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Accelerated UV Weathering of Polymeric Systems: Recent Innovations and New Perspectives

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Polymeric materials used in an outdoor environment are subjected to a wide variety of environmental factors, including solar ultraviolet (UV) radiation, temperature, and moisture, in a process known as weathering. Understanding the factors that govern the weathering performance of commercial polymeric materials has great practical importance, as does the ability to relate laboratory performance of a polymeric system to its performance in the field. At present, the full potential of these materials is inhibited by the absence of a methodology for accurately predicting their service life during exposure in their end-use environments. A reliability-based methodology utilizing total effective dosage as an exposure metric has been proposed as an alternative to the conventional methodology for carrying out laboratory and outdoor weathering studies. The use of this proposed methodology involves not only a shift in paradigm but also in the way that laboratory and outdoor weathering experiments are carried out. The concepts of reciprocity and additivity, which were first introduced by the photographic community and then studied by the medical and biological communities, are also proposed as models for synthetic polymeric systems.

INTRODUCTION

Synthetic and natural polymeric materials play an increasingly important role in today's society, and the versatility of these materials has been demonstrated through the breadth of their applications in almost every sector of the economy. The full potential of these materials is inhibited by the absence of a methodology for accurately predicting their service life during exposure in their end-use environments. This deficiency has been noted by industry and emphasized in a number of recent National Research Council (NRC) reports.[1,2]

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Over the last several decades, both industry and consumers have identified service life prediction of polymeric materials as a high priority research need. This high priority is justified given the high economic risk of introducing a poorly performing product into the market place. The number of class action suits initiated by product failures has escalated sharply since the 1960s,[3,4] thus making it riskier for manufacturers to provide service life estimates and warranty coverage, and/or introduce new products into the market.

Polymeric materials used in an outdoor environment are subjected to a wide variety of environmental factors, including solar ultraviolet (UV) radiation, temperature, and moisture. The physical and chemical degradation resulting from outdoor exposure is known in the materials community as *weathering*. Understanding the factors that govern the weathering performance of commercial polymeric materials has great practical importance, as does the ability to link laboratory performance of a polymeric system to its performance in the field. When this linkage can be accurately made, then the stage will be set for implementing a quantitative, scientifically based service life prediction methodology.

ACCELERATED LABORATORY VS. OUTDOOR WEATHERING EXPERIMENTS

For commercially viable materials, weathering is usually a slow and lengthy process, often taking five years or longer before failure occurs. These long testing periods carried out in real time are costly to the manufacturer and are also a major barrier to innovation and the timely introduction of new products into the market. A need exists for exposure strategies that can accelerate weathering, generate reliable performance data, demonstrate a linkage between laboratory and field exposure data, and permit valid extrapolations or predictions of service life from accelerated levels to in-service exposure conditions.

In recent years, the materials industry has made tremendous strides in terms of laboratory equipment for accelerated weathering and analytical techniques for characterizing the physical and chemical properties of polymeric systems. In terms of service life prediction capabilities, however, the current situation is not greatly changed from the previous century. At present, a commonly used materials weathering strategy consists of assigning specimens randomly between accelerated laboratory and outdoor exposure experiments. The accelerated laboratory testing conditions are adjusted to "simulate" as closely as possible the conditions encountered in the particular outdoor exposure, and the two sets of specimens are exposed for some predetermined amount of time. Within each study, the specimens are then ranked by performance (however that may be defined). The rankings of the two sets of samples are then correlated through a nonparametric statistic such as the Spearman Rank Correlation Coefficient—if the correlation coefficient is high, it is concluded that there is a high correlation of lab conditions to field, and vice versa.[5]

A review of field exposure results by Martin revealed the issues that plague this strategy.[6] Published correlation coefficients linking field and laboratory exposure results have not demonstrated a strong linkage between field and laboratory. It was observed that the repeatability and reproducibility of field exposure results is generally low, even in those studies that were carefully designed and executed. Trends in the weather are highly variable, and factors such as spectral UV radiation, temperature, relative humidity, precipitation, and atmospheric aerosols vary widely over relatively short periods of time. It was also difficult to obtain quantitative data from sample ranking information, as there was no common exposure metric that could be used to normalize the data. In a similar fashion, the lack of repeatability and reproducibility in laboratory exposures has also been documented.[7]

A NEW PARADIGM IN WEATHERING STUDIES

In general, industries that manufacture and utilize polymers rely on data from field exposures more than those obtained via accelerated laboratory testing. In the conventional methodology, outdoor weathering is the de facto standard of performance, as can be deduced from the use of words such as "primary," "real time," "decisive test," etc. in describing outdoor weathering studies of polymeric materials.[6] Although the outdoor weathering environment is not reproducible and is difficult to simulate, the linkage between field and laboratory experiments can still be made via an appropriate cumulative damage model if field and laboratory data can be made comparable. One such methodology is based on reliability theory, and has been successfully used in the electronics and aerospace industries.[5] In

Figure 1—NIST 2 m integrating sphere, shown with UV light source and environmental chambers.

this methodology, laboratory experiments are viewed as the standard of performance, and are not designed to simulate the outdoors but are designed to cover the entire range of expected exposure conditions. However, field and laboratory experiments are considered on an equal basis. Outdoor weathering variables cannot be controlled, but they can be measured and characterized in the same way that these variables are measured and characterized in the laboratory.[5]

Can critical weathering factors be converted into some common metric which is the same for both/all data sources? For ultraviolet radiation, the proposed metric for both outdoors and laboratory use is absorbed dosage, or better yet, *total effective dosage*. A cumulative damage model based on total effective dosage is capable of making predictions, as opposed to just establishing correlations. A more detailed discussion of total effective dosage is given in the following section.

CONCEPT OF TOTAL EFFECTIVE DOSAGE AND DAMAGE

The concept of total effective dosage, which has been applied successfully in the medical and biological fields, is based on the principles of photochemistry. Unlike time, total effective dosage is an absolute metric that can be used to compare specimens exposed in a variety of different environments. The use of total effective dosage, instead of total solar irradiance, incident dosage, or elapsed time as traditionally used, takes into account the fact that not all ultraviolet radiation is absorbed, and not all absorbed radiation participates in photolytic processes.[8] The total effective dosage, $D_{tot}(t)$, is related to changes in material properties, or damage, as follows:

$$D_{tot}(t)=\int_{0}^{t}\int_{\lambda_{min}}^{\lambda_{max}} E_0(\lambda,t)(1-10^{-A(\lambda,t)})\phi(\lambda)\,d\lambda\,dt \qquad (1)$$

where $E_0(\lambda, t)$ is the spectral irradiance, $A(\lambda, t)$ is the spectral absorbance of the sample, and $\phi(\lambda)$ is the spectral quantum yield of the material, which is the "weighting factor" for the photolytic effectiveness of a given wavelength in producing a chemical change. For a polymeric material, the quantum yield is primarily a function of its physical and chemical structure, as well as environmental factors such as moisture and temperature. The methodology developed at NIST for measuring UV irradiance and calculating absorbed dosage has been previously described.[9]

Damage in polymeric materials can be measured using a myriad of analytical instrumentation and techniques; the specific choice of damage metric is determined by the performance needs of the particular polymeric system in question. Thus, one of the keys to utilizing a reliability-based methodology for the weathering of polymeric materials is carefully monitoring the relationship between *dosage* and *damage*, in both outdoors and laboratory weathering experiments—if both are measured in exactly the same way, then data from both environments can be treated as equally valuable and valid for determining the service life of a polymeric system. Similar metrics for specimen moisture content and specimen temperature, as opposed to air temperature and air relative humidity, are also being considered in this evolving methodology.

THE RECIPROCITY QUESTION

It is well known that photochemical processes such as photodegradation can be accelerated by increasing the radiant flux to which the material is exposed. However, for polymeric systems, questions exist as to whether high irradiance exposure results can be correctly extrapolated to in-service exposure levels. Based on their experiments on photographic materials, Bunsen and Roscoe concluded that all photochemical reaction kinetics depend only on the total absorbed energy and are independent of the two factors that determine total energy: the intensity or irradiance, I, and the exposure time, t.[10] For a given photoresponse, the law of reciprocity states that

$$It = \text{constant} \qquad (2)$$

A few years later, Schwarzschild, an astronomer, proposed a modification of the reciprocity law that fit his low intensity, stellar data.[11] This model later became known as Schwarzschild's law and is given by

$$It^{p} = \text{constant} \tag{3}$$

where p is the Schwarzschild coefficient, hereafter referred to as the p-coefficient. Note that when $p = 1$, the Schwarzschild law and the reciprocity law are identical; hence, the Schwarzchild's law is a generalization of the reciprocity law. A number of graphical techniques have been proposed to determine whether a material obeys the reciprocity law, Schwarzschild law, or neither.[12-14]

Reciprocity experiments have been carried out on a small number of polymeric systems, with limited data reported in the literature. Much of the published data has been compiled in an extensive review by Martin et al.[15] For most of the polymeric systems studied, the Schwarzschild law appears to adequately model their response to reciprocity, with the p-coefficient generally falling between 0.5 and 1.0.

THE ADDITIVITY QUESTION

Polymers have been observed to exhibit wavelength, or spectral, sensitivity effects and previous research has documented that not all sources of polychromatic UV radiation produce the same type of degradation for a given polymer system. Both the failure mechanisms and kinetics involved in photodegradation may be affected by specific wavelengths in incident radiation. Thus, UV weathering results may vary widely depending on the type of radiation source that the material is exposed to. Many artificial light sources used in laboratory weathering equipment not only differ in spectral characteristics from natural solar UV, but also differ amongst themselves.

This wavelength sensitivity has been studied in polymers by a number of researchers, using broadband UV light sources with either cut-on filters,[16] spectrographs,[17] or monochromators[18,19] to break the incident radiation down into narrow wavelength bands. Plots of changes in material properties versus wavelength can be generated, allowing the most active wavelengths in the source spectrum to be identified. These plots can be used to calculate what are known as "action spectra" or "activation spectra."

A comprehensive understanding of the spectral sensitivity of a polymeric system has many practical implications in product development, including the selection of pigments, light absorbers, and other additives. However, wavelength sensitivity data is specific to a given UV light source, and the experiments must be repeated for each radiation source of interest. A higher goal is the capability to model the response of a polymeric system to any light source, based on the response to a specific source. This can be accomplished through yet another concept originating in the photographic community, the concept of *additivity*.

The van Kreveld addition law was one of the earliest attempts at modeling the sensitivity of a material (in this case, a photographic emulsion) to any type of light source, provided that spectral sensitivity data for one type of light source is available.[20] This law states that the spectral sensitivity of a material exposed to a mixture of wavelengths, $S_{m\lambda}$, is as follows:

$$S_{m\lambda} = \frac{\int S(\lambda)M(\lambda)d\lambda}{\int M(\lambda)d\lambda} \tag{4}$$

where $S(\lambda)$ is the spectral sensitivity of a material at wavelength λ, and $M(\lambda)$ is the energy distribution of the radiation source as a function of wavelength. In other words, any effect that can be produced independently by several specific wavelengths can be produced by a combination of these wavelengths applied simultaneously. This model has been validated by the photographic[21] and the medical/biological communities.[22] Deviations from this model are typically due to photorecovery[23] or wavelength interaction effects (synergistic or antagonistic).[24]

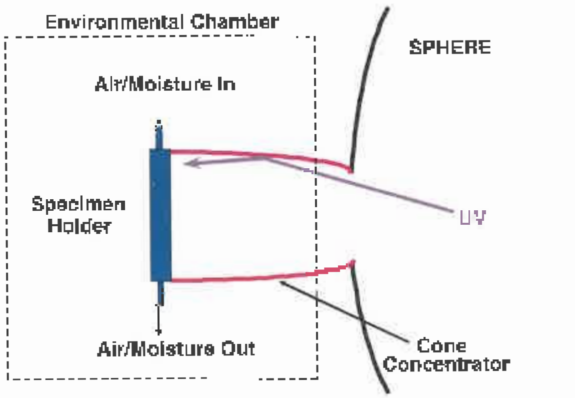
The potential impact of both the additivity and reciprocity laws on the polymeric materials community is tremendous. The validation of these two models, separately and combined, could potentially lead to the ability to model and accurately predict the properties of a polymeric system following exposure to any arbitrary source of radiation. Studies to achieve this objective are currently underway at NIST.

NIST INTEGRATING SPHERE-BASED WEATHERING DEVICE

One of the biggest obstacles in validating both the laws of reciprocity and additivity is the absence of laboratory weathering devices that consistently generate reproducible and repeatable data. Common sources of systematic errors associated with existing UV weathering devices include unnatural exposure conditions (e.g., excessively high specimen temperatures, non-terrestrial UV wavelengths), non-uniform spatial irradiance over the surface of a specimen, and unwanted temporal changes in exposure conditions.[7,25,26] Precise control and monitoring of temperature and relative humidity in weathering devices can also eliminate additional systematic errors in UV weathering experiments.

Since the reliability based methodology views laboratory experiments as the standard of performance, all of these errors must be eliminated or mitigated. To mitigate systematic errors and to prepare for the studies of

Figure 2—Location and orientation of CPC and specimen holder.



reciprocity and additivity, several novel UV weathering devices have been developed at NIST.[7,27] One such device, based on integrating sphere technology, has been designed, fabricated, and implemented for studying the accelerated weathering of polymers.[28,29] This device, known as the NIST SPHERE, has the capability of irradiating multiple test specimens with uniform, high-intensity UV radiation while simultaneously subjecting them to a wide range of precisely and independently controlled temperature and relative humidity environments (SPHERE is an acronym that stands for Simulated Photodegradation via High Energy Radiant Exposure).

The NIST SPHERE is based on a 2 m diameter integrating sphere equipped with a high intensity UV light source and environmental chambers, as shown in *Figure* 1. The exterior shell of the sphere is aluminum, and the interior surface is lined with poly(tetrafluoroethylene) (PTFE). The sphere currently contains 32 11.2 cm (4.4 in.) diameter ports, and a 61 cm (24 in.) diameter top port to accommodate the UV light source.

The lamp system that serves as the source of UV radiation is a microwave-powered six-lamp system with an output that is rich in the region between 290 nm and 400 nm. The total output flux of the six lamps operating at 100% power is approximately 8400 W in the spectral range integrated between 290 nm and 400 nm. Collimation and conveyance of the highly uniform radiation emitted from the sphere port to the specimen chambers is accomplished with minimal loss of uniformity and intensity using compound parabolic concentrators (CPC) that are more efficient than conventional image-forming optics in concentrating and collecting light.

Specimen holders are secured to the wide end of each CPC, and can be designed to hold a single specimen or multiple specimens. Both neutral density filters and bandpass filters are used to modify the UV intensity and spectral UV incident upon the specimens, respectively. *Figure* 2 shows the location and relative orientation of the integrating sphere, the specimen holder and the CPC.

A comprehensive understanding of UV effects on materials requires that specimens be irradiated over a range of exposure conditions. This has been accomplished by equipping each port with an environmental chamber in which temperature, relative humidity, and UV-visible irradiance can be precisely and independently controlled. With 32 ports and the capability of exposing 17 or more specimens in each port, a multiplicity of environmental conditions can be evaluated simultaneously. Temperature, relative humidity, and UV irradiance for each environmental chamber are independently monitored and controlled via microcontrollers on a PC network.

Additional capabilities include the application of mechanical stresses—either cyclic or static—to the specimens while they are undergoing UV exposure. This may be achieved by integrating a mechanical test frame, grips for securing specimens, and a servohydraulic or screw-driven loading device. Other unique exposure environments can also be created, including temperature cycling (including freeze/thaw), humidity cycling, and acid rain.

One of the first experiments to be carried out on the SPHERE was to ascertain the relationship between the UV irradiance and the photoresponse of a polymeric system, and to subsequently determine whether the reciprocity law is valid for this particular material.[30] In this

Figure 3—Changes in the FTIR absorbance of the band at 1085 cm^{-1} as a function of UV dosage at different UV irradiance levels. Each UV irradiance level is identified by the corresponding neutral density filter used. Error bars (± one standard deviation) shown for the 100% UV specimens are representative for all specimens.

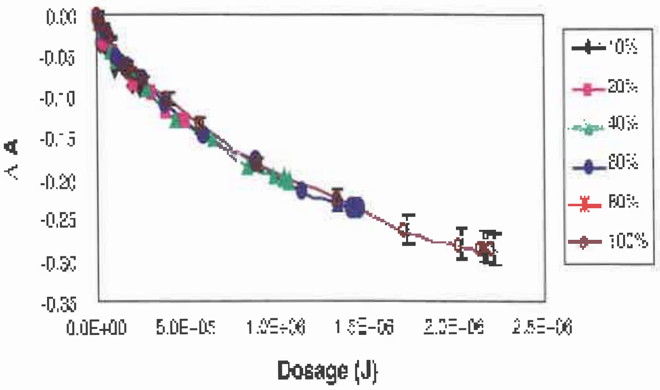


Table 1—Coefficients Calculated from Log Irradiance vs. Log Time Plots

FTIR Band (cm^{-1})	p-Coefficient ± One Standard Deviation
1085	1.09 ± 0.18
1670	1.22 ± 0.10
1730	1.05 ± 0.18
2960	0.97 ± 0.10

initial experiment, a non-pigmented, non-UV stabilized model acrylic-melamine coating was exposed to six different UV radiation intensities ranging from 36 W/m^2 to 322 W/m^2, in the spectral region between 290 nm and 400 nm. Neutral density filters with transmittance values of 10%, 20%, 40%, 60%, 80%, and 100% were used to control the UV irradiance incident on the specimens. Exposure was carried out at ambient temperature and relative humidity.

Changes in coating chemical structure during UV exposure were analyzed with transmission Fourier transform infrared (FTIR) spectroscopy and UV visible spectroscopy. Changes in the FTIR bands of interest were highlighted by subtracting the spectrum of the unexposed specimen from the spectrum of the UV-exposed specimen taken at time *t*. Changes in band absorbance were measured on the resulting difference spectrum, and are hereafter referred to as *damage*. The FTIR band at 1085 cm^{-1} was used to follow chain scission, and the band at 1670 cm^{-1} was used to follow photo-oxidation. Changes in coating mass loss due to degradation were followed by monitoring the intensity changes in the C–H stretching band at 2960 cm^{-1} and the acrylic ester C=O stretching band at 1730 cm^{-1}. Additional details on the photodegradation of this particular polymer system can be found in reference 31.

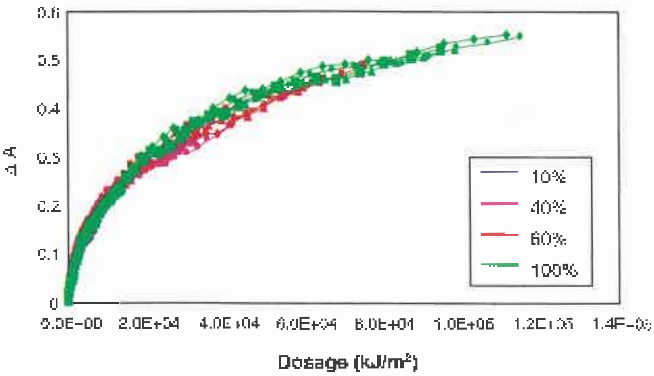
As an example, *Figure* 3 shows changes in the subtracted intensity of the infrared band at 1085 cm^{-1} as a function of absorbed dosage and UV irradiance level, where each irradiance level is identified by the corresponding neutral density filter. It is observed that the individual curves for each irradiance level superimpose onto a single curve. The superposition of data from all irradiance levels in the damage-dosage plots is indicative that any point on the master curve represents an equivalent level of damage for all specimens, independent of the UV irradiance that individual specimens were exposed to. Thus, it can be inferred that the dosage needed to cause a given level of damage is not a function of the incident intensity. Similar data and plots were obtained for the other FTIR bands of interest. Additional confirmation of reciprocity is provided by carrying out analyses according to the methods of Kron[13] and Arens and Eggert,[14] in which the p-coefficients for each of the FTIR bands of interest were determined to be approximately 1 (see *Table* 1).

A second reciprocity experiment on a non-pigmented, non-UV stabilized crosslinked epoxy was carried out following the completion of the acrylic-melamine reciprocity study. Additional factors in this study included temperature (25°C, 35°C, 45°C, 55°C), relative humidity (0%, 75%), and spectral UV. Bandpass filters and neutral density filters were used to control the wavelength ranges and UV irradiance levels, respectively.

The FTIR bands at 1510 cm^{-1} and 2925 cm^{-1} were used to follow mass loss, bands at 1658 cm^{-1} and 1728 cm^{-1} were used to follow photo-oxidation, and the band at 1250 cm^{-1} was used to follow chain scission. *Figure* 4 shows changes in the subtracted intensity of the infrared band at 1728 cm^{-1} for amine-cured epoxy specimens exposed under a bandpass filter with center wavelength 326 nm and neutral density filters. The superposition of all intensity levels on the same master curve when plotted as a function of dosage is once again indicative that reciprocity is obeyed. Similar results were obtained for other FTIR bands associated with photodegradation, and reciprocity was seen to be obeyed at elevated temperature and under spectral UV conditions.

In addition to studies of reciprocity and additivity, the NIST SPHERE is also being used to weather specimens that have counterparts in outdoor exposure experiments. As discussed earlier, temperature, relative humidity, and UV irradiance are measured in the same way in both the laboratory and the outdoor environment. In both environments, absorbed dosage is the normalizing metric. Eventually, these studies will play a dominant role in establishing a mathematical linkage between accelerated laboratory and outdoor weathering conditions.

Figure 4—Changes in absorbance for the FTIR band at 1728 cm^{-1} for amine-cured epoxy specimens exposed at 35°C/0% RH under a bandpass filter (center wavelength 326 nm) and neutral density filters.



SUMMARY

The ability to predict the service lives of polymeric materials used in outdoor environments is of great interest to producers, as well as to end-users, of polymeric materials. A reliability-based methodology utilizing total effective dosage as an exposure metric has been proposed as an alternative to the conventional methodology for carrying out laboratory and outdoor weathering studies. The use of this proposed new methodology involves not only a shift in paradigm but also in the way that laboratory and outdoor weathering experiments are carried out. Instruments such as the NIST SPHERE that are able to produce a high intensity, highly uniform UV flux are necessary to implement this methodology. In addition, the concepts of reciprocity and additivity, which were first introduced by the photographic community and then studied by the medical and biological communities, are proposed as models for synthetic polymeric systems.

The ability to weather polymeric materials at high UV irradiance levels in a laboratory device and confidently make the linkage to outdoor exposure results also has tremendous implications in UV weathering studies. Using the high irradiance UV source in the NIST SPHERE, experiments have been carried out to validate the reciprocity law for a non-pigmented, non-UV stabilized acrylic-melamine coating exposed to different broad band irradiance levels at ambient temperature and humidity, as well as an amine-cured epoxy exposed to spectral UV irradiance levels at elevated temperature. Reciprocity was observed to be obeyed in both studies. Studies to validate the law of additivity and to establish linkages between accelerated laboratory and outdoor environments are also underway at NIST.

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