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Chemical and Physical Aging of Epoxies

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Introduction

While "plastics" have a reputation of longevity in places that most of us do not want them-in our landfills and oceans,[1-5] they are falling apart in places that they are meant to last forever-in our national museums.[6] Many of the items in museums, such as Neil Armstrong's spacesuit, may not have been designed to last for decades. Yet the fact that the polymeric materials that make up these items can deteriorate under the relatively benign conditions of a museum display begs questions about what may be occurring in many Sandia National Laboratories' (SNL) applications, in which materials are asked to perform their required function(s) over multiple decades. Unlike the museum materials, the plastics in SNL applications are typically under a stress over this time period.

The high cross-link density of epoxy thermosets may lead some to regard the aging of these materials as a low priority, as it would require the severance of many covalent bonds within these materials to make them fall apart. However, the wide use of epoxy thermosets, often in regions of high consequence should the epoxy fail, makes it important to distinguish whether the aging of these materials affects their ability to meet performance requirements. Furthermore, it often does not require the material to "fall apart" in order to "fail". The gigapascal modulus of these materials means that even small strains, of order 0.01, can generate stresses that initiate "yield" in the material. Thus, it is important to be able to measure and predict the aging behavior of epoxies with high fidelity. In this presentation, we will report recent results assessing the aging of two epoxy thermosets relevant to SNL applications: one that has been widely used for decades but is still poorly understood [7,8] and one that has been introduced as part of recent modernization efforts.[9,10] The aging mechanisms observed in these materials will be presented along with data measuring the effect of these mechanisms on the mechanical response of the material. Initial assessments of the ability of current nonlinear viscoelastic models[11-13] to predict the effect of aging on the mechanical response of the material that has been widely used will be also be presented.

Experimental

The thermosetting epoxies used in testing will be referred to as DGEBA/DEA and DGEBA/T403. The first material is a mixture of EPON® Resin 828 (Momentive) - a diglycidyl ether of bisphenol A, and diethanolamine (Fisher Scientific). The second utilizes the same epoxy resin and mixes it stoichiometrically with Jeffamine T-403 (Huntsman). The chemical structure of the DGEBA resin, DEA curative and T403 curative are provided in Figure 1.

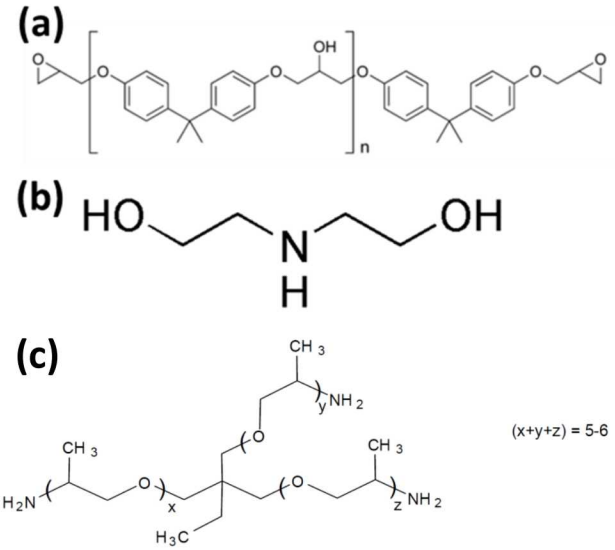

Figure 1. Chemical structure for (a) DGEBA, (b) diethanolamine and (c) Jeffamine T-403.

The DGEBA:DEA are mixed at a ratio of 100:12 parts by weight and cured at 70°C for 24 hours. This process gives a thermoset network that exhibits a T_g of ~70°C. During cure, the DEA first links to the epoxy via the secondary amine-to-epoxide reaction. This reaction is relatively fast and is followed by a much slower reaction that occurs through various pathways, including DEA hydroxyl reaction with the epoxide.[7] Both of these reactions (amine and hydroxyls with epoxide) are necessary to form the cross-linked network. The DGEBA:T403 are mixed at a ratio of 100:43 parts by weight and cured at 80°C for 24 hours. This process gives a thermoset network that exhibits a T_g of ~90°C.The cure process for both materials is completed in cylindrical molds and samples are cut to size (2-to-1

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length-to-diameter ratio for compression cylinders and thin cylindrical sections for differential scanning calorimetry) after cure. After cure and cutting, samples are annealed at 35°C above T_g and then cooled at 0.8°C/min to room temperature. This annealing process erases any previous thermal/mechanical history in the material and defines the thermal history of the "unaged" state. "Aging" was performed isothermally at temperatures of 55, 65, 76, 83 and 105°C for up to ~10,000 hours (over 400 days).

Compression testing was performed on a universal testing machine (Instron, 55R1125 or 5882) using a compression subpress. Samples were placed into the environmental chamber of the Instron and allowed to equilibrate for 30 minutes prior to compressing at 0.1 in/min to approximately 15% strain. Differential scanning calorimetry was performed on a Q2000 instrument (TA Instruments) in a heat-cool-heat experimental protocol with thermal ramps of 10°C/min between 5 and 145°C.

Results and Discussion

The uniaxial compression response for an epoxy glass during a ramped load experiment at a constant displacement rate exhibits at least four distinct features. Figure 2 schematically illustrates the stress-strain response and identifies these features as follows: (1) at small strains a linear regime exists where the stress is proportional to the strain and an "effective elastic" modulus can be defined, (2) at higher strain a local maximum is found that allows for a definitive definition of a "yield" stress for the material, (3) due to post-yield "strain softening" the yield peak has an associated width, and (4) at even higher strain a region where the "flow" stress is relatively independent of strain exists.

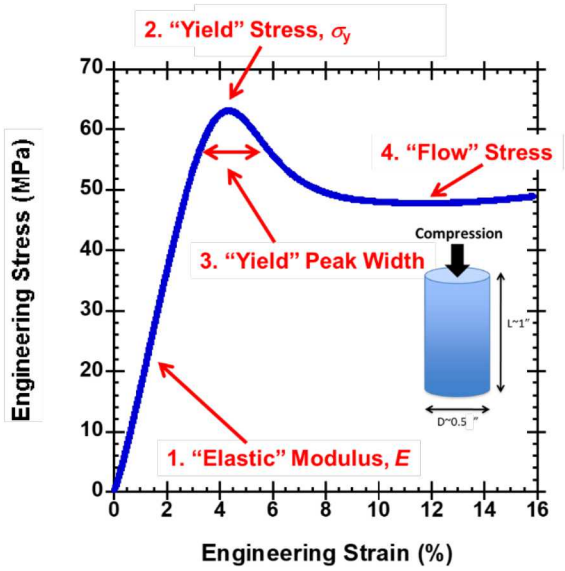

Figure 2. "Anatomy" of the compressive stress-strain response of a glassy polymer. The inset cylinder shows the sample geometry used in this testing.

How these characteristics of the DGEBA/DEA and DGEBA/T403 materials' stress-strain response evolve during isothermal "aging" is illustrated in Figure 3.

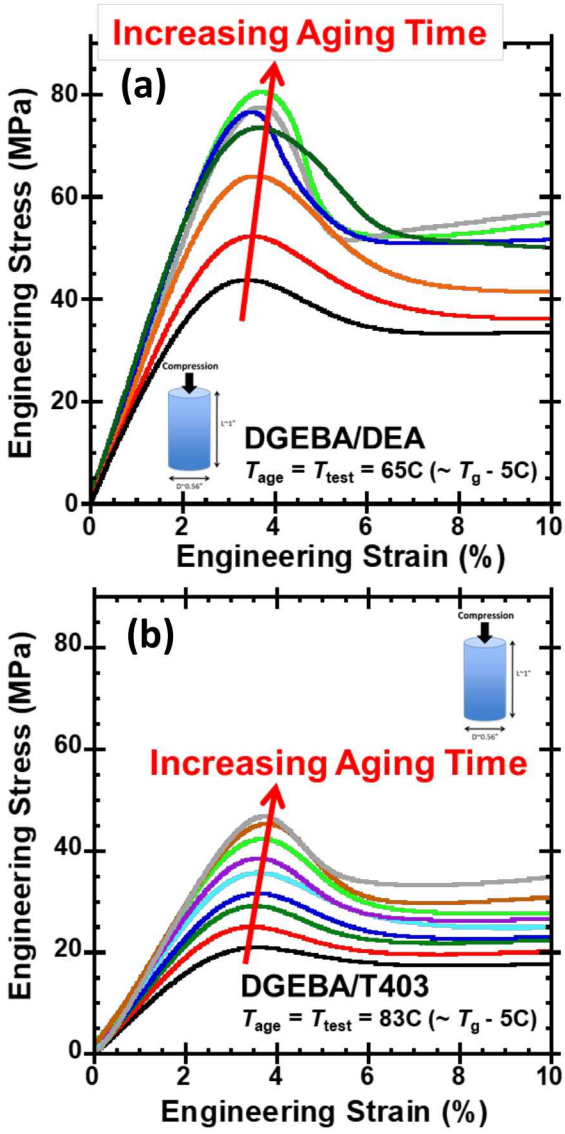

Figure 3. Evolution of the compressive stress-strain response of (a) DGEBA/DEA and (b) DGEBA/T403 during isothermal again at T_g-5°C. The inset cylinders show the sample geometry used in this testing.

From Figure 3, four distinguishable changes in the compressive stress-strain response include the following: (1) increase in initial compressive modulus, (2) increase in yield stress, (3) narrowing of yield peak, and (4) increase in flow stress. These results will be discussed in terms of the material volume and T_g changes observed during the aging, and the relative contributions of chemical and physical aging to the changes in compressive yield stress will be discriminated. Identifying the implications of the material aging effects on application performance over the lifetime of an engineering design is a long-term goal of this work. Continuum constitutive models that can predict the

material behavior and assess stress evolution in complicated geometries are key to the success of such a goal. Towards that goal, the ability of SNL's nonlinear viscoelastic model[11-13] to predict the change in material response with long-term aging will be assessed and discussed.

Acknowledgements

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