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The interplay of chemical and physical aging in a diglycidylether of bisphenol A (DGEBA) epoxy cured with diethanolamine (DEA)

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Introduction

Diethanolamine (DEA) cured diglycidyl ether of bisphenol-A (DGEBA) epoxies were formulated decades ago to provide a light-weight structural material amenable to encapsulation processing [1-5]. The formulation continues to maintain utility, and its longevity enabled a substantial amount of testing to characterize material properties during and after cure.[6-9] While some signatures of aging within this material have been documented,[7, 10] a detailed study of the material's performance over a prolonged service life had not been undertaken. In the present work, this deficiency is addressed by quantifying the effect of aging on the epoxy's thermal and mechanical properties.

A challenge in studying aging of the DGEBA/DEA material is the potential for the convolution of chemical and physical aging effects. After standard cure conditions (24 hours at T=70°C), the material is known to retain unreacted epoxide groups.[1] Thus, there is potential for continued reaction that would form additional cross-links and alter the physical properties of the material.[11] Of course, since the material is both glassy and highly crosslinked, the reaction rate after the initial 24 hours is slow. The slow, continued reaction results in a prolonged period of "chemical aging".

Furthermore, the material typically spends its life below the glass transition temperature (T_g). Under these conditions, material properties will also change with time due to "physical aging". In this process, the non-equilibrium glass generated in the manufacturing process will slowly evolve towards equilibrium. From a molecular perspective, the equilibration process consists of a physical reordering through available segmental motions to minimize free energy. The physical reordering results in a densification of the material. Importantly, because physical aging does not involve chemical changes, it can be "reversed" by thermally annealing above T_g.[12, 13]

In this work, the aging of DGEBA/DEA is quantified by tracking the glass transition temperature and the compressive stress-stain behavior during isothermal holds. The glass transition temperature of the material is measured after "erasing" the physical aging effects, and consequently, is a measure of chemical aging alone. The measured yield stress has contributions from both chemical and physical aging. To disentangle the two contributions, aged samples are thermally annealed above T_g to erase the physical aging effect and resolve only the contributions of chemical aging.

Experimental

The thermosetting epoxy used in testing will be referred to as DGEBA/DEA. The material is a mixture of EPON® Resin 828 (Momentive) - a diglycidyl ether of bisphenol A, and diethanolamine (Fisher Scientific). The chemical structure of the DGEBA resin and DEA curative are provided in Figure 1.

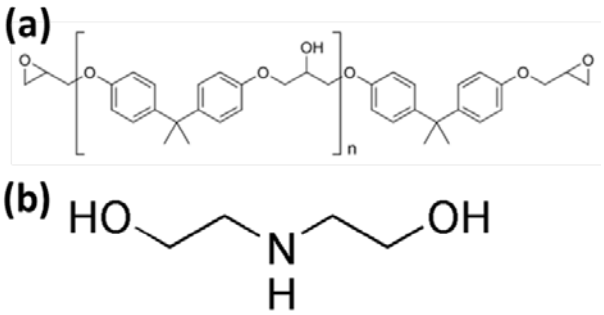

Figure 1. Chemical structure for (a) DGEBA and (b) diethanolamine.

The materials are mixed at a ratio of 100:12 parts by weight DGEBA:DEA 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. Both of these reactions (amine and hydroxyls with epoxide) are necessary to form the cross-linked network. The cure process is completed in cylindrical molds and samples are cut to size (2-to-1 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 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. How these characteristics of the DGEBA/DEA material stress-strain response evolve during isothermal "aging" will be demonstrated. The 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.

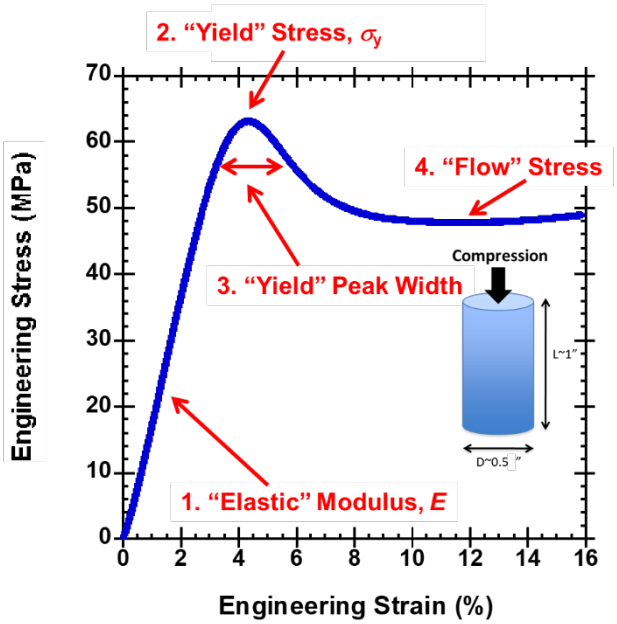

Figure 2. "Anatomy" of the compressive stress-strain response of a glassy polymer. The inset cylinder shows the sample geometry used in this testing.

Acknowledgements

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