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Explanation of the Exothermic Enthalpy Peak Exhibited by Glassy Polymers Following Loading-Unloading. GRIGORI MEDVEDEV, JAMES CARUTHERS, Purdue University — When a glassy material is heated at a constant rate, an endothermic peak is observed. In contrast, when a glass is subjected to a large loading-unloading deformation prior to heating, an exothermic peak emerges well below T_g and the conventional endothermic peak located near T_g disappears. The deformation induced exothermic peak is extremely broad where, depending on the material, it may begin more than 100 degrees below T_g . It has been speculated that the effect of deformation is similar to that of hyper-quenching, where the latter is known to also produce an exothermic peak in the heat capacity vs temperature curve. However, no existing model of glass contains a mechanism by which a loading-unloading cycle would produce the experimentally observed enthalpic response. In this communication we will show that the recently developed Stochastic Constitutive Model (SCM) does predict emergence of the exothermic peak following large loading-unloading deformation below T_g . According to the SCM, during a large deformation that takes the material into the post-yield flow state, the work of deformation is partially converted into excess non-equilibrium entropy which does not relax immediately upon unloading. During subsequent heating this excess entropy manifests as an exothermic peak.

Grigori Medvedev
Purdue University

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