OBSERVATION OF RHEOLOGICAL PROPERTIES OF POLYLACTIDE DURING CRYSTALLIZATION: MODELING QUIESCENT AND FIELD INDUCED CRYSTALLIZATION USING RHEOLOGICAL DATA

Y. Yuryev, P. Wood-Adams

Concordia University, Mechanical and Industrial engineering department, Montreal, Canada

y.v.yuryev@gmail.com

The polymer crystallization is one of the most significant phenomenon in polymer science and many different techniques were used for studying of different aspects of polymer crystallization. Linear viscoelastic properties of polymer melts are highly sensitive to any structural changes, including molecular weight changes and the formation and growth of crystallites. In this study we make use of this sensitivity to study the homogeneous crystallization of polylactide. Since this polymer is rather quickly susceptible to thermal degradation even at moderate temperatures it is essentially impossible to study homogeneous crystallization in the absence of degradation. Thus the evolution of complex viscosity of a polylactide during crystallization was studied taking into account complex viscosity decrease due to thermal degradation. A simple empirical model is used to characterize the variation of complex viscosity due to thermal degradation:

$$\eta_t^* = \eta_{t=\infty}^* + C\exp(-\frac{t}{\tau}) \tag{1}$$

where $\eta^*_{t=\infty}$ is a limiting complex viscosity at long times, C is the viscosity decay coefficient, and τ is the thermal degradation time constant.

The standardized residuals approach was used to determine the induction time of homogeneous crystallization at wide range of degrees of supercooling:

$$r_i = \frac{e_i}{\sqrt{\mathscr{e}^2}} = \frac{e_i}{\sqrt{\frac{1}{n-1}\sum_{i=1}^{i=n}(e_i-\bar{e})^2}} \tag{2}$$

where e_i is the real residual (the difference between measured zero shear viscosity and corresponding value of the fit equation) and the divider is the square root of the unbiased estimator. This technique allowed eliminating the errors which are intrinsic to previously implemented approaches based on detection of arbitrary viscosity increase during crystallization of polymer melt.

Based on this approach, a phenomenological model describing the viscosity evolution during homogeneous crystallization is proposed and validated:

$$\frac{\eta_{cryst}}{\eta_{melt}} = \frac{\eta_{filler}}{\eta_{melt}} \cdot \frac{\eta_{cryst}}{\eta_{filler}} = \frac{\exp\left[\frac{4\delta\phi}{3Gt(1-\phi)}\right]}{\left[1-\frac{\phi}{A}\right]^2} \tag{3}$$

where δ is physical entanglement factor, ϕ is relative melt crystallinity, G is spherulitic growth rate, A=0.68 is a shape factor.

The development of these experimental and theoretical approaches allowed extending the studies to flow induced crystallization under both continuous and step shear. The proposed technique demonstrated high repeatability and sensitivity in detection of crystallization onset.

Polylactide chains consist of highly polar repeat units which makes them susceptible to the presence of external electric field. Potentially, the electric field could affect the polymer chain orientation thus affecting polylactide melt crystallization. The development of the approach allowing modelling the viscosity at low melt crystallinity led to detecting and quantifying effects of electric field on polylactide crystallization parameters. It was found that the presence of electric field increases polylactide nucleation rate promoting crystallization. Further studies showed that the magnitude of this effect increases with the increasing crystallization temperature suggesting that the mobility of polymer chains plays main role in this effect.