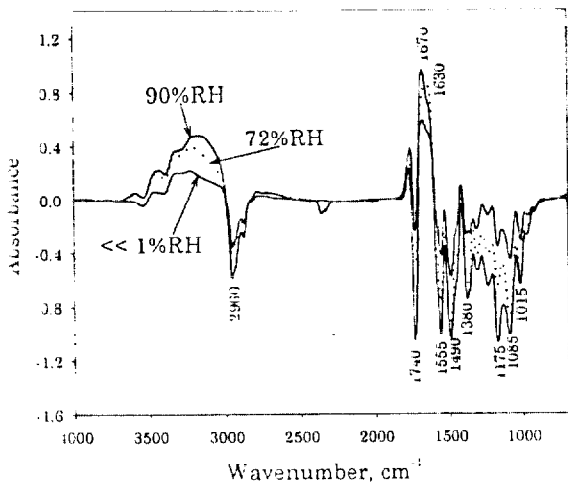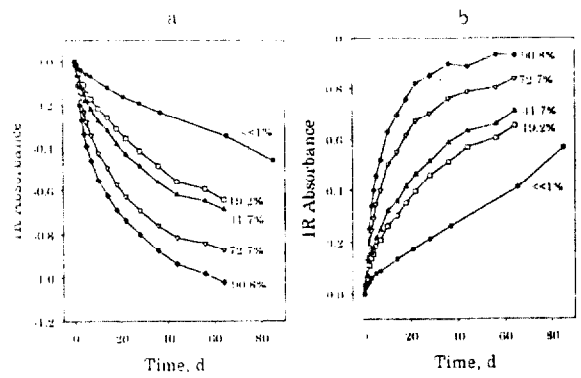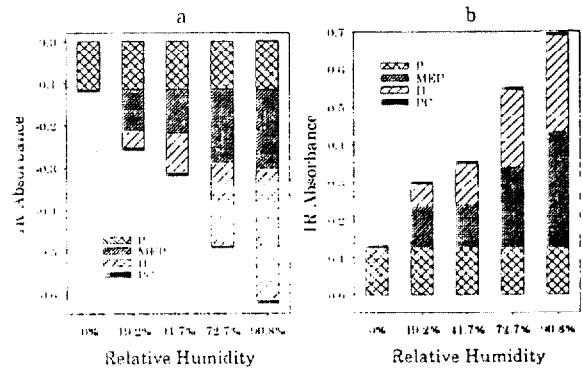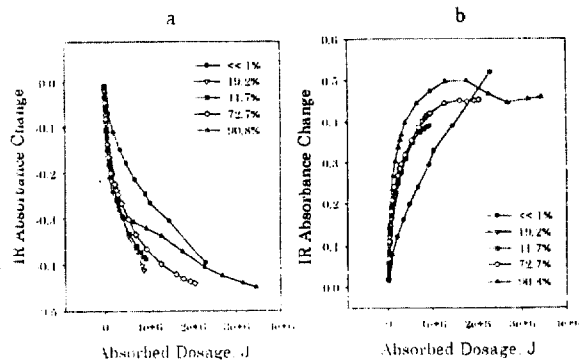

Figure 1. FTIR difference spectra for a partially-methylated melamine acrylic coating exposed to different relative humidities for 2040 h under "full UV"/50 condition.

Figure 4. Chain scission (1085 cm⁻¹ band) (a) and oxidation (1670 cm⁻¹ band) (b) as a function of absorbed dosage of a partially-methylated melamine acrylic coating exposed to different relative humidities under "full UV"/50 °C condition (only changes due to P and MEP are included).