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An XPS Study on the Effects of Pigment on the UV Degradation of an Epoxy System

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Abstract

X-ray photoelectron spectroscopy (XPS) is a powerful tool for monitoring the changes in the surface chemistry of many materials. In this study it was used to examine the chemical changes in an epoxy system formulated with and without pigment (TiO_2) in an effort to gain an understanding the role that pigment plays in polymer photodegradation. Epoxy degradation as a function of surface treatment on the pigment and pigment concentration was also investigated. Epoxy and pigment will be analyzed separately in an effort to understand the changes observed for the entire system (pigmented epoxy). Preliminary XPS results show that chemical changes have occurred on the epoxy surface and that the type of pigment affects the extent of degradation. The concentration of pigment appears to have no effect on the extent of degradation.

Introduction

TiO_2 and other pigments/fillers are heavily utilized in building and construction applications. For most applications these components are added to increase the opacity and improve the appearance of a coating system. However, the addition of pigments has been found to change the properties of the coating, especially its durability.[1-3] Basically, pigments can interact with their polymer binder in three different (but not mutually exclusive) ways. These are:

(a) Protect the resin from direct photochemical degradation. Some polymers, e.g. alkyd resins, are particularly susceptible to direct ultraviolet (UV) degradation, which has sufficient energy to break chemical bonds within the resin. In this case, the absorption of UV by TiO_2 mitigates direct photochemical attack. The absorption of UV by the pigment continues and will lead to photocatalytic attack as well, but is an initially less favored process.

(b) Degrade the resin by photocatalytic degradation. Radicals generated by the pigment oxidize the polymeric binder and is the process pigment manufacturers attempt to minimize via surface treatments of the pigment.

(c) Physical interactions with the resin. Degradation of a coating can lead to chalking, which is the physical separation/exposure of the pigment. Another factor, which is particularly important, especially in binders susceptible to photochemical attack, is the relative degree of dispersion of the pigment particles. Well-dispersed pigments absorb more UV and give a smoother surface resulting in enhanced gloss retention.

The aim of the present study is to examine the effects of the type (i.e. surface treatment) and concentration of pigment on the degradation of a resin system. A less durable, but well-characterized resin system, an amine-cured epoxy, was chosen for the investigation to limit the time necessary to detect degradation. The epoxy and pigment were analyzed separately to gain an understanding of their contributions to chemical changes observed for the entire system (pigmented epoxy). A number of studies on the weathering of polymers have focused on monitoring the mechanical properties and the surface morphology of the polymers using SEM.[1-4]

From our evaluation of the literature, no study has reported changes in the chemistry of a resin system as a function of the type of pigment, only the durability (chalking or gloss retention) of the resin. A surface-sensitive analytical technique, XPS (X-ray photoelectron spectroscopy) or ESCA (electron spectroscopy for chemical analysis), was utilized to monitor the degradation reactions that occur at the surface (~ 10nm) of the resin; the presence of TiO_2 also makes transmission spectroscopy techniques impossible to use due to the opacity of the film. ATR (attenuated total reflectance)-FTIR (Fourier transform infrared spectroscopy), which monitors the near surface (ca. 500 nm), was also used to help assign the elemental chemical shifts observed in the XPS spectra. Chemical analyses of the surface of the polymer systems [5-10] and the pigment[11-13], separately, have been made using ATR -FTIR and XPS. This study is one of the first to look at chemistry of polymer photodegradation and pigment data in conjunction.

Experimental[*]

Materials

TiO_2 pigment/epoxy polymer films were prepared by dispersing TiO_2 into an epoxy resin/curing agent mixture using a Dispermat mixer (BYK Gardner). Pigment surface treatments included alumina, silica, and no treatment. Pigment concentrations were 2.5 %, 10 %, and 15 % by volume based on a pigment volume concentration calculation. A mass ratio of 2.4: 1 for epoxy (EPON™ Resin 828, Resolution Performance Products) to curing agent (JEFFAMINE® T-403 polyetheramine, Huntsman). The pigment/epoxy mixture was degassed under vacuum for 2 h prior to film preparation. Films were prepared by applying the mixture onto release paper using a draw down blade. The films were cured at room temperature for 48 h followed by heat treatment at 130°C for 2 h.

UV Exposure Experiments

UV exposure experiments were conducted in the Building and Fire Research Laboratory at NIST using an Oriel Instruments solar simulator. The instrumentation uses a Xe arc lamp (1000 Watts) and has been described elsewhere. [14,15] Exposure conditions in this study were at full light intensity in the range of 270 nm to 800 nm and 50 % $\pm$ 3 % relative humidity (RH) at 33°C $\pm$ 1 %.

Measurements

XPS

All XPS measurements were performed with a Kratos Axis Ultra photoelectron spectrometer. Experiments were conducted at room temperature with a base pressure in the 1.3×10^{-6} Pa range. The monochromatic Al Kα x-ray source was operated at 140W (14 kV, 10 mA). The energy scale was calibrated with reference to the Cu $2p_{3/2}$ and Ag $3d_{5/2}$ peaks at binding energies (BE) of 932.7 eV and 368.3 eV. A coaxial charge neutralization system provided charge compensation. Initial and degraded polymer films were attached to the XPS sample holder using double stick tape. The analysis area for the high-resolution spectra was 2 mm x 1 mm. The O 1s, Ti 2p, N 1s, C 1s, and Si 2p spectra were acquired at a pass energy (PE) of 20 eV and a maximum acquisition time of 8 minutes per element. Peak BEs were determined by referencing to the

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[*] Certain instruments or materials are identified in this paper in order to adequately specify experimental details. In no case does it imply endorsement by NIST or imply that it is necessarily the best product for the experimental procedure.

adventitious C 1s photoelectron peak at 285.0 eV. Quantitative XPS analysis was performed with the Kratos VISION software (version 2.1.2). The atomic concentrations were calculated from the photoelectron peak areas by subtracting a linear-type background. The O 1s, N 1s, and C 1s regions were deconvoluted using mixed 70 % Gaussian/30 % Lorentzian components.

Attenuated Total Reflectance (ATR)-Fourier Transform Infrared Spectroscopy (FTIR)
ATR-FTIR was performed on the pigment epoxy resin films using a Magna-IR 560 (Thermo Nicolet) with an MCT detector and an ATR accessory with a Ge crystal (Spectra-Tech, Inc.). All sample spectra were acquired using the following conditions: 128 scans, 4 cm^{-1} resolution, and 1.928 cm^{-1} data spacing. A background scan was acquired before every sample scan.

Results and Discussion
Chemical changes were monitored as a function of irradiation time. Oxidation in the epoxy films with increasing irradiance time is indicated in Figure 1.   An increase in O 1s atomic
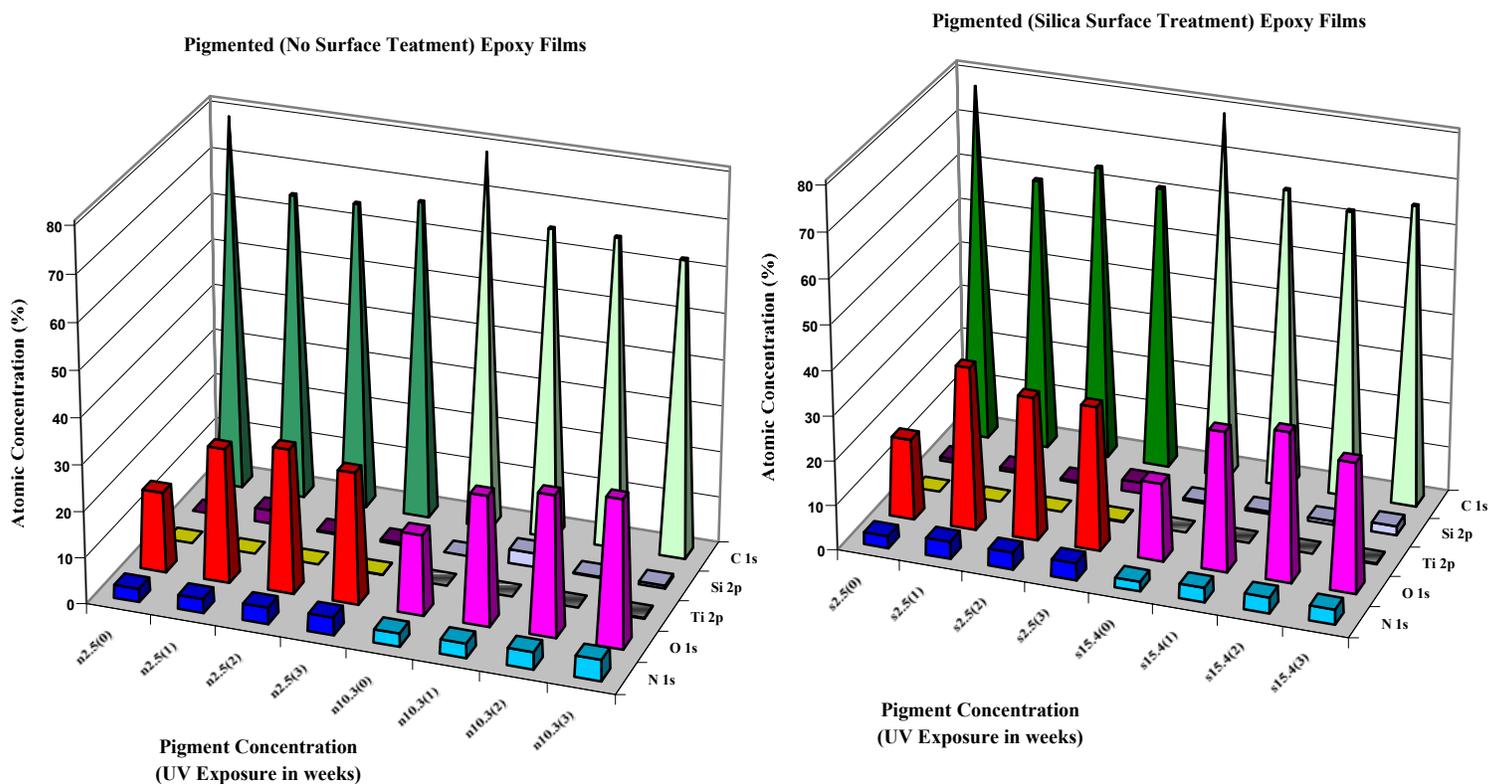

Figure 1. XPS element atomic concentrations for N 1s(blue), O 1s (red), Ti 2p (yellow), Si 2p (purple), and C 1s (green). The bar graphs with the lighter shades represent the higher pigment concentrations. The uncertainty in the values is ± 1 %.

concentration from 17.1 %-17.8 % to 27.6 % - 35.8 % was noted. The N 1s atomic concentration also increased by about 40 %. These changes coincide with the decreasing trends seen for the carbon region for the untreated pigment epoxy film. The C 1s atomic concentration

decrease ranged from 15 %-19 % and a slightly lower decrease was observed for the untreated pigment epoxy film. Traces of pigment were not observed until the third week of UV exposure. It should be noted that a trace amount of silicon (0.5 %) observed in the XPS results was due to the interaction of the epoxy under heat cure with the release paper. For the silica treated pigmented film, a marked increase in the Si concentration (2.0 % -2.4 %) was observed in the third week of UV exposure. This high Si concentration compared to the maximum Ti concentration (0.2 %) is not unusual as XPS is more surface sensitive, but it indicates that more pigment is exposed in this epoxy film. Epoxy films with alumina treated pigment and epoxy films containing no pigment have yet to be analyzed.   In general for the analyzed pigmented epoxy films, less degradation or oxidation was observed for the untreated pigment epoxy film. It appears that the untreated pigment is acting as a UV sink in the epoxy film and prevented degradation.

To get a complete look at the differences between the two films, the high-resolution regions of C 1s, O 1s, and N 1s were examined. Figure 2 shows the high-resolution C1s regions for the two epoxy films. There are changes in the C 1s peak shape with increasing irradiation, and the same peaks were observed for the two epoxy films with slightly different concentrations. A new band appears at higher binding energy with increasing photodegradation. This shift of 3.9 eV relative to the adventitious carbon peak at 285.0 eV, is indicative of carbonyl species containing C-O-C=O (4.0 eV) or HO-C=O (4.3 eV) or carbonyl species associated with nitrogen, i.e. O=C-N-C=O (3.6 eV) or N-C=O-N (3.8 eV).[16] Clark and Munro [17,18] also noted similar changes in the carbon region during photooxidation for a bisphenol A polysulphone system.
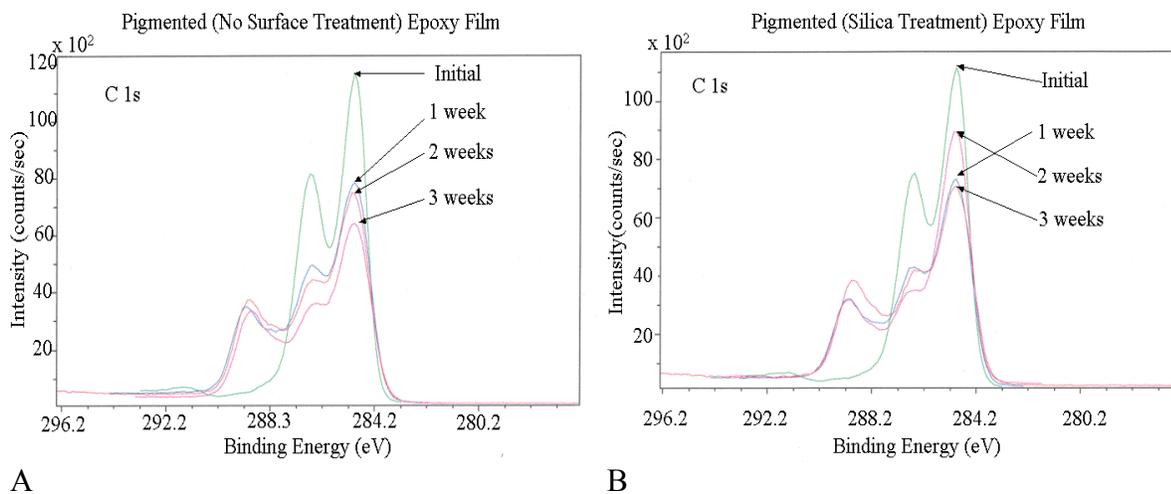
Figure 2. XPS spectra of the C 1s region for pigmented epoxy films with increasing UV exposure. Spectrum A: epoxy film with TiO_2 pigment (no surface treatment). Spectrum B: epoxy film with TiO_2 pigment (silica treatment). The green spectrum represents the initial pigmented epoxy film before UV exposure.

ATR-FTIR was used to validate the assignment of XPS C 1s, O 1s, and N 1s peaks. ATR-FTIR results before UV exposure show the presence of a ketone carbonyl band at 1720 cm^{-1}, of a C=N

band at 1654 cm^{-1}, and of an aromatic ester at 1510 cm^{-1}. With increasing UV irradiance time, an increase in the 1710 cm^{-1} and 1654 cm^{-1} bands were observed. Additionally, there was a marked decrease in the 1510 cm^{-1}, an indication of chain scission in the backbone of the epoxy system. To further elucidate the identity of the carbon shifts, the XPS N 1s region was

Pigmented (No Treatment) Epoxy Film
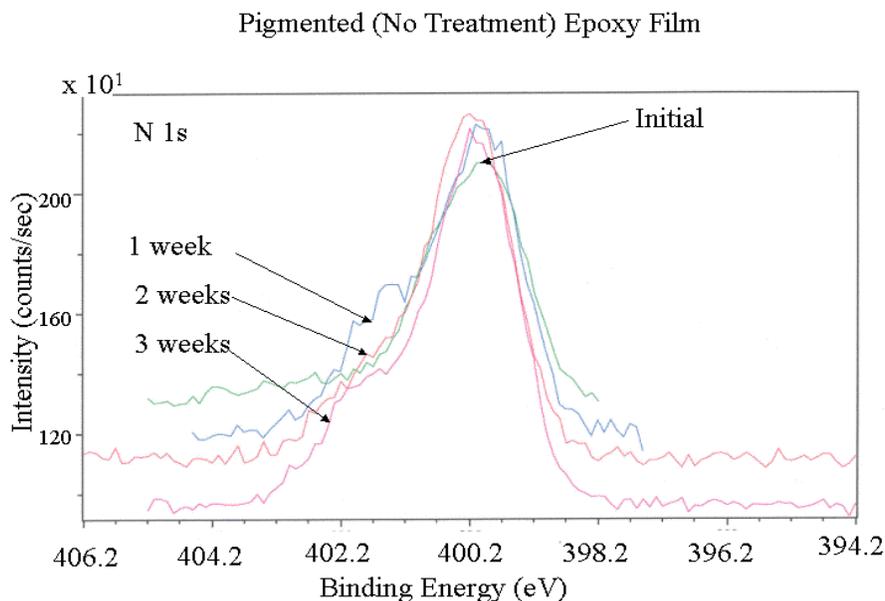
Figure 3. XPS spectra of the N 1s region for a pigmented epoxy films with increasing UV exposure. The green spectrum represents the initial pigmented epoxy film before UV exposure.

examined. Again, the N 1s regions showed similar changes for both epoxy films. Figure 3 shows that there is a new peak with a positive shift of 1.9 eV relative to the C-N peak at 399.9 eV that appears in the N 1s region. A shift of this magnitude relative to the C-N peak has been assigned to amine groups, NH_3^+ (1.7eV) or $N(CH_3)_3^+$ (2.4 eV).[16] Nitrogen groups containing an NO_2 species have shifts of 5.7 eV or higher and so this new band could not be assigned to this type of nitrogen species. An increase of ca. 1.0 eV in the FWHM (full-wide at half maximum) in the O 1s region with irradiance was observed for both polymer films. This is an indication of new oxygen species forming during photodegradation. Curve-fitting of all XPS high resolution element regions has yet to be completed for further interpretation of the degradation results. This will help to identify the chemical species in the film formed and/or lost during photodegradation.

Conclusions
XPS is a powerful technique for monitoring changes in polymer surfaces. It appears from the preliminary XPS results that chemical changes have occurred on the epoxy surface and that the type of pigment affects the extent of degradation. Untreated pigment may act as a UV sink and prevent early photooxidation of the epoxy system. The concentration of pigment appears to have no effect on the extent of degradation. More comparisons between the three types of pigments will be forthcoming upon completion of curve-fitting the high-resolution XPS data.

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