ABSTRACT

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Title: Effect of Temperature and Deformation on the Thermo-mechanical Properties of Thermoset Epoxies
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Linear viscoelastic behaviors for diglycidyl ether of bisphenol-A (DGEBA) epoxy resins cured with 4,4’-methylenedianaline (MDA) have been studied. For a particular DGEBA/MDA material with a glass transition temperature (T_g) of 102 °C, dynamic shear moduli were measured from 10^{-2} to $10^{1.7}$ Hz for 41 temperatures between −150 °C and 180 °C. Because DGEBA/MDA epoxies are thermorheologically complex, construction of master curves via time-temperature superposition is not applicable. Stress relaxation experiments were performed from 90 °C to 112.5 °C using the same specimen. A combination of Fourier transformed transient data and dynamic data extended the frequency window of an isotherm to 6 orders of magnitude. A new methodology was developed for determining the relaxation spectrum, where the spectral density changes under the constraint that all spectral components have the same strength. This new method accommodates thermorheological complexity. The analysis was performed throughout the entire temperature range, including sub-T_g low-temperature glassy state (i.e., γ region), sub-T_g “excess wing” (i.e., β region), glass-to-rubber transition zone (i.e., α region), and above-T_g plateau and terminal zones. In sub-T_g γ and β regions, dielectric relaxation data were analyzed using the same method.

Spectral analysis was applied to a variety of glassy-forming materials, including linear polymers, crosslinked polymers, oligomers and small molecules, with a focus on the relaxation processes in glass-to-rubber transition region (i.e., near and above α region). Spectra were constructed from (i) experimental data of a series of linear and crosslinked DGEBA polymers with different crosslink densities, and (ii) digitized literature data consisting storage and loss isotherms near and above T_g. A second relaxation process was found at higher temperatures and longer relaxation times than the main α peak, which is designated as the “α+” process, where the molecular mechanism of α+ is

unknown. For molecular glass formers no α+ process is observed. For other materials the α+ process is present as a shoulder on α peak.

In addition to temperature, deformation also affects mobility, where in the absence of deformation the mobility will decrease as the materials evolves towards the equilibrium state in a process called "physical aging". Two major ideas how mobility is affected by deformation: rejuvenation and accelerated aging. In accelerated aging, the molecular mobility is decreased after deformation. In rejuvenation, the mobility will increase. To discriminate these two models, a set of 4-step non-linear tensile experiments were performed on a crosslinked DGEBA polymer at T_g – 16 °C. The effect of deformation history was evaluated by comparing the mobility before and after the large deformation, where the mobility was quantified as the magnitude of stress overshoot on a stress-strain curve during reloading in the 4-step experiment. The experimental results at T_g – 16 °C are predominantly due to aging effect but the aging is not accelerated by the presence of deformation history.