Multimodal Analysis of Thermo-mechanical Behaviors of Glassy Polymers

Author: Hosup Song
Advisor: James M. Caruthers
Date: Nov. 29th, 2022, 12:30PM EST

The fundamental theory of the glass transition and the glassy state does not exist. Instead, over the years of research there have accumulated a vast number of experimental observations and phenomenological models developed in order to rationalize these observations. A case in point is the stress-strain behavior of a polymer glass during large constant strain rate deformation; for every feature of the stress-strain curve, such as yield, post-yield softening and post-yield hardening, a new mechanism is postulated. But do these mechanisms have a physical basis or are they merely curve-fits? The experiments included in this dissertation are purposefully designed to challenge the prevailing model assumptions. Four specific areas have been chosen: (1) the linear viscoelastic behavior above the glass transition temperature, Tg, (2) the effect of physical aging on the relaxation response of the glassy polymers well below Tg, (3) the behavior of the glassy polymers during a multi-step non-linear deformation, and (4) the effect of the large deformation of the glassy polymer on the enthalpy relaxation as measured by the DSC.

(1) Linear viscoelastic isotherms were analyzed by performing dynamic mechanical analysis on a thermoset epoxy, EPON1009F-MDA (Tg: 102.5°C). Storage and loss moduli for the material were investigated for isotherms ranging from 90°C (Tg-12°C) to 180°C (Tg+78°C) for frequencies ranging from 10^{-2} Hz to $10^{1.7}$ Hz. This linear viscoelastic dataset was augmented by performing stress relaxation experiments on the same material for temperatures ranging from 90°C (Tg-12°C) to 112.5°C (Tg+10.5°C). The transient results from the stress relaxation (SR) were converted to frequency domain. The resulting augmented dataset spanned 6 order of magnitude in frequency. The wide frequency window showed that the material is thermo-rheologically complex, precluding the creation of a master curve via horizontal shifting of the isotherms. This renders impossible the use of time-temperature superposition, and thus highlights the need for reevaluating its prominent use in glass studies.

(2) Existing beliefs on the diminishing effects of physical aging at low temperatures were studied. Linear viscoelastic isotherms of EPON825-MDA (Tg: 182°C) that have been annealed for 2 to 600 hours at temperature ranging from -100°C (Tg-282°C) to 185°C (Tg+3°C) were investigated. At temperatures near Tg, no tangible effects of annealing were identified. At the lowest temperature of -100°C, no differences could be identified between 2 hour and 6 hour annealed specimens; however, annealing effects could possibly be observed at longer aging times based on the results of other isotherms. For all other isotherms between -50°C to 170°C, clear differences could be observed between 2 hour and 6 hour annealed specimens, where the storage moduli increased while the loss moduli decreased. In addition, the effects of annealing were unidentifiable when the material went through a temperature up-jump, but persisted when the material went through a temperature down-jump. The results of this study show that contrary to popular belief, annealing effects are not frozen and persist deep in the glass state and is observable even within experimental limits. Additionally, deep glass aging is fundamentally different from physical aging in that no master curve can be achieved via horizontal shifting along the frequency axis unlike physical aging, due to the change in shape and magnitude of the isotherms.

(3) Many constitutive models that target prediction of mechanical behaviors are drawn from the results of single step deformation experiments. Multi-step non-linear deformation experiments were performed on a copolymer of PBMA and PMMA, to challenge the existing models, where the last step is a constant-strain-rate loading step that shows the effects of previous deformation histories on the stress overshoot. Various multi-step deformation histories were investigated, one being a sequence of constrain-strain-rate-loading/unload/creep/constant-strain-rate-loading. Contrary to previous literature reports, the results showed a dependence on the creep stress level of the last overshoot, which initially increased in peak magnitude with creep stress, reached a maximum, and decreased for further increase in creep stress. These results are not qualitatively predicted by any of the existing constitutive models, illustrating the need to rethink how the mechanisms behind stress-strain behaviors are approached. A new toy model is also discussed that can qualitatively predict these results as well as the results of other multi-step deformation histories that are discussed.

(4) A new methodology for analysis of the differential scanning calorimetry (DSC) traces was proposed. The DSC trace is known to be sensitive to the thermo-mechanical history a material is subjected to prior to the DSC test; but, the true effects are convoluted with the experimental scatter. The conventional method consists in shifting of the data obtained for different thermo-mechanical histories to the same glassy asymptote, but this has no physical basis. In fact, we argue that this misses the actual effects. We propose that the shifting must be to match the liquid, i.e., equilibrium, asymptote as it is in the equilibrium state which is independent of the history. The new methodology was used to confirm literature reports on the effects of aging. DSC scans of deformed specimens were also studied, where the results showed a systematic effect in the heat capacity traces of deformed specimens, where an endothermic peak followed by an exothermic peak is observed. The peaks are not present in the case of an undeformed material, where a larger degree of strain led to a larger endothermic peak. The results indicate the possibility of a systematic effect where the magnitudes of the additional endothermic and exothermic peaks are controlled by the amount of mechanical work performed during the deformation.