Polymer Bulletin 13, 271–276 (1985)

Polymer Bulletin

Constant Stretching Rate Experiments on Low Density Polyethylene

F.P. La Mantia, S. Piccarolo, A. Valenza, and D. Acierno[+]

Istituto di Ingegneria Chimica, Università di Palermo, I-90128 Palermo, Italy

ABSTRACT

A simple apparatus for elongational test of molten polymers is presented. Its realiability is demonstrated by means of stress growth in constant stretching rate experiments and relaxation test on a low density polyethylene sample.

INTRODUCTION

The evaluation of the elongational flow behaviour of the polymer melts has received more and more attention in the last twenty years (1). Many experimental apparatus have been used in order to obtain elongational data both at constant velocity (2-4) and at constant stretching rate (5-18) and at constant force or stress (19-24). Moreover also isothermal and non-isothermal melt spinning (25-27) or spinning-like experiments (17,28,32) have been adopted.

The response of the molten polymers to uniaxial stress is indeed not particularly simple and strongly depends on the polymer structure and on the test conditions. It is worth to notice for instance the strain hardening and the high elongation ratios to break of the low density polyethylene in isothermal constant stretching rate experiments (6-13), while in non isothermal conditions the breaking stretching ratios are very low (31-33). On the other hand the high density polyethylene show mostly opposite behaviour.

In this work a simple experimental apparatus similar to that described by Ide and White (13), is presented and its reliability is demonstrated by means of measurements on a low density polyethylene sample.

EXPRIMENTAL

Apparatus

A simple device for measuring elongational flow behaviour was designed and constructed following the suggestions of Ide and White (13).

[+] Present address: Istituto di Ingegneria Chimico-Alimentare, Università di Salerno, I-84100 Salerno, Italy

It consists of a thermostated oil bath, a rotating roll powered by a stepping motor controlled by means of a computer and a load cell connected to an electronic amplifier.

The molten polymeric rod, floating on silicon oil, is clamped between the roll and the jaw of the load cell and is stretched wounding-up around the rotating roll. The filament length was approximately 20 cm.

The rotation speed of the roll could be varied continuously by using a computer controlled stepping motor. This motor allowed elongational gradients, $\dot{\varepsilon}$, of 10^{-4}-1 s^{-1} with a 3 cm diameter roll. Elongational gradients values below 10^{-2} s^{-1} were allowed with the aid of a gearbox with a reduction factor of 28.

The thermostated oil bath was controlled through a PDI contoller Leeds & Northrup mod. ELECTROMAX III and continously stirred by means of a rotating stirrer. A small channel made by a thin sheet of copper surrounded the sample in order to avoid any disturbances of the stirring oil on the filament. The temperature gradient at the temperature of the tests was found to be about +/- 0.5 C over all the sample length. The silicon oil was chosen in order to compensate for much of the specimen gravity through buoyancy.

The force acting on the sample was revealed using a load cell TMI with a maximum capacity of 5.5 N, connected with an amplifer HBM mod. KWS 3072 . The force was recorded by means of the Hewlett-Packard oscillographic recorder mod. 7402A at low times, and with a Linseis recorder at high times.

Stable and reproducible measurements were obtained only when the force was not lower than 0.04 cN.

Material and sample preparation

The material used in this work was a commercial low density polyethylene known as EF5 2100 manufactured by ENICHEM (Italy). The main physico-chemical characteristics are reported in Tab I. A complete characterization of this polymer in shear flow has been reported in (34).

TABLE I

Physico-chemical properties of the low density polyethylene sample

M.F.I. (g/10min)[a]	$\bar{M}w\ 10^{-3}$ [b]	$\bar{M}w/\bar{M}n$ [c]	$[\eta]$ (dl/g) [d]	ϱ (gr/cm) [e]
0.7	220	6.9	1.05	0.919

a) ASTM D 1238-73.
b) from ligth sacttering at T= 135 C in α chloronaphtalene.
c) from GPC at T= 135 C in ortodichlorobenzene.
d) in THN at T= 130 C .
e) ASTM D 1505-78.

The filament was prepared by extrusion through a small scale piston-type extruder using a die of 2 mm and length to diameter ratio of 4. The extrusion was carried out at 200 C. The filament was collected in a water-ethanol solution to compensate the own weight and cut out in strands of about 30 cm.

The specimens were later remelted in the silicon oil at the same temperature of the test to allow them to shrink. After this operation the average diameter was about 0.4 mm and the cross section was constant over the whole sample length.

Procedure of the elongational tests

The specimes so prepared were fixed to the jaw of the laod cell and fastened to the roll attached to the motor. Given the desired stretching rate and the length of the filament, the input for the computer were found and the test could start.

The filament did not in general wind up irregularly, i.e. over itself at the end of each rotation. If however this happened, the run was discarded.

The actual cross sectional area at the test temperature is calculated taking into account the thermal expansion of the sample.

The stretching rate $\dot{\varepsilon}$ is

$$\dot{\varepsilon} = \frac{dv_1}{dx_1} = \frac{V}{L} = \frac{R\Omega}{L} \qquad (1)$$

and the elongational viscosity, η_{el} , was calculated through

$$\eta_{el} = \frac{\sigma_{el}}{\dot{\varepsilon}} = \frac{F(t)}{S(t)\dot{\varepsilon}} \qquad (2)$$

where σ_{el} is the true tensile stress, F(t) the recorder force and S(t) is the cross-sectional area which changes with time following the equation

$$S(t) = S_o \exp(-\dot{\varepsilon} t) \qquad (3)$$

where S_o is the initial cross section.

Stress relaxation experiment were carried out by stretching the filament at an elongational rate of 0.1 s^{-1} for about 0.3 s and recording the stress decay.

All the tests were carried out at 180 C.

RESULTS AND DISCUSSION

Fig.1 reports the transient viscosity curves for five values of the stretching rate. At very low value of $\dot{\varepsilon}$ the elongational viscosity increases with time to an asymptotic value which is the troutonian value, i.e. 3 η_o .

Increasing the stretching rate the curves show a sudden upturn and then the well known strain hardening of the low density polyethylene. At

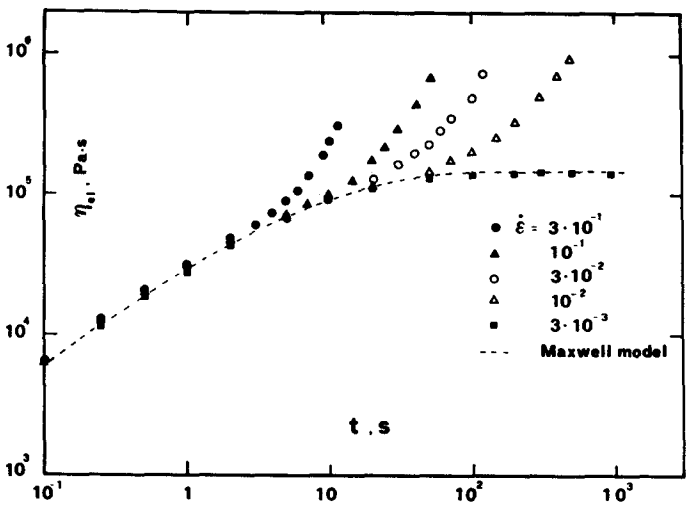

Fig. 1 Transient viscosity curves. T = 180 C.

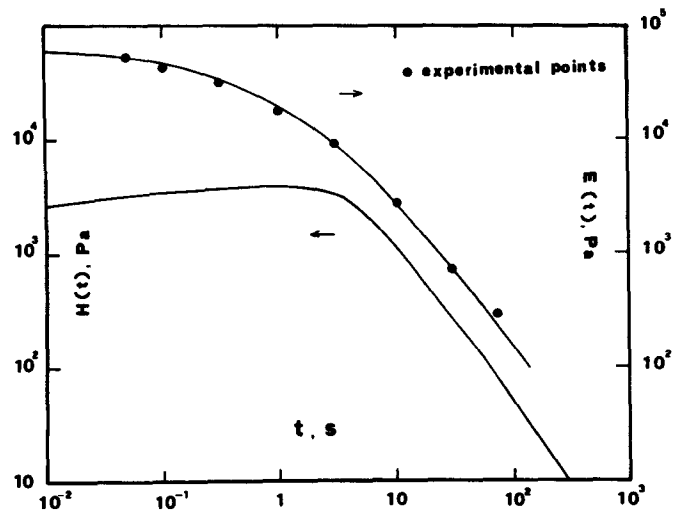

Fig. 2 Relaxation modulus, E(t), and relaxation times spectrum, H(t).

low times all the values lie on the curve relative to $\dot{\varepsilon} = 3 \cdot 10^{-3}\ s^{-1}$ that is for the linear viscoelastic case. The deviation from the troutonian curve occours at lower and lower increasing the extensional strain rate.

In order to evaluate the goodness of this apparatus, beyond the reaching the correct troutonian value obtained for the curves at $\dot{\varepsilon} = 3 \cdot 10^{-3} s^{-1}$, the theoretical transient curve in the linear range at the same stretching rate has been reported in the same figure.

For this aim the relaxation times spectrum has been derived from the relaxation modulus following the method outlined in (35). In Fig. 2 the experimental relaxation modulus and the curve calculated from the relaxation times spectrum have been reported indicating the goodness of the inversion. In the same figures the relaxation times spectrum is also reported.

The transient curve calculated through the Maxwell equation in the linear range superimpose very well to the experimental curve.

ACKNOWLEDGMENT

This work has been carried out with the financial support of "C.N.R. Progetto Finalizzato Chimica Fine e Secondaria".

REFERENCES

1) C.J.S. Petrie "Elongational Flow" Pitman, London (1979)
2) S. Middleman, Trans. Soc. Rheol. 13,123 (1969)
3) C. Goldstein, Trans. Soc. Rheol. 18,357 (1974)
4) D. Acierno, F.P. La Mantia, L. Nicodemo, Trans. Soc. Rheol. 21,261 (1977)
5) R.L. Ballman, Rheol. Acta, 4,137 (1965)
6) J. Meissner, Rheol. Acta, 8,78 (1969)
7) J. Meissner, Rheol. Acta, 10,230 (1971)
8) J. Meissner, Trans. Soc. Rheol. 16,383 (1972)
9) J. Meissner, J. Appl. Polym. Sci. 16,2877 (1972)
10) H.M. Laun, H. Munstedt, Rheol. Acta 15,517 (1976)
11) A.E.Everage and R.L. Ballman, J. Appl. Polym. Sci. 20,1137 (1976)
12) H.M. Laun, H. Munstedt, Rheol. Acta 17,415 (1978)
13) Y. Ide, J.L. White, J. Appl. Polym. Sci. 22,1061 (1978)
14) G.R. Cotton, J.L. Thiele, Rubber Chem. Technol. 51,749 (1978)
15) H.M. Laun, H. Munsted, Rheol. Acta 18,1061 (1979)
16) H. Munstedt, Trans. Soc. Rheol. 23,421 (1979)
17) T. Raible, A. Demarmelsm J. Meissner, Polymer Bullettin, 1,397 (1979)
18) H. Munstedt, Trans. Soc. Rheol., 24,847 (1980)
19) H.J. Karan, J.C. Bellinger, Trans. Soc. Rheol. 8,61 (1964)
20) F.N. Cogswell, Plastics and Polymers 36,109 (1968)
21) F.N. Cogswell, Trans. Soc. Rheol. 16,405 (1972)
22) G.V. Vinogradov, V.D. Fikhman, B.V. Radushkevich, Rheol. Acta

11,286 (1972)
23) T. Takaki, D.C. Bogue, J. Appl. polym. Sci. 19,419 (1975)
24) F.P. La Mantia, D. Acierno, Polym. Eng. Sci. 19,800 (1979)
25) D. Acierno, J.N. Dalton, J.M. Rodriguez, J.L. White, J. Appl. Polym. Sci. 15,2395 (1971)
26) C.D. Han, R.R. Lamonte, Trans. Soc. Rheol. 16,447 (1972)
27) I.J. Chen, G.E. Hagler, L.E.Abbot, D.C. Bogue, J.L. White, Trans. Soc. Rheol. 16,473 (1972)
28) A. Bergonzoni, A.J. Di Cresce, Polym. Eng. Sci. 6,45 (1966)
29) W.F. Busse, J. Polym. Sci. A2,5,1249 (1967)
30) K.F. Wissbrun, Polym. Eng. Sci. 13,342 (1973)
31) F.P. La Mantia, D. Acierno in "Polymer Processing and Properties" G. Astarita, L. Nicolais eds. pag 229 Plenum Press, New York 1984
32) F.P. La Mantia, D. Acierno, Polym. Eng. Sci. in press
33) F.P. La Mantia, D. Acierno, Plastics and Rubber Processing and Applications in press
34) D. Acierno, F.P. La Mantia, D. Romanini, A. Savadori, submitted for publication on Rheol. Acta
35) D. Acierno, F.P. La Mantia, G. Marrucci and G. Titomanlio J Non-Newtonian Fluid Mech. 1,125 (1976)

Accepted February 11, 1985