



The Spring 2007 Condensed Matter Seminar series presents:

Prof. Herve Marand
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“Secondary Crystallization: A Likely Mechanism for the Physical Aging of Semicrystalline Polymers above Their Glass Transition Temperature”

The crystallization of a polymer during cooling from the melt state is a complicated process, even when carried out under quiescent conditions. As a first approximation, crystallization can be viewed on the macroscopic level as occurring in two separate stages. During the primary stage, crystal nucleation and growth lead to the formation of semicrystalline superstructures (often, but not necessarily, spherulitic in nature), which grow until they impinge on each other. The secondary stage is then usually associated with the further increase in crystallinity within the primary superstructures. Secondary crystallization must be viewed as an inevitable consequence of *thermodynamic* and *kinetic* hindrances to the formation of equilibrium extended chain crystals. While profuse kinetic and morphological studies can be found in the literature for the primary crystallization stage, systematic attention has only been given recently to the secondary stage.

In this presentation, we combine results of differential scanning calorimetry, atomic force microscopy, small angle X-ray scattering and creep studies to propose a description of the secondary crystallization process and discuss a possible mechanism for the physical aging of semicrystalline polymers above their glass transition temperature.

Two mechanisms of secondary crystallization are envisioned conceptually: *secondary crystal formation* at low temperatures and *lamellar thickening* at high temperature. The crystallization time dependence of the melting behavior of secondary crystals is shown to be universal and strongly correlated with the temporal evolution of the glass transition temperature. These and related experimental observations are then rationalized in a qualitative model that considers 1) the thermal stability of crystals formed at different temperatures, 2) the influence of secondary crystallization on conformational constraints in the remaining amorphous fraction and 3) the magnitude of a scaled crystallization temperature defined by $\theta = (T_{ac} - T)/(T_{ac} - T_g)$, where T_{ac} and T_g are characteristic temperatures for the crystal and liquid phases.

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304 Robeson Hall

4:00 P.M.