Service Life Prediction of Polymeric Materials:

Vision for the Future

March 3-8, 2013
Monterey, CA

Q-LAB   NSF   UL   NIST National Institute of Standards and Technology U.S. Department of Commerce

Service Life Prediction of Polymeric Materials: Vision for the Future
March 3 – 8, 2013
Hyatt Regency Hotel and Spa
Monterey, California

On behalf of my co-organizers from **Underwriters Laboratories**, **Q-Lab**, and the **National Science Foundation**, I would like to welcome you all to *Service Life Prediction of Polymeric Materials: Vision for the Future!* This conference features a strong technical program of cutting edge research in service life prediction, including 42 presentations from across the globe with a diverse mix of industrial, academic and government perspectives, moderated panel discussions, a modeling workshop, and focused sessions involving proposed changes to the UL 746 process. The conference will end on Friday with a very important vision-setting wrap-up discussion of the future research directions for service life prediction.

Throughout the conference, there will be sessions led by our partners at Underwriters Laboratories to discuss modifications to the UL 746 process. These sessions will result in a draft of a white paper and road map for long-term thermal aging of polymers. The specific work items that will be addressed in these strategy sessions include:

- Round-robin testing parameters and expectations
- Detailed process for evaluation of compound variations using new program
- High temperature generated data following the principles of the new program
- Aging data for on-going aging projects at UL
- Statistical models to define acceptability
- Analytical methods to define acceptability
- Proposal for revision of UL 746A, Table 9.1 and Table 9.3
- Proposal of work needed to continue to work on long term evaluations of compounds beyond compound variations (e.g. rating increases, thickness reductions, etc.)

We invite everyone to come and participate in these sessions and contribute to this critical UL opportunity. This is a great time to come and learn more about how the standards process builds on fundamental research.

Following this meeting, all presenters are encouraged to submit a paper for publication in a peer-reviewed proceedings book to be published by Springer and co-sponsored by the Q-Lab Corporation. Previous proceedings volumes have been highly sought-after technical references. The paper submission deadline is <u>April 15, 2013</u>.

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 Monterey.

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

Monday Morning: Overview of the SLP Process

Time	Presenter	Title
8:00 AM - 8:30 AM	White	Introduction
8:30 AM - 9:00 AM	Reichert	Numerical Aging of Products Exposed to the Sun
9:00 AM - 9:30 AM	Hayes	The Effect of Non-Radiation Factors on the Weathering of Silicone Hardcoats
9:30 AM - 10:00 AM	White (Ken)	Laboratory-Based Predictions of Weathering in Outdoor Environments over the Entire Degradation Pathway
10:00 AM - 10:30 AM	Berry	An Improving Accelerated Weathering Protocols to Anticipate Florida Exposure Behavior of Transportation Coatings
10:30 AM - 10:45 AM	Coffee Break	
10:45 AM - 11:45 AM	Session Discussion	

Monday Afternoon: UL 746 Process

Time	Title
12:45 PM - 3:00 PM	Aging Data Analysis - Traditional
3:00 PM - 4:15 PM	Aging Data Analysis - New Program
4:15 PM - 5:30 PM	Analytical Methods

Monday Evening: Case Studies of Exposure

Time	Presenter	Title
6:30 PM - 7:00 PM	Patel	Ageing of adhesive binder materials in support of life assessment of sealed multi-material assemblies
7:00 PM - 7:30 PM	Srubar	Service-Life Prediction of Fully Biorenewable Wood-Plastic Composites: A Spatiotemporal Approach
7:30 PM - 8:00 PM	Wachtendorf	Development of a leaching test to estimate emissions from synthetic sports grounds into soil and ground water under weathering exposure
8:00 PM - 9:00 PM	Session Discussion	

Tuesday Morning: Service Life Prediction of Polymers Used in Energy Applications

Time	Presenter	Title
8:00 AM - 8:30 AM	Koehl	Accelerated Service Life Testing of Photovoltaic Modules
8:30 AM - 9:00 AM	Watson	Service Life of Electrical Cable and Condition Monitoring Methods
9:00 AM - 9:30 AM	Pickett	Hydrolysis Kinetics and Lifetime Prediction for Polycarbonate and Polyesters
9:30 AM - 10:00 AM	Yang (Edwin)	Polymer Degradation and Properties for Modeling Insulation Service Life of NM Cable
10:00 AM - 10:30 AM	Gu	Linking Accelerated Laboratory and Outdoor Exposure Results for Polymeric Materials used in Photovoltaics
10:30 AM - 10:45 AM	Coffee Break	
10:45 AM - 11:45 AM	Session Discussion	

Tuesday Afternoon: UL 746 Process

Time	Title
12:45 PM - 3:00 PM	Statistical Methods
3:00 PM - 4:15 PM	New Program - Process
4:15 PM - 5:30 PM	Aging - Round Robin Testing

Tuesday Evening: Tools and Techniques for Service Life Prediction

Time	Presenter	Title
6:30 PM - 7:00 PM	Costa	Polyolefin Lifetime Prediction
7:00 PM- 7:30 PM	Masayuki	Life time prediction of thermal aging of polyolefin by simple method
7:30 PM - 8:00 PM	Yang	Multi-detector GPC Characterization for Polymer Degradation
8:00 PM - 8:30 PM	Alig	Scanning acoustic microscopy for service life prediction of coatings
8:30 PM - 9:30 PM	Session Discussion	

Wednesday Morning: Limitations and Considerations

Time	Presenter	Title
8:00 AM - 8:30 AM	Wood	What are the Limitations on Using Accelerated Methods to Predict the Decorative Properties of PVDF-based Coatings?
8:30 AM - 9:00 AM	Thouless	Time-dependent crack growth in nano-composite coatings on polycarbonate
9:00 AM - 9:30 AM	Hardcastle	Ultra-Accelerated Weathering II: Considerations for Accelerated Data Based Weathering Service Life Predictions
9:30 AM - 10:00 AM	Glascoe	Predicting multi-material aging and degradation using reactive transport modeling
10:00 AM - 10:30 AM	Celina	Polymer Oxidation and Material Performance – A Critical Perspective on High Temperature Approaches
10:30 AM - 10:45 AM	Coffee Break	
10:45 AM - 11:45 AM	Session Discussion	

Wednesday Afternoon: UL 746 Process

Time	Title
12:45 PM - 3:00 PM	Revisions to UL746A, Table 9.1, and Table 9.3
3:00 PM - 4:30 PM	White Paper Drafting Session.

4:30 PM - 5:30 PM   Poster Session

Wednesday Evening: Accelerated Aging Predictions

Time	Presenter	Title
6:30 PM - 7:00 PM	Hartmann	Prediction of Thermal Aging of Materials Based on Limited Amount of Experimental Points. Modified Treatment of Kinetic Data
7:00 PM - 7:30 PM	Blair	Accelerated Aging Studies for the Lifetime Extension of O-rings Used in the SAVY-4000 Unit
7:30 PM - 8:00 PM	Quill	Test Method Development for Outdoor Exposure and Accelerated Weathering of Plastic Siding Specimens
8:00 PM - 9:00 PM	Session Discussion	

Thursday Morning, Session I: Modeling

Time	Presenter	Title
8:00 AM - 8:20 AM	Hsuan/ Dunn	Introduction
8:20 AM - 8:45 AM	Liechti	Shear Modified Free Volume Concepts for the Nonlinear Viscoelastic Behavior of Polymers
8:45 AM - 9:10 AM	Qi	Photo-mechanics of Polymer Structural Alteration Due to Light Irradiation
9:10 AM - 9:35 AM	Rajagopal	Modeling the non-linear response of polymeric solids undergoing microstructural changes due to the diffusion of solvents
9:35 AM - 10:00 AM	Caruthers	Development of Constitutive Models for the Long Term Performance of Glassy Polymers
10:00 AM - 10:25 AM	Keten	Solvent and Confinement Effects on the Thermomechanical Behavior of Amorphous Polymers
10:25 AM - 10:45 AM	Coffee Break	

Thursday Morning, Session II: Thermo-mechanical Effects in Polymeric Composites

Time	Presenter	Title
10:45 AM - 11:10 AM	Pochiraju	Long-Term Thermo-Oxidative Degradation of High-Temperature Polymers and their Composites
11:10 AM - 11:35 AM	Muliana	Coupled Heat Conduction and Thermo-viscoelastic Analyses of Polymeric Composites
11:35 AM - 12:00 PM	Bakis	Externally Bonded FRP Strengthening: Effects of Elevated Temperatures and Sustained Loads

Thursday Afternoon, Session III: Coupled Multi-field Problems, Damage, Experiment

Time	Presenter	Title
1:00 PM - 1:25 PM	Yun	Stochastic Characterization for Micromechanical Properties of Polymer Matrix
1:25 PM - 1:50 PM	La Saponara	A study on the impact of aerospace fluids on the durability of fiber-reinforced composite structures
1:50 PM - 2:15 PM	Bocchieri	A study of thermal damage to a variety of composite materials resulting in wide spread delamination as a function of applied thermal load
2:15 PM - 2:40 PM	Loyola	Time Dependency of Electrical Properties of MWCNT-PVDF Films Subjected to Temperature Cycling
2:40 PM – 3:45 PM	Session Discussion	
3:45 PM - 5:00 PM	Discussion on: Durability of Polymers and Polymeric Composites: Current Challenges and Future Prospects	

Thursday Afternoon: UL 746 Process

Time	Title
5:00 PM - 6:30 PM	White paper drafting session, discussion of next steps

Friday Morning: Modeling and Prediction

Time	Presenter	Title
8:00 AM - 8:30 AM	Kiil	Mathematical modeling of photoinitiated coating degradation: Effects of relative humidity, nano-size pigments, coating glass transition temperature, and light stabilizers
8:30 AM - 9:00 AM	Le Gac	Prediction of Mechanical Properties During Polychloroprene Oxidation Using Mechanistic Modeling
9:00 AM - 9:30 AM	Geburtig	PP Numerical Photoageing Simulation by Dose Response Functions with Respect to Irradiation and Temperature – ViPQuali Project
9:30 AM - 10:30 AM	Session Discussion	
10:30 AM - 10:45 AM	Coffee Break	
10:45 AM - 12:00 PM	Conference Wrap-up	

Monday Morning: Overview of the SLP Process

8:00 AM - 8:30 AM
Welcome and Introduction by Chris White

8:30 AM - 9:00 AM
Numerical Aging of Products Exposed to the Sun

Dr. Thomas Reichert[1], Dr. Axel Müller[2]; Teodora Vatahska[2], Gerhard Manier[3], Artur Schönlein[4], Anja Geburtig[5]

[1]Fraunhofer ICT, Pfinztal, Germany
[2]HTCO GmbH, Freiburg, Germany;
[3]Darmstadt, Germany;
[4]ATLAS MTT, Gelnhausen, Germany;
[5]BAM, Berlin, Germany

Abstract
In the partly funded collaborative project,ViPQuali[1], the aging of a polymer part was numerical simulated on the basis of geographical, geometrical, environmental, material data, and time. Starting point was the numerical construction of the part and the design. This construction is then exposed virtual in a box (Instrument Panel Box) to the environmental conditions described by the geographical data of the site and the calculated environmental conditions depending on day time, meteorological, material and geometrical data. The change in material properties (aging) of the part at any point of the surface will then be estimated by using the dose-response-functions for these properties and statistical evaluations for the environmental conditions. For the validation of the numerical simulation parallel measurements on real parts were done in IP/DP-Boxes in Arizona and in the artificial investigations in the laboratories.

[1] Collaborative project in the frame of "Key innovations for sustainability in economy" – Projektträger Forschung für die Nachhaltigkeit, Bonn, Germany

9:00 AM - 9:30 AM
The Effect of Non-Radiation Factors on the Weathering of Silicone Hardcoats

Robert Hayes, Jennifer David
Momentive Performance Materials
Waterford, NY, USA

Abstract

Artificial weathering methods using a Xenon light source (e.g. SAE J1960/J2527, ASTM G26/G155) are commonly used to evaluate materials used for exterior automotive applications. Over the last 20 years, improvements made to the methods have increased the acceleration factor (vs. natural weathering), refined the spectral distribution of the light to more closely match sunlight, and incorporated the effect of temperature and humidity on the degradation kinetics of the materials tested. These efforts have resulted in improvements in projection of natural weathering lifetimes based on artificial weathering tests. Despite these advances, significant challenges remain in applying artificial weathering methods to predict the service life of protective coatings. In the case of polycarbonate coated with weatherable silicone hardcoats, it has been observed that the accelerated natural weathering correlation factor is different depending on the mode of failure (e.g. coating adhesion vs. μ-cracking). This suggests that the key factors at play in weathering experiments (i.e. radiation, temperature, humidity, rate/time) influence the relative rates between different modes/mechanisms of failure, and need to be accounted for when projecting service life of the system under natural conditions. In addition, attention must be paid to the material properties of the coating and substrate, as interactions between the materials and the surrounding environment define a boundary to the service life.

9:30 AM - 10:00 AM
Laboratory-Based Predictions of Weathering in Outdoor Environments over the Entire Degradation Pathway

Kenneth M. White, David M. Burns, Travis Q. Gregar
3M Weathering Resource Center
St Paul, MN, USA

Abstract

A useful estimate of outdoor service life for a material or product based on laboratory weathering experiments requires a careful assessment of the degradation pathways that result from exposure. Furthermore, converting real-world conditions into parameters that serve as inputs to models based on the accelerated weathering stresses of radiation, heat, and moisture is not trivial. In an effort to study these relationships, a model material was weathered under accelerated conditions in the laboratory, from which mathematical formulas were derived to describe the resultant photodegradation as a function of irradiance and temperature. Calculations for a specific geographical location yielded degradation as a function of time that exhibited excellent agreement with actual outdoor weathering results over the entire degradation period. Variations on the method of calculation proved the mathematical model to be robust. Investigation of chemical degradation in the model material revealed the possibility of more than one reaction pathway. Such behavior is readily apparent in other polymer systems we have studied, wherein the exposure conditions employed can lead to a lack of synchronization of changes in the material or can produce significantly different degradation pathways, both of which affect lifetime estimates.

10:00 AM - 10:30 AM

An Improving Accelerated Weathering Protocols to Anticipate Florida Exposure Behavior of Transportation Coatings

Douglas H. Berry[1], Mark E. Nichols[2], Tony Misovski[2], Cindy A. Peters[2], and Jill E. Seebergh[1] John Boisseau[3], Lynn Pattison[3], Don Campbell[3], Jeff Quill[4], Jacob Zhang[5], Don Smith[5], Karen Henderson[6]

[1] The Boeing Company, Seattle , WA
[2] Ford Research and Advanced Engineering, Dearborn, MI
[3] BASF Coatings, Southfield, MI
[4] Q-Panel, Cleveland, OH
[5] Atlas Material Testing Technology LLC, Chicago, IL
[6] Bayer Material Science, Pittsburgh, PA

Abstract
An accelerated weathering protocol using Xenon arc light has been developed which closely replicates the performance of automotive and aerospace coating systems exposed in South Florida. For automotive basecoat-clearcoat, infrared and ultraviolet spectroscopy verified that chemical composition changes were similar between the accelerated protocol, which uses a glass filter to produce a high fidelity match to sunlight UV spectrum and water exposures to match absorption measured in Florida, and natural weathering. Both automotive and aerospace basecoat-clearcoat and aerospace monocoat systems were used to verify the failures - gloss loss, delamination, cracking, and blistering - as well as good performance correlated between the accelerated protocol and natural weathering in South Florida. For automotive paint systems, the new weathering protocol shows significant acceleration over both Florida and the SAE J2527 accelerated weathering standard. For aerospace systems, the new weathering protocol shows less acceleration than for automotive systems, but still an improvement over both Florida and SAEJ2527. Differences such as temperature, intensity of solar radiation and fluid exposure between the service environment for aircraft and automotive, including South Florida exposure, will also be discussed.

10:30 AM -10:45 AM
Coffee Break

10:45 AM - 11:45 AM
Moderated Discussion

11:45 AM - 12:45 PM
Luncheon

12:45 PM - 5:30 PM
UL-led 746 Discussion

5:30 PM - 6:30 PM
Dinner

Monday Evening: Case Studies of Exposure

6:30 PM - 7:00 PM
Ageing of Adhesive Binder Materials in Support of Life Assessment of Sealed Multi-Material Assemblies

Dr. Mogon Patel
AWE, Reading, UK

Abstract
Polyurethane and poly (ethylene-co-vinyl acetate) based materials are currently used in a number of commercial applications as adhesives and also as binders for specific filler particles. When used in specialised sealed multi-material assemblies, these materials experience a complex ageing regime with potential for significant age related changes. This paper will report our ageing and life assessment interests, and outline our studies to develop a predictive ageing model of the individual material and of the sealed multi-material assembly. A current technical challenge is how best to define the artificially induced accelerated age of a sealed multi-material system when each individual material potentially exhibits a different temperature induced acceleration or response. Without this information it is difficult to compare the results from accelerated multi-material assemblies with actual field trials (real-time) data.

The analytical challenges posed in baseline materials characterisation and quantifying age related changes of key properties, together with sensitivity studies, will be reported. In particular, a key objective of this paper is to highlight the link between age related changes to the individual material and the potential impact on the assembly as a whole. In specific cases, large age related changes (e.g. bond strength and/or volatile out gassing) can have little or no significant impact on the performance of the assembly, whilst in other cases small changes may cause dramatic changes in performance. This paper includes discussion on our approach to understand the 'failure criteria' or the 'amount of change that can be tolerated'. This information is a key requirement in order to assess remaining material or assembly life.

7:00 PM - 7:30 PM
Service-Life Prediction of Fully Biorenewable Wood-Plastic Composites: A Spatiotemporal Approach

Wil V. Srubar III, Sarah A. Miller, and Sarah L. Billington
Stanford University, USA

Abstract
Naturally occurring biopolymers have demonstrated suitability for use in wood-plastic composites (WPCs), which have found application in the construction industry as replacements for conventional petroleum-based plastics, wood, and engineered wood materials. However, widespread applicability of WPCs remains limited because of persistent concerns over their long-term durability performance, especially in high-humidity and wet environments. This presentation will discuss the development of analytical, numerical, and corresponding verification methods to predict the service-lives of both novel and conventional WPCs in outdoor applications. Using the design of an outdoor deck as a case-study example, simulation results from a lifetime prediction model that incorporates environmental exposure, moisture diffusivity, time, and material property degradation will be presented. In addition, the importance of service-life predictions on true material environmental impact assessments will be discussed.

7:30 PM - 8:00 PM
Development of a Leaching Test to Estimate Emissions From Synthetic Sports Grounds into Soil and Ground Water Under Weathering Exposure

Volker Wachtendorf, Ute Kalbe, Oliver Krüger, Wolfgang Berger, Anja Geburtig
BAM, Berlin, Germany

Abstract

In a project funded by the German Federal Institute for Sports Science, a test procedure had to be developed that aimed at estimating the emissions from synthetic sports surfaces into soil and ground water in a reliable, reproducible laboratory scale test, which is intended to be introduced into standardization.

Two different kinds of outdoor-use surfaces for sports grounds were chosen: artificial turf and running tracks. In both cases, scrap tires are often used as infill material or within sub-base layers while also much more expensive synthetic elastomers are applicable as an alternative. A variety of separate components and a number of resulting complete assemblies of sporting ground constructions were investigated as well as outdoor aged material.

The test to be developed had two main focuses: it should simulate the leaching of organic and inorganic substances into ground water in a field-like way and it should look at leaching as a function of the weathering exposure duration, characterizing at least the first few years of use. For the systems investigated a complex leaching behavior was found depending on the constituting components, their individual ageing behavior and the respective release functions of the leaving component, which superimposed to the observed accumulated release function.

8:00 PM - 9:00 PM
Discussion

Tuesday Morning: SLP of Polymers Used in Energy Applications

8:00 AM-8:30 AM
Accelerated Service Life Testing of Photovoltaic Modules

Michael Koehl
Fraunhofer ISE, Freiburg, Germany

Abstract
Temperature, temperature cycling, water and UV-radiation are considered as main degradation factor for PV-modules by causing hydrolysis and photo-degradation of polymeric components, corrosion of glass and of metallic components like grids and interconnectors. The type approval testing of PV modules according to the IEC standards takes these factors only qualitattively into account.

Basically absorption and mass transport of water into and within the module has to be considered. These phenomena depend on the ambient climate of the PV-module in use, the design (back-sheet, glass-glass, all polymer, e.g.), the operation conditions (rack-mounted, on rooftop, building integrated) and the material composition. We try to evaluate test conditions that are primarily based on the stresses occurring during the operation at specific locations by using monitored climatic data and applying phenomenological models for the estimation of the PV-modules as function of the module temperature. Simple time transformation functions were used for the design of appropriate accelerated service life tests. The evaluated testing times differ up to an order of magnitude for different climatic locations, depending on the kinetics of the dominant degradation processes.

8:30 AM - 9:00 AM
Service Life of Electrical Cable and Condition Monitoring Methods

Stephanie Watson
Engineering Laboratory
National Institute of Standards and Technology, Gaithersburg, MD, USA

Abstract

A number of premature electrical cable failures in nuclear power plants (NPPs) have been observed which have raised questions about long-term performance of electrical cables and renewed interest in investigating the service life of electrical cables. For new NPPs, assessing the integrity of electrical cables generates new concerns, which arise from the global nature of the cable market and from changes taking place in new construction of NPPs. From these studies, it has been concluded that for both new and existing NPPs, research is lacking for determining aging mechanisms of low voltage cables exposed to high RH and wet (submerged) conditions and for high voltage cables and new electrical cables subjected to temperature/radiation/wet conditions and validating methodologies for predicting the service life of electrical cable. In this paper, we will describe our new research program on cable condition monitoring and discuss results from a set of condition monitoring methods as a function of degradation on polymer cable insulation.

9:00 AM - 9:30 AM
Hydrolysis Kinetics and Lifetime Prediction for Polycarbonate and Polyesters

James E. Pickett[1], Joris Wismans[2], Frank Heessels[2], and Adrie Landa[2]

[1]GE Global Research, Niskayuna, NY
[2]SABIC Innovative Plastics, Bergen op Zoom, The Netherlands

Abstract
Plastic hot water modules can be designed using polycarbonate twin wall sheet glazing and a black absorber layer made from modified poly(phenylene oxide) blends. These blends are known to be subject to thermo-oxidative degradation resulting in brittleness, so accurate lifetime prediction is required. Embrittlement of these blends is closely associated with oxidation as shown by the correlation between Izod impact strength and oxygen uptake. We determined activation energies for the oxidation of two candidate blends. The activation energies can be used with modeled or measured module time/temperature profiles and a cumulative damage model to calculate the equivalent time at some benchmark temperature that would create the same amount of oxidative damage. The suitability of materials can then be judged based on measurement of property retention after oven aging at that temperature for the calculated time. We find that moderation of the stagnation temperature (periods of sun but no coolant flow) is key to successful module design, and that with effective stagnation temperature control, one blend is likely to be suitable for this application.

9:30 AM - 10:00 AM
Polymer Degradation and Properties for Modeling Insulation Service Life of NM Cable

Hsinjin Edwin Yang, Fan He, Tom Chapin, Pravinray Gandhi
Corporate Research, Underwriters Laboratories (UL-LLC), Chicago, Illinois, USA

Abstract

Over the service life, NM (Non-Metallic) cable may be exposed to a range of temperature and humidity conditions, with the insulation materials degrading with time (i.e., age). This variation in insulation composition is expected to change the dielectric breakdown voltage of the cable. Therefore, we may apply the degradation kinetics and properties change of the insulation materials to model the service life for NM cable.

Two approaches were used to study the degradation kinetics of the insulation materials: (1) TGA method with programmed heating rate to study the degradation kinetics at high temperatures called HT approach; (2) Isothermal low temperatures (LT) method is a direct measurement on both weight loss of the materials and breakdown voltage of the cables at temperatures below the dehydrochlorination of PVC around 150^0C. The activation energy was calculated by Arrhenius equation as a function of temperature at the critical weight loss at minimum voltage breakdown. The model for predicting service life of the cable can then be developed by the correlation among weight loss, activation energy and voltage breakdown. The comparison and understanding between these two approaches will be made.

We will further address how to select the effective polymer property to better predict the insulation service life of the cable.

10:00 AM - 10:30 AM
Linking Accelerated Laboratory and Outdoor Exposure Results for Polymeric Materials used in Photovoltaics

Xiaohong Gu
Engineering Laboratory
National Institute of Standards and Technology, Gaithersburg, MD , USA

Abstract
A reliable accelerated laboratory test that correlates to field performance is critical to the service lifetime prediction and quality assurance of PV products. To develop accelerated laboratory tests for PV polymeric materials and components, the fundamental understanding of degradation mechanism of PV materials under simultaneous multiple stresses (temperature, moisture, UV radiation) is significantly important. In this study, the NIST SPHERE (Simulated Photodegradation via High Energy Radiant Exposure) was used for accelerated laboratory tests of numerous PV polymers and components, such as ethylene vinyl acetate (EVA), poly (methyl methacrylate) (PMMA), ionomers, fronsheet fluoropolymers, and EVA/Polyester/Polyvinylidene (EVA/PET/PVF) backsheet materials. A factorial experiment was designed to evaluate the effects of temperature, relative humidity, and spectral ultraviolet (UV) irradiance, either applied individually or in combination, on the main degradation mechanisms of these materials. To make the linkage between the laboratory and outdoor exposure results, the outdoor exposure was carried out in Gaithersburg, Maryland. Multiscale chemical, optical, mechanical and morphological measurements were carried out to follow changes during accelerated and outdoor exposures. The results indicated that the UV radiation was the most important factor for the degradation of all studied materials. Synergistic effects between UV and moisture were observed for several materials such as EVA, ionomer, and EVA/PET/PVF multilayers. The results also indicated that a higher UV spectral intensity led to a higher degradation rate, but not the degradation mechanism for the studied PMMA. Same chemical degradation modes were also observed between accelerated laboratory and the outdoor exposures.

10:30 AM -10:45 AM
Coffee Break

10:45 AM -11:45 AM
Moderated Discussion

11:45 AM -12:45 PM
Luncheon

12:45 PM - 5:30 PM
UL-led 746 Discussion

5:30 PM - 6:30 PM
Dinner

6:30 PM - 7:00 PM
Polyolefin Lifetime Prediction

L. Costa
Torino University, Torino, Italy

Abstract
The life time of polyolefins is a function of the degradation process of the polymer and of the stabilization process of the additives. In order to have a correct prediction is necessary to know the degradation processes mechanism to be undergone by the polymers which generally is the oxidation process induced by thermal energy, radiation and mechanical stress.
Recently, the oxidation process of polyethylene has been revised. It has been demonstrated that the main reactive species are the macro alkyl radicals which may react with the double bonds imperfections in the polymer creating crosslinking; with oxygen to form, even at room temperature, all the oxidized species, but also with additives antioxidants in a termination reaction. In this work we present results on the stabilization of polyethylene with hindered amines and on the stabilization of polypropylene with vitamin E. The results are consistent with what has been described above for the polyethylene.

7:00 PM - 7:30 PM
Lifetime Prediction of Thermal Aging of Polyolefin by Simple Method

Masayuki Ito
Waseda University, Tokyo, Japan

Abstract

The thermal aging of polyolefin was performed at various constant temperatures in air oven. The weight of sample was measured periodically by using chemical balance at room temperature. The sample used was polyethylene (PE) and two kinds of ethylene-propylene elastomers (EPR). The weight of sample was increased after the induction period which was proportional to the concentration of antioxidant reagent. The weight increased up to a few percent and started to decrease after a maximum weight. This method could measure the induction period, the rate constant of weight increase and that of weight decrease and the activation energy of these three phenomena. The activation energy of induction period of PE was 136 kJ/mol and that of EPR was 110 kJ/mol.

These activation energies were compared with the data obtained by another method such as the count of chemiluminescence, the rate constant of thermal chain scission, increase of carbonyl group and thermogravimetry.

The result obtained suggested that the induction period of weight change could be considered to be an index of lifetime; the activation, which was calculated from the induction period was applicable to short time test.

7:30 PM - 8:00 PM
Multi-detector GPC Characterization for Polymer Degradation

Dali Yang, Annie Giambra, Darla Thompson
Los Alamos National Laboratory, Los Alamos, NM, USA

Abstract

Gel Permeation Chromatography (GPC) is often used to determine the molecular weight (MW) and the MW distribution of polymers. In a conventional GPC technique, a differential refractive index detector (DRI) is typically used to determine the MWs based on the concentration of the molecules eluting from a column against polymer standards, but does not provide any structural information of the polymer in its solution. Multi-detection employs a DRI with a viscometer and a light scattering detector. If a photodiode array detector is added into the characterization, a set of UV spectra of the eluted materials can be obtained as well. With four detectors, all the data are available and can be used to investigate the chain conformation and probe the structural changes over the MWs of the polymer in the solution. In this study, we used the multi-detector GPC characterization to study naturally and artificially aged Estane in PBX 9501. The gained scientific insights help to better understand the degradation mechanisms of Estanes aged at different conditions. LA-UR

8:00 PM - 8:30 PM
Scanning Acoustic Microscopy for Service Life Prediction of Coatings

Ingo Alig, Maike Bargmann, Harald Oehler, and Dirk Lellinger
Fraunhofer Institute, Darmstadt, Germany

Abstract
The first part of the lecture summarizes the basic principles of scanning acoustic microscopy (SAM) and discusses the possibilities of the method for service life prediction of coatings [1-6]. In the second part, examples for defect formation in paint systems of different layer structure and with different initial defects will be given. Time-evolution of disbonding, blister initiation and growth were investigated by analyzing SAM images after different times of exposure to a corrosive environment [3-6]. It was possible to differentiate between water/ion transport through the coating and along the coating-substrate interface. The propagation of the migration front - related to loss of adhesion - and nucleation of blisters are discussed by models for mass transport and growth of defects [4-7].

8:30 PM - 9:30 PM
Discussion

8:00 AM - 8:30 AM
What Are the Limitations on Using Accelerated Methods to Predict the Decorative Properties of PVDF-Based Coatings?

Kurt Wood
Arkema, King of Prussia, PA, USA

Abstract

Poly(vinylidene fluoride) (PVDF) resin is the dominant component of many of the most weatherable decorative coatings available. In commercial PVDF-based coatings, the binder system is almost invariably a blend of PVDF, plus a miscible acrylic co-resin, in some proportion. Since many of these coatings can retain color and resist chalking for decades, quantitative service life prediction models for their decorative properties are very much needed. We have recently outlined the elements of an SLP model for these kinds of coatings, based on the "contraction" theory of gloss loss and chalking, coupled with simple assumptions about the photochemical kinetics of the system. Because different mechanisms account for gloss loss, color change, and chalking, the relative rates of change for each of these properties can be different, in accordance with experimental observations. Rate differences related to coating film inhomogeneity, such as latex blend and pigment flocculation effects, can also be accounted for at least in a qualitative fashion. This talk will review the basic elements of the SLP model for PVDF coatings, and look critically at the extent to which some common accelerated weathering test methods can be harnessed to give reliable SLP information for this particular class of coatings.

8:30 AM - 9:00 AM
Time-dependent Crack Growth in Nano-composite Coatings on Polycarbonate

F. Meng[1], J. David[2], M. Nichols[3] and M. D. Thouless[1]
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[2]Momentive Performance Materials, Waterford, New York, USA
[3]Ford Motor Company, Dearborn, Michigan, USA

Abstract
The use of polymeric glazing would enable many breakthrough designs for automotive applications that are not achievable with glass, and would have the added advantage of providing considerable weight savings. However, polymeric materials glazing suffer from two critical limitations: ultra-violet (u.v.) degradation, and low scratch resistance. This has necessitated the development of transparent nano-composite coatings that are both hard and absorb u.v. radiation. Current coatings do not yet meet satisfactory performance metrics, owing to premature failure by cracking. The time-dependent nature of this crack growth has been studied. Using the approaches of fracture mechanics for thin films, we have developed a procedure for determining the relationship between crack velocity (v) energy-release rate (G) and crack velocity for nano-composite coatings. Plots of velocity against energy-release rate of interest show the classic kinetic features of crack growth, with a clear threshold-energy-release rate and a crack growth rate that increases with both energy-release rate and temperature.

9:00 AM - 9:30 AM
Ultra-Accelerated Weathering II: Considerations for Accelerated Data Based Weathering Service Life Predictions

Henry K. Hardcastle III
Atlas Material Testing Technology LLC, Chicago, Illinois, USA

Abstract
This paper discusses the effect of varying UV intensity on weathering degradation rates of materials. The effects of increasing intensities of solar UV on materials obeying strict reciprocity and materials deviating from strict reciprocity are considered. A second new high intensity natural UV weathering device is introduced based on ASTM G90. The paper presents data from two materials degrading under different intensities of UV and compares natural weathering with data obtained at increasing levels of UV intensity with implications on SLP calculations.

9:30 AM -10:00 AM
Predicting Multi-material Aging and Degradation Using Reactive Transport Modeling

Elizabeth A. Glascoe, Stephen J. Harley, Chuanhe Lu, Yunwei Sun, and Richard Gee
Lawrence Livermore National Laboratory, Livermore, California, USA

Abstract

Predicting the aging and degradation of polymeric materials is important to almost every industry (e.g., automobile, food packaging, defense applications, satellites, biomedical, etc). One key problem with many prediction methods is the fact that materials are usually assembled and used as multi-material assemblies. Hence, we need a tool sophisticated enough to predict the aging of the assembly, and, specifically, long term compatibility issues of multiple materials in contact with each other and with the surrounding environment. We are developing a computational tool for simulating the aging and chemical compatibility of multiple material assemblies. Our code is a modification of a reactive transport code, which is traditionally used by the geo-chemistry and earth science community. Our model uses fundamental physical parameters (e.g., sorption, diffusion, Arrhenius based chemical kinetics, etc) in a 1D or 3D mesh in order to simultaneously simulate the transport and chemical reactions of mobile species through polymeric materials. This talk will discuss our approach and our progress to date, which will include, model development and experimental work 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. LLNL-ABS-607995

10:00 AM - 10:30 AM
Polymer Oxidation and Material Performance – A Critical Perspective on High Temperature Approaches

Mathew Celina, Adam Quintana, Angela Dayile, Nick Giron
Sandia National Laboratories, Albuquerque, New Mexico, USA

Abstract
This presentation offers a review of oxidative polymer degradation and its relationship with lifetime prediction approaches. Oxygen will degrade polymers, it is just an issue of time and how individual properties may change, whether we should care or won't have to worry about it. We will review the key aspects, i.e. our basic understanding of thermo-oxidative degradation, measuring oxidation rates, how degradation modeling can be of benefit, and how oxidation reactions depend on temperature. Examples will show how knowledge of oxidation sensitivity can be translated into a frame work for material lifetimes. We will then focus on the complications that arise when the temperature is raised and thermo-oxidative degradation is conducted very rapidly, for example when using TGA or DSC. This requires an angle on temperature effects and a clear understanding of mechanistic variations in the development of bulk property degradation. We will review the currents trends in modeling degradation heterogeneity and predictions towards high temperature regimes where the polymer degrades mostly under inert conditions, and hence the consequences for very fast qualification tests.

10:30 AM - 10:45 AM
Coffee Break

10:45 AM - 11:45 AM
Moderated Discussion

11:45 AM - 12:45 PM
Luncheon

12:45 PM - 4:30 PM
UL-led 746 Discussion

4:30 PM - 5:30 PM
Poster Session (see separate program for abstracts)

5:30 PM- 6:30 PM
Dinner

Wednesday Evening: Accelerated Aging Predictions

6:30 PM - 7:00PM
Prediction of Thermal Aging of Materials Based on Limited Amount of Experimental Points-Modified Treatment of Kinetic Data

Bertrand Roduit[1], Marco Hartmann[1], Patrick Folly[2], Alexandre Sarbach[2], Pierre Guillaume[3], Laurence Jeunieau[4], Hansgeorg Haupt[5]

[1]AKTS AG, Siders, Switzerland
[2]armasuisse, Thun, Switzerland
[3]PB Clermont s.a., Engis, Belgium
[4]Royal Military Academy, Bruxelles, Belgium
[5]Technische Universitaet, Darmstadt, Germany

Abstract

The investigation of materials aging process at ambient temperatures is experimentally very difficult due to its very low rates and small changes of physicochemical properties. Commonly applied methods of thermal-aging determination are therefore based on measuring material properties at several elevated temperatures followed by plotting log of time-to end-of-life at each temperature against the reciprocal of absolute temperature and, finally, calculating best-fit straight line by regression analysis. In this study we propose a modified method for the kinetic analysis of experimental data. In proposed modification both, n^{th} order and autocatalytic kinetic models are applied, what results in much better fit of experimental data. The method used to compare different models takes into account not only the quality of regression fit, but also the number of data points and number of parameters in specific models. Such procedure allows concluding which model is more likely to be correct. The proposed method delimits also the borders of the prediction band (e.g. 95%) showing scatter of the data and allows considering uncertainty of the best-fit curve being very important for thermal aging predictions. Advantages of new method will be illustrated by results of investigations of thermal aging process of some polymers and energetic materials.

7:00 PM - 7:30 PM
Accelerated Aging Studies for the Lifetime Extension of O-rings Used in the SAVY-4000 Unit

Michael W. Blair, Eric M. Weis, D. Kirk Veirs, Tim A. Stone, Paul H. Smith, Jeanne M. Ball
Los Alamos National Laboratory, Los Alamos, New Mexico, USA

Abstract

A new plutonium storage container, 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 are undertaking 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 will rely on changes in mechanical properties of the O-rings, such as sealing force decay, 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.

7:30 PM - 8:00 PM
Test Method Development for Outdoor Exposure and Accelerated Weathering of Plastic Siding Specimens

Jeffrey Quill and Sean Fowler
Q-Lab Corporation, Cleveland, Ohio, USA

Abstract
This paper provides an overview of significant research conducted by the Vinyl Siding Institute (VSI) on the development of new test methods for exterior plastic building products. The purpose of the VSI study was to develop a robust testing protocol for use in approving materials and certifying products. This paper describes the process of developing an outdoor test program and a robust accelerated weathering test method that could be used to predict actual outdoor durability with a greater degree of confidence. Outdoor weathering tests were conducted in Florida, Arizona and Northern temperate locations to obtain baseline data for comparison. This part of the research led to the development and subsequent publication of ASTM D6864. Accelerated laboratory tests were performed in Fluorescent UV/Condensation test apparatus and Xenon Arc test chambers. The process involved the examination of multiple types of equipment, multiple cycles, and multiple conditions, and comparing the various results to the outdoor exposures. Preliminary exposures suggested that for this particular material, one method was more suitable than the other. The proposed method was verified with repeat testing and rugged statistical analysis. Round robin testing was conducted to determine repeatability and reproducibility. The proposed method allows for a pass/fail threshold that greatly reduces the occurrence of false positives, and the user has much greater confidence that materials passing the accelerated test will pass the outdoor test. False negatives were also minimized in the new protocol. This paper will show how outdoor weathering and accelerated testing can work together to create a robust testing program.

8:00 PM - 9:00 PM
Discussion

8:00 AM - 8:20 AM
Introduction by Grace Hsuan and Martin Dunn

Session 1: Modeling (8:20 AM - 10:25 AM)

8:20 AM - 8:45 AM
Shear Modified Free Volume Concepts for the Nonlinear Viscoelastic Behavior of Polymers

Kenneth Liechti
University of Texas at Austin, Austin, Texas, USA

Abstract
Many structural polymeric materials exhibit a nonlinear viscoelastic response. Over the years, several models have been developed to account for this behavior. Some are based on the Doolittle concept that the "free volume" controls the mobility of polymer molecules and, thus, the inherent time scale of the material. It then follows that factors such as temperature and moisture, which change the free volume, will influence the time scale. Furthermore, stress-induced dilatation will also affect the free volume and hence the time scale, thereby leading to the nonlinear effect. However, Popelar and Liechti [1, 2] found that dilatational effects alone were insufficient in describing the response of near pure shear tests of an epoxy. Thus, the free volume approach was modified to include distortional effects in the inherent time scale of the material. Since then the model has been successfully applied to a number of other types of polymers.

The approach builds naturally on the small strain viscoelastic response which has lately been based on master curves of shear and bulk relaxation moduli determined on one specimen in combined compression tests. Ramp testing in shear and tension is then conducted in order to extract the free volume parameters. The effects of thermal and solvent expansion have also been incorporated. The shear modified free volume model has been incorporated in the ABAQUS finite element code via a user-defined material subroutine. Successful validation of the model has been achieved through a variety of multiaxial stress states, strain rates, temperatures and solvent contents.

The challenge now is to determine the mechanisms for this effect of shear on the free volume from theoretical and novel experimental developments.
1. *Popelar, C.F., and Liechti, K.M., Multiaxial Nonlinear Viscoelastic Characterization and Modeling of a Structural Adhesive. J. Engineering Materials and Technology., Transactions of the ASME, 1997: p. 119, 205-210.*
2. *Popelar, C.F., and Liechti, K.M., A Distortion-Modified Free Volume Theory for Nonlinear Viscoelastic Behavior. Mechanics of Time-Dependent Materials, 2003. 7(2): p. 89-141.*

8:45 AM - 9:10 AM
Photo-mechanics of Polymer Structural Alteration Due to Light Irradiation

R. Long[1,2], M. L. Dunn[1], H. Jerry Qi[1]
[1]University of Colorado, Boulder, Colorado, USA
[2]University of Alberta, Edmonton, Alberta, Canada

Abstract

The development of light activated polymers, which undergo network structural alternation and consequent mechanical deformation responding to light, promises to offer exciting, innovative, and unique material capabilities. Currently, several light-activated polymers have been developed with very different underlying photo-mechanical mechanisms. Such materials include: photo-radical mediated cleavage and reformation of the polymer backbone in cross-linked elastomers that results in local stress relaxation; photo-switching cross-links in shape memory polymers. This paper developed a thermodynamically consistent constitutive framework to model photo-mechanical behaviors of these polymers. This framework was applied to a cross-linked elastomeric system that is able to undergo cleavage/reformation of the polymer backbone and photo-switching cross-links. In these systems, the presence of radical species is modeled to locally relieve stress through network rearrangement. Modeling this photo-radical-mechanical behavior constitutes a multi-physics problem with three primary constituents: the optical penetration and attenuation throughout the material; the photo-chemistry and associated radical concentration field; and the radical concentration-coupled mechanical behavior of the material. These three processes have been implemented in a finite element code. Experimental data are used to calibrate the photo-mechanical model. Model prediction simulations of novel actuators are compared with experimental results. Finally, a few examples of applications are demonstrated.

9:10 AM - 9:35 AM
Modeling the Non-linear Response of Polymeric Solids Undergoing Microstructural Changes Due to the Diffusion of Solvents

K. R. Rajagopal
Texas A&M University, College Station, Texas, USA

Abstract
The degradation/healing/oxidation of polymeric solids capable of undergoing large deformations due to the diffusion of solvents will be discussed. First, a new and novel class of constitutive models for describing the non-linear elastic and non-linear viscoelastic response of solids will be introduced and then a class of models will be developed for describing the changes in the microstructure, and hence the properties of the polymeric solid, due to the absorption of the diffusing fluid. The governing equations for the problem under consideration, namely a system of coupled partial differential equations or a system of partial differential and integral equations, for the displacement field and the concentration of the diffusing fluid, will be derived and specific initial-boundary value problems of technological significance will be discussed.

9:35 AM - 10:00 AM
Development of Constitutive Models for the Long-term Performance of Glassy Polymers

J.M. Caruthers
Purdue University, West Lafayette, Indiana, USA

Abstract
The development of accurate constitutive models for glassy polymers remains an outstanding problem in polymer engineering, where there is a need to both describe the diversity of nonlinear relaxation behavior exhibited by these materials as well as acknowledge the underlying molecular deformation processes. Both experiments and molecular simulation clearly indicate that glassy polymers exhibit fluctuations at the nanoscale, where there are order-of-magnitude differences in the mobility between neighboring meso-domains, i.e. dynamic heterogeneity. A new constitutive approach has been developed that explicitly acknowledges the nanoscale fluctuations present in the glassy state. This stochastic constitutive model (SCM) only has a single relaxation time, but can describe the complex nonlinear relaxation behavior exhibited by glassy polymer including yield. Of particular significance is the ability of the SCM to predict post-yield softening – a phenomena that heretofore has not been predicted by existing constitutive models. The evolution of the fluctuating internal variables provides a mechanistic picture of what is controlling the macroscopic behavior of glassy polymers in complex thermal-deformation histories. Because fluctuations are explicitly included, the SCM may provide a bridge between molecular simulations of polymer behavior and traditional continuum mechanics.

10:00 AM - 10:25 AM

Solvent and Confinement Effects on the Thermomechanical Behavior of Amorphous Polymers

Wenjie Xia, Shawn Mishra, Sinan Keten
Northwestern University, Evanston, Illinois, USA

Abstract

The effect of low molecular weight solvents on polymer microstructure and mechanical behavior is a central problem with broad implications to nanofabrication, biomechanics and multifunctional polymers. Ever present water molecules in the form of humidity, as well as retained solvents after materials processing alter the anticipated behavior of materials significantly by shifting thecharacteristic relaxation times and glass transition temperature. Additionally, surfaces and interfaces in polymer nanostructures and nanocomposites show strong changes in mechanical behavior due to free surface and substrate effects, which compound the complexity of predicting thermomechanical behavior in these emerging applications. The fundamental understanding of these effects call for new bottom-up predictive modeling approaches that can capture molecular structure and dynamics to accelerate advancements in nanofabricated devices and polymer nano fibers. In this study, we present atomistic and coarse-grained molecular simulations that explain how solvent and confinement effects govern the relaxation and glass-transition temperature (T_g) of amorphous polymers, specifically poly(methyl methacrylate) (PMMA). First, we present an approach for quantifying solvent induced T_g suppression using atomistic simulation derived parameters in conjunction with free-volume theory (*Mishra, Keten, APL, 2013*). We build on this approach to establish an analysis of the spatial variation of glass-transition temperature in thin films, illustrating competing effects of attractive substrates and free surfaces using experimentally validated coarse-grained models. Functional usage of heterogeneities to control solvent diffusion and material properties will be discussed. Our results can be directly combined with theoretical models to directly quantify variation in thermomechanical properties without empirical inputs, and corroborate recent experimental findings. Our investigations provide basis for a positive outlook on the potential of applying multi-scale, predictive, simulation-based design approaches to the discovery process of new specialty polymers.

10:25 AM - 10:45 AM
Coffee Break

Session 2: Thermo-mechanical Effects in Polymeric Composites, Modeling/experiment (10:45 AM - 12:00 PM)

10:45AM-11:10 AM
Long-term Thermo-Oxidative Degradation of High-Temperature Polymers and their Composites

Kishore Pochiraju[1], Gyaneshwar Tandon[2,3] and Gregory Schoeppner[3]

[1]Stevens Institute of Technology, Hoboken, New Jersey, USA
[2]University of Dayton, Dayton Ohio, USA
[3] Wright Patterson Air Force Base, Dayton Ohio, USA

Abstract

Thermal oxidation is a significant degradation mechanism that limits the service life of high-temperature polymers and their composites. The diffusion and reaction of atmospheric oxygen with the polymer cause morphological and mechanical behavior changes, which lead to damage initiation and eventual failure. A methodology that considers the coupled physical, chemical, and mechanical interactions taking place in the material during oxidation is required for accurate prediction of in-service life. We have developed a diffusion-reaction-conversion model that predicts the oxidation state in the material at any time and temperature. Furthermore, we coupled a mechanics model that determines the stress fields and damage state to simulate degradation. Both oxidation and damage growth predictions are verified with isothermal aging experiments on several high-temperature polymer systems. Using the developed framework, the oxide layer growth can be predicted for neat resins and their composites at lamina and laminate scales. Results are presented for polyimide and bismaleimide polymer systems and their composites reinforced with carbon fibers.

11:10 AM-11:35 AM
Coupled Heat Conduction and Thermo-viscoelastic Analyses of Polymeric Composites

Anastasia Muliana
Texas A&M University, College Station Texas, USA

Abstract

Polymer matrix composites exhibit significant viscoelastic behaviors when exposed to coupled mechanical and thermal effects. Viscoelastic materials are dissipative materials and deformations in the viscoelastic bodies could generate significant amount of heat, increasing the temperature of the bodies, and elevated temperatures accelerate creep/relaxation in the body, leading to a fully coupled thermo-mechanical response. This study presents a multi-scale material model for analyzing coupled nonlinear heat conduction and thermo-viscoelastic deformation of multi-layered fiber reinforced polymeric composites. The multi-scale material model is implemented in finite element (FE) and used for analyzing time-dependent responses of composite structures under coupled mechanical and thermal stimuli. Short-term (30 minutes) creep tests on off-axis multi-layered specimens are also conducted under combined stresses and temperatures to calibrate in-situ fiber and matrix properties and verify the predictions of the multi-scale framework. A time-shifting method is applied to create long-term material behaviors from the available short-term creep data. Furthermore, the multi-scale model is modified to incorporate the dissipation of energy from the viscoelastic constituents. The dissipation effect is important when the composite structures are subjected to cyclic mechanical loading over a relatively long period of time, which will be useful in determining fatigue life of composite structures.

11:35 AM - 12:00 PM
Externally Bonded FRP Strengthening: Effects of Elevated Temperatures and Sustained Loads

Charles E. Bakis and Maria M. Lopez
Penn State University, University Park, Pennsylvania, USA

Abstract

Fiber reinforced polymer (FRP) composites are gaining widespread acceptance as an economical way to repair or strengthen existing concrete, masonry, steel, and timber structures. Design guides for the application of FRP composites for strengthening (and repair) have been published by several organizations around the world. Typically, high strength synthetic fibers such as carbon or glass are impregnated with an ambient-curing epoxy resin and attached to the structure on-site. Alternatively, pre-cured composite plates manufactured off-site by the pultrusion process are bonded to the structure using an ambient-curing epoxy. Both of these techniques are rapid by virtue of the light weight and easy handleability of the FRP material, which reduce labor costs and minimize the out-of-service time of the structure. Also, by extending the service life of a functionally obsolete or deficient structure, replacement costs are avoided, including environmental costs related to demolition and replacement. One outstanding issue with FRP strengthening is the long-term durability of the material that connects the stiff, strong fibers to the substrate: i.e., the ambient-cured epoxy. In fact, the organizations that develop guidelines have been wrestling with this issue for the past several years. It is widely known that the degree of cure (chemical cross-linking) and mechanical performance of ambient cured epoxies depends significantly on time along with the ambient temperature and perhaps moisture over the service history. It is also known that the environmental conditions along with applied stress level dictate the time-dependent deformation (creep and relaxation) of the epoxy, which in turn can affect the stress state in the all-important adhesive layer between the FRP and substrate. If debonding of the FRP from the substrate (the typical failure mode) is to be avoided, a better understanding of the implications of sustained loads and environmental conditions on the long-term performance of the strengthening systems is needed. An investigation of the combined effects of elevated temperatures and sustained loads is underway at Penn State, with a focus on a wet-laid carbon/epoxy FRP system bonded to concrete. It has been determined that exposure of the FRP material to moderately elevated temperatures increases the mechanical properties of the epoxy resin not by advancement of cure but, rather, by advancement of physical aging. In turn, it has been observed that the bond strength between the FRP and concrete can increase as well. Thus, it is clear that performance of the strengthening system over extended periods of time is a complicated process governed by physical changes in the epoxy resin and changes in the local stress distributions at the interface between the FRP material and substrate. The full paper will present specific experimental and numerical modeling results behind these observations, and will also suggest avenues for further advancement of our understanding of this important problem.

12:00 PM -1:00 PM
Lunch

Session 3: Coupled Multi-field Problems, Damage, Experiment (1:00 PM - 2:40 PM)

1:00 PM -1:25 PM
Stochastic Characterization for Micromechanical Properties of Polymer Matrix

G.J. Yun
The University of Akron, Akron, Ohio, USA

Abstract

A stochastic characterization method was presented that can micromechanically derive stochastic information about spatially varying local matrix properties of fiber-reinforced composite lamina. The statistical information (mean, variance, covariance and correlation length) of the random matrix properties was used to generate statistically equivalent distributions of matrix properties. For reliable design and use of materials, accurate characterization of materials and structures are required. Traditionally, averaged effective properties with considerations of constituent volume fractions, properties of different material constituents and a simplification of the microstructure have been assumed for large selection of macro-scale material samples. However, initiations and evolutions of many critical damage phenomena in materials are closely linked to local stresses that can be associated with local variations and features in the material microstructure. Close observations of microscopic material features reveal significant heterogeneities in various forms such as inclusions, pores, local flaws, microcracks, and in random variations of local residual stresses and diffusivities for moisture ingress. For fiber reinforced polymer matrix composites and ceramic matrix composites, these heterogeneities are mainly caused by random fiber distributions, manufacturing process and damaging process of material properties under uncertain loadings. Therefore, under different potential combinations of these causes of heterogeneities, the matrix material has spatially varying gradients of local stiffness, strength properties and physical damage variables. The effects of the microstructure variability on transverse strength of the lamina can be evaluated by using sophisticated damage models.

1:25 PM - 1:50 PM
A Study on the Impact of Aerospace Fluids on the Durability of Fiber-Reinforced Composite Structures

C. Winkelmann, V. La Saponara
University of California, Davis, California, USA

Abstract

We present results of a multi-year investigation on the thermo-mechanical impact of fluids commonly used in aerospace operations, over the durability of epoxy-based structural adhesive (approved for maintenance and repairs) and woven carbon fiber-reinforced polymeric composites. These structural materials were individually immersed in water and undiluted/unmixed jet fuel, anti-icing jet fuel additive, hydraulic fluid. Gravimetric tests were carried out at three conditioning temperatures typical of those experienced by a composite aircraft structure in service: room temperature, 70 deg. C and 85 deg. C. The effect of post-curing of the structural adhesive was also studied. Hardness test data, statistical analysis and microscopy showed a significant loss of hardness for the structural adhesive samples treated in jet fuel additive or in hydraulic fluid, with irreversible phenomena that may be ascribed to diffusion-driven chemical reactions. The carbon/epoxy specimens experienced more limited damage, in particular due to jet fuel additive.

The moisture uptakes were modeled with two simple diffusion models used in the literature (Fickian, two-stage sorption or 'Langmuir'). Despite limitations inherent in these models, reasonably good fits were obtained, that captured the trends for adhesive and carbon/epoxy specimens immersed in water (as expected) or anti-icing additive (new result). On the other hand, the mass gain caused by hydraulic fluid could not be fitted by either model. The suitability of an Arrenhius trend is also assessed, since this is a common model in multiphysics software packages that may be used for this problem.

The results of this investigation appear to confirm the concerns of the US National Transportation Safety Board regarding hydraulic fluid exposure of aerospace composites (in fact, a warning was recently issued about delamination of the composite rudder of Airbus A300 aircraft due to hydraulic fluid leaks).

1:50 PM - 2:15 PM
A Study of Thermal Damage of a Variety of Composite Materials Resulting in Wide Spread Delamination as a Function of Applied Thermal Load

R. Bocchieri[1], D. Dierdorf[1], K. Cozart[1], S. Wells[1], J. Hawk[2]

[1]Applied Research Associates, Inc., Albuquerque, New Mexico, USA
[2]Air Force Research Laboratory, Tyndall AFB, Tyndall, Florida, USA

Abstract
In this study, we have examined thermal damage to a series of aerospace composite materials exposed to controlled radiant fluxes over periods ranging from seconds to minutes. Three major classes of matrix resins were evaluated for comparison purposes. Three IM7 carbon fiber composites were evaluated, with epoxy 977-3, modified bismaleimide (BMI) RM3002 and condensation polyimide AFR-PE-4.

Composite plates with quasi-isotropic layup were exposed to controlled radiant heat fluxes on one face for specified time periods. Plates were thermally insulated on the back side and around the edges, to minimize edge damage. Thermal exposure was mild and the primary source of heating was radiant heating. Thermocouples were placed throughout the thickness during manufacture. After exposure, the plates were machined into 4-point bend and tensile samples and mechanically tested. Mechanical degradation in terms of reductions in tensile and flexural modulus and strength were documented as a function of exposure level. Microscopy of the machined sections was performed to document the observed damage.

In all materials and heat flux magnitudes tested, it was found that the composite plates experienced sudden and catastrophic damage, prior to any significant charring or mass loss, in the form of delaminations, sometimes throughout the entire thickness. Delaminated samples displayed little residual mechanical strength in flexure (up to 85% strength loss) and greatly reduced tensile strength (up to 40% strength loss). Samples exposed to similar heat flux and durations, but removed from heat prior to delamination, showed little reduction in mechanical strength. The time at which delamination occurred was indicated by thermocouple data and global buckling of the plate. The delamination time was affected by the water moisture content of the plate, with delamination occurring at shorter exposure times for plates with higher moisture content. High pressure gases in the plate from water vapor and resin outgassing are postulated to cause this delamination.

2:15 PM- 2:40 PM

Time Dependency of Electrical Properties of MWCNT-PVDF Films Subjected to Temperature Cycling

Bryan R. Loyola, Rachel Barth, Timothy M. Briggs, Greg O'Bryan, and Marianne Laford
Sandia National Laboratories, Livermore, California, USA

Abstract
Since their discovery, carbon nanotubes have been utilized to impart electrical conductivity into non-conductive polymers at very low weight percentages. In this study, multi-walled carbon nanotubes (MWCNTs) have been added to a PVDF-based coating for the purpose of static dissipation and structural health monitoring. Due to the uncertain environments that these coatings may see in service, it is imperative to fully understand how the electrical properties of the films will change with environmental conditions over time. In this preliminary study, MWCNT-PVDF films with three different percent loadings of MWCNTs are tested, as well as the effect of the location of the electrodes. The films were subjected to thermal cycles bounded by -70 °C and 80 °C, while maintaining conditions to ensure that the electrical response of the films is due solely to temperature change. The results of this study will show some of the sensitivities due to the electrical properties of the MWCNTs as well as the impact of the PVDF matrix on the electrical properties of the film as a whole.

Acknowledgments

2:40 PM - 3:45 PM
Session Discussion

3:45 PM - 5:00 PM
Discussion/Summary in Durability of Polymers and Polymeric Composites: Current Challenges and Future Prospects

5:00 PM - 6:30 PM
UL-led 746 Discussion

6:30 PM - 9:00 PM
Group Celebratory Dinner

Friday Morning: Modeling and Prediction

8:00 AM- 8:30 AM
Mathematical Modeling of Photoinitiated Coating Degradation: Effects of Relative Humidity, Nano-Size Pigments, Coating Glass Transition Temperature, and Light Stabilizers

Søren Kiil
Technical University of Denmark, Lyngby, Denmark

Abstract
A mathematical model, describing coating degradation mechanisms of thermoset coatings exposed to ultraviolet radiation and humidity at constant temperature, has been verified against available experimental data for epoxy-amine coatings [1]. The model was used to conduct a parameter study simulating the effects of relative humidity, nano-size pigments (carbon nano-tubes and SiO_2), coating glass transition temperature, and light stabilizers on the rate of degradation [1,2]. The model includes photoinitiated oxidation reactions, intrafilm oxygen permeability, water absorption and diffusion, reduction of crosslink density, absorption of ultraviolet radiation, a radical scavenger reaction, and simulates the transient development of an oxidation zone. Both relative humidity and nano-size pigments can have a strong influence on the degradation rate. Furthermore, it was found that the degradation rate of a non-stabilized coating with a low glass transition temperature was influenced significantly by the diffusion rate of oxygen in the oxidation zone, whereas light absorption by the photoproducts formed was only a secondary effect. On the other hand, the degradation rate of a stabilized coating was mainly influenced by the light absorption capability of the coating and in this case there was no oxygen diffusion resistance. Finally, simulations showed that the rate constants of the photoinitiating and oxidation reactions, taking place within the epoxy-amine family of coatings, are strong functions of the specific crosslinker used and must be estimated, in each case, by calibration of the model against adequate experimental data series.

References
[1] Kiil, S. (2012), Model-based analysis of photoinitiated coating degradation under artificial exposure conditions, JCT Research, 9(4), 375-398.
[2] Kiil, S. (2012), Mathematical modelling of photoinitiated coating degradation: Effects of coating glass transition temperature and light stabilizers, Prog. Org. Coat., accepted for publication.

8:30 AM - 9:00 AM
Prediction of Mechanical Properties During Polychloroprene Oxidation Using Mechanistic Modeling

Pierre Yves Le Gac[1,3], Peter Davies[1], Mat Celina[2], Lida Audouin[3], and Bruno Fayolle[3]

[1]French Ocean Institute, Plouzane, France
[2]Sandia National Laboratories, Albuquerque, New Mexico, USA
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Abstract
Life time prediction of polymers is usually complicated, both because of the complexity of chemical mechanisms involved in the degradation and also due to the difficulty to relate material chemistry to mechanical properties such as modulus or elongation at break. Furthermore, predictions are generally based on time/temperature superposition using an Arrhenius law. However, this approach may not be valid, either due to the fact that each chemical mechanism involved in the oxidation process has a different activation energy value or because the degradation is limited by oxygen diffusion. Our purpose is to build a muti-scale model based on a mechanistic approach, which describes the main chemical reactions involved in the overall degradation and their kinetics as a function of temperature. Thus it is possible to set up a non-empirical model based on chemistry. In this study polychloroprene oxidation has been characterized and modelled from a chemical point of view in order to set up the mechanistic model. In order to predict mechanical properties, relationships between crosslink density increase due to oxidation and modulus and fracture properties are proposed. As a result, lifetime modelling is proposed, by coupling oxidation kinetic modelling and these structure-properties relationships

9:00 AM-9:30 AM

PP Numerical Photoageing Simulation by Dose Response Functions with Respect to Irradiation and Temperature – ViPQuali Project

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Abstract

The aim of the joint project ViPQuali (Virtual Product Qualification) was to describe a components ageing behavior in a given environment, by numerical simulation. By choosing polypropylene as a moisture insensitive material, the relevant weathering parameters of the dose response functions could be limited to spectral irradiance and temperature.

In artificial irradiation tests, for PP plates of varied stabilizer content, spectral sensitivity as well as temperature dependence of irradiation caused crack formation was quantified. For that purpose, samples were exposed both to artificial weathering tests at various constant temperatures and to spectrally resolved irradiation. The temperature dependence could be modeled by an Arrhenius fit. For fitting the spectral sensitivity, a plateau function was chosen. Subsequently, the stabilizer content was parameterized and extrapolated.

The formed dose response functions were incorporated into a CFD program, simulating the environment within a Phoenix exposed IP/DP box, based on sun position and weather conditions, including radiation interactions. Observed local effects as well as the general ageing advance of PP pylons are compared with respect to simulation and experiment.

Resulting from this project, for this most simple example of PP of varied stabilizer content, the time to failure can be estimated for each weathering exposure environment with known time-resolved irradiance and temperature conditions.

9:30 AM -10:30 AM
Session Discussion

10:30 AM -10:45 AM
Coffee Break

10:45 AM -12:00 PM
Discussion of Future Directions and Research Needs

12:00 PM
Adjourn

Author Index

Time	Sunday	Monday	Tuesday	Wednesday	Thursday	Friday
7:00		Group Breakfast				
7:30						
8:00		Intro (White)	Koehl	Wood	Hsuan/Dunn	Kiil
8:30		Reichert	Watson	Thouless	Liechti	LaGac
9:00		Hayes	Pickett	Hardcastle	Qi	Geburtig
9:30		White (Ken)	Yang (Edwin)	Glascoe	Rajagopal	Session Discussion
10:00		Berry	Gu	Celina	Caruthers	
					Keten	
10:30		Coffee Break				
10:45						
11:00		Session Discussion			Pochiraju	Conference Wrap-up
11:30					Muliana	
11:45		Group Lunch			Bakis	
12:00					Group Lunch	
12:30						
12:45						
1:00		Aging Data Analysis - Traditional	Statistical Methods	Revisions to UL 746A, Table 9.1, and Table 9.3	Yun	
1:30					La Saponara	
2:00					Bocchieri	
2:15					Loyola	
2:30						
2:45						
3:00		Aging Data Analysis – New Program	New Program - Process	White Paper Drafting Session	Session Discussion	
3:30						
4:00						
4:15		Analytical Methods	Aging Round Robin Process			
4:30				Poster Session		
5:00					UL 746a Wrap-up	
5:30		Group Dinner				
6:00	Reception					
6:30		Patel	Costa	Roduit	Group Dinner	
7:00		Srubar	Masayuki	Blair		
7:30		Wachtendorf	Yang	Quill		
8:00		Session Discussion	Alig	Session Discussion		
8:30			Session Discussion			
9:00						