

**NIST Special Publication 1255**

**Polymer Surface/Interface Consortium  
2018 Workshop Report**

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## Executive summary

The Polymer Surface/Interface (PSI) consortium held a two-day workshop on “Polymer Surface and Interface Characterization: Metrology Development and Applications” at the National Institute of Standards and Technology (NIST) in Gaithersburg, MD on October 17<sup>th</sup> & 18<sup>th</sup>, 2018. Day 1 of the workshop was open to PSI members, prospective industrial partners, and the general NIST community. It was structured around invited speakers and short presentations (10 min to 15 min in length) in the morning, followed by two open panel discussions in the afternoon. Day 2 of the workshop was reserved for PSI business for consortium members and interested prospective members only.

Participants in this workshop included PSI’s present members (NIST Engineering Laboratory, Eastman Chemical, Anton Paar, The Boeing Co. (invited but unable to attend), Dow Chemical, SABIC, and Saint-Gobain) as well as prospective industrial partners and other NIST researchers from the Materials Measurement Laboratory (MML). The purpose of this workshop, as articulated to members and invitees, was to (1) discuss the current state of the science for service life prediction (SLP) of polymeric systems exposed to environmental stresses; (2) freely exchange recent developments in characterization tools, test methods, modeling approaches, and environmental stress simulation for plastics, coatings, interfaces, and composites; and (3) facilitate industrial collaborations with NIST to establish weathering correlations on industrial-relevant chemistries and exposure sites/conditions in conjunction with SPHERE exposure experiments.

During two days of thoughtful discussion and enthusiastic participant engagement, workshop participants were presented with both research achievements and technical innovations since the last PSI consortium workshop in 2017 (such as publication of a PSI study of reciprocity in *Polymer Degradation and Stability* and the ongoing development of a new ASTM standard, respectively) realized by their fellow consortium members and workshop participants. As well, PSI consortium members capitalized on the opportunity afforded by the workshop to collectively discuss the future direction of PSI and identified potential useful next steps such as working towards improving metrologies that examine complex failure modes and designing artificial weathering protocols that incorporate more dynamic exposure conditions (*e.g.*, freeze-thaw cycling).

The objectives of this report are to summarize the broad array of topics presented at the 2018 PSI consortium workshop and communicate the major themes, research needs, and future technological and collaborative directions covered during the panel discussions.

Further description of the workshop, a history of the PSI consortium, and information on previous workshops may be found at the following URL:

<https://www.nist.gov/el/materials-and-structural-systems-division-73100/polymer-surfaceinterface-consortium>

## Key Words

Aging; Coating; Interface; Polymer; Surface; Testing; Weathering.

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## 1 Introduction

Consumer products utilized in outdoor applications will inevitably deteriorate, degrade, and often become unusable as a result of weather exposure. Polymeric materials, such as plastics, paints, and composites, are particularly vulnerable to weathering due to their susceptibility to a variety of degradation processes (*i.e.*, photochemical, oxidative, thermal, scratch/abrasion). While polymeric material degradation may occur through one or more of these pathways, it is generally slow (*i.e.*, over the course of many years) and, therefore, challenging to study experimentally. One approach towards overcoming this challenge – determining the duration of functionality of a given product on an experimentally accessible timescale – is the application of accelerated aging scenarios for service life prediction (SLP).

Service life prediction (SLP) is a continuously evolving field, focused primarily on the identification and evaluation of relevant material transformations by physical and/or chemical means in order to quantify the useful service life of a given product. While SLP can be utilized to examine the longevity of materials used in outdoor settings, it is important to note that SLP studies conducted within PSI are *not* intended to exactly mimic a product's exposure to natural weather conditions. Rather, such SLP studies within PSI and carried out at NIST use the Simulated Photodegradation via High Energy Radiant Exposure (SPHERE) device to obtain key parameters for specific material types (*e.g.*, the degradation mode, activation energy, the reciprocity factor, humidity effects) to help design natural exposure experiments that predict long-term product performance. With SPHERE exposure data, and regression models developed therefrom, NIST provides the knowledge necessary to accurately predict the service life of existing and emerging polymeric coatings, paints, and composites exposed to environmental stresses.

Meaningful SLP is predicated not only on well-designed studies but also on the accurate characterization of samples throughout SLP studies. Research efforts towards the advancement of characterization strategies, through both improved instrumental capabilities and methodological design, can be more broadly regarded as research towards advances in measurement science (a topic central to the NIST mission<sup>a</sup>). Work within PSI towards such advancements includes the validation of SPHERE laboratory data with field data/industrial performance testing, the development of novel non-destructive measurements, the development of predictive modeling techniques to study polymer surfaces/interfaces, the design of studies that examine how the failure of a given interface is dependent on environmental and mechanical stresses, and the establishment of standards and standard reference materials for testing and characterizing polymer-substrate interfaces. Indeed, advances in measurement science, as they related to SLP, are essential to the success of the PSI consortium and its members.

The PSI consortium, originally named the Polymer Interface/Interphase Consortium (PIC), first began in 2001 and comprised four companies – Dow Chemical, Pittsburgh Plate and Glass (PPG), Visteon, and MTS. Since its genesis, PSI has gone through five complete phases, each spanning three to four years. Presently, in Phase VI, PSI membership included NIST

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<sup>a</sup> To promote U.S. innovation and industrial competitiveness by advancing measurement science, standards, and technology in ways that enhance economic security and improve our quality of life.

Engineering Laboratory, Eastman Chemical, Anton Paar, The Boeing Co., Dow Chemical, SABIC, and Saint-Gobain. PSI has several ongoing research objectives: facilitation of industrial collaborations with NIST to establish correlations among outdoor exposure of industrial relevant polymers to SPHERE exposure experiments, improvement of methodologies and tools for accelerated weathering/aging studies, and establishment of industrial collaborative comparison experiments on a target system (*e.g.*, emerging polymeric/coating products) within ASTM G03. Working towards these and other goals, the two-day PSI consortium workshop convened on October 17<sup>th</sup> & 18<sup>th</sup>, 2018; the knowledge shared and topics discussed at the workshop are recounted in this report.

## 2 Meeting agenda

Speaker	Affiliation	Topic
Jason Averill	NIST	Opening Remarks
Li-Piin Sung	NIST	Research Program at PMG/NIST
Rose Ryntz	IAC	Challenges in Interior Automotive Component Manufacturing
Ken Strawhecker	ARL	Tools, Methods, Approaches: Nanostructure and Deformation Behavior of High Performance Fibers
Jennifer David	Momentive	Studies of Coating Stress as a Function of Exposure
Olivier Rosseler	Saint-Gobain	Saint-Gobain Research North America
Yuming Lai and Maryus Chyashnavichyus	Dow Chemical	How to study filler-binder synergy for elastomeric materials during degradation?
Joe Fay	BASF	Development to Improve the Correlation of Natural and Accelerated Weathering
Matt McGreer	Atlas Material Testing Technology	The usefulness of weathering reference materials. What they are, how they can be used, how not to use them
Andy Francis	Q-Lab Corporation	Water delivery for improved accelerated testing (ASTM D7869) and expanding this concept into tests designed for other classes of materials
Doug Vermillion	Eyelightning	Eyelightning's involvement with the ASTM MH (metal halide) standard
James E. Pickett	Schenectady, NY	Annual outdoor solar spectral energy distributions from spectroradiometer data
Ron Jones	NIST	n-Soft and neutron research @NIST
Andrew Detwiler	Eastman/Anton Paar/NIST	Fundamentals and characterizations of scratch resistance on automotive clearcoats
Olivier Rosseler and Paul Elziere	Saint-Gobain/NIST	Weathering of polypropylene
James E. Pickett and Olga Kuvshinnikova	SABIC/NIST	Reciprocity and activation energies—NIST Round 2

### 3 Highlighted topics

The following highlighted topics are not intended to serve as a detailed recitation of all material presented and discussed. Rather, this overview serves to communicate topics that spurred engaging discussions and/or were frequently revisited throughout the workshop.

#### 3.1 SPHERE

The NIST SPHERE (Simulated Photodegradation via High Energy Radiant Exposure, Figure 1) was developed over 15 years ago and provides a precise and reproducible means to irradiate multiple test samples with high intensity ( $> 160 \text{ MJ/m}^2$ ) uniform UV radiation (295 nm to 400 nm) while simultaneously exposing samples to precise, specified temperature and relative humidity environments.[1, 2]

The SPHERE is an indispensable instrument within both the PSI consortium and the Infrastructure Materials Group, as it enables high-throughput material degradation studies to be carried out on an experimentally tractable timescale. Furthermore, the precise control over exposure conditions such as UV dose, uniformity of UV irradiance, exposure temperature, and relative humidity allow for the explicit investigation of degradation pathways, kinetics, and more subtle degradation behaviors (*e.g.*, reciprocity, activation energies ( $E_a$ )).

Ongoing SPHERE exposure studies will be utilized to identify key environmental factors that most strongly regulate material degradation of different classes of polymers (*e.g.*, polyesters, polyurethanes) at the mechanistic level. SPHERE studies also include efforts to correlate SPHERE exposure to natural weathering, populating property-performance databases, and validating statistical models for SLP of polymeric materials.

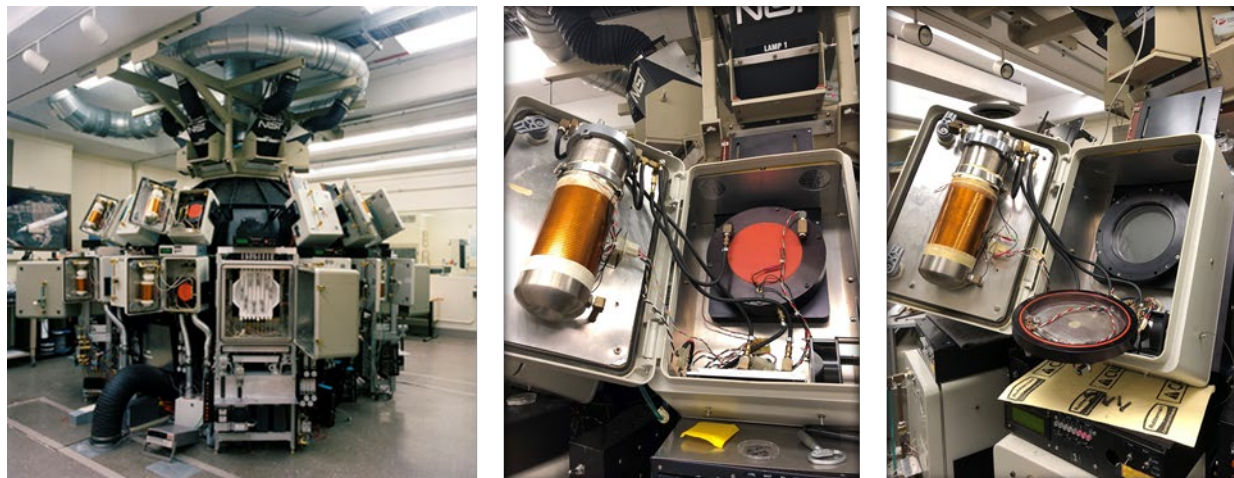


Fig. 3-1: Photo of NIST SPHERE and individual environmental chamber (environmental chamber photos courtesy of Alexander Conrad), which can independently control temperature and relative humidity.

#### 3.2 Quantifying natural exposure

While the SPHERE has a well-defined spectral power distribution (SPD) that can be readily modulated (through the application of various filters) and monitored, the SPD of sun light reaching the surface of the Earth – and a given coating or polymer of interest – does not provide nearly the same degree of control to the researcher interested in investigating how irradiation conditions impact sample degradation due to variable weather conditions such as cloud cover,



precipitation, *etc.* Instead, one must take the approach of accurately measuring the SPD reaching their samples to then relate natural exposure to accelerated exposure.

The accurate measurement of outdoor SPD is not a trivial task, however, and on-going efforts towards this end were presented and discussed during the PSI consortium. The pressing barrier to a complete description of outdoor SPD is incomplete SPD data (*i.e.*, gaps in collected data/missing days of outdoor SPD measurements).

Jim Pickett, Patrick Neale, and Jacob Pickett took a comprehensive approach to address this shortcoming: first they gathered spectroradiometric data collected by SR-18 radiometers located in Miami, FL, Madison, WI, and Phoenix, AZ, from 1997 to 2012.<sup>b</sup> These data were then collated into a usable form by identifying and removing missing data points, examining annual SPD data with > 300 complete days of data collected, and filling in missing days with corresponding data collected from other years to complete annual data sets, converting measured irradiance values in annual data sets to joules, summing daily energy at each wavelength to obtain total annual energy at each wavelength measured, and fitting the data to calculated and weighted SPD values. With this approach, a more complete description of annual solar irradiance could be developed.

While work is ongoing to evaluate the robustness of this method to reliably produce useful SPD values, achievements with this approach were presented, such as agreement of this data set with USDA SPD data collected from nearby locations and good fits of the SPD profile of this data set with previously developed calculated and weighted SPDs. As well, this discussion also included achievements in accuracy realized with SMARTS 2.9.5 (defined below<sup>c</sup>), for the Miami, FL location. Accuracy with the SMARTS model is extremely valuable, as it allows for the natural SPD at 340 nm to be determined – this metric is necessary to accurately and quantitatively compare the power output of natural exposure conditions to a given artificial UV exposure setup.

### 3.3 Advancements in artificial exposure protocols

The ongoing efforts to improve artificial weathering devices and exposure strategies were a reoccurring topic of discussion throughout the PSI consortium. A major challenge one faces when designing an artificial weathering exposure scenario is balancing increased acceleration factors with decreased realism. Generally, the upper limit of any acceleration factor (*e.g.*, increased UV intensity, elevated temperature) is the point above which the degradation mechanism of the material is fundamentally altered from the degradation mechanism that occurs during natural exposure.

Metal halide weathering light sources operating at high UV irradiance were presented as one such strategy towards increasing the acceleration of polymer degradation through increasing UV intensity, but without altering the polymer degradation pathway. Specifically, a new metal halide exposure approach, *Super UV*, described by Doug Vermillion, would provide up to 25 times greater UV irradiance than existing Xenon arc lamps. A challenge with metal halide lamps, however, is that they are sometimes unstable and can emit light < 290 nm as their overall

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<sup>b</sup> The SR-18 radiometer instrument measures light intensity from 290 nm to 324 nm and this network of instruments was operated by both NIST and the Smithsonian Environmental Research Center.

<sup>c</sup> SMARTS: Simple Model of the Atmospheric Radiative Transfer of Sunshine. <https://www.nrel.gov/grid/solar-resource/smarts.html>

power output fluctuates. Given the emerging development and use of high irradiance devices such as *Super UV*, ASTM Subcommittee G03.03 is developing a Work Item to standardize their use and application. Further details regarding this emerging testing strategy may be found in ASTM Working Item *New Practice for Standard Practice for Operating Metal Halide Light Apparatus for Exposure of Non-Metallic Materials*, (WK46431).

As work continues to advance artificial exposure scenarios, another strategy discussed during the PSI workshop was improved water delivery systems during artificial weathering. More specifically, fixed relative humidity (RH) is often utilized to simultaneously expose samples to moisture, UV and elevated temperatures. However, RH does not accurately replicate water exposure during rainfall events. Water delivery devices that provide a realistic replication of rainfall during artificial exposure would greatly enhance the capabilities of existing artificial weathering devices to accurately emulate natural exposure conditions. For example, natural precipitation events can remove loosely bound degraded material from the surface, thereby exposing pristine material beneath. This process of surface regeneration via rainwater exposure is otherwise challenging to reproduce in the laboratory without simulated rainfall water delivery devices, and the development of such devices would be a great advance in producing more realistic laboratory based aging studies.

### 3.4 Activation energy and reciprocity

All materials and products engineered for outdoor use will age, degrade, and deteriorate due to natural weathering. While this process is inevitable, it is not necessarily rapid, and depending on the material, may occur over decades or centuries. This poses a unique challenge in the study of polymeric coatings and materials, as investigators must develop artificial exposure methods and strategies that accelerate the degradation of a material of interest but do so without altering the degradation pathway the material would experience outdoors. In short, this requires researchers to consider how the material of interest will respond to selected acceleration factors (*e.g.*, increased UV dose, elevated temperature).

There exist many testing strategies and protocols for accelerated weathering/degradation of materials. The SPHERE, however, is uniquely – and deliberately – designed to permit the explicit investigation of varying acceleration factors on the rate and mechanism of sample degradation. More specifically, the SPHERE permits the investigation of reciprocity and determination of activation energy for a given material. A material obeys reciprocity if the rate of material degradation increases proportionally with increased irradiance. Activation energy of a material informs the extent to which an increase in exposure temperature will accelerate the rate of change of a measurable material/chemical property. Both reciprocity and activation energy are frequently studied for a variety of materials within the PSI consortium via sample exposure in the SPHERE, where precise control over UV dose, exposure temperature, and relative humidity is achieved.

One such study presented during the PSI workshop, and recently published, detailed the examination of reciprocity and activation energy of bisphenol A polycarbonate (PC), poly(butylene terephthalate) (PBT), a 55:45 PC/PBT blend, and poly(styrene-co-acrylonitrile) (SAN), all pigmented with 3 % (by mass) rutile TiO<sub>2</sub>.<sup>[3]</sup> As shown in Figure 2, two of the four aforementioned polymers obeyed reciprocity with respect to color shift ( $\Delta E$ ) up to at least 300 MJ/m<sup>2</sup> of SPHERE exposure, with PBT and PC/PBT obeying reciprocity up to approximately 100 MJ/m<sup>2</sup>. This divergence from reciprocity at higher irradiances has been

observed previously for poly(ethylene terephthalate) (PET) and was attributed to diffusion limited oxidation (DLO).[4] Important parameters for evaluating polymer degradation, such as activation energy ( $E_a$ ), can also be extracted from SPHERE aging data. As shown for PC in Figure 3a, the rate of change of color-shift during UV exposure increased with increasing temperature. A shift-factor (*i.e.*, multiplicative constant) is applied to the x-axis to overlay the experimentally collected data during the initial period of exposure with increasing change in appearance (Figure 3b). The natural log of the shift-factor applied to data from each temperature can then be plotted as a function of  $1/T$  (Figure 3c); the slope of this line is the activation energy for colors-shift ( $E_a$ ), as defined by the Arrhenius equation.

The role of relative humidity (RH) in regulating polymer degradation and changes in polymer appearance were also explored in this study. Appearance measurements performed after

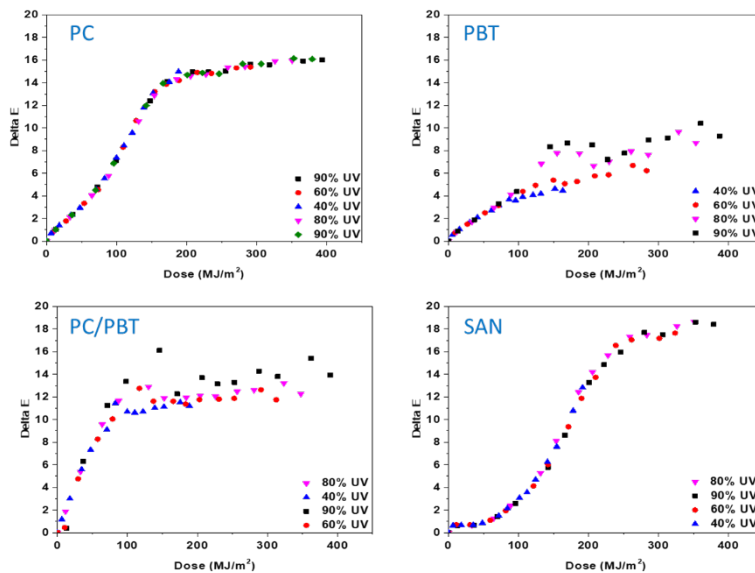


Fig. 3-2: Color shift data of four polymers after SPHERE exposure, at 35 °C, 10% RH, and four irradiance levels. Error bars in the graphs represent one standard deviation from four measurements on the same specimen, and the error bars are smaller than the size of the symbols. Note that measurement uncertainties for different specimens from the same batch on the same exposure conditions are smaller than 2 % according to previous experiments. Final results published in Pickett et al. Polym. Degrad. Stab. 166 (2019) 135-144

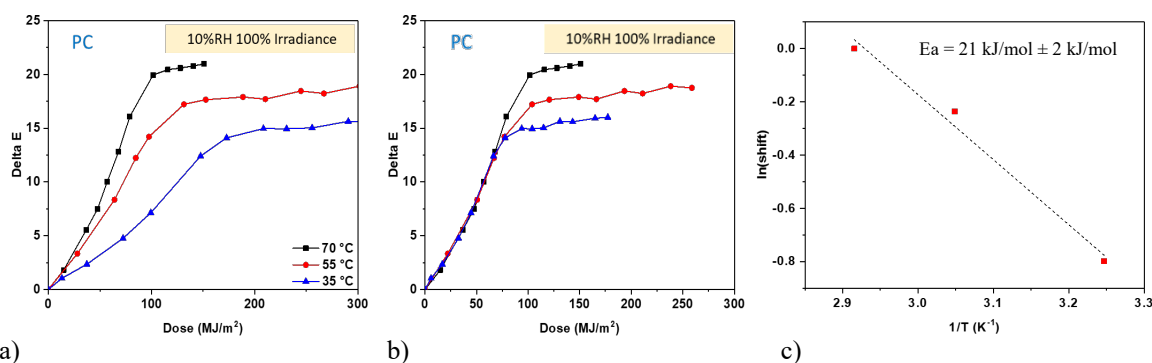


Fig. 3-3: a) Measured color shift of PC samples after SPHERE exposure at three different temperatures. b) Overlay of color shift data to extract temperature dependent shift factor. c) Arrhenius plots obtained after PC exposure in the SPHERE at three temperatures. Error bars in the graphs represent one standard deviation from four measurements on the same specimen, and the error bars are smaller than the size of the symbols. Note that measurement uncertainties for different specimens from the same batch on the same exposure conditions are smaller than 2 % according to previous experiments. Final results published in Pickett et al. Polym. Degrad. Stab. 166 (2019) 135-144

exposure at 100 % UV intensity and varying RH levels indicated that changes in appearance of PC, PBT, PC/PBT blend, and SAN showed little to no dependence on RH.

Samples were also exposed to varying RH conditions at 40 % UV intensity; the color shift data for PC, PBT, and PC/PBT blend continued to show little to no sensitivity to RH. In contrast, appearance measurements of SAN after exposure to 40 % UV intensity demonstrated a well-defined sensitivity to relative humidity and indicated that the color shift and gloss loss of SAN occurred most rapidly under dry UV exposure conditions. Although the chemical mechanism for this observed behavior is presently unresolved, this observation highlights the necessity to examine the role of moisture in regulating the degradation of a given polymer during different exposure conditions (*i.e.*, irradiance intensities). Indeed, more accurate service life predictions of polymers require the design of studies that explicitly examine the confluence of multiple simultaneous exposure conditions in driving material degradation, as probing only a single variable at a time (*e.g.*, RH at a single irradiance) runs the risk of obfuscating more subtle polymer degradation behavior and pathways.

To that end, the value of reciprocity, activation energy, and multi-variable studies was further demonstrated at the PSI workshop during a presentation and discussion regarding the degradation of polypropylene. In this study, irradiance (I), temperature (T), and relative humidity (RH) values were selected for a series of exposure experiments to develop an equation predictive of aging:

$$\text{degradation rate} \propto I^p * e^{\frac{-E_a}{RT}} * [RH]^n$$

By selecting systematic combinations of irradiance, temperature, and relative humidity during exposure, power factors indicating the extent to which each exposure condition regulates the rate of degradation ( $p$  – Irradiance,  $E_a$ , - Temperature, and  $n$  – Relative Humidity) can then be determined from the experimentally measured degradation rate. While this study is ongoing, preliminary findings indicate that experimental data collected over a span of irradiance values, temperatures, and humidity values can be modeled to fit and share the same rate of degradation.

Overall findings from these studies demonstrated the ability of SPHERE exposure experiments conducted within PSI to: a) identify exposure factor(s) most important for accelerated weathering, b) inform the selection of appropriate exposure conditions (*e.g.*, exposure temperatures should be similar to use temperatures), and c) develop models that are predictive of material degradation across a range of exposure conditions. Such findings are necessary in the design and execution of SLP studies to ensure that findings from the lab are indicative of outdoor performance and degradation behavior.

### 3.5 Correlation to the natural environment

When interpreting SPHERE exposure data, it is imperative to keep in mind that the SPHERE is designed to permit precise control over specific acceleration factors and is *not* intended to mimic exact outdoor weathering conditions – this is largely due to the fact that the spectral power distribution of the SPHERE is similar to but not exactly the same profile of natural sunlight. Therefore, while generally all materials studied in the SPHERE are susceptible to UV driven degradation (*i.e.*, 300 nm to 400 nm exposure), some materials can exhibit wavelength dependent degradation modes and may respond differently during SPHERE exposure than would otherwise occur outdoors. That stated, comparison of SPHERE exposure data to natural exposure data is a reliable strategy used to inform what weather factors are most

important to predict the service life of a given product (*i.e.*, what exposure condition(s) lead to the most rapid loss of material efficacy).

As discussed by Joseph Fay, data collected from SPHERE exposure plays an integral role in identifying the interdependent relationship among indoor accelerated weathering, outdoor exposure, and the use-phase of a given product. Importantly, findings from each compartment must not be examined in isolation but instead should be considered together. With this holistic approach, indoor accelerated weathering studies can be designed to more accurately accelerate naturally occurring failure modes. Indoor accelerated weathering studies can also first be used to determine what material properties/composition might be most susceptible to natural aging outdoors. Ultimately, this approach provides the data necessary for advancement in design of coating products with improved durability and increased service life.

### 3.6 Fillers

Particulate filler materials, both on the nanoscale and microscale, are added to polymeric matrices to confer desirable material properties to the resulting composite material. Fillers may be added to a given coating (or polymer in general) to act as a pigment, impact modifier, UV-stabilizer, flame retardant, gas or water barrier, electrical insulator or conductor, or mechanical reinforcer. The specific role of a given filler is largely dictated by the size, composition, morphology, surface functionalization, and concentration of the selected particle.

As discussed by Yuming Lai and Maryus Chyasnayichu, the efficacy and durability of a given composite material through its service life depends strongly on filler-binder synergy. Persistence of this synergy is of particular importance with respect to composite weathering, as weather-driven degradation can negatively impact the interaction of a given filler with its surrounding polymer matrix through a variety of pathways such as inhibited stress transfer or producing an anisotropic distribution of particles (*e.g.*, aggregation, surface accumulation as the surrounding polymer matrix degrades). As well, depending on composition and other intrinsic properties, fillers may also impact the kinetics of matrix aging by either accelerating[5] or mitigating[6] the rate of degradation. Furthermore, composite materials can experience diffusion limited oxidation (DLO) as they age. DLO contributes to the generation of a heterogeneous material that is more challenging to characterize, as chemical and material properties of the material will vary from the surface of the sample into the bulk. Due the variety of complex failure modes and processes like DLO that arise in composite systems, innovative characterization techniques and strategies are required to investigate weather-driven changes to particle-polymer and particle-particle interactions. Such data are necessary for more well-informed service life predictions of composite materials.

### 3.7 Coating stress

Stated most simply, automotive coatings (and most coatings in general) are engineered to provide a barrier to the outside environment by resisting natural degradation pathways, while maintaining desirable aesthetic properties (*e.g.*, color and gloss). Cracking is a prevalent failure mode of coatings as they age and is the result of a given applied instantaneous stress ( $\sigma_i$ ) exceeding the stress threshold ( $\sigma_{max}$ ) of the coating.

As efforts continue to improve coating crack resistance, Jennifer David discussed four primary factors that have been identified as most readily influencing cracking: intrinsic material

properties, internal stresses, external stressors (*e.g.*, UV, thermal, humidity/moisture), and the presence of defect/propagation sites. Investigation of these factors, and more specifically, the role of weathering in both contributing to external stresses as well as reducing the stress threshold of a given coating, is necessary to develop coatings with improved resistance to crack initiation and crack propagation. Broadly, such a coating – were it formulated to exhibit increased elasticity or increased resistance to photodegradation, for example – would demonstrate an improved cracking lifetime via shifting the crossover point ( $\sigma_i = \sigma_{max}$ ) by reducing the magnitude of instantaneous coating stresses and/or increasing the threshold coating stress prior to failure.

Andrew Detwiler and Rose Rytz both discussed one of the most well-known and often encountered external stressors that can lead to coating cracking: scratching. Scratching can occur in a broad range of scenarios (*e.g.*, car wash, key scratch, belt buckle, shopping cart) and applied forces (*i.e.*, 2 N to 35 N). As a result, several laboratory-based testing methodologies have emerged to study scratching phenomena.[7] However, these strategies span several orders of magnitude of scale – in both indenter size and scratching force applied. Therefore, careful consideration must be given when selecting a scratch testing methodology, so that the scratch behavior measured is relevant to real-world scratch performance of the coating of interest. For example, while nano-scratch techniques provide a means to investigate surface scratch improvement of a given coating formulation, consumers are still more sensitive to larger (*i.e.*, macro) scratches and thus improvements in coating technologies must be realized at the macroscopic level as well.

As measurement tools and strategies for the accurate study of the cracking and scratch behaviors of coatings continues to advance, several broad areas of future investigation were identified and discussed during the PSI consortium. They included measuring both the modulus of weathered samples and the stress threshold as a function of temperature, examining the role of humidity on overall coating stress, and validating an approach that includes weathering properties in coating stress analysis.

### **3.8 Panel discussions**

In addition to prepared presentations, the PSI consortium workshop also featured two open panel discussions. Included below are summaries prepared from notes collected during each open panel discussion.

#### **3.8.1 Panel Discussion I: Challenges in weathering testing and prediction**

A primary challenge associated with the variety of testing methods (*i.e.*, aging and weathering protocols) available today is that different testing methods often lead to different results. For example, Reactive Oxygen Species (ROS), or precursors to ROS such as ozone, can form in a given testing chamber and their contribution to material degradation may be overlooked if not all together not considered. One solution to the oft encountered variety of results produced from different testing methods would be to develop a reference material that degrades/behaves similarly across all testing scenarios. Alternatively, and with respect specifically to ROS and ozone formation, depending on the light source, proper filtering of the source of light could limit their production. Indeed, more subtle differences in testing methods,

exposure conditions, and material response to both must be considered so that results across different weathering studies can be meaningfully compared.

Towards developing new aging and weathering protocols, it is important that testing conditions are applicable to a broad range of different materials and different classes of material. For example, a novel testing method should ensure that a given set of exposure conditions that are applicable for assessing the aging of polyolefins are equally applicable for aromatic polymers. A challenge in developing widely applicable testing methods is that many classes of materials/polymers possess distinct intrinsic chemical and material properties and therefore, polymer response to exposure conditions can be different depending on these properties. Additionally, changes to a given material during simulated weathering and/or accelerated degradation strategies should have some meaningful correlation to changes that would have occurred during natural exposure.

It is also important to keep in mind that existing accelerated weathering strategies based on standardized exposure methodologies do not necessarily predict service life. Such strategies are primarily used to develop standards. An alternative approach to designing new accelerated weathering strategies would be to do so with the focus more centered on obtaining fundamental knowledge on failure modes present in a material. However, breaking away from legacy standards is also a pressing challenge in the development of new testing strategies.

Along with new testing methods, a database(s) that collates testing strategies and findings for different classes of materials would be very valuable to the community. Moreover, while data are good, actionable information is what is needed.

### **3.8.2 Panel Discussion II: Research needs on surface/interface characterization – tools, test methods, modeling**

It is challenging to correctly characterize and understand failure mechanisms at interfaces. For example, in emerging pigment/fiber composites – how can one distinguish/determine if it is the matrix that is failing or the interface between the filler/fiber and the matrix that is failing? As we (the polymer, interface, and coatings community) look to the future, what is going to fail in the next 10 years: the pigment itself, the matrix, the fiber, the interface? And how can we accurately study such failures on laboratory tractable timescales?

Towards addressing such challenges, when examining a coating failure, one must strive to distinguish adhesion failure from fracture failure. For example, scratching through layers provides a means to examine which layer most easily delaminates; pull-off tests are also very common for examining cohesive vs. adhesive coating failure. To examine material failure after some period of aging/degradation, nanoindentation or microindentation across a cross section of the material can be used to probe the extent/gradient of degradation. More broadly, characterization methods should be applicable for a variety of substrates (*e.g.*, metals and even building materials). Additionally, characterization methods should also be capable of determining the extent – and possibly the rate – of complex processes such as diffusion limited oxidation and/or filler migration.

## 4 Future of PSI

As the PSI consortium prepares to begin its third decade of coordinated and collaborative research efforts, it is presented with many opportunities to advance measurement science as it works towards a more complete understanding of polymer/surface interface behavior and performance in the natural environment. Two broad areas of advancement were identified during the workshop: improved metrologies for examining complex failure modes (such as scratching/mar, adhesion failure) and the design and implementation of artificial weathering devices/protocols that produce more dynamic exposure conditions, such as freeze-thaw cycling. Listed below are more specific recommendations for continuing research and new areas of focus for PSI consortium, and it is planned as a statement of work in the next phase of PSI consortium.

- Scratch, adhesion, weathering, corrosion resistance.
- Weathering – Pigment matrix interfaces
- Corrosion – Accelerating corrosion resistance of coatings adhered to metal substrates.
- Freeze thaw cycling, thermal cycling in combination with UV weathering
- Building materials on steel
- Working towards a more quantitative adhesion test
- Composites weathering
- Scratch metrology and how it connects to chemistry of coating
- Development of less invasive and/or non-destructive test methods (*e.g.*, any alternative test method assessing mechanical performance to replace tensile testing)

## 5 Concluding Remarks

The study of polymer weathering, aging, and degradation towards advancing service life prediction is as equally challenging as it is necessary. A principle challenge is finding the appropriate balance between accelerating degradation while maintaining relevance to natural exposure: as debated during open panel discussions of this workshop, accelerated weathering will never perfectly predict outdoor performance – but how good is good enough? Relatedly, commercial standards for products can result in the – sometimes harmful – notion that compliance is indicative of accurate service life prediction. As measurement science of polymer surfaces and interfaces continues to advance, these considerations should be kept in mind, as improvements in instrumentation and characterization strategies will be rendered null if the data acquired are simply reported without providing context for the strengths and limitations of such data as they relate to natural exposure and natural degradation modes. The PSI consortium is uniquely suited, however, to lead the advancement of this field due to the comprehensive approach it takes towards designing and executing laboratory exposure studies of commercially relevant polymer chemistries and the equally rigorous data analysis that is performed to ensure laboratory findings accurately represent outdoor performance.



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## Appendix A: Workshop Attendee List (Non-NIST Attendee)

Polymer Surface and Interface (PSI) Workshop

October 17-18, 2018; 101 West Square

Last Name	First Name	Company
Pickett	James	SABIC
Kuvshinnikova	Olga	SABIC
Detwiler	Andrew	Eastman Chemical
Bhattacharya	Deep	Eastman Chemical
Baker	Leslie	Eastman Chemical
Morel	Pierre	Anton Paar
Rosseler	Olivier	Saint-Gobain
Chyasnovichyus	Maryus	Dow Chemical
Lai	Yuming	Dow Chemical
Hua	Hong	Momentive
David	Jennifer	Momentive
Fay	Joseph	BASF
Hall	Michael	SABIC
Sharma	Ravi	Eastman Chemical
Strawhecker	Kenneth	ARL
Francis	Andrew	Q-lab
Vermillion	Douglas	EYE Applied Optix
McGreer	Matthew	Atlas Material Testing Technology
Rose	Ryntz	IAC

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