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Towards a Solid-State Constitutive Model for Polymer Products with Process-Induced Molecular Orientation

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There is much interest at present in the use of numerical modelling for predictive simulation of the solid-state performance of polymers, to assist in the design of products and their processing. Moreover, in view of the number of available degrees of freedom in the creation of synthetic polymer systems (monomer and comonomer chemistry, MWD, molecular shape etc), it would be especially attractive for such modelling to be “molecularly aware”, so that the roles of such structural details could be factored in. The work to be described is aimed at achieving this ambitious goal.

Some years ago, this laboratory proposed the only general constitutive model for amorphous polymers applicable right through the glass transition: the “glass-rubber constitutive model”. This is a fully 3-D, finite deformation, constitutive model, capable of capturing many features of the elastic, viscoelastic and viscoplastic deformation of amorphous polymers. Its central tenet is that perturbation of free energy of deformation A (and hence stress) in these materials has two, independent, parts – a ‘bond-stretching’ component (b) and a ‘conformational’ component (c). In spite of its success when applied to isotropic amorphous polymers, the model has sometimes been shown to be inaccurate when applied to polymers containing molecular orientation. There is currently no published constitutive model for polymers that is adequate for this important task.

To meet this need, we are investigating a new form of the GR model. The key new feature is recognition that the viscoplastic flow process by which segmental molecular relaxation takes place is likely to be intrinsically anisotropic. During melt-state processing, preferential molecular alignment occurs, but this relaxes on a spectrum of length and time-scales. When orientation remains on the scale on the segment, i.e. at the sub-entanglement length scale, there will remain a degree of alignment of the flow-process units, leading to anisotropy of the viscoplastic flow process by which A_b relaxes. In addition, residual chain stretch in processed products leaves A_c perturbed from its equilibrium value, and nonlinearity of the conformational response then causes additional anisotropy, especially apparent in the strain stiffening regime.

In the work to be described, the new model has been tested against measurements of the solid-state constitutive response of amorphous polymers containing process-induced molecular orientation, taking account of the different length and time-scales on which orientation relaxes. These, and comparisons with previous results in the literature, indicate that the new model can rationalise previously unexplained features of the solid-state mechanical response of oriented polymers, and provides a promising vehicle for predictive modelling of processed polymer products.