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# Polymer Prize Talk: Segmental Dynamics in Polymers : From Cold Melts to Aging and Stressed Glasses

KENNETH SCHWEIZER, University of Illinois @ Urbana-Champaign

Polymers are excellent glass formers. In the cold molten state they exhibit chemically-specific and strongly non-Arrenhius segmental relaxation which sets the time scale for the generic chain scale dynamics. In the amorphous solid or plastic state the temperature dependence of the alpha relaxation time changes, physical aging emerges, and a rich mechanical response occurs characterized by the dynamic yielding, strain softening and strain hardening processes. We have developed a statistical mechanical theory of activated segmental relaxation in cold melts by combining and extending methods of mode coupling, dynamic density functional and activated hopping theories. The approach is built on the concept of a confining nonequilibrium free energy which quantifies local dynamical constraints and the barrier hopping process. The localizing consequences of interchain caging forces are quantified by the amplitude of nanometer scale density fluctuations (compressibility) and backbone stiffness. Predictions for the kinetic glass and dynamic crossover temperatures, dynamic fragility, and thermal dependence of the segmental relaxation time are consistent with experiments. The theory has been generalized to treat alpha relaxation, physical aging, and nonlinear mechanical properties in the glass. The structural component of density fluctuations become (partially) frozen resulting in a crossover to Arrenhius relaxation. Physical aging is modeled based on a kinetic equation for collective density fluctuations. At intermediate time scales the relaxation time (shear modulus) grows as a power law (logarithmic) function of aging time with a temperature dependent exponent. Applied stress weakens dynamical constraints thereby accelerating relaxation and softening the elastic modulus. A constitutive equation has been constructed from which the temperature dependent dynamic yielding and mechanical response under constant strain rate, constant stress (creep), and other modes of deformation can be calculated. This work was done in collaboration with Drs. Kang Chen and Erica J. Saltzman.