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Stress and Recovery Maxima in LDPE Melt Elongation

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Summary

By means of a new tensile rheometer for polymer melts, stress-strain curves $\sigma(\varepsilon)$ and the elastic recovery $\varepsilon_R(\varepsilon)$ of a low density polyethylene melt were measured up to total strains $\varepsilon = 7$, i.e. stretch $\lambda = 1097$, at 150°C and two strain rates, $\dot{\varepsilon}_o = 0.03$ and $0.1\ s^{-1}$. Tensile tests up to very high strains ε give relevant results only if the test performance is characterized by quality parameters which are defined and given in this paper. The test results show a maximum in σ as well as in ε_R at about $\varepsilon = 5.5$. Hence, in the range of ε investigated, a rheologically steady-state of flow does not exist.

1. Introduction

In tensile rheometry of polymer melts substantial progress could be achieved during the past decade (a) by floating the rod-like molten polymer sample on silicone oil to remove the effects of gravity, and (b) by the application of 'rotating clamps' (MEISSNER 1969). With a constant speed of rotation, these clamps provide a linear increase of the HENCKY strain ε with time t,

$$\varepsilon = \dot{\varepsilon}_o t, \quad \text{where} \quad \varepsilon = \ln \lambda \qquad (1).$$

$\dot{\varepsilon}_o$ is the tensile strain rate, kept constant during the tests discussed here, and λ is the stretch of a material element residing between the clamps during the whole test.

With the first version of this rheometer, stress-strain diagrams could be measured for melts of low density, i.e. branched polyethylene (LDPE) up to total strains of $\varepsilon = 4$, i.e. $\lambda = 54.6$ (MEISSNER 1971, 1972a). After a smooth linear-viscoelastic stress growth, the stress-strain curves showed a remarkable increase followed by a transition into an apparently constant, i.e. steady-state stress. However, this transition could be found only after a modified version of the rheometer allowed measurements up to total strains of $\varepsilon = 6$, i.e. $\lambda = 403$ (LAUN and MUENSTEDT 1976, 1978).

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The maximum strain obtainable in these tests is limited by the temperature constancy which has a direct influence on the homogeneity of the deformation. For further improvement, a new tensile rheometer of the same type was built with a constant temperature along the sample within less than 0.1^oC at 150^oC. This new instrument allows measurements up to a total strain $\varepsilon = 7$, i.e. $\lambda = 1097$ with an excellent homogeneity of deformation. In this paper results obtained from this rheometer for LDPE are published.

In addition to the tensile stress σ, the recoverable portion ε_R of the total strain ε is determined by cutting the sample into short pieces at the end of the tensile test as described formerly (MEISSNER 1969, 1972a). The mass of the cut-offs is connected with the cross-sectional area of the sample at the end of the test and allows one to characterize the quality of the test. Only with such quality parameters, do tensile tests with large strains give relevant results.

2. Experimental, Quality of Test Performance

The LDPE used for our tests had a density at 20^oC of $\rho = 0.919\ g/cm^3$ and a melt flow index of MFI 190/2,16 = 1.37 g/10 min (German standard DIN 53735). The samples were prepared by extrusion. The initial cross-sectional area q_o at test temperature was about 55 mm^2. All tests were performed at 150^oC.

The tensile force F(t) is recorded with a standard deviation of less than 5×10^{-5} N. From F and the cross-sectional area q(t), the tensile stress is obtained: $\sigma(t) = F(t)/q(t)$, where $q(t) = q_o \exp(-\dot{\varepsilon}_o t)$. The last relation makes use of the incompressibility assumption. As rheological material function the time dependent tensile viscosity $\mu(t)$ is defined by

$$\mu(t) = \sigma(t)/\dot{\varepsilon}_o \qquad (2).$$

Two parameters characterize the quality of the test performance:

(1) The relative error of the total strain $\Delta\varepsilon/\varepsilon$, which is the relative difference between the true strain $\bar{\varepsilon}$ and the nominal strain $\varepsilon_1 = \dot{\varepsilon}_o t_1$, where $\bar{\varepsilon}$ follows from the measured cross-sectional area average $\bar{q}$ of the sample at the end of the tensile test, $t = t_1$, and the initial area q_o by $\bar{\varepsilon} = \ln(q_o/\bar{q})$. The relative error of the total strain is equal to that of the strain rate and defined by

$$\frac{\Delta\varepsilon}{\varepsilon} \equiv \frac{\bar{\varepsilon}-\varepsilon_1}{\varepsilon_1} = \frac{(\bar{\dot{\varepsilon}}-\dot{\varepsilon}_o)t_1}{\dot{\varepsilon}_o t_1} = \frac{\Delta\dot{\varepsilon}}{\dot{\varepsilon}_o} \qquad (3).$$

(2) The homogeneity of the deformation determined at t_1 and defined by

$$\Delta q/\bar{q} \equiv (q_{max} - q_{min})/\bar{q} \qquad (4).$$

q_{max}, q_{min} correspond to the thickest and the thinnest of the 13 cut-offs, respectively, into which the sample is cut at $t = t_1$. The q-values follow from the mass of the cut-offs. The cutting length is 50 mm, the distance between the centers of the two rotating clamps is L_o = 710 mm and corresponds to the sample length.

In the following table the quality measures $\Delta\varepsilon/\varepsilon$ and $\Delta q/\bar{q}$ are given for tensile tests performed with $\dot{\varepsilon}_o$ = 0.03 and 0.1 s^{-1}. From the data it follows that even at the very large total strain of ε = 7, the new rheometer works satisfactorily. (The exception in $\Delta\varepsilon/\varepsilon$ for test 72 is caused by an error in the speed of rotation of the clamps.)

Table 1: Quality of Test Performance

$\dot{\varepsilon}_o = 0.03\ s^{-1}$					$\dot{\varepsilon}_o = 0.1\ s^{-1}$				
test	symbol (fig.1)	ε_1	$\Delta\varepsilon/\varepsilon$(%)	$\Delta q/\bar{q}$(%)	test	symbol (fig.1)	ε_1	$\Delta\varepsilon/\varepsilon$(%)	$\Delta q/\bar{q}$(%)
43	○	4.0	-1	3	56	◐	6.0	+1	8
45	△	5.0	+1	3	58	●	6.0	+3	7
46	◘	5.0	0	3	72	⊖	3.0	-7	3
48	■	6.0	+1	6	74	◒	7.0	+2	6
50	▽	7.0	+2	6					
51	●	7.0	0	5					
52	▲	7.0	-2	7					
54	▼	7.0	+1	13					

From the shrinkage of the cut-offs, the recoverable portion ε_R of the total strain $\varepsilon_1 = \dot{\varepsilon}_o t_1$ is determined. However, at large total strains the action of the interfacial tension between molten LDPE and silicone oil requires a correction, the details of which will be published in a forthcoming paper. The recovery data of Figure 3 represent the corrected results of ε_R.

3. Stress-Strain Relations

The stress-strain relations $\sigma(\varepsilon)$ are given up to ε = 7 in Figure 1. For both strain rates, $\dot{\varepsilon}_o$ = 0.03 and 0.1 s^{-1}, and small ε the well-known curves are found with a transition into a horizontal level at about ε = 5, as reported by LAUN and MUENSTEDT (1976, 1978). But for ε > 5.8 the stress decreases from that level, such that a maximum of the $\sigma(\varepsilon)$-relation is found. For both strain rates the stresses measured at ε = 7 are equal to the ones at ε = 3.8. Considering the excellent quality of the test performance, the existence of a maximum in the stress-strain relation is experimentally well established. (Adiabatic heating can be neglected because at $\dot{\varepsilon}_o$ = 0.1 s^{-1} the temperature rise during the deformation from ε = 6 to ε = 7 would be smaller than 0.05°C.

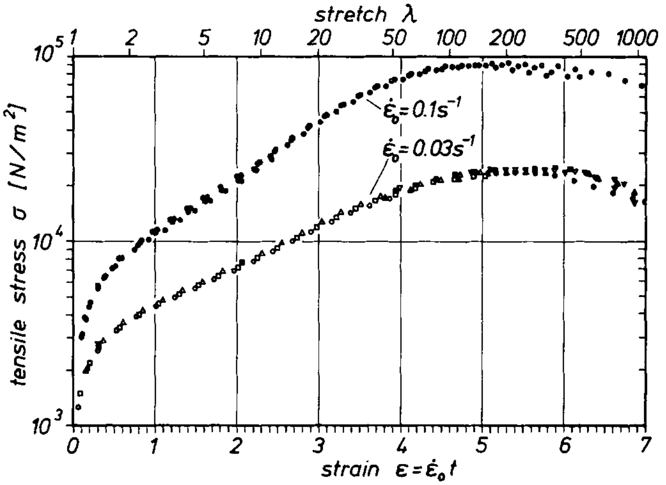

Figure 1: Stress-strain relations σ(ε) of the LDPE melt investigated. Test temperature 150°C.

From the data of Figure 1, the tensile viscosity μ(t) is calculated with eq. (2). This function is plotted on a logarithmic time scale in Figure 2, in which the maximum of each curve is more clearly to be seen than in Figure 1.

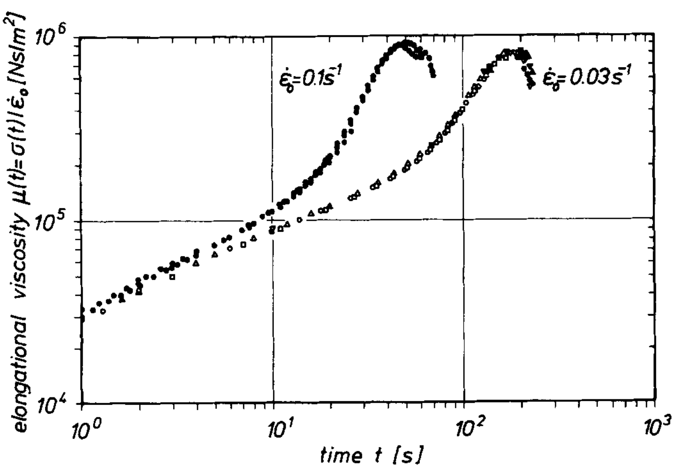

Figure 2: Tensile viscosity μ(t) from the data of Figure 1.

4. Recoverable Strain

In order to find out whether the maximum in stress is connected with a maximum in the elastic portion of the strain, the recoverable strain ε_R was measured at $\dot{\varepsilon}_o = 0.03\ s^{-1}$ at different total strains ε_1. The resulting function $\varepsilon_R = f(\varepsilon_1)$ is given in Figure 3, where ε_R is already corrected for the influence of the interface tension. The curve of Figure 3 shows a maximum also, at approximately the same total strain $\varepsilon = 5.6$ at which the maxima of the stress and the tensile viscosity are located for this strain rate.

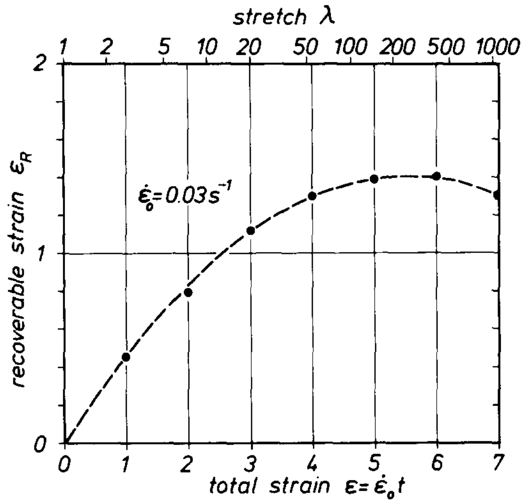

Figure 3: Recoverable portion ε_R of the total strain $\varepsilon_1 = \dot{\varepsilon}_o t_1$. Material and test conditions see Figure 1.

5. Conclusion

The conclusion which must be drawn from the results presented here is that in constant tensile strain rate flow of the LDPE melt investigated, even up to very high total strains $\varepsilon = 7$ ($\lambda = 1097$), a rheologically steady-state flow does not exist. Instead, there is a maximum in tensile stress and in the recoverable portion of the tensile strain. These maxima for elongational flow find their correspondence in shear flow of a similar melt, where maxima occur in shear stress, first normal stress difference and recoverable shear strain (MEISSNER 1972b, 1975). Obviously, these maxima indicate a change of the physical structure of the polymer melt during and because of the deformation in flow (WAGNER 1976, 1979).

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References

LAUN, H.M. and MUENSTEDT, H.: Rheol. Acta 15, 517 (1976)

LAUN, H.M. and MUENSTEDT, H.: Rheol. Acta 17, 415 (1978)

MEISSNER, J.: Rheol. Acta 8, 78 (1969)

MEISSNER, J.: Rheol. Acta 10, 230 (1971)

MEISSNER, J.: Trans. Soc. Rheol. 16, 405 (1972a)

MEISSNER, J.: J. Appl. Polym. Sci. 16, 2877 (1972b)

MEISSNER, J.: Rheol. Acta 14, 201 (1975)

WAGNER, M.H.: Rheol. Acta 15, 136 (1976)

WAGNER, M.H.: Rheol. Acta 18 (1979), in press

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