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Materials Compatibility and Migration in Polymer Systems

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Abstract

This is the final report of a one-year, Laboratory-Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL). The purpose of this project to study the effects of materials migration by direct measurement of the diffusion and convective migration processes in complex polymeric materials and to develop appropriate predictive models. The use of isotopically tagged probe molecules to measure in-situ the diffusion of water in estane was demonstrated. A special environmental cell with a thin window was fabricated to enable real time measurements to be made under realistic conditions simulating actual operating parameters. Depth profiles were measured quantitatively using ion beam methods available at the Los Alamos Ion Beam Materials Laboratory. The Williams-Landau-Ferry model was adopted as a general expression for diffusion of a volatile material in a polymer. This model contains both thermal activation and free-volume change effects to account for the changes in polymeric structure with temperature and physical properties as embodied in the glass-transition temperature. A theoretical simulation of water migration in polyurethane was performed and compared to the ideal 1-D, constant temperature, constant-boundary concentration test problem, for which an analytical solution is known. The transport code works properly and indicates that time steps on the order of 10 minutes are permissible, which is the order of the time required to collect data for one measurement in the ion beam.

Background and Research Objectives

Lifetime prediction capability is an important component of the Stockpile Stewardship Program. Separate polymeric materials are being studied and evaluated independently, but the effects of materials migration are not being directly addressed in composite and loaded materials. This results in the potential for reduced reliability or performance degradation in complex assemblies and multi-component operational units. The compromised performance may be due to a "self-poisoning" migration of minor component materials. In this work we studied the effects of materials migration by direct measurement of the diffusion and convective migration processes in complex polymeric materials and developed appropriate predictive models.

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The approach is based on the direct experimental measurement of diffusion and convective migration processes and the simultaneous development of a model to describe and ultimately yield predictive capability. Selectively deuterated probe molecules were used with ion beam analysis to map the migration processes in an environmental cell. The research intended to demonstrate: 1. The use of ion beam analysis and deuterium-tagged molecules to study diffusion in mock HE and solid silicone materials. 2. The feasibility of in-situ methods for the measurement in non-vacuum conditions. 3. The application of the technique to the study of multi-component layered structures. 4. Development of a phenomenological model for the transport of molecular species in open-celled foams and solid-loaded polymers based on the statistical concept of overlapping rigid spheres and rods. 5. Coupling of the theoretical models to describe multi-layered composite structures.

Importance to LANL's Science and Technology Base and National R&D Needs

Composite materials using polymer binders and polymer materials exhibit aging effects that eventually affect the performance of the composite or material itself or of some collateral unit of a device or machine due to deleterious interactions with a volatile material. Examples of composites that we have in mind are grains of explosive compound in polymer binder and open polystyrene foams. Classic examples include degradation of binders in structural powder compacts, evolution of water in otherwise anhydrous environments, sintering processes for glass seals and advanced aircraft components, and embrittlement of foams.

By their nature composite materials usually possess a random character to their structure due to forming or synthesis conditions. With respect to modeling, this random character lends itself to analogy with random porous media, including polymer foams. That is, polymer binders take the place of void space. In simulating transport processes, the governing equations take on the same structure as for random porous media, but the transport coefficients must be replaced by those appropriate for a polymeric system. Because of this analogy, it is possible to use similar representations of randomness in both types of systems, thereby yielding a unifying point for the associated models.

Validation of the simulations by direct measurement of isotopically tagged migrating species in pure polymers and composites will directly support the understanding of aging in polymeric materials used in weapons systems. The resulting data and models are expected to be of significant value in deciding possible performance degradation, safety concerns, and materials replacement issues.

Scientific Approach and Accomplishments

The purpose of this project was to study the effects of materials migration by direct measurement of the diffusion and convective migration processes in complex polymeric materials and to develop appropriate predictive models. The central approach is to measure transport properties of various volatile components in polymer-plasticizer systems and then to use those measurements to predict the overall transport behavior of combinations of composite materials derived from those polymeric systems. Direct measurement of the concentration profile of the migrating species in the pure polymeric material as a function of time, temperature, and environmental exposure provides the input data for the simulations. Similarly, direct measurement of the transport of migrating species in the composite systems of interest will validate the model and resulting simulations.

The basic idea is to use isotopically tagged probe molecules to measure in-situ the diffusion of the potential volatile species of interest. Low energy nuclear reaction techniques are used to follow the behavior of the tagged molecules. A special environmental cell with a thin window was fabricated to enable real time measurements to be made under realistic conditions simulating actual operating parameters. Depending on the migrating species to be followed, the depth resolution needed, and the sensitivity required, the stable isotopic tag may be deuterium, ^{13}C , ^{15}N , or ^{18}O . The depth profiles were measured quantitatively using ion beam methods available at the Los Alamos Ion Beam Materials Laboratory. The low energy nuclear reactions that are particularly useful for these measurements are the positive Q-value reactions such as $\text{d}(^3\text{He}, \alpha)\text{p}$, $^{13}\text{C}(\text{d}, \text{p})^{14}\text{C}$, $^{15}\text{N}(\text{d}, \alpha)^{13}\text{C}$, and $^{18}\text{O}(\text{p}, \alpha)^{15}\text{N}$.

The permeability of each polymer to the various probe molecules can be measured in thin films of the pure polymers to determine the diffusion coefficients. Deuterated water was the obvious first probe molecule because the atomic properties of water are relatively well understood and the ion beam analysis of deuterium has the required sensitivity and depth resolution.

There are two dimensional regimes over which measurements must be made. The near surface region within a few microns of the surface is amenable to the usual ion beam analytical methods that rely on the energy loss of the ion beam to determine the distribution of the migrating molecule below the surface. The second involves transport over centimeter distances in bulk material. By making a series of spatially resolved measurements in a direction perpendicular to the diffusion direction the required information can be obtained. Sub-mm spatial resolution is easily available at the IBML and has been demonstrated in the environmental cell.

The goals of modeling activities were: (1) Development of an expression for the diffusion constant for the various volatile species in a elastomeric polymer; (2) Introduction into a simulation code of the required spectrum random media models to address the situation of

diffusion of volatile substances through multiple random materials, both composite and open-foam in nature; (3) Calibration of the diffusion model through comparison to experimental measurements of the diffusion process; (4) Use of the calibrated diffusion model of volatile migration in a random composite such as PBX.

The Williams-Landau-Ferry model was adopted as a general expression for diffusion of a volatile species in a polymer. This model contains both thermal activation and free-volume change effects to account for the changes in polymeric structure with temperature and physical properties as embodied in the glass-transition temperature. As a specific case, a full initial parameter set for water migration in polyurethane was deduced from the data of Pissis et al. The parameters were used in an ideal 1-D, constant temperature, constant-boundary concentration test problem, for which an analytical solution is known, to assure the functioning of the diffusive transport section of the code. The code worked properly. In addition, the test case also showed that time steps on the order to 10 minutes are permissible, which is the order of the time required to collect data for one measurement in the ion beam.

All models of diffusion in random media were represented as an effective diffusion constant D_{eff} of the form:

$$D_{eff} = D_{pure} \cdot \epsilon / \tau$$

where D_{pure} is the diffusion constant in the pure material, ϵ is the volume fraction for the medium in which the diffusion is taking place and τ is called the tortuosity factor. D_{pure} is assumed to be known and modeled as describe above. ϵ is also considered to be known. The models then deal solely with the form of the tortuosity factor. The random media tortuosity modules that have been assembled for subsequent testing on PBX-elastomer composites are:

- (1) $\tau = 3$
- (2) $\tau = \tau_0 \cdot \epsilon_0 / \epsilon$
- (3) $\tau = 1 / \epsilon$
- (4) $\tau = f(\text{connectivity})$

(1) is valid at small polymer fractions. (2) is valid when there is only small variations in the tortuosity from system to system or sample to sample. $\tau_0 \cdot \epsilon_0$ are values that have been measured for a representative case of a particular class of composites. (3), the Smith-Wacko model, is valid for intermediate polymer fractions, and (4), the Friedman-Seaton model, is appropriate for composites that map onto a network model with a constant connectivity. The tortuosity is expressed as a function of the connectivity and the aspect ratio of typical geometric

features in the composite. The exception is the model of Mater *et al.* which uses a volume-weighted average of diffusion through multiple media and is appropriate for diffusion through foams. The value of the various random media models with respect to PBX-elastomer composites and extensions to multiple-layered materials can be assessed when the appropriate experimental data becomes available.