Prediction of yield stress development using structural relaxation

Citation for published version (APA):

Document status and date:
Published: 01/01/2005

Document Version:
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher’s website.
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• The final published version features the final layout of the paper including the volume, issue and page numbers.

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Introduction

In previous work [1] we showed that by extrapolating the results of the development of yield stress due to annealing treatments on a glassy polymer below the glass transition temperature, $T_g$, towards the development of properties during processing, we were able to predict the resulting distribution of yield stresses. In this previous approach, however, $T_g$ was used as an input parameter. In the approach presented here [2], structural relaxation kinetics are used to describe the relaxation kinetics of the solidifying glass, and thus describing $T_g$.

TNM-Model

Structural relaxation has already been extensively used to describe a number of relaxation phenomena observed in polymers, e.g. volume and enthalpy. In figure 1 (left) relaxation of a property $P$ (volume) with temperature is shown. Figure 1 (right) shows how this can be translated to the relaxation of the zero-viscosity.

\[ T_f(T, \xi) = T - \int_0^\xi M_\nu(\xi - \xi') \frac{dT}{d\xi} d\xi' \]  

\[ M_\nu(\xi) = \exp \left( - \left( \frac{\xi}{T_\nu} \right)^3 \right) \]  

\[ \gamma_f(T, T_f) = A \exp \left( \frac{x \Delta H}{RT} + \frac{(1-x) \Delta H}{RT_f} \right) \]  

\[ \log_{10}(\gamma_f(T, \xi)) = \log_{10} \left( \frac{A_0 \xi^2 V^3}{R V^3} \right) + \log_{10}(T) + \frac{1}{2 \cdot 303} \left( \frac{\Delta H}{R} \right) \left( \frac{1}{T} - \frac{1}{T_f(\xi)} \right) \]  

\[ \sigma = \sigma_t + \sigma_r \]  

\[ \sigma_t = 3 \alpha \sigma_0 \quad ; \quad \sigma_r = G_0 \left( \lambda^2 - \lambda_{\infty}^{-1} \right) \]

Experimental

From a commercial grade of polycarbonate, Lexan 141R, injection molded samples were made. Mold temperatures were varied from $30^\circ C$ to $130^\circ C$. Subsequently tensile bars were machined from the injection molded samples to determine the resulting yield stress, see figure 2 below.

![Figure 2 Injection molded part and tensile bars made thereof](image)

Results

The results show that both annealing close to $T_g$, and prediction of the yield stress distribution as it develops due to processing conditions can be described accurately by our approach.

![Figure 3 Annealing close to $T_g$: symbols are experimental results, lines are model predictions (left); development of zero viscosity versus temperature, $T_f$, is a reference temperature, here equal to $T_g$ (right)](image)

Conclusions

With the use of structural relaxation kinetics yield stresses can be predicted from processing conditions. This makes it possible to design a product for performance without ever doing a single experiment.

References:


T.A.P.Engels, L.E.Govaert, G.W.M.Peters and H.E.H.Meijer

PO Box 513, 5600 MB Eindhoven, the Netherlands