A MODEL FOR STRESS-INDUCED CRYSTALLIZATION OF POLYMERS

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The study deals with constitutive relations for rubbery polymers partially crystallized due to the mechanical treatment. This subject is of crucial importance for applications in polymer engineering, since stress-induced crystallization is observed in such wide-spread manufacturing processes as melt spinning, extrusion drawing, film blowing, blow molding, and injection molding. Mechanically induced crystallization produces internal inhomogeneity in materials, leads to a significant redistribution of stresses in polymeric articles, and may cause their failure. Stress-induced crystallization is demonstrated by polybutadiene, polyethylene, poly(ethylene terephthalate), poly(ethylene terephthalate glycol), polypropylene, and natural rubber, to mention a few.

Crystallization of polymers has been the focus of attention in the past four decades. Despite a number of experimental and theoretical studies, it is difficult to mention a constitutive model which

1. Correctly predicts experimental data.

2. Reflects an adequate physical scenario of mechanically induced crystallization.

3. Is relatively simple to be used in the numerical analysis of stresses built up in polymeric articles during their manufacture.

Two approaches may be mentioned to the analysis of stresses in crystallizized polymeric media. According to the first, the kinetics of crystallization is prescribed *a priori*, whereas the stresses are calculated as sums of stresses in an amorphous part of the material and stresses in crystallites. An advantage of this approach is that it provides a simple way to account for viscous and plastic phenomena in constitutive relations. Its shortcoming is that this method cannot describe coupling between mechanical and thermodynamic processes which is the essence of mechanically induced crystallization.

According to the other approach, a polymer is treated as a network of long chains connected to junctions. Stretching of chains entails an increase in their free energy. When macro strains reach some threshold level, the free energy of a partially crystallized chain falls below that of an amorphous chain. With the growth of strains, the concentration of crystallites (per unit mass) also increases to ensure minimum of the total free energy. This scenario has been proposed by Flory (1947) to predict crystallization of natural rubber. Its advantage is that the constitutive relations account for coupling between mechanical stresses and the level of crystallization. However, the following shortcomings may be mentioned:

1. The Flory theory is restricted to uniaxial extension of specimens.

2. It assumes that end-to-end vectors of all chains lie along the direction of loading.

3. This method neglects the viscoelastic phenomena in rubbery polymers and it can be applied when the rates of strains are rather small to guarantee that at any time t chains reach their thermodynamic equilibrium, on the one hand, and are relatively large to ensure that the stress relaxation can be neglected, on the other hand.

In the present work, the Flory model is extended to arbitrary three–dimensional loadings. It is assumed that long chains are located arbitrarily with respect to the strain tensor, which implies that the local concentration of crystallites c becomes a function of a point in a medium and two spherical angles which determine the position of the end-to-end vector with respect to the eigenvectors of the strain tensor. To account for the viscoelastic response of semicrystalline polymers, we combine the Flory approach with the concept of transient polymeric networks.

New constitutive relations are derived for rubbery polymers subjected to stress-induced crystallization under nonisothermal three-dimensional loading. Thermodynamic potentials of a network are calculated based on the Flory concept, and the stress–strain relations are developed using the laws of thermodynamics. Adjustable parameters of the model are determined for poly(ethylene terephthalate) in uniaxial extension. It is demonstrated that the constitutive relations correctly predict experimental data in uniaxial tensile tests at deformations up to 300%.