Kinetic model for tensile deformation of polymers.
Part IV: Effect of polydispersity*)

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Abstract: A previously introduced molecular model for tensile deformation of solid, flexible chain polymers is used to study the effect of the molecular weight distribution on the strain at break, or maximum draw ratio. The parameters in the model are chosen to represent melt-crystallized linear polyethylene. We focus, in particular, on the relation between the maximum draw ratio and two distribution characteristics: the $M$ molecular weight average, first introduced by Graessley, and the polydispersity ratio $M_d/M_w$. For a log-normal molecular weight distribution, an increase in polydispersity at constant $M$ leads to a broadening of the optimum rate (or temperature) window for achieving maximum elongation, but is accompanied, however, by a substantial decrease in the maximum attainable draw ratio. Studies on the deformation of systems having a bimodal molecular weight distribution indicate that blends made of equal weight fractions of long and short chains exhibit an unexpectedly high elongation at break. These results are explained in terms of the model and possible technological implications are discussed.

Key words: Model; Deformation; Polymer.

1. Introduction

The present paper is a continuation of a previous series [1–3] on the development of a theoretical, kinetic model for tensile deformation of solid, flexible polymers. The model, its basic physics and critical assumptions were described in detail in Parts I and II [1, 2]. In the first part [1], it was applied to study the effects of molecular weight on the deformation of melt-crystallized, linear polyethylene; in the subsequent Part II [2] the model was employed to examine the influence of entanglement spacing on the deformation behavior of (solution-crystallized) high molecular weight polyethylene. The important effects of temperature and rate of deformation on the drawability of melt-crystallized polyethylene were reported at length in Part III [3]. In the latter study, we made the interesting observation that, for each molecular weight, there exists a narrow temperature or elongation rate window within which maximum drawability occurs, i.e., where a maximum value of the elongation at break is observed. This finding is of obvious practical importance in view of the strong dependence on draw ratio of the stiffness of oriented flexible polymers. It is important to point out that the above results obtained with the kinetic model were restricted to systems of monodisperse chains.

It was already mentioned in Part III [3] that the previous predictions are likely to be strongly affected by polydispersity. Although the effects of a distribution of chain lengths on the tensile strength...
of highly oriented polymer filaments have been investigated at length, both theoretically [4] and experimentally [5–6], relatively few studies dealt with the influence on the drawability of unoriented polymers. Experimental work on the deformation behavior of melt-crystallized polyethylene, performed by Capaccio and Ward [7], focused primarily on the effect of the molecular weight and its distribution on the morphology of the initial material and its indirect correlation with tensile drawing. The particular role of the high molecular weight component in the structure development of melt extruded polyethylene was emphasized by Bashir et al. [8].

It is the purpose of the present paper to extend the results obtained in [1–3] to include the important effects of the molecular weight distribution on the maximum draw ratio of (melt-crystallized) polyethylene. Special attention will be given to bimodal distributions which were recently found to yield unusual deformation properties of cross-linked networks [9].

2. Theory

We briefly recapitulate the essential features of our approach. The reader is referred to [1–3] for a detailed description of the model and its parameter values. In the model at hand, the polymer solid is represented by a loose network of entangled chains that are tied together through numerous, weak (Van der Waals) bonds (Fig. 1). The latter represent the crystallinity that provides the initial stiffness to the material. Upon tensile deformation, these bonds are broken, the chains are deformed and are allowed to slip through entanglements with the help of Monte-Carlo processes based on the Eyring chemical activation rate theory. At regular, short time intervals, the network is relaxed to its minimum energy configuration using a series of fast computer algorithms, which steadily reduce the net residual force acting on each entanglement.

As was stated in the introduction, previous applications of this model were restricted to polymers of a monodisperse molecular weight distribution. Here, we present a detailed study of the effects of polydispersity of the deformation behavior.

Several analytical equations have been utilized to represent molecular weight distributions of polymers (for a review, see, e.g., [10]). Of particular use and, therefore, the subject of this work, is the log-normal distribution. This distribution may be represented by

\[ w(M) = \frac{\phi}{M} \exp \left[ -\left( \frac{1}{\beta^2} \right) \ln^2 \left( \frac{M}{M_0} \right) \right] . \]  

Here \( w(M) \) is the weight fraction of polymer with molecular weight \( M \). The parameter \( \beta \) in Eq. (1) increases with the increase of the width of the distribution, whereas \( M_0 \) together with \( \beta \) determine the average molecular weight of the distribution. The number, weight and z-average molecular weights, expressed in terms of \( \beta \) and \( M_0 \) are

\[ M_n = M_0 \exp \left( -\frac{\beta^2}{4} \right) \]  
\[ M_w = M_0 \exp \left( \frac{\beta^2}{4} \right) \]  
\[ M_z = M_0 \exp \left( 3\frac{\beta^2}{4} \right) . \]  

In view of its academic and potential commercial interest [4, 11], the present work concerns also another molecular weight distribution, i.e., a