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Linear Viscoelastic Characterization of Polymer Melts with Long Relaxation Times[†]

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ABSTRACT: Melts of linear polyethylenes (HDPE) have broad retardation and relaxation spectra that can be determined by combining oscillatory and long duration creep/creep recovery tests. For a commercial HDPE the necessary sample preparation (stabilization), testing (at 170 °C), and data conversion are described. For long time testing *incomplete* creep/creep recovery is preferred because the strain is kept within the linear range and reaches a final, constant value. The measured recoverable compliance, $J_e^0(t)$, is converted into a discrete retardation spectrum $\{L_i, \tau_i'\}$. For the short time range the dynamic moduli are measured and converted into the dynamic compliances and finally the retardation spectrum $L(\tau')$. Both spectra overlap and form a *combined* spectrum over 7.5 decades of retardation time τ'. From this the dynamic compliances are recalculated and converted into the dynamic moduli. These are used for computing the weighted relaxation spectrum, $\tau H(\tau)$, ranging from $\tau = 0.01-2.5 \times 10^5$ s. $\tau H(\tau)$ has a maximum at $\tau = 10^4$ s, explaining the difficulties in characterizing HDPE melts. The viscosity functions $\eta(t)$ and the first normal stress functions $\Psi_1(t)$ are measured at shear rates between 10^{-3} and 10 s^{-1} and compared with their limits for zero shear rate, $\eta^0(t)$ and $\Psi_1^0(t)$, respectively, predicted from $H(\tau)$. The measured results are close to these predictions, but only at short times, such that the equilibrium values for $t \to \infty$, η_0 and $\Psi_{1,0}$, are never reached in such tests. In contrast, creep/creep recovery reveals $\eta_0 =$ 113.5 kPas, the (high!) linear equilibrium compliance $J_e = 0.05$ Pa^{-1}, and $2\eta_0{}^2 J_e = \Psi_{1,0} = 1.3 \times 10^9$ Pa s^2. The latter value coincides well with the one calculated from the second moment of $H(\tau)$.

1. Introduction

Rheological studies of melts of linear polyethylene (HDPE) are rare in the literature[1,2] despite the practical importance of this material in polymer engineering[3] and as a reference melt for theoretical studies. Already in 1969 Lee[4] pointed out that at a temperature of 220 °C in a start-up test (step function shear rate) different HDPE samples did not show a constant equilibrium shear stress but instead the shear stress, after some tendency to level-off, started to steadily increase again. In 1979 Plazek and Raghupati[2] performed long time creep measurements with HDPE melts after a careful stabilization. Today, there is no doubt that only after such a stabilization do HDPE melts reveal rheological results that refer to the "as-received" material, but only within an experimentally established "residence time−temperature field" within which the melt under testing is sufficiently stable. Otherwise, the results are not exclusively physical in nature, but influenced or even falsified by chemical reactions in the material during the rheological investigation.

The latter aspect is especially important when the linear viscoelastic behavior is used for characterizing commercial HDPE products by melt rheology because these melts can have extremely long relaxation times.[5] Therefore, the conventional range of oscillatory tests is often not broad enough, such that creep tests followed by creep recovery must be performed as well. In this paper we show results from creep/creep recovery tests combined with those from oscillatory tests, resulting in dynamic moduli that range over a sufficiently broad frequency range. The weighted relaxation spectrum, $\tau H(\tau)$, reveals a maximum at a very long relaxation time (several hours), reflecting a very long transient behavior and—in the molecular weight distribution—the probable existence of molecules of such a high molecular mass that they cannot be detected by the conventional gel permeation chromatography (GPC). A previous study of melt elongation with several HDPE samples revealed an unexpected strain hardening, different for each sample.[6] This hardening was also attributed to a few, very long molecules not detectable in GPC, or to the existence of a few long-chain branches.

For the linear viscoelastic studies described here the shear strain is kept within 1 shear unit. The different steps for performing oscillatory and creep/creep recovery tests are described, and so is the combination of the results until finally the weighted relaxation spectrum is obtained over a broad enough time scale. It is the purpose of this paper to show in detail how such a broad spectrum can be determined for an important commercial polymer that is experimentally difficult to handle. Additional tests in the nonlinear range (start-up tests with constant shear rates between 0.001 and 10 s^{-1}) show that the measured shear stress and first normal stress difference follow predictions from linear viscoelasticity and the Lodge theory if the strain is less than 1 shear unit, but they never reach the predicted equilibrium values. With the same HDPE melt the rheological anisotropy induced during shear flow was studied[7,8] and the behavior in simple (uniaxial), equibiaxial, and planar elongations.[9] For the latter, a constitutive analysis was given.[10]

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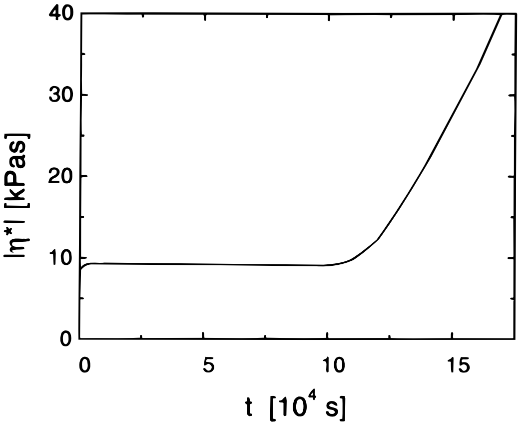

Figure 1. Magnitude of the complex viscosity of the stabilized HDPE melt at 170 °C. The angular frequency was kept constant throughout the test at $\omega = 1\ \mathrm{s}^{-1}$.

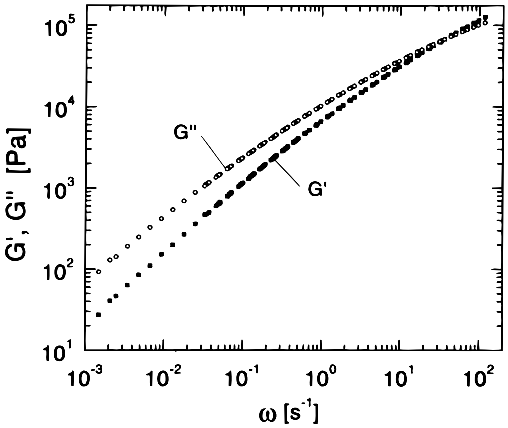

Figure 2. Storage modulus G' and loss modulus G'' measured at or shifted to the reference temperature $T_0 = 170$ °C. The amplitude of the shear oscillations was $\hat{\gamma} = 0.05-0.07$.

2. Experimental Procedures

2.1. Test Material and Sample Preparation. For this study a commercial grade of HDPE (STATOIL 870 H, lot no. 85579) has been used. After stabilization, the melt flow index is MFI = 0.84 g/10 min.[11] Infrared measurements revealed that this material consists of linear molecules,[7] at least within the resolution of the present-day IR technique. For long-time stability in the molten state and protection against oxygen a stabilizer (0.1% IRGANOX B 215) was added.[12] The resulting granules were compression-molded into sheets from which the test samples with the required dimensions were re-molded. From the molecular mass distribution, obtained by GPC, of this material after stabilization, the following number-, weight-, and z-averages resulted: $M_n = 18\,900$, $M_w = 104\,000$, and $M_z = 422\,000$, respectively.[13]

To establish the residence time range during which this material did not change its structure at the test temperature of 170 °C, we followed the already described procedure,[14] viz. performing oscillatory measurements at a constant angular frequency of $\omega = 1\ \mathrm{s}^{-1}$ during a long enough time range until deviations from the constant linear viscoelastic properties were visible.[15] As an example, Figure 1 shows the resulting magnitude of the complex viscosity, $|\eta^*|$, as a function of the residence time of the melt. It follows from this result that the stabilized HDPE melt remains stable at the test temperature of 170 °C during a period of 110 000 s, that is, approximately 30 h.[16]

2.2. Shear Oscillations. For shear oscillations a mechanical spectrometer (Rheometrics RMS 800) was used that had been modified to allow also for normal stress measurements by a temperature constancy of <0.01 °C within the sample.[17] The cone-and-plate configuration (0.1 rad gap angle) was applied and different sample diameters were used to adjust the torque amplitude. The resulting storage and loss moduli G' and G'', respectively, measured at temperatures between 142 and 190 °C, were shifted to the reference temperature $T_0 = 170$ °C by means of the well-known shifting procedure for linear viscoelastic data.[18] Figure 2 shows these master curves; they reach from $\omega = 0.001-100\ \mathrm{s}^{-1}$. This range is given by the frequency range of the rheometer and the temperature dependence of the shift factor a_T that for linear polyethylene has the relatively low activation energy of 27.0 kJ/mol. The crossover point of the curves has the value $G' = G'' = 7 \times 10^4$ N/m^2 and is located near the high-frequency end of the test range. We should mention that Zeichner and Patel[19] used this crossover point for material characterization. For polypropylene samples they could attribute its value to the ratio M_w/M_n and its location to the molecular weight M_w. For polyethylene melts, such a correlation has not been reported.

The small curvature of the curves of Figure 2 indicates the insufficient frequency range of the rheometer because, at the lowest frequencies at which only the molecular motions with the longest relaxation times contribute to the viscoelastic behavior, the predictions for the frequency dependence are as follows:

$$G' \propto \omega^2 \quad \text{and} \quad G'' \propto \omega \tag{1}$$

From Figure 2 it follows that much lower frequencies are required to achieve the transition into such a frequency dependence. But these frequencies are experimentally not accessible. By means of creep/creep recovery tests, however, linear viscoelastic long time results can be obtained that can be converted into the desired quantities.

2.3. Creep and Creep Recovery. The creep/creep recovery tests were performed in a cone-and-plate constant stress rheometer (Rheometrics RSR 8600 with a modified heating similar to that of our RMS 800)[17] with a 0.1 rad cone angle. The sample diameter was approximately 20 mm and the temperature was set to 170 °C. To work with a high enough stress and not to exceed the range of linear viscoelastic response (approximately within 1 shear unit as a rule of thumb for polyethylene melts), furthermore to detect relatively easily the transition of the curved creep response into the linear behavior with the slope $1/\eta_0$, where η_0 is the zero shear viscosity, an *incomplete creep test* was performed with the following stress history:

$$p_{21}(t) = p_{21}[h(t) - h(t - t_1)] \tag{2}$$

with $p_{21} = 20$ Pa, $t_1 = 4000$ s; $h(t)$ is the unit step function.

Preliminary incomplete creep tests were performed with a variation of the shear stress, p_{21}, and the creep duration, t_1, to find the optimal test conditions (sufficiently small stress, but sufficient resolution of the stress signal, sufficient resolution of the strain signal, and sufficient mechanical and thermal stability of the rheometer). These tests resulted in the same value of the zero shear viscosity, indicating that the condition of linear viscoelastic response was given and the "rule-of-thumb" was valid. Another proof that this condition is fulfilled is the overlapping of data from shear oscillations and creep, as will be shown in Figure 5. Plazek and Raghupathi used for their "complete" creep tests with melts of HDPE a shear stress of 15 N/m^2 at 138 °C and concluded that under this condition their HDPE samples respresented linear viscoelastic behavior for times shorter than 1000 s and, furthermore, that "...the departure of the higher molecular weight samples from linear behavior is deferred to longer times...".[2]

$p_{21}(t)$ consists of two step functions, the first step occurring at $t = 0$ and the second at $t = t_1$. Correspondingly, the shear strain measured between $t = 0$ and t_1 due to $p_{21}h(t)$ is the same, only with an opposite sign (negative), due to $p_{21}h(t - t_1)$ for the time span between t_1 and $2t_1$. Hence, the creep strain calculated for the linear viscoelastic response only for the first step, $p_{21}h(t)$, during the period $t_1 < t < 2t_1$, is the sum of the measured, decreasing strain during this period and the strain

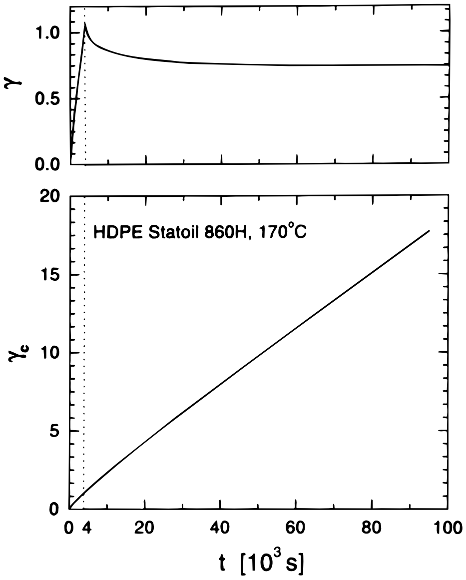

Figure 3. Incomplete creep test followed by creep recovery at 170 °C. Shear stress $p_{21} = 20$ Pa during $0 < t < 4000$ s; for $t > 4000$ s the shear stress was zero. Upper graph: shear strain, γ, measured during the total test period of 10^5 s (approximately 28 h). Lower graph: shear strain, γ_c, calculated for a creep test with $p_{21} = 20$ Pa completely performed in the linear viscoelastic range during the total test period. For this calculation Boltzmann's principle of superposition was applied as described by Meissner.[14]

(positive sign) due to $p_{21}h(t - t_1)$ during the same period. For $t > 2t_1$ this procedure of applying Boltzmann's superposition principle is repeated several times as has been derived and is explained more in detail elsewhere.[14]

It should be mentioned that Meissner proposed, in 1978, an analogous test procedure for stress relaxation after cessation of *incomplete* constant shear rate flow (i.e., a flow at the termination of which the developing shear stress has not reached or could not reach its equilibrium value).[20] Both procedures, viz. stress relaxation after incomplete flow and retardation after incomplete creep, have been analyzed also in Tschoegl's book.[21] Their application is especially recommended if the relaxation or retardation times are very long and/or the stability of the liquid under test causes problems.

For the incomplete creep/creep recovery test performed with our test material, Figure 3 shows in the upper graph the measured shear strain $\gamma(t)$. We see the rapid increase up to the instant $t_1 = 4000$ s and the following recovery until a horizontal level is achieved at long times. It should be pointed out that one advantage of this test procedure is that the final part of the measured curve has to be a *horizontal* straight line such that the difficulty in determining the slope of the creep strains at the end of complete creep tests is avoided. The second advantage of the incomplete creep test is that the measured strain, $\gamma(t)$, stays always within the linear viscoelastic limit, whereas the calculated shear strain, $\gamma_c(t)$, for the corresponding complete creep test may reach much higher values, as is shown in the lower graph of Figure 3. To make it clear to the unfamiliar reader: The meaning of $\gamma_c(t)$ is the shear strain for a complete creep test, $p_{21}(t) = p_{21}h(t)$, under the assumption that within the duration of such a test the material response remains linear viscoelastic. From this $\gamma_c(t)$ the linear viscoelastic shear creep compliance, $J^0(t)$, is calculated. $J^0(t)$ consists of the recoverable, elastic portion, $J_e^0(t)$, and the irrecoverable, viscous portion, t/η_0:

$$\gamma_c(t)/p_{21} \equiv J^0(t) = J_e^0(t) + t/\eta_0 \qquad (3)$$

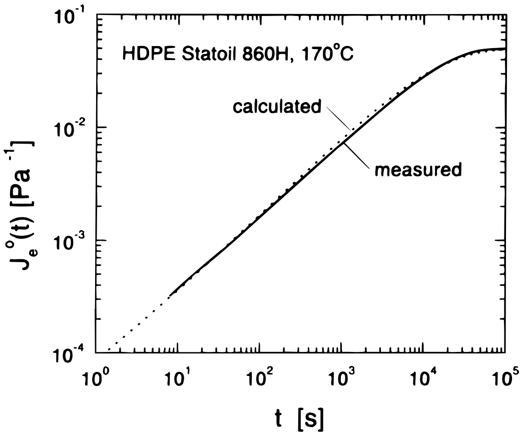

Figure 4. Linear viscoelastic recoverable shear creep compliance of the HDPE melt at 170 °C, measured by incomplete creep/creep recovery and calculated from the "combined retardation spectrum" of Figure 5.

When the measured strain, $\gamma(t)$, has reached its constant equilibrium value at long recovery times, then the calculated strain, $\gamma_c(t)$, starts to follow a straight line and, consequently, also the compliance, $J^0(t)$, does so; the slope of the latter is $1/\eta_0$. In addition, $J_e^0(t)$ has reached its final equilibrium value J_e (i.e., the complete or equilibrium recoverable shear creep compliance). For obtaining the equilibrium values η_0 and J_e, the extrapolation procedure proposed by Ninomiya was helpful by plotting $J^0(t)/t$ versus $1/t$.[22] The resulting equilibrium quantities are

$$\eta_0 = (113.5 \pm 4)\ \text{kPa s} \quad \text{and} \quad J_e = 0.050\ \text{Pa}^{-1} \qquad (4)$$

Figure 4 shows as the final result the recoverable creep compliance, $J_e^0(t)$, of our melt measured up to $t = 10^5$ s (28 h!). From this curve it follows that only after a duration of 50 000 s is the equilibrium value J_e reached. This value is very large. We like to add that Meissner published a previous result obtained with the melt of another commercial HDPE (Marlex 600) at 150 °C that had an equilibrium compliance $J_e = 0.016$ Pa^{-1}, and the onset of the linear increase of $J_e^0(t)$ occurred at 45 000 s. Plazek and Raghupathi found similar large values.[2] The conclusion must be that the linear viscoelastic behavior of commercial HDPE melts can be governed by very long relaxation times.

These long relaxation times are not reflected in oscillatory investigations but call for creep tests as well. The application of both types of tests has the advantage that there is a sufficiently large range of overlapping results that allow for a mutual control of the test performance quality. In what follows we combine the results from oscillatory and creep/creep recovery tests by using the interconversion relations of linear viscoelastic material functions.

3. Conversion of Viscoelastic Material Functions

To combine the results from oscillatory and creep (= *incomplete* creep)/creep recovery tests, the obtained frequency and time-dependent linear viscoelastic material functions must be converted such that one retardation or relaxation spectrum results over a sufficiently wide range of retardation or relaxation times. In fact, we perform two such procedures:

First, from the complex modulus, $G^* = G' + iG''$, the complex compliance, $J^* = J' - iJ''$, is calculated and, by means of a regularization procedure, the continuous retardation spectrum, $L(\tau')$, is determined. From the creep/creep recovery results, a discrete spectrum $\{L_i, \tau_i'\}$ can be derived and is added to the first one obtained from oscillations such that the *combined* spectrum reaches over 7.5 decades of the retardation time, as is shown in Figure 5.

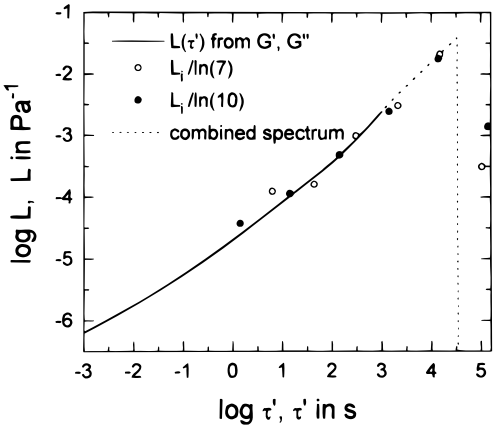

Figure 5. Retardation spectrum of the HDPE melt at 170 °C in a double-logarithmic plot. The symbols are the values $L_i/(\ln b)$ obtained from creep tests; the solid curve is the continuous spectrum based on oscillatory data after using a regularization procedure; the dotted line shows the "combined spectrum".

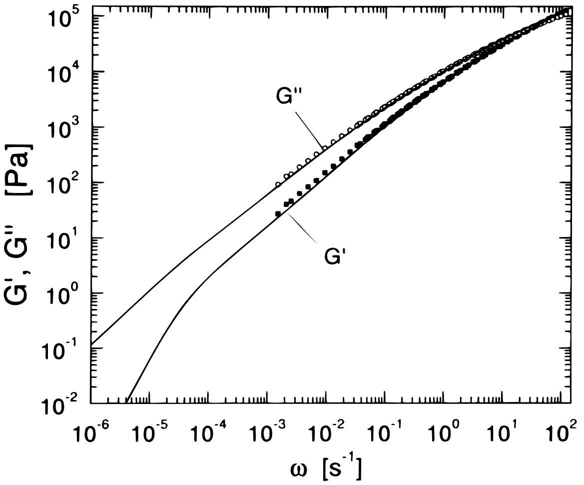

Figure 6. Storage and loss modulus of the HDPE melt at 170 °C in a double-logarithmic plot. Symbols: Measured results from shear oscillations. Solid curves: Calculated from the combined retardation spectrum via the real and imaginary parts, J' and J'', respectively, of the compliance $J^*(\omega)$.

Second, from this combined retardation spectrum the complex (oscillatory) compliance, J^*, is calculated and converted into G^*. The resulting data are plotted in Figure 6 together with the G' and G'' measured by shear oscillations. The comparison of the calculated and directly measured data shows that the combined spectrum expands the frequency range of information tremendously. With the combined data of G^* the application of the regularization procedure results in the sufficiently broad weighted relaxation spectrum, $\tau H(\tau)$, of Figure 7. In the following, the individual steps discussed so far shall be described in more detail. For the basic relations of the theory of linear viscoelasticity reference is made to the standard books of Ferry and Tschoegl.[18,21]

3.1. Retardation Spectrum. For the conversion of the measured G^* into J^* the relation $G^*(\omega)\ J(\omega)^* = 1$ is used with the results

$$G'(\omega) = J'(\omega)/|J^*(\omega)|^2 \tag{5a}$$

$$G''(\omega) = J''(\omega)/|J^*(\omega)|^2 \tag{5b}$$

where $|J^*(\omega)|^2 = J'^2 + J''^2$. The retardation spectrum,

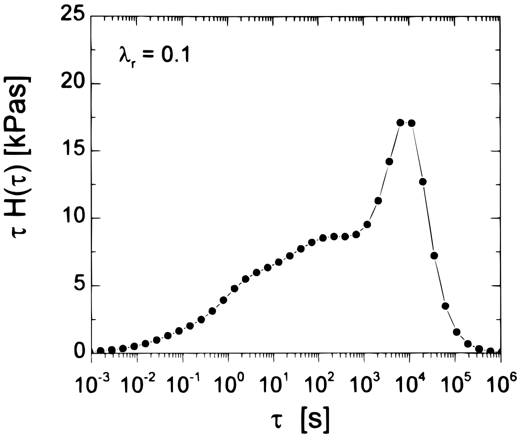

Figure 7. Weighted relaxation spectrum of the HDPE melt at 170 °C in a semilogarithmic representation.

$L(\tau')$, is introduced and defined by its relation to the elastic, recoverable portion, $J_e(t)$, of the creep compliance, $J(t)$:

$$J_e(t) = J_0 + \int_{-\infty}^{+\infty} L(\tau')\,(1 - e^{-t/\tau'})\ d\ln\tau' \tag{6}$$

J_0 is the instantaneous recovery, mostly neglegted in polymer melt viscoelasticity because, like here, of its minute magnitude. The conversion of the integral (i.e., the calculation of $L(\tau')$ from $J_e(t)$) is an ill-posed mathematical problem, as described by Honerkamp.[23] For the solution of this problem regularization procedures together with the corresponding computer programs were developed by Weese and Honerkamp and Weese.[24−26] For our calculations their nonlinear NLREG program was used.[27] The result is the curve $L(\tau')$ in Figure 5 ranging from $t' = 0.001$ to 1000 s.

From the directly measured creep compliance $J(t)$, after subtracting the flow term t/η_0, a discrete retardation spectrum is obtained, defined by

$$J_e(t) = \sum_{i=1}^{N} L_i (1 - e^{-t/\tau_i'}) \tag{7}$$

such that a line spectrum results, following a procedure published by Kaschta and Schwarzl.[28] The continuous spectrum, $L(\tau')$, and the discrete spectrum, $\{L_i,\tau_i'\}$, are related as follows:

$$L_i(\tau_i') \approx L(\tau')\ \Delta \ln \tau' = L(\tau') \ln b \qquad \text{with } \tau_i' = \tau' \tag{8}$$

In fact, two sets $\{L_i,\tau_i'\}$ are established for the discrete retardation spectrum with six terms each. In each set the individual retardation time is separated from the next by a constant factor, $b = 7$ in the first and $b = 10$ in the second set. The resulting spectra are given in Table 1 and shown as symbols in Figure 5. To compare the discrete compliances L_i with the values of the continuous spectrum, L, eq 8 must be observed; in other words $L_i/(\ln b)$ (and not L_i) must be compared with the values L of the continuous spectrum.

We notice from Figure 5 that there is agreement of the data in the overlapping region of the continuous spectrum, obtained from the oscillatory measurements, and the values $L_i/(\ln b)$ of the discrete spectrum obtained from the creep results. These two spectra are united in a *combined spectrum* by means of the following procedure: For short retardation times, $\tau' < 1000$ s, the spectrum obtained from shear oscillations is used. In

Table 1. Two Sets $L_i(\tau_i')$ for the Discrete Retardation Spectrum of the HDPE Melt Investigated, $T_0 = 170$ °C[a]

$b = 7$		$b = 10$	
L_i [10^{-3} Pa^{-1}]	τ_i' [s]	L_i [10^{-3} Pa^{-1}]	τ_i' [s]
0.244	6.17	0.0874	1.41
0.315	43.9	0.266	14.1
1.93	307	1.131	141
5.97	2 150	5.72	1 410
40.9	15 100	41.1	14 100
0.608	105 000	3.22	141 000

[a] In the left spectrum the values τ_i' are separated by a factor $b = 7$; in the right spectrum by $b = 10$.

the graph of Figure 5 this spectrum is extrapolated as a straight line through the points obtained from the creep results. The abrupt termination due to the idea that there must be a maximum retardation time is smoothed by a narrow parabola. The location of this termination is determined by the condition that the area under the curve must be equal to the measured equilibrium recoverable shear compliance, J_e. More precisely, the transient function $J_e^0(t)$, calculated from this combined spectrum, must give good agreement with the measured function, and this is the case, as is shown in Figure 4. The equations for the straight line and the steeply decreasing parabola (dotted line) terminating the spectrum in the double logarithmic plot of Figure 5 are as follows:

$$\log L = a \log \tau' + b \qquad \text{with } a = 0.51,\ b = -3.89 \quad (9)$$

$$\log L = a \log \tau'^2 + b \log \tau' + c \qquad \text{with } a = -2.7,\ b = 22.77,\ c = -49.81 \quad (10)$$

Finally, we point out that by combining shear oscillations and creep/creep recovery tests, the range of retardation (and relaxation) times in the spectrum can be remarkably extended as Figure 5 demonstrates. One more comment refers to the points in Figure 5 for $\tau' >$ 100 000 s. They probably reflect the "smearing-out" found by Kaschta and Schwarzl when they introduced a discrete spectrum for the replacement of a continuous spectrum that was terminated by a sudden jump.[28]

3.2. Relaxation Spectrum. To determine the relaxation spectrum, we use the combined retardation spectrum and calculate the real and imaginary parts of the complex compliance (by numerical integration) using

$$J'(\omega) = J_0 + \int_{-\infty}^{+\infty} L(\tau')(1 + \omega^2\tau'^2)^{-1}\, \mathrm{d}(\ln \tau') \quad (11)$$

$$J''(\omega) = \int_{-\infty}^{+\infty} L(\tau')\omega\tau'(1 + \omega^2\tau'^2)^{-1}\, \mathrm{d}(\ln \tau') \quad (12)$$

Equation 5a,b allow us to convert these results into the storage and loss modulus, G' and G''. Both functions calculated from the combined retardation spectrum are drawn as lines in Figure 6 together with the moduli, directly measured in oscillatory tests. There is an excellent coincidence of both sets of results. It is remarkable that the data calculated from the combined retardation spectrum extend to frequencies by more than 3 decades lower than the measured data. At the lowest frequencies the frequency dependences of eq 1 are reached.

With the calculated moduli G' and G'', in other words with the values of the solid curves of Figure 6, ranging from $\omega = 10^{-6}$ to 100 s^{-1}, the relaxation spectrum $H(\tau)$ is determined. Again, we appply the nonlinear regularization program of Honerkamp and Weese.[27,29] In Figure 7 the result is shown as the *weighted relaxation spectrum*, $\tau H(\tau)$. The area under this curve represents the zero shear viscosity, $\eta_0 = \int_{-\infty}^{+\infty}\tau H(\tau)\ \mathrm{d}(\ln \tau)$.

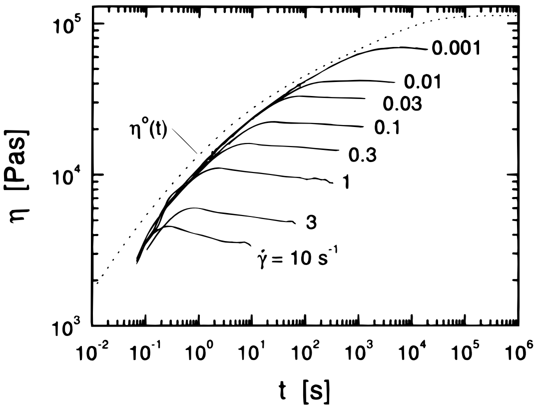

Figure 8. Transient viscosities of the HDPE melt at 170 °C for different shear rates, measured in a modified mechanical spectrometer. The linear viscoelastic transient viscosity, $\eta^0(t)$, was calculated from the spectrum by means of eq 13.

The range of confidence of these data (compare, for example, Honerkamp and Weese[26]) corresponds to the range within which the experimental data were taken. According to Figure 6 this range is $4 \times 10^{-6} < \omega < 100$ s^{-1} which corresponds in Figure 7 to a range of relaxation times $0.01 < \tau < 2.5 \times 10^5$ s. The most remarkable result is that the weighted spectrum has a maximum at a relaxation time that is out of the range of any conventional testing except creep combined with creep recovery, but only if a sufficiently long chemical stability of the sample and an excellent thermal and mechanical stability of the rheometer are established. It is this maximum and its location of why the zero shear viscosity can be measured only in such tests, and also the equilibrium recoverable creep compliance, J_e, with its high value, eq 4.

4. Predictions for Shear Flow and Comparison with Experiment

When the spectrum is known, the linear viscoelastic material functions—defined by the response to well-defined deformation or stress histories—can be calculated. From linear viscoelasticity the following relation exists between the transient linear viscoelastic viscosity and the relaxation spectrum:[18,21]

$$\eta^0(t) = \int_{-\infty}^{+\infty} \tau H(\tau)(1 - \mathrm{e}^{-t/\tau})\ \mathrm{d}\ (\ln \tau) \qquad (13)$$

with the zero shear visosity $\eta_0 = \int_{-\infty}^{+\infty}\tau H(\tau)\ \mathrm{d}(\ln \tau) = \int_0^{+\infty} H(\tau)\ \mathrm{d}\tau$ as the equilibrium value. To measure $\eta^0(t)$, step function shear rate tests were performed with the HDPE sample in the improved cone-and-plate shear rheometer.[17]

The results are shown in Figure 8 for different shear rates together with the function $\eta^0(t)$ calculated from the continuous spectrum using eq 13.[30] It follows from this graph that the curves measured at different shear rates have $\eta^0(t)$ as their envelope, but do not reach this limit at long times, even at the smallest shear rate (0.001 s^{-1}) applied in these tests. All the measured curves show a well-developed maximum, indicating the breakdown of the physical structure due to the deformation. The measured curves do not exactly match $\eta^0(t)$.

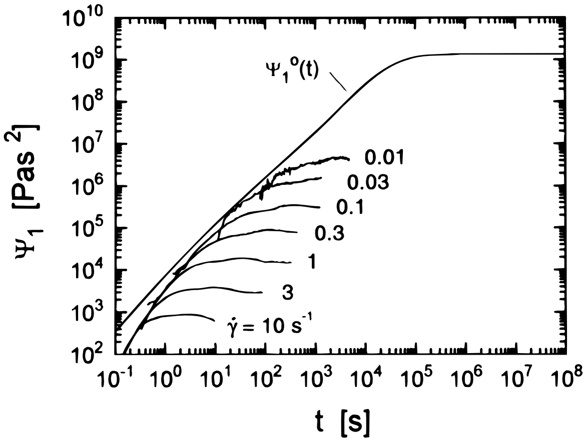

Figure 9. Measured transient first normal stress functions $\psi_1(t)$ and limiting transient $\psi_1^0(t)$, calculated from the spectrum by eq 15, for the HDPE melt at 170 °C.

For short times this may well be due to experimental difficulties in starting such start-up tests, as has been found also for melts of branched polyethylene (LDPE) and was discussed in detail;[31] but for times $t > 10$ s the differences between the measured curves and $\eta^0(t)$ cannot be explained presently.

The same results for $\eta^0(t)$ can be obtained from the rubberlike liquid theory of Lodge.[32,33] Wagner and Meissner applied this theory to the "Melt I"-LDPE and found good agreement with the measured transient viscosity, but only at the lowest shear rate of 0.001 s^{-1}.[34] At higher shear rates, the curves fell together at short times (i.e., small shear strains) only; at longer times, the measured viscosity functions were increasingly smaller with increasing shear rates.

In these step function shear rate tests, in addition to the shear stress the first normal stress difference, $N_1 \equiv p_{11} - p_{22}$, could be measured from which the "first normal stress function" $\Psi_1(t)$ resulted:[35]

$$\Psi_1(t) \equiv (p_{11} - p_{22})/\dot{\gamma}_0^{\,2} \qquad (14)$$

Here, p_{11} is the tensile stress component in the direction of flow, p_{22} is the tensile stress in the direction of the velocity gradient, $\dot{\gamma}_0$ is the magnitude of the step function shear rate test with the shear rate history $\dot{\gamma}(t) = \dot{\gamma}_0 h(t)$, where $h(t)$ is the unit step function. Figure 9 shows the functions $\Psi_1(t)$ measured with different shear rates.

The Lodge theory predicts, independent of the shear rate:

$$\Psi_1^0(t) = 2\int_{-\infty}^{+\infty} \tau^2 H(\tau)[1 - (1 + t/\tau)e^{-t/\tau}]\, d(\ln \tau) \qquad (15)$$

This function is calculated from the relaxation spectrum, $H(\tau)$, and is shown as the dotted curve in Figure 9. Again, the predicted and the measured curves come together at short times, and they differ remarkably at longer times. The lowest shear rate (0.01 s^{-1}) is not yet small enough to reach the limiting value:[36]

$$\Psi_{1,0} = \lim \Psi_1^0(t \to \infty, \dot{\gamma}_0 \to 0) \qquad (16)$$

From eq 15 it follows that $\Psi_{1,0}$ is twice the second moment of the relaxation spectrum:

$$\Psi_{1,0} = 2\int_{-\infty}^{+\infty} \tau^2 H(\tau)\, d(\ln \tau) \qquad (17)$$

whereas η_0 is equal to the first moment of the relaxation spectrum, as was shown in connection with eq 13.

From the theory of linear viscoelasticity it can be derived that the second moment of the spectrum is connected with the equilibrium recoverable creep compliance, such that, with eq 17, the following relation holds:

$$J_e = \Psi_{1,0}/(2\eta_0^{\,2}) \qquad (18)$$

Performing the integration on the right-hand side of eq 17, $\Psi_{1,0} = 1.34 \times 10^9$ Pa s^2 is obtained. With η_0 from eq 4, the calculated compliance following from eq 18 is $J_e = 0.052$ Pa^{-1}. The measured compliance according to eq 4 is $J_e = 0.05$ Pa^{-1}. The agreement of these two values is very good, especially when the difficult and lengthy procedure is taken into consideration by means of which the relaxation spectrum has been determined. With the measured $J_e^0 = 0.05$ Pa^{-1} and eq 18 the limiting value, eq 16, of the first normal stress function turns out to be $\Psi_{1,0} = 1.29 \times 10^9$ Pa s^2.

5. Discussion and Conclusions

This paper demonstrates that for the melt of a commercial HDPE the retardation and relaxation spectra can be determined in a sufficiently broad time range by linear viscoelastic tests of adequate long duration. But one requirement is that during this duration at test temperature the sample material does not change chemically, otherwise an adequate stabilizer must be added.

For such long tests, the *incomplete* creep/creep recovery test turns out to be helpful (i.e., a creep test with the constant shear stress p_{21} during a period t_1, within which the creep strain has not yet reached its linear dependence on t). p_{21} and t_1 can both be selected such that the maximum strain, $\gamma(t_1)$, is rather large, but still within the limit of linear viscoelastic behavior. At t_1, the recovery starts with a shear strain signal that is large and of sufficient resolution. Furthermore, at very long times the measured recovering strain finally becomes constant. This helps to determine long retardation times because in conventional creep tests of very long duration the separation of the recoverable portion from the linearly increasing viscous flow term is difficult, especially when small variations of the rheometer and material properties occur during such long experimental times.

The importance of the additional oscillatory tests should also be mentioned: they extend the test range to higher frequencies (i.e., shorter relaxation times) and in the overlapping range of oscillatory and creep results a check is possible of whether basic errors have been made. The conversion of the linear viscoelastic results is standard; however, the calculation of the spectra requires special procedures, such as the Honerkamp−Weese method. Other methods might be applicable too, but to check them was not the objective of this study. The conversion of the creep data into a discrete spectrum by the Kaschta−Schwarzl procedure, the conversion of the compliances into the moduli and the following application of the Weese−Honerkamp procedure in order to obtain the very broad weighted relaxation spectrum seems to be long-winded but it turns out to be successful with the tools we had at the time of our investigation.

The results obtained are unexpected, viz. that a melt of a conventional standard commercial polyethylene has a maximum of the weighted spectrum, $\tau H(\tau)$, at a relaxation time of $\tau = 10\,000$ s. This is the reason why the zero shear viscosity cannot be measured in conventional "start-up tests", because in conventional rheometers the smallest shear rate is too high and the required residence time might be too long, viz. >100 000 s, as follows from Figure 8. The recoverable creep compliance increases steadily with time, and its final value is unexpectedly high, $J_e = 5 \times 10^{-2}$ Pa^{-1}. For melts of polystyrene and poly(methyl methacrylate) at 170 °C Gramespacher and Meissner[37] measured $J_e = 1.5 \times 10^{-4}$ and 3.6×10^{-5} Pa^{-1}, respectively. For melts of linear polymers, including polyethylene, with narrow molecular mass distributions, Graessly[38] listed even smaller J_e (between 2×10^{-6} and 1.75×10^{-5} Pa^{-1}).

The last comment is related to the question of the extension of the linear viscoelastic range. The assumption that this range is limited by 1 shear unit is supported by the fact that the start-up curves of the transient viscosity, $\eta(t)$, follow the linear viscoelastic $\eta^0(t)$ up to a total strain between 0.5 and 1. The first normal stress function follows its limiting curve, $\Psi_1^0(t)$, also in this deformation range. However, the existence of the latter shows how limited the "linear viscoelastic concept" is because $\Psi_1^0(t)$ should be zero. Hence, we should speak more precisely of the range of the "Lodge-theory-validity".

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