Original Contributions  ·  Originalarbeiten

© 1978 Dr. Dietrich Steinkopff Verlag, Darmstadt
ISSN 0035-4511 / ASTM-Coden: RHEAAK

Meß- und Prüflaboratorium der BASF Aktiengesellschaft, Ludwigshafen am Rhein

Description of the non-linear shear behaviour of a low density polyethylene melt by means of an experimentally determined strain dependent memory function*)

H. M. Laun

With 12 figures and 3 tables  

(Received July 12, 1977)

1. Introduction

The description of the nonlinear viscoelastic behaviour of polymer melts by means of an appropriate and mathematically simple constitutive equation is very helpful for the rheological characterization of polymer melts. The rheologist has to choose a set of tests which is sufficient to characterize the flow behaviour of a material rather completely. From these measurements he wants to predict the rheological behaviour of the melt at quite different flow situations. The constitutive equation is a guidance for the selection of the most suitable experiments for this characterization and makes it possible to calculate the material functions for a great variety of deformation histories.

During the last years many experiments have been performed to examine the applicability of a single integral constitutive equation given by Lodge (1, 2):

\[ \sigma(t) + p \mathbf{1} = \int_0^\infty \bar{\mu}(t - t') C^{-1}(t,t') d(t - t'). \]

[1]

Here \( \sigma \) is the extra-stress tensor at the current time \( t \), \( p \) the hydrostatic pressure, \( C^{-1} \) the Finger relative strain tensor between the states \( t \) and \( t' \), and \( \bar{\mu} \) is the memory function specific for the material. The zero superposed on symbols is used to distinguish the material functions describing the linear viscoelastic behaviour from those describing the nonlinear behaviour.

Recently a straightforward generalization of the rubberlike-liquid constitutive equation was proposed by Wagner (3, 4), where the memory function for the nonlinear behaviour \( \mu(t - t'; I_1; I_2) \) is expressed as a product of the memory function for the linear behaviour \( \bar{\mu}(t - t') \) and a so-called damping function \( h(I_1; I_2) \) depending on the first and second invariants of the Finger tensor:

\[ \mu(t - t'; I_1; I_2) = \bar{\mu}(t - t') h(I_1; I_2). \]

[2]

The aim of this paper is to give an experimental justification for assumption [2] and to show how the complete memory function describing the shear behaviour can directly be determined by rheological measurements. The predictions of the constitutive equation making use of the experimentally determined memory function are compared with measurements. It is important to test the predictions by means of quite different measuring quantities, as some material functions are rather insensitive to the special form of the memory function.

2. Experimental

The shear flow data reported in this paper were obtained using a Weissenberg Rheogoniometer Model R 12/15 modified by Meissner. Details of the apparatus can be found in (5, 6). A cone angle of 8° was used. The plate diameters were 24 mm, 50 mm, and 72 mm. All measurements have been carried out on a stabilized LDPE melt formerly called 'Melt I' (7). The zero shear viscosity at T = 150°C is \( \eta_0 = 5.0 \times 10^4 \) Pa s. An extensive series of rheological measurements on Melt I has been performed by Meissner (5, 6, 8, 12). The data already available from these measurements have been completed by additional experiments.

3. Linear viscoelastic behaviour

3.1. Time dependence

For simple shear flow the well known relations for the shear stress \( p_{12} \) and the primary normal-stress difference \( p_{11} - p_{22} \)

\[
p_{12}(t) = \int_0^\infty \mu(t - t') \gamma_{i,t'} dt'(t - t') ,
\]

\[
[p_{11} - p_{22}](t) = \int_0^\infty \mu(t - t') \gamma_{i,t'}^2 dt'(t - t')
\]  are obtained from eq. [1] (1). Here \( \gamma_{i,t'} \) is the relative shear strain between the states \( t' \) and \( t \). It is convenient to approximate the memory function by a sum of exponential functions with time constants \( \tau_i \) and coefficients \( a_i \) (9, 2):

\[
\mu(t - t') = \sum_i a_i \exp \left( -\frac{t - t'}{\tau_i} \right).
\]

Using [5], for oscillatory shear flow of angular frequency \( \omega \) the following expressions for the storage modulus \( G'(\omega) \) and the loss modulus \( G''(\omega) \) are derived from [3]:

\[
G'(\omega) = \sum_i a_i \tau_i \frac{\omega^2 \tau_i^2}{1 + \omega^2 \tau_i^2},
\]

\[
G''(\omega) = \sum_i a_i \tau_i \frac{\omega \tau_i}{1 + \omega^2 \tau_i^2}.
\]

To each relaxation time \( \tau_i \) a relaxation strength \( \gamma_i = a_i \tau_i \) is attributed. Figure 1 shows measurements of \( G'(\omega) \) and \( G''(\omega) \) performed by Zosel (10). The moduli measured at different temperatures are plotted as functions of the reduced angular frequency \( \alpha_T = a_T \omega \) to get master curves at a reference temperature of \( T_0 = 150°C \) (11), \( a_T \) being the shift factor. For the approximation of the memory function eight relaxation times \( \tau_i \) between \( 10^{-4} \) s and \( 10^3 \) s with decimal

![Diagram showing shear moduli of LDPE Melt I as functions of the reduced angular frequency. Reference temperature \( T_0 = 150°C \). The full lines were calculated according to [6] and [7] using the constants of table 1.](image-url)