

THERMOMECHANICS OF POLYMERS UNDER CONDITIONS OF RELAXATION AND PHASE TRANSITIONS

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ABSTRACT

Most of polymeric articles are produced during polymerization at elevated temperatures. After completion of the polymerization process there may occur glass transition and crystallization processes singly or in combination, depending on the polymer type and cooling regime. Polymerization proceeds non-isothermally over the entire volume and the front, as such, is absent. Similar phenomena are also observed in crystallization. Furthermore, polymerization and crystallization processes may go on concurrently. It is essential that such factors as crystallization shrinkage and strong temperature dependence of physicomechanical and thermophysical properties of the material should be taken into account. The process of glass transition is of relaxation nature and, unlike crystallization, is not a phase transition. Glass transition occurs in a certain temperature range and does not involve shrinkage, and heat absorption or heat release. During glass transition the elastic moduli and relaxation times change by several orders of magnitude. All these phenomena are eventually responsible for generation of residual stresses.

The proposed model involves two problems: thermophysical and thermomechanical. To simulate the space-time temperature distribution and the degrees of polymerization and crystallization we use the system of differential equations which consists of the equation of non-stationary heat conductivity, the kinetic equation of polymerization and the kinetic equation of crystallization. The system is supplemented with appropriate boundary and initial conditions.

In the framework of the accepted phenomenological approach the crystallizing polymeric material is represented as a two-component mixture of amorphous and crystalline structures, whose specific fractions are defined by the degree of crystallization. It is assumed that at the instant of transition to the crystalline state each part of the amorphous structure of the polymer, proportional to the increment of the

crystallization degree, has a zero stress state and is consistent in its strain state with an early formed structure.

The strain-stress state of amorphous and crystalline phases is characterized by a specific elastic-hereditary potential. The procedure of deriving the expression for the specific potential of the composition is proposed. Setting particular forms of the potential for amorphous and crystalline phases, we obtain the constitutive relation.

As an example of the obtained relation, consideration is given to a particular but widely met in practice case, when the characteristic times of the crystallization process and the external action are less than relaxation times of the crystalline phase but greater than those of the amorphous phase. This allows us to neglect the rheology aspects and to apply the elastic approximation of material properties in the form of an instantaneous modulus to the crystalline phase and in the form of equilibrium modulus to the amorphous phase.

The experimental verification of the model related to identification of the model parameters involves traditional thermophysical tests, differential scanning and adiabatic calorimetry. It is also necessary to conduct traditional mechanical experiments to define elastic and viscoelastic characteristics of amorphous and crystalline phases.

The constitutive relations are constructed under the assumption that the isotropic uniform polymer exhibits perfect elastic properties in a highly elastic state and viscoelastic properties in a glassy state.

For description of glass transition occurring within a certain temperature range, it is suggested to introduce a variable characterizing the degree of completion of glass transition. A number of equations determining the relationship between the temperature, the rate of its variation and the degree of glass transition have been obtained.

A special procedure has been developed to derive constitutive relations for the specific potential of the vitrifying material, which is the result of the limiting transition from successive series of glass transition states.

An experimental procedure for identifying model parameters in thermomechanical tests is described. The proposed model is compared with the other known models of polymer behavior under conditions of relaxation transitions observed in experiments on cyclic cooling/ heating of the constrained specimen. The analytical solution is constructed for a model problem on generation of residual stresses in a non-uniformly cooled packet of polymeric bars undergoing glass transition.

For the models proposed, the finite-element procedures of solving the boundary-value problems have been developed. These procedures are found to be rather effective for estimating the evolution of thermomechanical behavior of polymers from the melting stage to the solid phase in a number of particular polymeric articles. Some example problems have been solved numerically: cooling of a circular polyethylene plate, curing of a short cylinder made of epoxy resin.

To demonstrate validity and applicability of the model, the obtained solutions have been compared with experimental data.

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