SERVICE LIFE PREDICTION OF POLYMERIC MATERIALS

★ Over the Horizon ★

MARCH 20 - 24, 2016

SANTA FE
NEW MEXICO

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

UL

Q-LAB

Service Life Prediction: Over the Horizon
March 20-24, 2016
Hilton Santa Fe Historic Plaza
Santa Fe, NM

On behalf of the technical organizing committee and the sponsors from **Underwriters Laboratories**, **Q-Lab**, and the **National Institute of Standards and Technology**, I would like to welcome you all to ***Service Life Prediction: Over the Horizon.*** This conference features a strong technical program of cutting edge research in service life prediction, including presentations from across the globe with a diverse mix of industrial, academic and government perspectives, moderated panel discussions.

The organizing committee has designed this meeting to address two areas of Service Life Prediction: scientific and standards.

In the scientific area, benchmarking the current state of the art is an important outcome of this meeting. Additionally, the discussion sections will focus on identifying areas where additional research is required.

The same questions apply to the standards area. The focus here will be on barriers to including this state-of-the-art science in industry consensus standards. These activities will also identify areas where additional research is required. These standard focused sessions will be held between lunch and dinner.

The meeting has an active social/networking component. This starts on Sunday with a welcoming reception. Monday will start with a continental breakfast and series of moderated talks and discussion. After a provided lunch, the standards session will focus on feedback from the Standards Technical panel on a current standard effort. In the evening there will be a light reception followed by two talks and more discussion. This pattern remains similar with Tuesday having a banquet dinner and Wednesday having a poster session and dinner at the hotel. The conference wraps up on Thursday morning.

Following this meeting, all presenters are encouraged to submit a paper for publication in a peer-reviewed volume edited by C. White, K. White, and J. Pickett to be published by Elsevier. Previous proceedings volumes have been highly sought-after technical references. Everyone with a full registration for this meeting will be mailed a copy of this volume. The paper submission deadline is June 1, 2016.

Many thanks to all of the authors, session chairs, organizers, and participants for making this conference possible. Wishing you all an enjoyable and productive time in Santa Fe, NM.

Dr. Christopher C. White
Polymeric Materials Group
Engineering Laboratory
National Institute of Standards and Technology

Picture view of 2016 program

Time	Sunday	Monday	Tuesday	Wednesday	Thursday
7:00		Breakfast			
7:30					
8:00		C. White	Sung	Celina	Scott
8:30		Berry	Lewicki	Schlothauer	Pintar
9:00		Wood	Hayes	Chen	Tedds
9:30		Coffee Break			
10:00		Quill	Alig	Pickett	Libby
10:30		Ken White	Redline	Blair	Baxamusa
11:00		Watson	Ito	Koehl	Wu
11:30		Discussion			
11:45					
12:30		Lunch			
1:00					
1:30					
2:00		2000 hour	IEC	Roadmapping	
2:30		working draft	60216-7	SLP into	
3:00		and proposal	discussion	UL, IEC	
3:30		Break		standards	
4:00			Begin	Poster	
4:30			Roadmap	Session	
5:00			Discussion		
5:30		Reception		Dinner	
6:00	Reception		Banquet		
6:30		Sun	Dinner	Stull	
7:00		Bora		Old	
7:30		Discussion		Discussion	
8:00					

List view of 2016 program.

Monday Morning: Weathering and Validation
Discussion Leaders: Pickett and Jennifer David

Time	Presenter	Title
7:00AM-8:00AM		Continental Breakfast.
8:00 AM-8:30 AM	C. White	Intro
8:30 AM-9:00 AM	Berry	Challenges in Accelerated Weather Testing, Method Development, and Service Life Prediction of Exterior Commercial Airplane Coatings
9:00 AM-9:30 AM	Wood	Accelerated testing and risk minimization for exterior building product finishes-Part 1
9:30 AM-10:00 AM	Coffee Break	
10:00 AM-10:30 AM	Quill	Development of Weathering Cycles for Qualitative Service Life Analysis as a Precursor to Accurate Service Life Prediction Protocols: Contemporary Examples
10:30 AM-11:00 AM	K. White	Case Studies to Assess the Effects of Accelerated Weathering Stresses Used to Predict Service Life
11:00 AM – 11:30 AM	Watson	Weathering of Polymeric Materials in Trace Forensic Evidence and its Effect on Identification Measurements
11:30-12:30		Panel Discussion
12:30-2:00	LUNCH	

Monday Afternoon: UL 746 Process

Time	Title
2:00 PM-5:30 PM	Noé P. Navarro 2000HR Program working draft and proposal: This is a working session for members of the UL 746B LTTA Forum and it is open to SLP attendees interested in participating. The objective of this session is to develop a final draft of a UL 746 Standard Technical Panel (STP) proposal that can be ready to be submitted for ballot by the end of the session.

Reception

Time	Title
5:30- PM-7:00 PM	Reception

Monday Evening: Water and Moisture
Discussion Leaders: Watson and Sutter

Time	Presenter	Title
6:30PM-7:00 PM	Sun	Modelling Sorption and Diffusion for Lifetime Assessment: Surrogate Models of Langmuir Sorption Kinetics Coupled with Vapour Diffusion in Polymers
7:00 PM - 7:300 PM	Bora	Spectroscopic measurement of water in polymeric materials
7:30PM – 8:300PM		Panel Discussion and Open (cash) Bar (6:30 PM-8:30PM)

Tuesday Morning: Mechanical Changes Related to Exposure
Discussion Leaders: Celina and Lewicki

Time	Presenter	Title
7:00AM-8:00AM		Continental Breakfast.
8:00 AM-8:30 AM	Sung	Characterizing surface damage of nano-filled polymer coatings under accelerated ultraviolet degradation
8:30 AM-9:00 AM	Lewicki	Towards a predictive, multi-scale aging model for complex silicone architectures - Insights into structural control and response to environmental stressors
9:00 AM-9:30 AM	Hayes	A Study of Nano-mechanical Test Methods as Predictive Tools for Coating Changes in Weathering
9:30 AM-10:00 AM	Coffee Break	
10:00 AM-10:30 AM	Alig	Combination of material characterization and cyclic fatigue testing for investigation of elastomer aging
10:30 AM-11:00 AM	Redline	Unusual Aging Behaviour of Elastomers in High Temperature Environments
11:00 AM – 11:30 AM	Ito	Degradation of ethylene-propylene-diene elastomer by heat and/or radiation
11:30-12:30		Panel Discussion
12:30-2:00	LUNCH	

Tuesday Afternoon: UL 746 Process

Time	Title
2:00 PM-5:30 PM	Jun Haruhara, Noé P. Navarro, and Dr. Thom Fabian IEC 60216-7: Applicability & next round robin plans. This is a working session to discuss the potential applicability of newly published IEC Technical Specification (TS) 60216-7-1 and IEC Test Report (TR) 60216-7-2 for the determination of Relative Thermal Indices (RTIs). Plans for additional round robins incorporating different materials will be discussed.

6:00 PM Tuesday Evening: Banquet Dinner at Rio Chama Steak House
414 Old Santa Fe Trail, Santa Fe, NM 87501

Wednesday Morning: Chemical Changes Related to Exposure
Discussion Leaders: Berry and K. White

Time	Presenter	Title
7:00AM-8:00AM		Continental Breakfast.
8:00 AM-8:30 AM	Celina	An overview of DLO modelling and relevance for polymer aging predictions
8:30 AM-9:00 AM	Schlothauer	Prospects of 2D-luminescence spectroscopy for aging investigations of the embedding EVA polymer in PV modules: Revealing DLO conditions.
9:00 AM-9:30 AM	Chen	Investigation of PDSC applicability to evaluate polymer thermo-oxidative stability
9:30 AM-10:00 AM	Coffee Break	
10:00 AM-10:30 AM	Pickett	Forbidden Chemistry: Non-Free Radical Oxidation Mechanisms
10:30 AM-11:00 AM	Blair	Lifetime Prediction of O-rings Used in the SAVY-4000 Actinide Storage Vessel
11:00 AM – 11:30 AM	Koehl	Evaluation of the time-transformation function from a round robin weathering test of various back-sheets for PV-modules with different ultra-violet radiation sources and sample temperatures
11:30-12:30		Panel Discussion
12:30-2:00	LUNCH	

Wednesday Afternoon: UL 746 Process

Time	Title
2:00 PM-4:30 PM	Noé P. Navarro, Dr. Chris White, Dr. Tom Fabian Roadmap for SLP into UL, IEC, and other standards. This is working session to discuss how to continue incorporate lessons from SLP meetings into the development of standards used to determine temperature ratings. A white paper outline is the goal from this session.

4:00PM -5:30 PM Poster Session.

Poster #	Presenter	Title
1	Li*, Morris †, Sahlani‡, Tietsort*, Lim §, Bruckman*, French	Lifetime and Degradation Science Studies of Exterior Coatings.
2	Tony Misovski & Mark Nichols	Visualization and Quantification of Impact Events on Automotive Paint Systems
3	Wang Eun Lee	Accelerated fluorescence photobleaching of conjugated polymer film under wet state
4	. Rodriguez, Lewicki, Alviso, Chinn,. Wilson & Maxwell	NMR Methodologies for the detection and quantification of nano-structural defects in Silicon Networks

5	Judovits Kowal	Comparison of TGA Methods to Determine Decomposition Kinetic Parameters
6	C. White[1], Byrd[1], Thomas[2], Clerici[1], Kaetzel	Predicting Field Panel Temperature

5:30 PM – 6:30 PM Dinner at Hotel

Wednesday Evening: Radiation
Discussion Leaders: Glascoe and Baxamusa

Time	Presenter	Title
6:30 PM-7:00 PM	Stull	Informed Design of Aging Experiments via CW and Pulse EPR Spectroscopy
7:00 PM - 7:30 PM	Old	Material Property changes following neutron and Gamma irradiation of Carborane-co-PDMS composites.
7:30PM - 8:30 PM		Panel Discussion and Open (Cash) Bar (6:30-8:30)

Thursday Morning: Modelling and Prediction
Discussion Leaders: Quill and Wood

Time	Presenter	Title
8:00 AM-8:30 AM	K. Scott	Selecting a statistical method for validation of life prediction models
8:30 AM-9:00 AM	Pintar	Predicting Field Degradation of Sealants Using Accelerated Tests from the NIST Solar Sphere.
9:00 AM-9:30 AM	Tedds	Validating laboratory-based models and scaling-up for service life prediction
9:30 AM-10:00 AM	Coffee Break	
10:00 AM-10:30 AM	Glascoe	Predicting chemical compatibility and aging of materials in a system: a combined experimental and modelling approach
10:30 AM-11:00 AM	Baxamusa	Photo-oxidation under visible light: the strange case of plasma polymers
11:00 AM – 11:30 AM	Wu	Highly Accelerated UV Testing and Its Correlation to Mild Test Conditions of Polymeric Materials
11:30-12:30		Panel Discussion and wrap up.

Table of Contents

Monday Morning: Weathering and Validation

Author name(s): Douglas H. Berry[1], Erik D. Sapper
Douglas H. Berry, 3 Erik D. Sapper, 3
[2], and Brian Hinderliter[3]

Job title: [1]Associate Technical Fellow, [2]Research Chemical Engineer, [3]Associate Professor

Affiliation: [1,2]Boeing Research & Technology, [3]University of Minnesota Duluth

Contact information including physical address, phone and email:
Douglas Berry
Boeing Research & Technology
7701 14th Avenue South2-122 Building, Door N-8
Seattle, WA 98108
Or
PO Box 3707, MC 19-LX
Seattle WA 98124-2207
206-310-0804
douglas.h.berry@boeing.com

erik.d.sapper@boeing.com
bhinderl@d.umn.edu

Abstract Title:

Challenges in Accelerated Weather Testing, Method Development, and Service Life Prediction of Exterior Commercial Airplane Coatings

Abstract :
Exterior commercial airplane coating systems serve both decorative and protective functions so must retain gloss and color properties as well as provide corrosion and fluid resistance in severe service environments. Commercial aircraft can make up to eight flights per day and cruise at ceilings as high as 12 kilometers for up to 18 hours per day. Ultraviolet radiation exposure can increase by a factor of four and surface temperature can range from as high as 70 °C down to -60 °C between ground and cruise altitudes. Additionally moisture levels may vary from 100% relative humidity and rain on the ground to bone dry conditions at cruise. At a minimum the effects of the changes in UV, temperature, and moisture on photo-oxidation and hydrolysis must be considered and balanced in accelerated test method development, damage mechanism understanding, modeling for service life prediction of these coating systems, and design of future generation coatings with a desire of twelve year service life to correspond with the heavy maintenance checks for the 787. This presentation will discuss recent advances in achieving these goals through development of more realistic accelerated weathering tests, simulation of water diffusion in coatings, and modeling of the sensitivity of damage from overlap of polymeric absorption peaks with UV spectral irradiance.

Author name(s): Kurt Wood

Job title: Principal Scientist

Affiliation: Arkema, Inc.

Contact information including physical address, phone and email:

900-1st Avenue
King of Prussia PA 19406 USA
+1 610 878-6914
Kurt.wood@arkema.com

Accelerated testing and risk minimization for exterior building product finishes- Part 1

Abstract :

While outdoor exposure in Florida has long been the primary standard used to evaluate and qualify premium finishes for exterior building products, accelerated weathering test methods are a valuable complement to outdoor weathering, not only for R&D screening, but also as tools for reducing risk. Since accelerated test conditions cannot, by their very nature, uniformly accelerate every stressor involved in material weathering, they can produce false positives and false negatives compared to outdoor performance. To reduce risk, these two cases of false positives and false negatives must be managed quite differently. These principles will be illustrated by reviewing recent weathering data comparing several premium building product finish chemistries, in south Florida exposure, and using several accelerated test methods including the new ASTM D7869-13 method. Specifically, we will consider the case of formulations with little or no pigment in the topcoat- i.e. formulations similar in spirit to those used to develop ASTM D7869-13.

Development of Weathering Cycles for Qualitative Service Life Analysis as a Precursor to Accurate Service Life Prediction Protocols: Contemporary Examples

Jeffrey Quill, Sean Fowler--Q-Lab Corporation

The major international test standards for accelerated weathering of materials for outdoor use are ISO 4892 & ISO 16474, ASTM G15*X* series and D2565. Despite the longevity of each of these standards and their predecessors, polymer scientists often express mistrust of the data produced from tests run according to these practices. Entire conferences and research programs dedicated to service life prediction lament the slow developmental progress of accurate models for predicting or estimating with reasonable accuracy the outdoor service life of polymers. One reason for the slow progress is the difficulty of the task. The interdependent effects of environmental stresses are not well enough understood, and the data collection necessary for progress on this front is both prohibitively expensive and logistically daunting for most organizations.

However, there may be another far more basic reason why accelerated weathering tests are not yet capable of providing reliable data useful in predicting or estimating long term performance. The exposure cycles themselves have rarely been validated to determine if they truly represent what happens to polymeric or other synthetic materials exposed to sunlight, moisture, heat, and outdoor environmental cycling. One reason for this is the over-reliance of under-developed cycles in major international weathering test standards, many of which are 50 to 100 years old. One fundamental principle that is often ignored is that before you can develop a test protocol that provides a quantitative service life prediction for a material you must first have a test procedure that provides a qualitative service life prediction.

This paper will explore the most commonly run weathering test cycles for weathering of polymeric materials and how they fail in the goal to provide accurate acceleration of outdoor weathering. The major weathering standards will go on trial. However, not all weathering standards have been created equally, and recent examples of proper development of standardized weathering cycle will be detailed. These examples will demonstrate how a small dedicated group of researchers can initiate the development of new accelerated weathering test cycles that achieve the intermediate goal of providing qualitative service life predictions. This information should provide fuel for thought for future standards development and the ongoing work to develop accurate and useful SLP models.

Kenneth M. White
Lead Senior Research Specialist
3M Company, St Paul, MN, USA

Hyun-Jin Koo
Director of Overseas Business Division
FITI Testing & Research Institute, Seoul, Korea

Karnav Kanuga
Product Development Specialist
3M Company, St Paul, MN, USA

Contact information including physical address, phone and email:

Kenneth M. White
3M Center, Building 0235-B-B-44
St Paul MN 55144-1000
Phone: 651-736-3119
Email: kmwhite@mmm.com

Abstract Title:

Case Studies to Assess the Effects of Accelerated Weathering Stresses Used to Predict Service Life

Abstract description:

Taking service-life prediction to the next level demands a better understanding of how the effects of accelerated weathering compare with results obtained under natural weathering conditions. Useful service-life estimates require that degradation pathways stemming from the two methods be the same. Potential deviation from this requirement is particularly an issue when accelerated testing is conducted at high levels of stress. Using poly(ethylene terephthalate) film as a model material, the impact of irradiance, temperature, and humidity on degradation has been evaluated in a series of accelerated laboratory exposures. Results reveal multiple failure modes, each of which displays a unique dependence on the applied stresses. Comparison to degradation observed from natural outdoor exposures enables assessment of the limitations, determination of the constraints, and interpretation of the data relating to accelerated weathering, all of which must be considered for service-life prediction.

Author name(s): Stephanie Watson

Job title: Research Chemist

Affiliation: NIST

Contact information including physical address, phone and email: 100 Bureau Drive, Stop 8615, Gaithersburg, MD 20899; 301-975-6448; stephanie.watson@nist.gov

Weathering of Polymeric Materials in Trace Forensic Evidence and its Effect on Identification Measurements

Abstract description (500 words or less): Trace evidence is perhaps the broadest and least defined area of forensic science. The analysis of trace evidence seeks to connect people, places, things, times, and activities to help identify criminals and understand crimes. While trace evidence has been used since the beginning of forensic science, it has become controversial due to over interpretation of the evidence and the human-based observational methods that are hard to characterize for accuracy and precision. Research groups at NIST are developing reliable methods including valid interpretation that will help make trace evidence useful. As an example, for paint collected at a hit-and-run scene, the class may be a manufacturer or model or year of vehicle, but seldom will point to an individual vehicle. Is there a way to improve the selectivity of trace analysis to move closer to individualization?

Our research group at NIST is focusing on paint and fiber trace evidence measurements. One aspect of this research is to determine how aging or weathering of evidence can be incorporated into measurement protocols to distinguish evidence within the same class to more uniquely and realistically compare real world trace evidence. This talk will discuss the role of weathering in the forensics field, the importance of the design of experiments for the NIST work and preliminary results for paint samples.

Monday Evening: Water and Moisture

Author name(s):

Yunwei Sun, Charles Tong, Stephen J. Harley, and Elizabeth A. Glascoe

Job title:
Computational Physicist in Material Aging and Compatibility, Deputy Group leader of geochemical, hydrological, and environmental science

Affiliation:
Lawrence Livermore National Laboratory

Contact information including physical address, phone and email:
L-223
7000 East Ave., Livermore, CA 94550
925-422-1587
Sun4@llnl.gov

Abstract Title:

Modelling Sorption and Diffusion for Lifetime Assessment: Surrogate Models of Langmuir Sorption Kinetics Coupled with Vapour Diffusion in Polymers

Abstract description (500 words or less):
The sorption and diffusion of vapors in materials are important to the predictions of lifetime and compatibility of polymeric materials in multi-material systems as the vapors may be incompatible with the materials. Here, we present a methodology for approximating reaction kinetics coupled with vapor diffusion in polymer materials. The ordinary differential equations representing reaction kinetics is solved in concentration and parameter space and the corresponding concentration changes due to the reaction kinetics are statistically approximated by using computationally cheap surrogate models (e.g., algebraic polynomials). The polynomials replace the ODEs of reactions and are coupled with the diffusion equations. Since the polynomial presentation of the reaction term is obtained in a standard format prior to modeling reactive diffusion, the reaction operator can be coded as input data in the reactive transport code. Compared to conventional operator-splitting methods, the polynomial approximation (PA) of reaction kinetics offers better computational efficiency. Taking an example of Langmuir sorption kinetics, the advantage of the proposed method is demonstrated for vapor sorption and diffusion in polymeric materials. The computer code of reactive transport in polymer materials has been developed with the user's option of ODE solution or surrogate approximation of Langmuir adsorption kinetics. This talk will cover model development, solution methods, system simulation and calibration.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

Author name(s): Mihail Bora, Vincenzo Lordi, Joel B. Varley

Job title: Scientist

Affiliation: Lawrence Livermore National Laboratory

Contact information including physical address, phone and email: 7000 East Ave., Livermore, CA 94501, (925) 324-2042, bora1@llnl.gov

Spectroscopic measurement of water in polymeric materials

Abstract description

We investigate development of a non-invasive optical detection technique to determine moisture content in polymer materials based on absorption bands of water at 1.4, 1.9 and 2.8 μm. Experimental measurements are performed in transmission for transparent samples and transflection (double pass transmission and reflection) for reflective samples. Spectroscopic data is calibrated with independent assessment of water concentration through Karl-Fischer titration. The method is employed to assess diffusion profile of water in glass-polymer-glass laminates and to estimate polymer transport properties of saturation and diffusion coefficient.

Prepared by LLNL under Contract DE-AC52-07NA27344.

Tuesday Morning: Mechanical Changes Related to Exposure

Author name(s): Lipiin Sung, Ching-Hsuan Chang, and Po-Jui Su
Job title: Research Physicist

Affiliation: Polymer Materials Group, Engineering Laboratory, NIST

Contact information including physical address, phone and email:
Lipiin Sung
100 Bureau Dr. Stop 8615,
Gaithersburg, MD 20899-8615
(301)975-6737
lipiin@nist.gov

Abstract Title:

Characterizing surface damage of nano-filled polymer coatings under accelerated ultraviolet degradation

Abstract description

It is known that surface is the first point of attack in any degradation process initiated by ultraviolet (UV) radiation, temperature, and/or moisture. Surface damage caused by environmental can lead to the changes in optical, morphological, and mechanical properties, pathways for ingress of moisture and corrosive agents, and/or cracks as stress concentrators. The objective of this study is to investigate how the controlling environmental factors (such as temperature and humidity) affect the photodegration process and the relationships between the resulting surface mechanical property and surface morphology in a nanocoating. An acrylic polymer matrix containing nano-titanium dioxide (nanoTiO_2) system was selected. Effects of nanoTiO_2 crystal structures on dispersion and surface properties were also investigated. Film specimens were exposed using NIST SPHERE at different temperature and humidity conditions. Surface morphology and mechanical properties were monitored at sequential intervals in various exposure conditions. Laser scanning confocal microscopy was employed for surface morphology and RMS roughness measurements, and nanoindentation for surface modulus and hardness. UV degradation rate in different relative humidity conditions can be estimated from the changes in the surface properties. Correlations between surface mechanical properties and surface roughness were found, but different correlation functions were observed for coatings containing different nanoTiO_2 crystal structures.

Author name(s): James P. Lewicki*, Cynthia T. Alviso, Sarah, C. Chinn, Eric B. Duoss, Stephen J. Harley, Amitesh Maiti, Ward Small, Todd Weisgraber, Thomas S. Wilson, Jennifer N. Rodriguez and Robert S. Maxwell

Job title: Staff Scientist

Affiliation: Materials Science Division, Lawrence Livermore Natl. Laboratory

Contact information including physical address, phone and email: James P. Lewicki, 7000 East Ave. L-231, Livermore, CA 94550 lewicki1@llnl.gov tel. 92596065100

Towards a predictive, multi-scale aging model for complex silicone architectures - Insights into structural control and response to environmental stressors

Lawrence Livermore National Laboratory develops and utilizes silicone formulations and foams for a variety of service applications. We manufacture these components using traditional blowing or sacrificial pore forming processes to yield ‘stochastic foams’ with a range of properties. In addition, depending on the application, a wide variety of fillers have been added to modify mechanical and chemical properties. However we are also pursing new additive manufacturing methods for the formation of low density silicone materials with *3D micro-architected structures*. A number of applications require that these formulations remain viable in relatively harsh environments for many years. In order to better predict lifetime performance and failure of these complex materials, we are using a range of experimental and modeling techniques to investigate changes in network, interfacial and microstructure in siloxane elastomers and their correlations with engineering performance. Advanced Multiple Quantum Nuclear magnetic resonance (MQ-NMR), for example, has shown excellent promise for providing insight into changes in crosslink density and motional dynamics. And at much larger size scales, X-ray Micro-CT imaging provides data on the effects of the service environment on material microstructure. Through multi-scale modeling we are beginning to link chemical & network level aging /degradation processes with meso- to micro structural changes, to predict macroscale response in silicone architectures.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

Author name(s):
Jennifer David, Robert Hayes

Job title:
Senior Scientist Coatings Technology, Senior Manager Coatings Technology

Affiliation:
Momentive Performance Materials

Contact information including physical address, phone and email:
260 Hudson River Road
Waterford, NY 12188
Jennifer.David@momentive.com (518-233-3509)
Rob.Hayes@momentive.com (518-233-3591)

Abstract Title:

A Study of Nano-mechanical Test Methods as Predictive Tools for Coating Changes in Weathering

Abstract description (500 words or less):

Service life prediction models that follow the chemical degradation of species within a coating to predict delamination failure are well known and used extensively. For prediction of coating failure by cracking, however, similar types of models have yet to be developed. Although measurements of coating cracking by visual inspection of the coating surface can provide semi-quantitative comparative information on coating performance, the data obtained are not sufficient for building predictive models. This work tracks the fundamental physical properties of several coatings (modulus, hardness, storage modulus, loss modulus) as a function of accelerated weathering through the use of nano-mechanical measurement techniques. Several of these measurements highlight differences between coatings before such differences are observed by traditional methods of visual inspection. Identifying measures that are quantitative and predictive of cracking failure is the first step towards the goal of a service life prediction model for cracking.

Author name(s): Ingo Alig*, Dirk Lellinger, Frank Malz, Marc Reinhardt, Torsten Bitsch, Kai Kühne, Thomas Kroth, and Marc Wallmichrath

Affiliation: Division Plastics, Fraunhofer Institute for Structural Durability and System Reliability LBF

Contact information including physical address, phone and email:
Fraunhofer LBF, Division Plastics,
Schlossgartenstr. 6, 64289 Darmstadt, Germany
Phone: +49 6151 705-8659, Fax: +49 6151 705-8601
Ingo.Alig@lbf.fraunhofer.de, www.lbf.fraunhofer.de

Combination of material characterization and cyclic fatigue testing for investigation of elastomer aging

Abstract description (500 words or less):
Degree and type of crosslinks are well known to determine physical properties of elastomers. Both, chemical crosslinks due to vulcanization and physical crosslinks (entanglements, polymer-filler and/or filler-filler interaction) have to be taken into consideration.
In this study cyclic fatigue testing and elastomer characterization were combined to study changes in network structure and material properties of elastomers with and without filler by thermal aging. As model materials natural rubber (NR) with and without carbon black (CB) and containing a typical additive package were studied. The NR compounds were aged at different temperatures in air or under nitrogen atmosphere.
The mean times to failure (MTTF) were determined from strain and stress controlled fatigue tests on specimen after different times of aging. For strain controlled fatigue testing it was found that the MTTF decreases with aging time. However, significant differences in the stress-number (S/N) curves were found between strain and stress controlled fatigue tests.
Changes of mechanical properties and crosslink density were studied during and after thermal aging by continuous or discontinuous detection. For this purpose tensile tests, stress relaxation experiments, dynamic mechanical analysis (DMA), measurements of compression setting, swelling measurements and solid-state NMR were performed. In addition, chemical analysis on extracts (MALDI-TOF, NMR, IR) and pyrolysis-GC were performed. Chemical analytics of extracts and after pyrolysis were used to study degradation of additives. Combining different characterization methods allowed differentiating between aerobe and anaerobe aging mechanisms in rubbers such as thermo-oxidative degradation or different cross-linking reactions. The changes in crosslink densities were related to the interplay of breakdown of existing crosslinks and the formation of new crosslinks. The higher the aging temperature, the faster are both reactions. Chemical analysis of extracted organic components and by pyrolysis-GC allows discussing the property changes in relation to chemical reactions. The molar mass of the network chains derived from DMA, tensile tests, solid state NMR and swelling experiment show the same trend for all methods with aging time: an initial increase of the network density is followed by a decrease at longer aging. The same trend was found for MTTF in stress controlled fatigue tests: an increase of MTTF at short aging times followed by a decrease at longer times. Thermal aging under nitrogen shows similar results. The results can be used for improvement of aging models for elastomers. From comparison with fatigue tests, customized test procedures can be derived.

Unusual Aging Behaviour of Elastomers in High Temperature Environments

Erica M. Redline [1], Mathias Celina[1], Toshifumi Sugama[2], and Tatiana Pyatina[2]
[1]Sandia National Laboratories, Albuquerque, NM, USA
[2]Brookhaven National Laboratory, Upton, NY, USA

The movement to reduce reliance on fossil-based fuels has garnered much attention on renewable energy sources, including geothermal. Geothermal technology requires the use of high temperature wells, often around 150°C or more, in addition to high pressures and exposure to harsh chemical environments. While evaluating elastomers in simulated geothermal environments at elevated temperature and pressure, an unexpected trend was observed in the aging of EPDM and FEPM materials. Namely, the polymers experienced degradation and disintegration in an oxidative thermal cycle environment, but maintained mechanical performance and shape during oxidative thermal cycling in the presence of steam. This trend was further explored by investigating the oxidative and hydrolytic degradation of EPDM and FEPM and how these processes interact to impact thermo-mechanical stability of the polymers.

Author name(s): Masayuki Ito
Job title: Dr.
Affiliation: Waseda University
Contact information
Address: 227-4 nakamachi, Kodaira Tokyo, 187-0042 Japan
Phone: +81-42-346-3467
e-mail: masayuki@kurenai.waseda.jp

Degradation of ethylene-propylene-diene elastomer by heat and/or radiation

Abstract:

Nine kinds of ethylene-propylene-diene elastomer (EPDM) that has different compounding formula were used in this experiment.

The samples were thermally aged at 125℃ and 140℃ to investigate thermal resistant properties of the samples ; the maximum period of time was 384 hours.

For the purpose of investigating the effect of temperature on radiation induced degradation, Co-60 γ ray was irradiated to EPDM at constant temperature and constant dose rate of 5.0 kGy/h. Temperature ranged from room temperature to 150℃. The maximum dose was 1.8 MGy.

Tensile properties were measured at room temperature after aging by heat and/ or irradiation.

Result was summarized as follows.

1. All of the base polymer used in this experiment was Nodel 1070 (du pont); the degradation behavior caused by heat and/or radiation, however, largely depended on the compounding formula of the samples.
2. The correlativity between heat resistant property and radiation durability was not observed among nine samples when we compared the result obtained by the measurement of ultimate elongation of thermally aged samples at 140^{o}C and that of radiation aged at 70^{o}C.
3. Effect of temperature below 90^{o}C was not observed on decrease in ultimate elongation along with dose.
4. The rate of decrease in ultimate elongation by irradiation increased with increasing temperatures above 90^{o}C; on the other hand the temperature dependence of the changes in tensile strength was relatively small.
5. The ratio of scission and crosslinking occurred during irradiation was analyzed by using “modulus-ultimate elongation profile”.

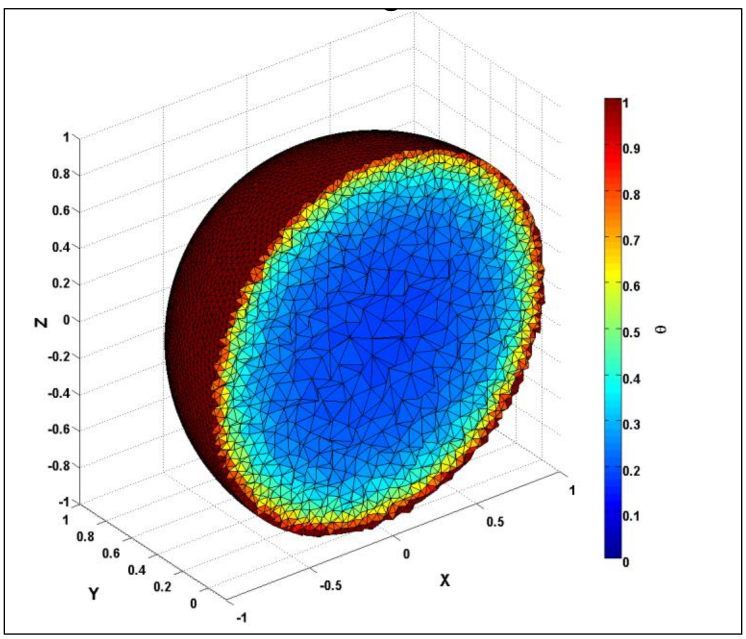
Wednesday Morning: Chemical Changes Related to Exposure

An overview of DLO modelling and relevance for polymer aging predictions

Mat Celina, Adam Quintana, and Nick Giron
Organic Materials Science Dept.
Sandia National Laboratory, Albuquerque, New Mexico, 87185
mccelin@sandia.gov, 1-505-8453551

Abstract:

Environmental polymer aging and accelerated aging studies, as well as material degradation models depend on spatially dependent oxygen availability in the material. It is well known that as a consequence of intrinsic oxidation rates and slow diffusion, polymer aging often proceeds in a heterogeneous manner. This presentation will provide an overview for the experimental approaches and material parameters that are needed, including a brief perspective on oxidation, permeation rates and diffusivity, and avenues for appropriate material characterization. The discussion of DLO phenomena will focus on the mechanistic description and mathematical approaches for DLO simulations, which range from 1D differential equations that can be numerically solved, to solutions for 3D FEM models. Examples will demonstrate how DLO modelling enables a perspective on spatially resolved material aging phenomena, for specific geometries and multi-material configurations in many applications.



3D representation of reactive diffusion phenomena resulting in material surface degradation

Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000. Unlimited release under SAND2015-xxxx A.

To be presented at the conference "Service Lifetime Prediction of Polymeric Materials: Over the Horizon" March 20th 2016, Santa Fe, NM, USA

Author name(s): Jan C. WachF, Beate Röder
Job title: Scientific Assistant, University Professor
Affiliation: Humboldt-Universität zu Berlin
Contact information including physical address, phone and email:
Humboldt-Universität zu Berlin
Inst. für Physik, Photobiophysik
Newtonstr. 15
12489 Berlin, Germany
jan.schlothauer@physik.hu-berlin.de (+49 30 2093 7893)
beate.roeder@physik.hu-berlin.de (+49 30 2093 7625)

Abstract Title:

Prospects of 2D-luminescence spectroscopy for aging investigations of the embedding EVA polymer in PV modules: Revealing DLO conditions.

Abstract description:

The characterization of the aging of the encapsulation polymer in PV modules is an especially challenging task. On the one hand it is important, to conduct aging experiments on complete modules, because the composition of different materials in the PV module affects the degradation processes. On the other hand conventional characterization methods cannot be applied for practical and economic reasons since samples of the embedding material must be taken destroying the PV module.

The ability to follow and characterize degradation processes of different materials in the intact PV module is a fundamental prerequisite for degradation investigations and lifetime prediction. This needs the development of suitable characterization methods. Luminescence as a non-invasive cheap method was used to investigate the most common embedding material, ethylene vinyl acetate (EVA) in intact PV modules. The correlation of the luminescence pattern to aging has been investigated and will be discussed in detail.

Extensive investigations of commercial PV modules show that specific luminescence pattern occur upon aging which are specific for the aging conditions. It is found, that UV aging and outdoor weathering show similar patterns, while exclusive thermal aging results in a fundamentally different luminescence pattern.

We evaluate the correlation of photoluminescence and different destructive methods. EVA samples were extracted systematically at different locations from two different sets of modules. Differential scanning calorimetry (DSC) as well as a dynamic mechanical analysis (DMA) was conducted on the extracted samples.

A correlation of the photoluminescence intensity and parameters obtained from DSC as well as DMA is found. The results point to the fact that location-dependent differences in the crosslinking develop upon aging. Furthermore, the spatial profiles are in accordance to kinetics of diffusion limited oxidation processes.

This work provides the first comprehensive experimental evidence of DLO in the embedding material in PV modules. Apparently DLO kinetics of 1st order match the aging behavior of only-thermally aged PV modules, while in UV aged and outdoor weathered modules more complex degradation kinetics are observed.

The result imply that photoluminescence can be used to assess DLO-related inhomogeneous material aging. Prospective applications for the investigation of material aging of such complex products arise, as this will greatly help to improve drawing a connection between accelerated aging and outdoor weathering.

Author name(s): Li-Ju Lillian Chen

Job title: Research scientist

Affiliation: Underwriters Laboratories

Contact information including physical address, phone and email:
Address: 333 Pfingsten Rd, Northbrook, IL, 60062-2096 USA
Email: Lillian.Chen@ul.com
Phone: +886-2896-7790 ext. 62589

Investigation of PDSC applicability to evaluate polymer thermo-oxidative stability

Abstract description (500 words or less):

Oxidation Onset Temperature (OOT) and Oxidation Induction Time (OIT) are two relative measures of oxidative stability of polymeric materials conducted by Pressure Differential Scanning Calorimeter (PDSC). Thus, OOT and OIT values may be compared from one material to another or to a reference material to obtain relative oxidation stability information. Temperature and oxygen pressure are two control factors for PDSC tests. Therefore, understanding the influences of temperatures and oxygen pressures on polymer thermo-oxidative stability will benefit the development of proper PDSC test programs.

In this investigation, a total of thirteen polymers were used as test samples, including PP, PVC, FEP, EVA, ECTFE, PA12, PBT, PVDF, PS, ETFE, PC, PMMA and ABS. Conventional TGA test methods were applied to all polymers at a heating rate of 10K/min from 50 to 800°C in nitrogen and dry air environments. The differences of the onset decomposition temperatures and maximum weight loss rates measured between nitrogen and dry air environments were calculated in three oxygen-oxidative degree ranks: low, medium, and high. Eight polymers ranked high in oxygen-sensitivity, including PP, EVA, ETFE, ECTFE, PS, PA12, PC, and PMMA, were conducted OOT tests by referring to the ASTM E2009 method A, to determine the appropriate isothermal temperatures for OIT tests.

Each polymer, including PP, EVA, PS, PC, PA12, and PMMA, was conducted an OIT test at different isothermal temperatures and oxygen pressures. Experimental results demonstrated that both temperature and oxygen concentration influenced polymer thermal oxidative degradation. When the polymer was conducted at higher isothermal temperatures, OIT values affected by oxygen pressures were small; but at lower temperatures, OIT values decreased significantly with increased oxygen pressures. This phenomenon was found on PP, EVA, and PMMA.

Polymer initiated radicals (R*) adjacent allylic bond or atoms with long pair electrons were ratiocinated to be stabilized by radical resonance. These radicals had lower radical energy due to the resonance stabilization. The stabilized radicals slowed down the oxidation resulting in low enthalpy changes which could not be detected by DSC. This phenomenon was found on PS, PC and PA12.

Author name(s): James E. Pickett

Job title: Principal

Affiliation: James Pickett Consulting

Contact information including physical address, phone and email: 4331 Buckingham Drive, Schenectady, NY 12304. e-mail: dr.james.pickett@gmail.com. Cell: 518-322-6187

Forbidden Chemistry: Non-Free Radical Oxidation Mechanisms

Abstract description (500 words or less):

The free radical chain autoxidation mechanism is very successful in describing oxidation of aliphatic materials, but other mechanisms are possible in some cases. The literature shows that oxygen can add thermally to some electron-rich compounds to produce singlet oxygen-like products that clearly are not the result of free radical autoxidation. We have found similar results for triaryloxazoles, which slowly but smoothly give products apparently arising from a 4 + 2 cycloaddition with oxygen in the dark at 150 °C, even though this is a formally spin-forbidden process. Triphenyloxazole gives high yields of benzonitrile and benzoic anhydride with kinetics that are first order in oxygen. Oxygen also seems to abstract benzylic hydrogens from poly(2,6-dimethyl-1,4-phenylene oxide) and related model compounds both thermally and photochemically by mechanisms that do not appear to be classic free radical autoxidation. Direct abstraction of a hydrogen atom by molecular oxygen generally is considered to be unfavorable, but the kinetics of the thermal reaction are linear from the start and first order in oxygen, indicating that oxygen is directly involved in the rate determining step. The photochemical oxidation can be intercepted by hydrogen-donating solvents to give products difficult to explain by a free radical mechanism. These types of reactions are important because they can define an ultimate limit to the oxidative stability and useful the lifetime of some materials.

Author name(s): Michael W. Blair*, Eric M. Weis, Mathew J. Herman, Jennie Keller, Joseph A. Torres, Stephanie L. Edwards, Nikolaus L. Cordes, Jude M. Oka, Tristan Karns, Austin D. Brown, Tim A. Stone, Paul H. Smith, D. Kirk Veirs

*Corresponding Author

Job title: Scientist 3

Affiliation: Los Alamos National Laboratory

Contact information including physical address, phone and email:
Los Alamos National Laboratory
P.O. Box 1663
MST-7, MS E549
Los Alamos, NM 87545

Lifetime Prediction of O-rings Used in the SAVY-4000 Actinide Storage Vessel

Abstract description (500 words or less):

An actinide storage container used throughout the DOE complex, designated SAVY-4000, uses a Viton-based O-ring to form a seal between the lid and body, and this O-ring is the lifetime-limiting component of the unit. Preliminary studies have established that the SAVY-4000 O-rings are viable for at least 5 years, but there is a pressing need to extend this service lifetime to 40 years or longer. We have undertaken accelerated aging studies, for both thermal stress and radiation exposure, in order to predict the service lifetime of the Viton-based O-rings.

The lifetime prediction relies on changes in mechanical properties of the O-rings, such as compression set, during accelerated aging studies. However, an important component of the program is surveillance of O-rings from service containers, and these O-rings are not expected to display changes in mechanical properties for some time. In order to anticipate the expected changes in the surveillance data, we are measuring spectroscopic properties of O-rings from the accelerated aging studies. These spectroscopic properties will be correlated with changes in mechanical properties in an attempt to provide a more sensitive predictor of O-ring performance that can be detected at an earlier stage of the surveillance program, thereby enhancing the service lifetime prediction. The presentation gives our results to date along with our best understanding of the O-ring service lifetime.

Evaluation of the time-transformation function from a round robin weathering test of various back-sheets for PV-modules with different ultra-violet radiation sources and sample temperatures

Michael Koehl
Fraunhofer Institute for Solar Energy Systems (ISE), Heidenhofstrasse 2, 79110 Freiburg, Germany
Michael.koehl@ise.fraunhofer.de, Phone +49-761-4578-5124

Summary:
Fraunhofer ISE organised an inter-laboratory comparison of testing different back-sheets with different UV-light sources in various test laboratories using different UV-sources. The interaction of the UV-radiation with the polymers used in PV-modules is main subject of this round robin. Laminates were produced by using solar glass (130mm * 200mm) and a respective EVA encapsulant combined with 7 different back-sheets. The sample was exposed in a sample holder equipped with a couple of different filters in order to investigate roughly the spectral sensitivity by means of 3 edge filters and the intensity impact by two grating filters. The sample temperature was measured by thermo-couples.
The degradation was followed by spectral reflectance and transmittance measurements and calculation of the yellowness-index. Clear differences in the degradation behaviour of the different products were found.

Purpose of the work:
Durability testing of materials exposed to natural weathering requires testing of the UV stability, especially for polymeric materials. The spectral distribution of the radiation source is very important since the samples show a very individual spectral sensitivity for the radiation offered. Less than 6% of the intensity of solar radiation comes in the UV range. In case of an increase of the intensity of the light source for accelerating the UV-test the overheating of the samples would have to be prevented more strictly and the temperature of the samples have to be measured in order to avoid misinterpretation of the test results.

Approach:
Fraunhofer ISE organised an inter-laboratory comparison of testing different back-sheets with different UV-light sources in various test laboratories using different UV-sources. The interaction of the UV-radiation with the polymers used in PV-modules is main subject of this round robin. Laminates were produced by using solar glass (130mm * 200mm) and a respective EVA encapsulant combined with 7 different back-sheets. One special laminate was produced with a thermoplastic silicone and an appropriate back-sheet for comparison. Besides the laminates single back-sheet samples were exposed with the side dedicated to adhere to the encapsulant in addition to the laminates that had been exposed via the glass-side and the unprotected back-side, both.

Results and conclusion:
Some samples did not change after a UV-dose of 120 kWh/m², while other showed heavy discoloration (figure 2). Figure 2 also shows the effect of the edge filters. No discoloration was found behind the 360nm and 400nm filters. The shading by the intensity filters reduced the discoloration clearly.

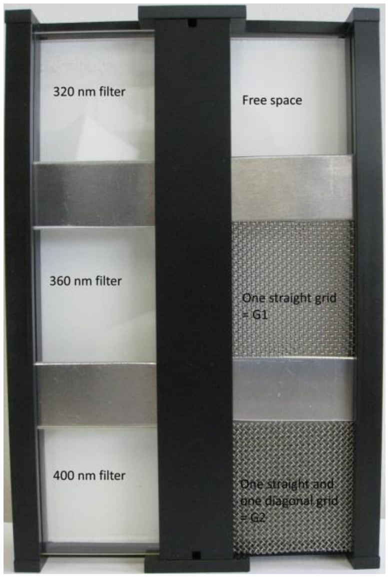
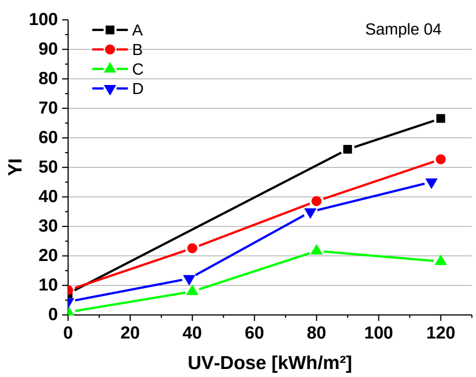


Figure 1: Sample holder equipped with edge filters (left side) and intensity filters (right side)

Figure 2: Example of yellowing of a back-sheet below different filters after a UV-irradiation of 120 kWh/m²

The sample was exposed in a sample holder equipped with a couple of different filters (50mm*50mm each) in order to investigate roughly the spectral sensitivity by means of 3 edge filters and the intensity impact by two grating filters (see figure 1 and figure 2). The sample temperature was measured by thermo-couples and the plan is to achieve different sample temperatures in order to evaluate the temperature dependence of the photo-degradation.

The degradation was followed by spectral reflectance and transmittance measurements and calculation of the yellowness-index. Clear differences in the degradation behaviour of the different products were found.



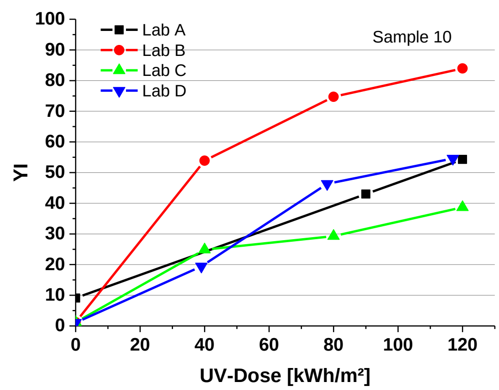


Figure 3: Example of the changes of the yellowness index of a two back-sheets in different test labs up to a UV-dose of 120 kWh/m²

Poster Session.

Author name(s):
Donghui Li*, Emily Morris †, Marc Sahlani‡, Noah Tietsort*, Allen Lim §, Laura Bruckman*, Roger French* ‡
Job title:
Graduate assistant, Undergraduate, Undergraduate, Undergraduate, Research Assistant Professor, Professor

Affiliation:
*Department of Material Science and Engineering, Case Western Reserve University, OH, 44106
†Department of Chemistry, Case Western Reserve University, OH, 44106
‡Department of Macromolecular Science and Engineering, Case Western Reserve University, OH, 44106
§Department of Mathematics, Applied Mathematics and Statistics, Case Western Reserve University, OH, 44106

Contact information including physical address, phone and email:
Roger H. French, Ph.D
F. Alex Nason Professor
216 3683655
roger.french@case.edu
538 White Building, Department of Material Science, Case Western Reserve University, OH, 44106-7204

Abstract Title:

Lifetime and Degradation Science Studies of Exterior Coating**s**

Abstract description:
Driven by the social and political awareness, coupled with the strict environmental legislation, waterborne coating plays an important role in the global coating market. The class of resin known as acrylics is of importance to the waterborne exterior coating application. Although waterborne acrylic coatings have better durability than other types of polymeric coating, these coatings degrade over long period of outdoor exposure time. Moreover, the additives, such as coalescent, extenders, surfactants, thickeners and dispersants have been found to have effect on the durability properties and life time of coatings.

The first step of this research was to investigate the amount of titanium dioxide (TiO_2) pigments on the durability and lifetime of polymeric exterior waterborne coatings. Waterborne acrylic coatings with different amount of TiO_2 were exposed in outdoor exposure and accelerated exposures in lab. And the accelerated exposures are artificially-controlled conditions of temperature, humidity and solar irradiance based on ASTM G154 and G155. The physical and chemical degradation of coating were monitored by Fourier transform infrared spectroscopy (FTIR-ATR), UV-Vis spectroscopy, colorimetry and glossmetry to evaluate the degradation of coatings. These data were collected stepwise as the degradation occurring during long term exposure. Data were acquired and exploratory data analysis and semi-gSEM model constructed to predict the degradation mechanisms and build up a novel efficient accelerated aging test to specific waterborne acrylic coatings. It was observed that the amount of TiO_2 strongly affected the durability of waterborne acrylic coating system. Further studies on the effect of the other type of additives in waterborne coatings, such as surfactant and coalescent etc., are underway using same exposure with additional accelerated outdoor exposure.

Author name(s): Tony Misovski & Mark Nichols

Job title: Research Engineer

Affiliation: Ford Motor Company

Contact information including physical address, phone and email:

MD 3182/RIC Building
PO Box 2053
Dearborn, MI 48121
tmisovsk@ford.com
313-337-3195

Abstract Title:

Visualization and Quantification of Impact Events on Automotive Paint Systems

Abstract description:

The damage induced on automotive paint systems by high-speed projectiles was quantified using high-speed photography and image analysis. The projectile's shape, in particular the angle of the projectile's face in relation to the angle of the painted panel's surface, played a large role in the type and extent of damage induced in the paint. Damage types included surface scuffing, gouging, skiving of paint layers, and delamination to various depths in the paint system. Higher impact velocities led to greater paint system damage. Different paint process techniques (traditional three-coat two bake vs. compact three-coat one bake) also led to differences in the mode of failure. The different mechanisms for absorbing energy during a chip event have been qualitatively determined and analyzed for different test geometries and conditions.

Author name(s): **Wang Eun Lee**

Job title: **Senior Researcher**

Affiliation: **Reliability Assessment Center for Chemical Materials, Korea Research Institute of Chemical Technology (KRICT)**

Contact information including physical address, phone and email:
141 Gajeong-ro, Yuseong-gu, Daejeon 305-600, Korea
E-mail : welee@krict.re.kr
Photo: +82) 42-860-7701, Fax: +82) 42-860-7704

Abstract Title:

Accelerated fluorescence photobleaching of conjugated polymer film under wet state

Abstract description:

Accelerated photodegradation methods of conjugated polymers are great interest in academy as well as real industry. Here, we present an accelerated photo-degradation phenomena of a polymer under wet state by various solvents. Films of a microporous conjugated polymer were studied and their photo-degradation rate compared. The polymer film is rapidly swollen in polar and non-polar solvents by large fractional free volume. The evaluated degradation rates of the polymer film in various solvents were, in turn, compared to the degradation rates in air condition. Interestingly, the film showed accelerated photobleaching phenomena at wet (swollen) state in polar solvents such as methanol. However, the photobleaching rate was retarded in non-polar solvents such as hexane. Photobleaching rate is proportional to the polarity of solvents. This means that a highly stable, long-lived quenching site such as polymer—solvent charge transfer complex was formed instead of polymer - oxygen complex under intensive UV light. This poster presentation will discuss the unique solvent-mediated rapid photobleaching and its recovery system in detail.

Jennifer N. Rodriguez, James P. Lewicki, Cynthia T. Alviso, Sarah, C. Chinn, Thomas S. Wilson & Robert S. Maxwell

Postdoctoral Researcher

Materials Sciences Division, Lawrence Livermore National Laboratory

7000 East Avenue, L-231, Livermore, CA 94550. rodriguez96@llnl.gov 925 724 9106.

Abstract Title:

NMR Methodologies for the detection and quantification of nano-structural defects in Silicon Networks

Abstract description (500 words or less):

Polysiloxanes are one of the most utilized non-carbon backboned polymeric materials today. However, polysiloxane elastomers require chemical & physical modification in order to form materials that are useful in commercial applications. This modification results in a final polymeric structure that is complex, hierarchical and often poorly defined. The current understanding of network structure in these materials - in relation to service lifetime, performance and degradation, is limited. Furthermore, the chemical origins of the aging and degradation processes occur at molar levels, which challenge the detection limits of many conventional analysis techniques. Here we present and discuss a direct and sensitive means of detecting and quantifying network defects and other trace chemical signatures of degradation in siloxane based materials by means of solution state Nuclear Magnetic Resonance (NMR). We have designed model siloxane based networks with controlled levels of 'defect' sites, meant to simulate the aging process that were tagged with reactive organo-fluorines, which can be readily detected and quantified via ^{19}F NMR. We also discuss the application of this method as a tool to measure the degradation of commercial engineering polysiloxane materials

This work was supported by Lawrence Livermore National Laboratory under the auspices of the U.S. Department of Energy under Contract DE-AC52-07NA27344, IM Release No: LLNL-ABST-XXXXXX.

Comparison of TGA Methods to Determine Decomposition Kinetic Parameters

L. Judovits and E. Kowal
Arkema
900 First Avenue
King of Prussia, PA 19406
larry.judovits@arkema.com, elizabeth.kowal@arkema.com

A service life is commonly used to estimate how long a product will last. The UL Standard for Safety for Polymeric Materials – Long Term Property Evaluations, UL 746B is a testing procedure that employs lifetime calculation. It assigns a relative temperature index (RTI), which represents an upper use temperature where a material withstands degradation that would render it unfit for service over its lifetime. To determine an RTI, samples with a control material are subjected to oven aging at a variety of temperatures over various time periods and their loss of a particular physical property is monitored. The property loss versus time is determined at the 50% reduction of that property and then a lifetime is determined based on an Arrhenius plot extrapolation.

Modifications to a material can trigger the need to redo the RTI determination. The cost of an RTI is expensive and may take multiple years. Not only the oven time is an issue but oven availability as well as the time needed to make sample forms for testing. Therefore, a fast track methodology is needed when slight modifications are made to an existing formulation rather than subjecting the material once again to a full testing program. The effort so far has centered on a one-point physical reduction test by conventional oven aging accompanied with an activation energy determined from thermogravimetric analysis (TGA) kinetics (for additional confirmation). Modulated TGA (MTGA) has the capability to also determine a decomposition activation energy but with a faster determination. This work will compare kinetic constants for poly(methyl methacrylate-co-ethyl acrylate) determined from standard TGA techniques and MTGA.

Author name(s): Chris White[1], Eric Byrd[1], William Thomas[2], Cyril Clerici[1], and Larry Kaetzel[1]

Job title: Research Chemist

Affiliation: NIST, Virginia Tech

Contact information including physical address, phone and email:

100 Bureau Drive
National Institute of Standards and Technology
Gaithersburg, MD 20816
(301) 975-6016
Christopher.white@nist.gov

Abstract title:

Predicting Field Panel Temperature

Abstract description:

This work presents the development of accurate model predictions for panel temperature of model coatings. The model predictions are favorably compared with experimentally obtained field data. The panel temperature model is an analytical solution of first order differential equation aggregated-capacity thermal model expressions. Predictions for both white and black panel temperature are presented. The development of these two models allows for accurate prediction of the actual sample temperature and sample moisture content.
.

Wednesday Evening: Radiation

Author name(s): Jamie A. Stull

Job title: Postdoctoral Fellow

Affiliation: Los Alamos National Laboratory

Contact information including physical address, phone and email:
2264 35th St. Apt. A
Los Alamos, NM 87544
(505) 695-8948
jamie.stull@lanl.gov

Abstract Title:

Informed Design of Aging Experiments via CW and Pulse EPR Spectroscopy

Abstract description (500 words or less):

Currently the majority of studies of thermolytic- and radiolytic-accelerated aging of polymers are based upon the *empirical* Arrhenius equation. To be valid, the mechanism of aging must not change during the test conditions (i.e. all temperatures or irradiation doses). However, currently, these accelerated aging test conditions are primarily determined by expert judgment and can only be evaluated for adherence to the relationship *at the end of the study*. This method often leads to wasted experimental time, effort and resources. Since free radical processes (crosslinking, chain scission) are responsible for the majority of aging for polymeric materials, we have used a combination of continuous wave (CW) and pulse electron paramagnetic resonance (EPR) spectroscopic techniques that excel in identification of unique radical species and their surrounding electronic environment. Our intent is to identify radicals involved in aging processes and determine the conditions under which a particular degradation pathway dominates. With this information, we can design aging experiments such that we avoid non-Arrhenius behavior and concentrate our efforts on those conditions that will produce useful information.

We have used CW EPR methods, in combination with spin trapping techniques, to monitor the presence of radicals produced during different aging conditions including irradiation (gamma and X-ray) and heat. Whilst spectra from CW EPR can typically be inhomogeneously broadened, pulsed EPR, including electron nuclear double resonance (ENDOR) spectroscopy excel in directly probing the nuclear transitions dependent on not only the atom with the unpaired electron, but also ligands with a nuclear spin (I) ≥ ½ (i.e. ^{14}N, ^{1}H, ^{13}C). These measurements probe the strength of the covalency between the bonding interactions. The information gained is similar to that of powerful multinuclear NMR measurements; however, typically NMR spectroscopy can be very difficult to use on samples that contain paramagnetic species. We have tested a wide variety of polymeric materials for which aging, lifetime prediction or laboratory exposures are of interest; these include polyolefins, poly(ester urethane)s and cyanate esters.

Extreme aging conditions can lead to a variety of degradation mechanisms. Understanding how these mechanisms differ between accelerated aging and field exposures is imperative to correctly and

accurately predict material lifetimes and allow us to determine whether the polymer degradation mechanisms are changing within the aging studies. These would constitute pivotal insights that would lead to the design of more successful accelerated aging programs.

Material Property changes following neutron and Gamma irradiation of Carborane-co-PDMS composites.

Robert Old, Peter Beavis, Mathew Robinson.

Highly specialised polymers have applications in nuclear, medical and aerospace industries as shielding materials against ionising radiation. A number of carborane-*co*-PDMS polymers were synthesised in-house using a novel route then blended with PDMS to give solid elastomeric networks; these materials were then exposed to ionising radiation using the Gamma Irradiation Facility and Annular Core Research Reactor facilities (SNL).
The extent of material property changes which occur are dependent upon the adsorbed dose of radiation. For samples irradiated in the ACRR, the presence of elements with a large neutron capture cross section will increase the effective adsorbed dose due to additional emitted gamma radiation. The changes in material properties have been studied using a range of techniques to probe both the thermal and mechanical responses. Under these harsh conditions of high flux radiation it is know that additional thermally accelerated chemical reactions take place which would not necessarily be observed through life; therefore these can be considered as worst case ageing scenarios. Material property changes expected throughout life under more moderate irradiation conditions will be discussed.

Robert Old
Materials Scientist
AWE
Direct: 0118 9827133
Email: rob.old@awe.co.uk
AWE, Aldermaston, Reading, RG7 4PR

Thursday Morning: Modelling and Prediction

Author name(s):
K. Scott

Job title:
Mathematical Modeller

Affiliation:
AWE

Contact information including physical address, phone and email:
Telephone: +44 (0) 118 9850867
Email: Kathy.Scott@AWE.co.uk
Address: AWE, Aldermaston, Reading, UK. RG7 4PR

Abstract Title:

Selecting a statistical method for validation of life prediction models

Abstract description (500 words or less):
Validation is a crucial part of the model development process. A number of statistical techniques are available with which to quantitatively assess the data derived from model validation experiments; these methods all have advantages and disadvantages but the suitability of the technique will depend upon the validation problem being considered. One important characteristic of the data obtained from the life prediction validation experiments at AWE is the multivariate nature of the data; the experimental output will be recorded as a function of time. As such, any chosen validation method must be capable of assessing the global predictive capability of the model over the timeframe of interest. A range of validation methods were assessed, including classical hypothesis testing, Bayesian hypothesis testing and the area metric. The down selected methodology for validation of life prediction models, based upon the area metric, is presented along with examples of applications to both illustrative test cases and life prediction data.

Author name(s): Adam L. Pintar[1], Christopher White[2], and Donald Hunston[2]

Job title: Mathematical Statistician[1] and [2] Engineering Laboratory

Affiliation: National Institute of Standards and Technology

Contact information including physical address, phone and email:
100 Bureau Drive
Mail Stop 8980
Gaithersburg MD, 20899
Phone: 301-975-4554
Email: adam.pintar@nist.gov

Abstract Title:

Predicting Field Degradation of Sealants Using Accelerated Tests from the NIST Solar Sphere.

Abstract description
Field testing of sealants, used for instance in construction, is a slow process due primarily to the good durability of these materials. The tempo of the development cycle for such materials could be greatly increased by accelerating their degradation in laboratory conditions and then translating that degradation to a field prediction. Efforts to this end have been, and continue to be, explored at the National Institute of Standards and Technology (NIST) as part of the sealant consortium. The results so far are mixed, but the final goal of accurate field predictions has yet to become reality. In this presentation, efforts to date as well as future plans will be described. Efforts to date include empirical modeling of accelerated degradation data from the NIST solar sphere as well as an initial approach to translating predictions from the empirical model to the field. They also include a process for creating maps of predicted field degradation throughout the contiguous United States. Future plans include adding complexity to the model used for converting predictions from the lab into the field so it better represents physical reality. For example, modeling the change in the cross-link density as a function of time/solar exposure can help relate constant, high intensity solar exposure over long time periods in the lab to lower level solar exposure over short time periods in the field.

Author name(s):
S. Tedds, P. Monks, K. Scott and P. Morrall

Job title:
Material Scientist

Affiliation:
AWE

Contact information including physical address, phone and email:
Telephone: **+44 (0) 118 9850409**
Email: Steven.Tedds@AWE.co.uk
Address: **AWE, Aldermaston, Reading, UK. RG7 4PR**

Abstract Title:

Validating laboratory-based models and scaling-up for service life prediction

Abstract description (500 words or less):
Computational models are under development to aid the lifetime prediction of individual materials within closed system environments. Examples include simple numerical models, based on empirical rate expressions, which provide good foundations. However in order to fully describe system chemistry, mathematical and mechanistic models are required for each individual material.

The computational model is built to describe long-term ageing/corrosion/degradation and therefore requires accurate knowledge of numerous properties and parameters. Laboratory-based experiments have been used to determine such values as model inputs. In order to have confidence in the use of computational models for life prediction applications, validation of the model is required. The model validation methodology adopted utilises a three stage approach, which tests the basic fundamental assumptions of the model to progressively validate the model from lab-based “ideal” experiments to “in-service” conditions.

Author name(s):
Elizabeth A. Glascoe, Stephen J. Harley, and Yunwei Sun

Job title:
Project leader in Material Aging and Compatibility, Deputy group leader in the energetic materials group

Affiliation:
Lawrence Livermore National Laboratory

Contact information including physical address, phone and email:
L282, 7000 East Ave., Livermore, CA 94550
925-424-5194
Glascoe2@llnl.gov

Abstract Title:

Predicting chemical compatibility and aging of materials in a system: a combined experimental and modeling approach

Abstract description (500 words or less):
Predicting the aging and compatibility of materials in a system or sub-system is important to establishing the lifetimes and viability of current assembly and screening new materials for future designs. In addition to traditional screening methods and analytical tools for investigating material compatibility and aging, LLNL is developing a novel tool to predict the compatibility using reactive transport modeling. The challenge with multi-material assemblies is that the degradation products of one material may initiate a chain-reaction that could not be simulated with binary combinations of materials. Experiments on multi-material assemblies are critical to establishing compatibility on a system level. However, it is often difficult to establish the problem material or materials because of the complexity of the system. We are developing a reactive transport modeling capability in order to address these kinds of issues. Our model includes (1) a triple-mode sorption model that includes absorption, adsorption, and pooling of species, (2) molecular diffusion, and (3) chemical reaction kinetics. Using a 1D or 3D mesh we can simultaneously simulate the transport and chemical reactions of mobile species through polymeric and organic materials. This talk will discuss our overall approach to compatibility and aging at LLNL, with an emphasis on our modeling approach. We will report on our progress to date, which will include, model development and experimental work using polymeric systems to parameterize and validate the model.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

Author name(s):

Salmaan Baxamusa, Ted Laurence, Paul Ehrmann, Steve Haan, Matthew Worthington, Jeff Hayes, Michael Stadermann

Affiliation:

Lawrence Livermore National Laboratory

Contact information including physical address, phone and email:

7000 East Avenue,L-470
Livermore, CA 94550 USA
baxamusa1@llnl.gov
925-422-0378 (O)
925-321-8860 (M)

Photo-oxidation under visible light: the strange case of plasma polymers

Abstract description (500 words or less):

Plasma polymers are amorphous hydrogenated carbon networks that are synthesized and cast through the decomposition of an organic gas in a hydrogen plasma (chemical vapor deposition, or CVD). The ability to deposit hard, chemically inert, and adherent films from inexpensive hydrocarbon feedstocks has made them attractive candidates as protective, tribological, biocompatible, and insulating coatings. One of the disadvantages of plasma polymers is their tendency to oxidize over their service lifetime. The resulting change in the physical and chemical properties has limited the adoption of plasma polymers in several applications despite their many intrinsic benefits.

The thermomechanical stability, low film stress, and low average atomic number make hydrocarbon plasma polymers suitable ablators for high energy density (HED) and inertial confinement fusion (ICF) experiments at high peak-power laser facilities such as the National Ignition Facility in Livermore, California and the Omega Laser in Rochester, New York. The plasma polymer ablates as it absorbs high intensity lasers or x-rays, causing it to drive a compression that leads to very high pressures. These ablators have stringent requirements on the total amount of acceptable oxygen as well as spatial variations in oxygen content, motivating us to understand the oxidation pathways of plasma polymers.

Plasma polymers have long been known to exhibit optical absorption of visible light, with optical gaps of 1-2 eV commonly reported in the literature. Little, if any, work has reported on the associated photochemistry of these polymers. We will show that that optical absorption in the plasma polymers used in ICF and HED experiments is accompanied by rapid (within minutes) photo-oxidation. This reaction in the plasma polymer chemically resembles classical photo-oxidation as scission of the carbon network results in the incorporation of oxygen in the form of carbonyl and hydroxyl species. However, the spectral response of the photo-oxidation is unique: rather than requiring ultraviolet light, the plasma polymer readily photo-oxidizes under visible light illumination at wavelengths as low as 530 nm (green light).

Huang Wu

Job Title:
Associated Research Scientist

Affiliation:
The Dow Chemical Company

Contact information including physical address, phone and email:

433 Building
The Dow Chemical Company
Midland, MI 48642
9896365809
wu352d14@dow.com

Abstract Title:

Highly Accelerated UV Testing and Its Correlation to Mild Test Conditions of Polymeric Materials

Abstract description (500 words or less):
Many industries such as The Dow Chemical Company rely on accelerated weathering techniques to determine failure modes, product performance and service lifetimes. The accelerated UV lifetime test can speed time to market and reduce costs associated with long term outdoor exposure test. The commonly used UV weatherometers provide reasonable acceleration over the outdoor exposure but may not be enough for products with long intended lifetime, which has urge the development of faster UV acceleration capabilities. Recent efforts towards increase the accelerating factor can result in unrealistic failure modes, thus investigation of the correlation between the high acceleration test and the standard tests are necessary. In this work, a UV chamber equipped with a metal halide lamp that is capable of providing 25 times of maximum outdoor UV intensity is used to study the degradation of several polymeric materials, the result of which is compared to an Atlas Ci weatherometer. A lifetime prediction model based on effective dosage is used to calculate the acceleration factor between the two chambers. To account for the difference in the light source spectra, wavelength sensitivity is studied through experiment in both chambers. The wavelength sensitivity, activation energy of the degradation and the degradation profile of the materials were then compared between the highly accelerated chamber and the Ci weatherometer. It was found that the highly accelerated test methods are capable of predicting the failure more than 30 times faster than the Ci weatherometer within the same degradation profile. The wavelength sensitivity and the activation energy obtained in both tests agree well with each other.

Appendix A: List view of 2016 program.

Monday Morning: Weathering and Validation
Discussion Leaders: Pickett and Jennifer David

Time	Presenter	Title
7:00AM-8:00AM		Continental Breakfast.
8:00 AM-8:30 AM	C. White	Intro
8:30 AM-9:00 AM	Berry	Challenges in Accelerated Weather Testing, Method Development, and Service Life Prediction of Exterior Commercial Airplane Coatings
9:00 AM-9:30 AM	Wood	Accelerated testing and risk minimization for exterior building product finishes-Part 1
9:30 AM-10:00 AM	Coffee Break	
10:00 AM-10:30 AM	Quill	Development of Weathering Cycles for Qualitative Service Life Analysis as a Precursor to Accurate Service Life Prediction Protocols: Contemporary Examples
10:30 AM-11:00 AM	K. White	Case Studies to Assess the Effects of Accelerated Weathering Stresses Used to Predict Service Life
11:00 AM – 11:30 AM	Watson	Weathering of Polymeric Materials in Trace Forensic Evidence and its Effect on Identification Measurements
11:30-12:30		Panel Discussion
12:30-2:00	LUNCH	

Monday Afternoon: UL 746 Process

Time	Title
2:00 PM-5:30 PM	Noé P. Navarro 2000HR Program working draft and proposal: This is a working session for members of the UL 746B LTTA Forum and it is open to SLP attendees interested in participating. The objective of this session is to develop a final draft of a UL 746 Standard Technical Panel (STP) proposal that can be ready to be submitted for ballot by the end of the session.

Reception

Time	Title
5:30- PM-7:00 PM	Reception

Monday Evening: Water and Moisture
Discussion Leaders: Watson and Sutter

Time	Presenter	Title
6:30PM-7:00 PM	Sun	Modelling Sorption and Diffusion for Lifetime Assessment: Surrogate Models of Langmuir Sorption Kinetics Coupled with Vapour Diffusion in Polymers
7:00 PM - 7:300 PM	Bora	Spectroscopic measurement of water in polymeric materials
7:30PM – 8:300PM		Panel Discussion and Open (cash) Bar (6:30 PM-8:30PM)

Tuesday Morning: Mechanical Changes Related to Exposure
Discussion Leaders: Celina and Lewicki

Time	Presenter	Title
7:00AM-8:00AM		Continental Breakfast.
8:00 AM-8:30 AM	Sung	Characterizing surface damage of nano-filled polymer coatings under accelerated ultraviolet degradation
8:30 AM-9:00 AM	Lewicki	Towards a predictive, multi-scale aging model for complex silicone architectures - Insights into structural control and response to environmental stressors
9:00 AM-9:30 AM	Hayes	A Study of Nano-mechanical Test Methods as Predictive Tools for Coating Changes in Weathering
9:30 AM-10:00 AM	Coffee Break	
10:00 AM-10:30 AM	Alig	Combination of material characterization and cyclic fatigue testing for investigation of elastomer aging
10:30 AM-11:00 AM	Redline	Unusual Aging Behaviour of Elastomers in High Temperature Environments
11:00 AM – 11:30 AM	Ito	Degradation of ethylene-propylene-diene elastomer by heat and/or radiation
11:30-12:30		Panel Discussion
12:30-2:00	LUNCH	

Tuesday Afternoon: UL 746 Process

Time	Title
2:00 PM-5:30 PM	Jun Haruhara, Noé P. Navarro, and Dr. Thom Fabian IEC 60216-7: Applicability & next round robin plans. This is a working session to discuss the potential applicability of newly published IEC Technical Specification (TS) 60216-7-1 and IEC Test Report (TR) 60216-7-2 for the determination of Relative Thermal Indices (RTIs). Plans for additional round robins incorporating different materials will be discussed.

6:00 PM Tuesday Evening: Banquet Dinner at Rio Chama Steak House
414 Old Santa Fe Trail, Santa Fe, NM 87501

Wednesday Morning: Chemical Changes Related to Exposure
Discussion Leaders: Berry and K. White

Time	Presenter	Title
7:00AM-8:00AM		Continental Breakfast.
8:00 AM-8:30 AM	Celina	An overview of DLO modelling and relevance for polymer aging predictions
8:30 AM-9:00 AM	Schlothauer	Prospects of 2D-luminescence spectroscopy for aging investigations of the embedding EVA polymer in PV modules: Revealing DLO conditions.
9:00 AM-9:30 AM	Chen	Investigation of PDSC applicability to evaluate polymer thermo-oxidative stability
9:30 AM-10:00 AM	Coffee Break	
10:00 AM-10:30 AM	Pickett	Forbidden Chemistry: Non-Free Radical Oxidation Mechanisms
10:30 AM-11:00 AM	Blair	Lifetime Prediction of O-rings Used in the SAVY-4000 Actinide Storage Vessel
11:00 AM – 11:30 AM	Koehl	Evaluation of the time-transformation function from a round robin weathering test of various back-sheets for PV-modules with different ultra-violet radiation sources and sample temperatures
11:30-12:30		Panel Discussion
12:30-2:00	LUNCH	

Wednesday Afternoon: UL 746 Process

Time	Title
2:00 PM-4:30 PM	Noé P. Navarro, Dr. Chris White, Dr. Tom Fabian Roadmap for SLP into UL, IEC, and other standards. This is working session to discuss how to continue incorporate lessons from SLP meetings into the development of standards used to determine temperature ratings. A white paper outline is the goal from this session.

4:00PM -5:30 PM Poster Session.

Poster #	Presenter	Title
1	Li*, Morris †, Sahlani‡, Tietsort*, Lim §, Bruckman*, French	Lifetime and Degradation Science Studies of Exterior Coatings.
2	Tony Misovski & Mark Nichols	Visualization and Quantification of Impact Events on Automotive Paint Systems
3	Wang Eun Lee	Accelerated fluorescence photobleaching of conjugated polymer film under wet state
4	. Rodriguez, Lewicki, Alviso, Chinn,. Wilson & Maxwell	NMR Methodologies for the detection and quantification of nano-structural defects in Silicon Networks

5	Judovits Kowal	Comparison of TGA Methods to Determine Decomposition Kinetic Parameters
6	C. White[1], Byrd[1], Thomas[2], Clerici[1], Kaetzel	Predicting Field Panel Temperature

5:30 PM – 6:30 PM Dinner at Hotel

Wednesday Evening: Radiation
Discussion Leaders: Glascoe and Baxamusa

Time	Presenter	Title
6:30 PM-7:00 PM	Stull	Informed Design of Aging Experiments via CW and Pulse EPR Spectroscopy
7:00 PM - 7:30 PM	Old	Material Property changes following neutron and Gamma irradiation of Carborane-co-PDMS composites.
7:30PM - 8:30 PM		Panel Discussion and Open (Cash) Bar (6:30-8:30)

Thursday Morning: Modelling and Prediction
Discussion Leaders: Quill and Wood

Time	Presenter	Title
8:00 AM-8:30 AM	K. Scott	Selecting a statistical method for validation of life prediction models
8:30 AM-9:00 AM	Pintar	Predicting Field Degradation of Sealants Using Accelerated Tests from the NIST Solar Sphere.
9:00 AM-9:30 AM	Tedds	Validating laboratory-based models and scaling-up for service life prediction
9:30 AM-10:00 AM	Coffee Break	
10:00 AM-10:30 AM	Glascoe	Predicting chemical compatibility and aging of materials in a system: a combined experimental and modelling approach
10:30 AM-11:00 AM	Baxamusa	Photo-oxidation under visible light: the strange case of plasma polymers
11:00 AM – 11:30 AM	Wu	Highly Accelerated UV Testing and Its Correlation to Mild Test Conditions of Polymeric Materials
11:30-12:30		Panel Discussion and wrap up.

Author Index

Time	Sunday	Monday	Tuesday	Wednesday	Thursday
7:00		Breakfast			
7:30					
8:00		C. White	Sung	Celina	Scott
8:30		Berry	Lewicki	Schlothauer	Pintar
9:00		Wood	Hayes	Chen	Tedds
9:30		Coffee Break			
10:00		Quill	Alig	Pickett	Libby
10:30		Ken White	Redline	Blair	Baxamusa
11:00		Watson	Ito	Koehl	Wu
11:30		Discussion			
11:45					
12:30		Lunch			
1:00					
1:30					
2:00		2000 hour	IEC	Roadmapping	
2:30		working draft	60216-7	SLP into	
3:00		and proposal	discussion	UL, IEC	
3:30		Break		standards	
4:00			Begin	Poster	
4:30			Roadmap	Session	
5:00			Discussion		
5:30		Reception		Dinner	
6:00	Reception		Banquet		
6:30		Sun	Dinner	Stull	
7:00		Bora		Old	
7:30		Discussion		Discussion	
8:00					