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Influence of the MWD of Poly(vinylidene Fluoride) on its Viscoelastic Behaviour in the Melt, Part II: Relaxation Time Spectra

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The study of the viscoelastic behavior of molten polyvinylidene fluoride (PVDF) was performed in oscillatory shear flow and analyzed in terms of relaxation time distribution. Continuous spectrum having a log normal distribution of relaxation time and discrete spectrum with a limited number of relaxation modes were investigated. Attention was also paid to the correspondence between the two types of spectra. Material parameters such as the broadness of the relaxation spectrum can be related to the polydispersity of the samples. In the limit of monodisperse samples, the broadness of the relaxation time distribution was found to be in agreement with values from the literature ranging from 1.7 to 6.0, while the Newtonian viscosity is influenced mainly by the molecular weight. These dependences are combined in a relation between the average relaxation time and the parameters of the molecular weight distribution. In addition, this enables us to get an estimate of the plateau modulus of PVDF. The melt strength and breaking stretch ratio that describe the extensional behavior of the molten material in a spinning experiment can be correlated only with the average relaxation time of the material.

Keywords: Relaxation spectrum; PVDF; Melt; MWD; Plateau modulus

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1. INTRODUCTION

In a previous paper^[1], empirical relationships describing the influence of the molecular weight distribution of some samples of polyvinylidene fluoride (PVDF) on the viscoelastic behavior of these polymers in the molten state were derived. These relations were concerned with parameters relative to shear properties such as the zero-shear viscosity or relaxation time and parameters relative to extension during the melt spinning such as the melt strength and breaking stretch ratio.

The relevant parameters in shear were obtained from empirical equations widely used for polymer melts such as the Cole–Cole equation or the Carreau–Yasuda equation. Though these equations can give an appropriate fit of the experimental data in the terminal zone, they generally suffer from large limitations. The Carreau–Yasuda equation can be used to describe only one of the viscoelastic functions (either the real part of the complex viscosity η' or η^*). However, the Cole–Cole equation does not satisfy the limiting behavior of the linear viscoelasticity in the low frequency range since the predicted limiting slope of the loss and storage moduli in a double logarithmic plot are respectively $1-h$ and $2-h$, which prevents us from obtaining a value for the limiting elastic compliance. In addition, no stable value of the plateau modulus can be predicted by the model. Consequently, only values of the Newtonian viscosity and of one characteristic relaxation time have been obtained.

For these reasons, in this paper, attention has been focused on the various technique that enable the recovery of the relaxation time spectrum in the terminal zone, which normally contains the whole information on the linear viscoelastic behavior. Numerous authors have developed numerical methods that recover the relaxation time spectrum either in a continuous or discrete form from transient or oscillatory data in the linear viscoelastic domain. Continuous spectra were obtained from a complex algebra formula, by approximations, or by prescribing a mathematical form to the continuous distribution function of relaxation times^[2,7]. Methods for the determination of discrete relaxation spectra were proposed in the '90s by different authors^[6,8,14]. Correspondence between discrete and continuous forms have also been proposed^[9].

In this study, two different techniques have been compared: One is working with a continuous function and uses an a priori form of distribution function of the log normal type; the other one is working on discrete spectra without setting any assumptions on the number of relaxation modes or on the parameters of the modes (time and modulus contributions).

From these spectra, viscoelastic parameters were calculated and the influence of the molecular weight distribution was revisited.

2. EXPERIMENTAL

Six samples (A1, A2, A3, S1, S2, E) of industrial origin are investigated. Most of the characterizations were described in the previous paper^[1]. The molecular weight characterization was obtained from SEC data, osmometry in dimethyl formamide (DMF) at 80°C, and viscosimetry at room temperature (25°C) in dimethyl acetamide (DMAC) as described in the previous paper^[1]. Absolute values of the molecular weight are reported in Table I.

Oscillatory shear measurements were performed in a Rheometrics Dynamic Analyzer RDA 700 using a parallel plate geometry with frequencies ranging from 0.01 to 100 rad/s and temperatures ranging from 200 to 250°C to get mastercurves at 200°C. Elongational properties were estimated at 200°C using a nonisothermal spinning device on a capillary rheometer Instron 3211 equipped with a capillary die (diameter = 1.25 mm, $L/D = 50$, flow rate = 7.13 mm³/s) according to the procedure described in^[1].

3. RESULTS AND DISCUSSION

3.1. Continuous Spectrum

The relaxation modulus $G(t)$ is related to the continuous relaxation spectrum $H(\lambda)$ through

$$G(t) = \int_{-\infty}^{+\infty} H(\lambda) \exp(-t/\lambda) d \ln \lambda \quad (1)$$

TABLE I Molecular Characteristics of the Samples (from SEC in DMF at 80°C)

Sample	Absolute Values (After Correction)		
	M_w [g/mol]	M_n [g/mol]	M_w/M_n
S1	123000	60000	2.1
A1	131000	61000	2.2
A2	153000	71000	2.2
A3	154000	64000	2.4
S2	174000	71000	2.5
E	213000	62000	3.5

where $H(\lambda)d\ln\lambda$ is the contribution to the modulus of relaxation modes whose characteristic times lay between λ and $\lambda + d\ln\lambda$. The dynamic modulus is given by

$$G^*(\omega) = \int_{-\infty}^{+\infty} H(\lambda) \frac{j\omega\lambda}{1 + j\omega\lambda} d\ln\lambda \quad (2)$$

Starting from the Cole–Cole equation^[15] for the complex viscosity

$$\eta^* = \frac{\eta_0}{1 + (j\omega\bar{\lambda})^{1-h}} \quad (3)$$

the use of the classical rules of complex algebra leads to the following spectrum^[16]

$$H(\lambda) = \frac{2\eta_0}{\pi\lambda} \frac{(\bar{\lambda}/\lambda)^{1-h} \sin(h\pi/2) \cos(h\pi/2)}{1 + (\bar{\lambda}/\lambda)^{2(1-h)} + 2(\bar{\lambda}/\lambda)^{1-h} [\sin^2(h\pi/2) - \cos^2(h\pi/2)]} \quad (4)$$

with η_0 the zero-shear viscosity, $\bar{\lambda}$ the characteristic relaxation time, and h a parameter for the relaxation time distribution ($0 \leq h \leq 1$).

Applied to the Carreau–Yasuda^[17,18] equation:

$$\eta'(\omega) = \frac{\eta_0}{[1 + (\omega\lambda_0)^{2a}]^{(1-n)/(2a)}} \quad (5)$$

the same method gives^[19]

$$H(\lambda) = \frac{2\eta_0}{\pi\lambda} \left[1 + (\lambda_0/\lambda)^{4a} + 2(\lambda_0/\lambda)^{2a} \cos(a\pi) \right]^{\frac{n-1}{4a}} \\ \times \sin \left\{ \frac{1-n}{2a} \sin^{-1} \left[\left[1 + (\lambda_0/\lambda)^{4a} + 2(\lambda_0/\lambda)^{2a} \cos(a\pi) \right]^{-1/2} \right. \right. \\ \left. \left. \times (\lambda_0/\lambda)^{2a} \sin(a\pi) \right] \right\} \quad (6)$$

where η_0 is the zero-shear viscosity, λ_0 is a characteristic relaxation time, n is the flow index at high shear rates, and a characterizes the smoothness of the transition between the Newtonian and non-Newtonian behavior.

Exponents $1-n$ and $2a$ were calculated from the results on the different samples (Table II) and are always found to be lower than 1 which means that, except for the zero-shear viscosity Equation (7a), the integrals for the calculation of the parameters of the terminal zone, namely the steady-state compliance and plateau modulus Equations (7b) and (7c), never converge and these parameters can not be calculated in this case.

TABLE II Parameters for the Cole-Cole and Carreau-Yasuda Equations at 200°C

Sample	Equation (13)			Equation (15)			
	η_0 [Pa s]	$\bar{\lambda}$ [s]	h	η_0 [Pa s]	λ_0 [s]	a	n
S1	5060	0.21	0.50	5000	0.19	0.30	0.38
A1	7930	0.21	0.51	7730	0.18	0.30	0.39
A2	16100	0.58	0.51	15600	0.44	0.29	0.37
A3	17500	1.24	0.51	17100	1.09	0.30	0.41
S2	29000	2.20	0.51	28800	1.88	0.30	0.38
E	46500	8.53	0.52	47100	8.18	0.29	0.40

$$\eta_0 = \int_{-\infty}^{+\infty} \lambda H(\lambda) d \ln \lambda \tag{7a}$$

$$J_e^0 = \int_{-\infty}^{+\infty} \lambda^2 H(\lambda) d \ln \lambda \tag{7b}$$

$$G_N^0 = \int_{-\infty}^{+\infty} H(\lambda) d \ln \lambda \tag{7c}$$

Thus, the number average and weight average relaxation times of equation can not be evaluated, and the limiting slope of $G'(\omega)$ and $G''(\omega)$ can not be retrieved.

To avoid these problems, the log-normal form of the relaxation spectrum was preferred^[4]:

$$H(\lambda) = \frac{\eta_0}{\lambda \sqrt{2\pi \ln(\lambda_w / \lambda_n)}} \exp \left\{ - \left[\frac{1}{\sqrt{2\pi \ln(\lambda_w / \lambda_n)}} \ln(\lambda / \sqrt{\lambda_w \lambda_n}) \right]^2 \right\} \tag{8}$$

Three material parameters are involved in this equation: the newtonian viscosity η_0 , the number average relaxation time λ_n , and the weight average relaxation time λ_w . The function satisfies the normalization condition:

$$1 = \int_{-\infty}^{+\infty} \lambda \frac{H(\lambda)}{\eta_0} d \ln \lambda \tag{9}$$

Using a logarithmic scale for the time axis, the plot of $\lambda H(\ln \lambda)$ yields a symmetrical bell-shaped curve centred on $\ln(\lambda_w \lambda_n)/2$. Moreover the functions $H(\ln \lambda)$ and $\lambda^2 H(\ln \lambda)$ are also symmetrical bell-shaped curves with the same width, but having their median values shifted towards longer times. Table III summarizes the values of the parameters for the PVDF samples. The values of the plateau modulus, which should normally be independent of the molecular weight, range from 0.42 MPa to 0.92 MPa. This discrepancy is related to the overlap between the transition and terminal zone that occurs in the case of polydisperse samples. On the other hand, the variation of the low-frequency parameters is consistent since the zero-shear viscosity increases with the molecular weight and since the equilibrium elastic compliance increases significantly with the polydispersity. Figures 1a and 1b show the plot of the continuous spectrum and related functions for samples S1 and E. Figure 2 shows the comparison between the experimental values and those recalculated using these spectra.

3.2. Discrete Spectrum

The relaxation modulus $G(t)$ is related to the discrete relaxation spectrum, which is a set of N pairs of (λ_i, g_i) or (λ_i, η_i) with $\eta_i = g_i \lambda_i$ through

$$G(t) = \sum_{i=1}^N g_i \exp(-t/\lambda_i) \quad (10)$$

The dynamic modulus is given by

$$G^*(\omega) = \sum_{i=1}^N g_i \frac{j\omega \lambda_i}{1 + j\omega \lambda_i} \quad (11)$$

The discrete spectra were obtained using the technique developed by Carrot et al.^[11], which lets the number of modes, times, and contributions to the

TABLE III Parameters of the Log-normal Continuous Spectrum at 200°C

Sample	η_0 [Pa s]	λ_n [s]	λ_w [s]	λ_w/λ_n	G_N^0 [MPa]	J_e^0 [Pa ⁻¹]
S1	4770	0.010	2.8	283	0.48	5.9×10^{-4}
A1	7530	0.008	3.5	433	0.92	4.7×10^{-4}
A2	15300	0.019	10.9	588	0.82	7.2×10^{-4}
A3	16200	0.032	25.2	788	0.51	1.6×10^{-3}
S2	27000	0.065	41.4	641	0.42	1.5×10^{-3}
E	48500	0.116	1150	9990	0.42	2.4×10^{-2}

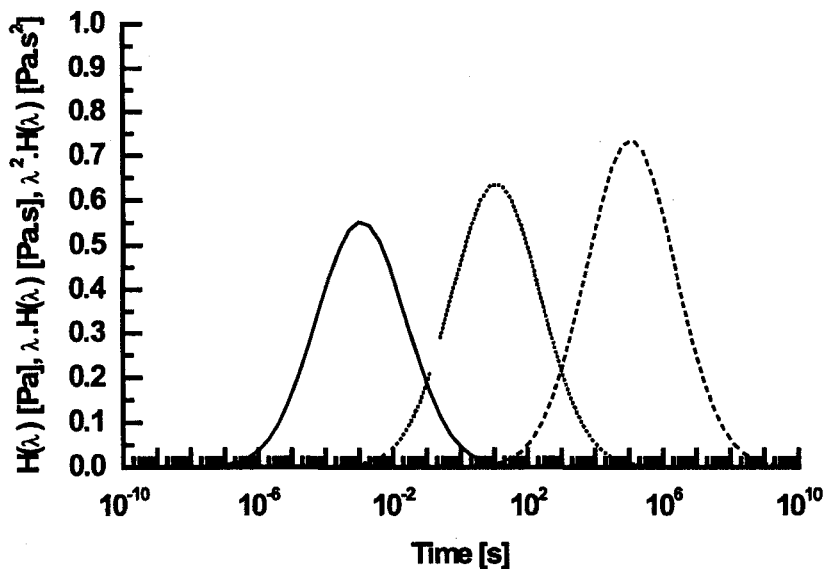


FIGURE 1A Log-normal continuous relaxation spectrum of sample S1 at 200°C (—: $H(\lambda) \times 10^{-5}$, ...: $\lambda \cdot H(\lambda) \cdot 10^{-3}$, - - -: $\lambda^2 \cdot H(\lambda) \cdot 10^{-4}$).

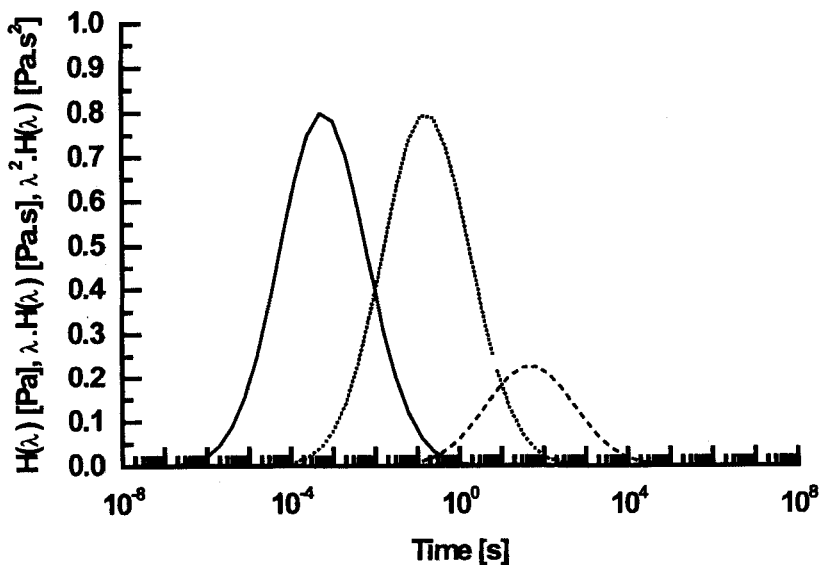


FIGURE 1B Log-normal continuous relaxation spectrum of sample E at 200°C (—: $H(\lambda) \cdot 10^{-5}$, ...: $\lambda \cdot H(\lambda) \cdot 10^{-4}$, - - -: $\lambda^2 \cdot H(\lambda) \cdot 10^{-7}$).

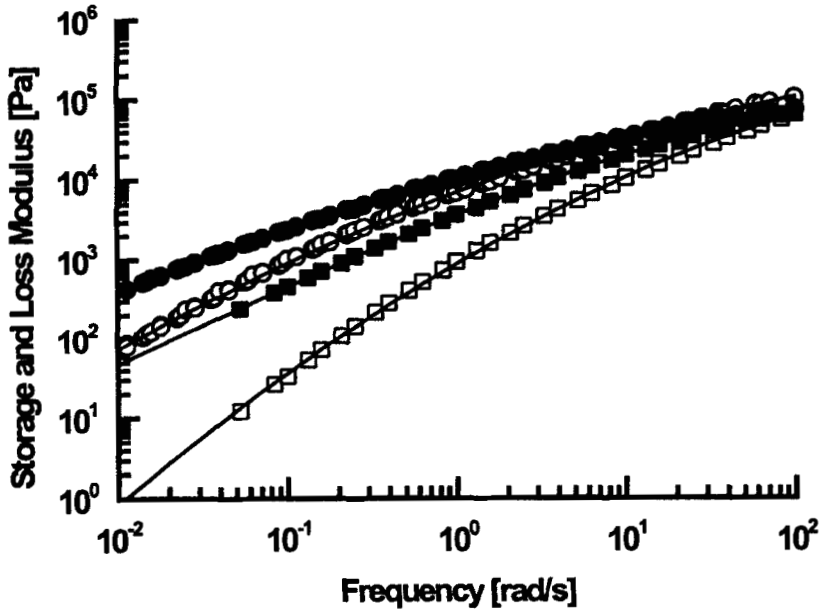


FIGURE 2 Storage (filled symbols) and loss modulus (open symbols) of samples S1 (■, □) and sample E (●, ○) at 200°C from experiments and calculation (—) with the spectrum from Eq. 17 and parameters of Table 3.

modulus be freely adjustable. Table IV gives the spectra of samples S1 and E. In most of the cases, except for sample E, the spectra are quite symmetric on a logarithmic time scale and the information is quite complete both in the short and long time range. For sample E, there is an evident lack of information in the long time range even when using high temperatures for the building of the master curve. Table V shows the different parameters that can be calculated. Though problems similar to those evoked in the case of the continuous spectrum may be expected, the range of the values of the plateau modulus is narrower. Also, the dependence of the equilibrium compliance is not so sharp, which seems more realistic. Figures 3a and 3b show the discrete spectra that are calculated, and Figure 4 shows the experimental and calculated dynamic moduli.

3.3. Interrelation Between the Continuous and Discrete Spectra

In Figure 5 the discrete and continuous relaxation spectra of sample S1 are plotted on the same time axis. Baumgaertel and Winter^[9] have shown that these spectra can be related through integration. Indeed

TABLE IV Discrete Relaxation Spectra of Samples S1 and E at 200°C

Sample S1		Sample E	
λ_i [s]	g_i [Pa]	λ_i [s]	g_i [Pa]
0.00436	158000	0.00224	250000
0.0277	31500	0.0259	60600
0.129	8680	0.146	23100
0.578	2030	0.754	8630
2.57	266	3.74	2810
14.6	14	19.2	620
		116	79.7

TABLE V Parameters of the Discrete Spectra at 200°C

Sample	η_0 [Pa s]	λ_n [s]	λ_w [s]	λ_w/λ_n	G_N^0 [MPa]	J_e^0 [Pa ⁻¹]
S1	4730	0.024	1.2	50	0.20	2.5×10^{-4}
A1	7430	0.023	1.3	53	0.32	1.7×10^{-4}
A2	15000	0.049	2.7	55	0.31	1.8×10^{-4}
A3	15900	0.061	4.4	72	0.26	2.8×10^{-4}
S2	26800	0.098	8.8	90	0.27	3.3×10^{-4}
E	43600	0.126	30.8	244	0.35	7.0×10^{-4}

considering a discrete series of $N + 1$ ($0 \leq i \leq N$) relaxation times λ_i separated by the factors a_i defined as

$$a_i = \lambda_i / \lambda_{i+1} \tag{12}$$

with $\lambda_i > \lambda_{i+1}$, the continuous spectrum can be integrated around each time λ_i of the series in a window $[\lambda_i^+, \lambda_i^-]$ such as

$$\lambda_i^+ = \sqrt{\lambda_{i+1} \lambda_i} \quad \text{and} \quad \lambda_i^- = \sqrt{\lambda_{i-1} \lambda_i} \tag{13}$$

For sufficiently narrow spacing, the contribution g_i of each mode to the relaxation modulus can be calculated from the continuous spectrum $H(\lambda)$ owing to

$$g_i = \ln \sqrt{\lambda_{i-1} / \lambda_{i+1}} H(\lambda_i) = \ln \sqrt{a_{i-1} a_i} H(\lambda_i) = \xi H(\lambda_i) \tag{14}$$

Table VI shows as examples for samples S1 and E that the parameter ξ is nearly constant and consequently, the relaxation spectrum $H(\lambda)$ can be obtained from the discrete g_i values by a vertical shift of $\ln a$:

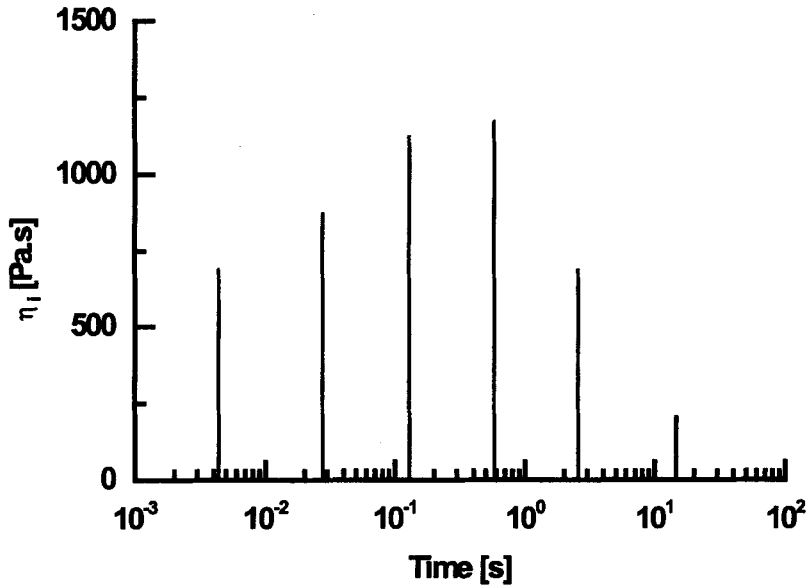


FIGURE 3A Discrete relaxation spectrum of sample S1 at 200°C.

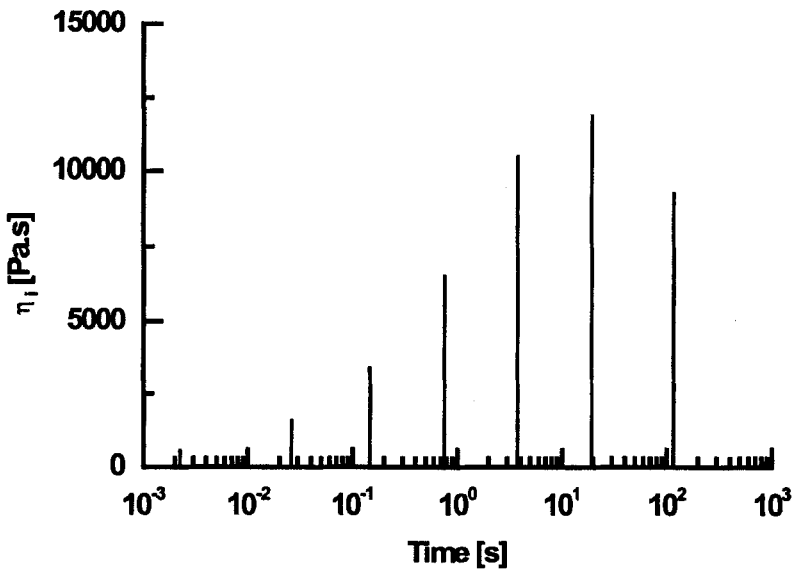


FIGURE 3B Discrete relaxation spectrum of sample E at 200°C.

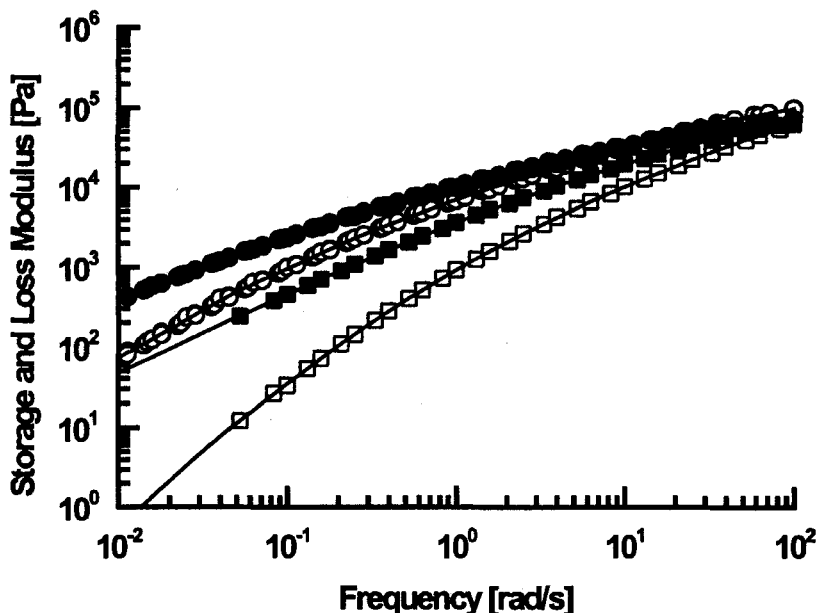


FIGURE 4 Storage (filled symbols) and loss modulus (open symbols) of samples S1 (■, □) and sample E (●, ○) at 200°C from experiments and calculation (—) with the discrete spectrum from Table 4.

$$H(\lambda_i) = g_i / \ln \sqrt{\lambda_{i-1} / \lambda_{i+1}} = g_i / \ln \sqrt{a} \quad (15)$$

Figure 6 gives some example of such a shift for samples S1 ($\ln a = 1.614$) and E ($\ln a = 1.716$).

3.4. Structure Property Relationships in Shear

From the previous results on the spectra, some useful relations connecting the microstructure of the polymers with their rheological behavior in the melt can be deduced. First, the polydispersity effect on the relaxation times is clearly displayed by the broadness of the relaxation time spectrum through the ratio λ_w / λ_n . Indeed, the latter is connected to the equilibrium elastic compliance, which is known to be very susceptible to the polydispersity as can be seen on Tables III and V. A plot of the ratio λ_w / λ_n as a function of the polydispersity index M_w / M_n (Figure 7) yields the following relations depending whether a discrete or continuous spectrum is used:

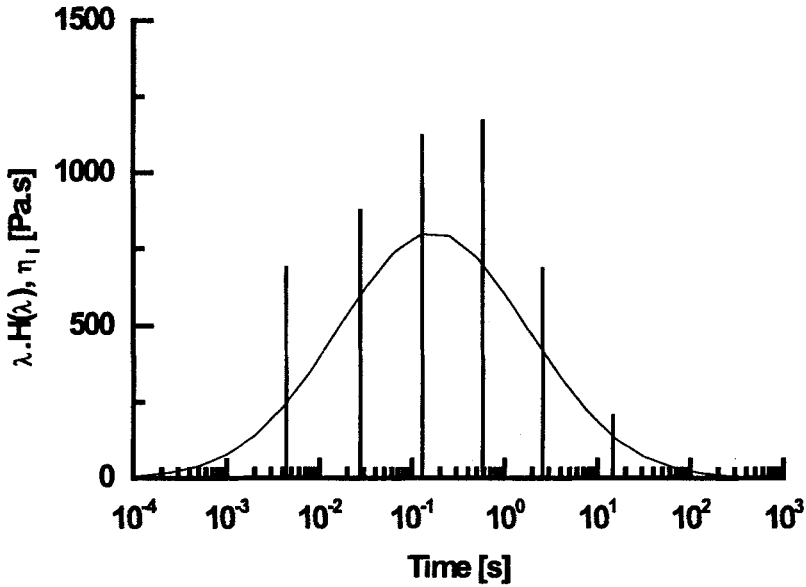


FIGURE 5 Comparison between the discrete and continuous spectra for sample S1 at 200°C.

TABLE VI Factors for the Correspondence Between the Discrete and Continuous Spectra of Sample S1 and E at 200°C

Sample S1			Sample E		
λ_i [s]	g_i [Pa]	ξ	λ_i [s]	g_i [Pa]	ξ
0.00436	158000	–	0.00224	250000	–
0.0277	31500	1.69	0.0259	60600	2.09
0.129	8680	1.52	0.146	23100	1.69
0.578	2030	1.50	0.754	8630	1.57
2.57	266	1.61	3.74	2810	1.62
14.6	14	–	19.2	620	1.72
			116	79.7	–

$$\lambda_w/\lambda_n = 2.59(M_w/M_n)^{6.57} \quad (16a)$$

or

$$\lambda_w/\lambda_n = 4.82(M_w/M_n)^{3.17} \quad (16b)$$

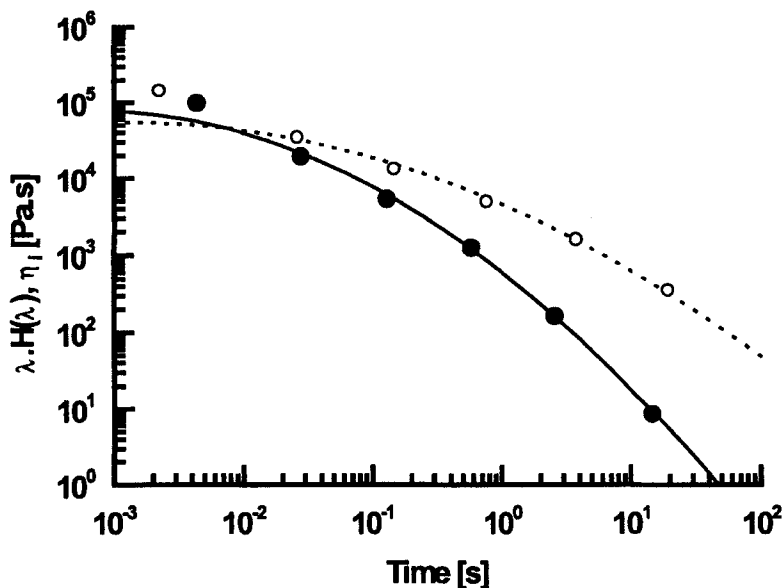


FIGURE 6 Interconversion between the discrete and continuous spectra at 200°C (—: sample S1, continuous spectrum, ●: sample S1, discrete spectrum converted with Eq. 15 with $\ln a = 1.614$, ○: sample S1, discrete spectrum converted with Eq. 15 with $\ln a = 1.716$).

Extrapolation of these in relation to monodisperse samples leads to a reasonable broadness of the relaxation spectrum for monodisperse samples ranging from 2.59 to 4.82 in agreement with experiments on various monodisperse species reporting values between 1.7 and 6^[20].

An average relaxation time $\bar{\lambda}$ can be obtained from the log normal equation for the continuous relaxation time spectrum:

$$\bar{\lambda} = (\lambda_w \lambda_n)^{1/2} \quad (17)$$

This relaxation time is similar to the characteristic relaxation time that can be obtained from the Cole–Cole equation. Indeed, the double logarithmic plot of $\lambda \cdot H(\lambda)$ as a function of the relaxation time λ is centered on the average relaxation time $\bar{\lambda}$. Since according to Equation (7a) the area under the curve equals η_0 , the relaxation time $\bar{\lambda}$ corresponding to the maximum of the bell-shaped curve also corresponds to $\eta_0/2$, which is exactly the definition of the reciprocal frequency for $\eta'(\omega) = \eta_0/2$ in Equation (3).

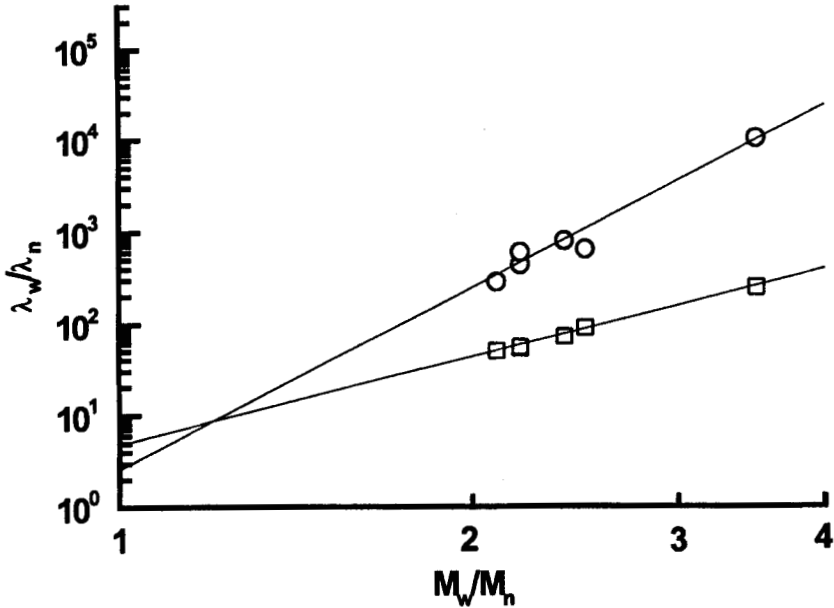


FIGURE 7 Broadness of the continuous (○) and discrete (□) relaxation spectrum as a function of the polydispersity (full line indicating Eqs. 16a and 16b).

In the previous paper^[1], it was shown that the Newtonian viscosity of the PVDF samples has the following dependence of the MWD:

$$\eta_0 = 3.7 \times 10^{-14} M_w^{3.4} \left(\frac{M_w}{M_n} \right)^{0.0034} \quad (18)$$

which means that in the range of MWD under investigation, the zero-shear viscosity is a good estimator of the molecular weight, whereas the ratio λ_w/λ_n gives a good idea of the polydispersity.

Moreover, combining Equations (16b), (17), and (18) with $\lambda_n = \eta_0/G_N^0$ and $\lambda_w = \eta_0 J_0^e$ yields:

$$\bar{\lambda} = \frac{5.95 \times 10^{-14}}{G_N^0} M_w^{3.4} \left(\frac{M_w}{M_n} \right)^{3.28} \quad (19)$$

Thus, the average relaxation time is strongly related to the polydispersity and to the molecular weight.

As a consequence, the influence of the polydispersity can be well displayed by a plot of the reduced relaxation spectrum $\lambda \cdot H(\lambda)/\eta_0$ as a

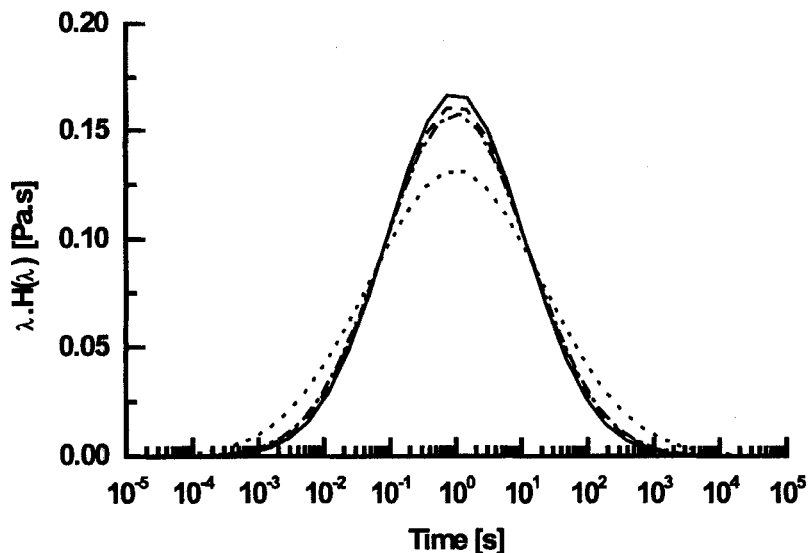


FIGURE 8 Comparison of the reduced relaxation spectra (—: S1, ---: A1, ···: S2, ····: E).

function of the reduced relaxation time $\lambda/\bar{\lambda}$. Figure 8 shows such a plot for the various samples.

At least according to Equation (19), a plot of the average relaxation time as a function of $M_w^{3.4}(M_w/M_n)^{3.2}$ should help to obtain the plateau modulus of the PVDF samples. Such a calculation gives the value of 0.6 MPa which is reasonable compared to the values for polystyrene (0.2 MPa) and for polyethylene (2.6 MPa).

3.5. Structure Property Relationships in Extension (Melt Spinning)

It has been shown in a previous paper that the melt strength (MS) and breaking stretch ratio (BSR) are related to the molecular weight distribution. However it has also been shown that the relative influence of the weight average molecular weight or of the polydispersity can hardly be distinguished, since an increase of any of these parameters increases the melt strength and decreases the BSR. Taking into account the remarks of the previous paragraph, it might be stated that the BSR and MS are linked to the zero-shear viscosity and to the broadness of the relaxation time distribution, but in an indistinguishable manner and that correlations can only be found with the average relaxation time, which includes both the

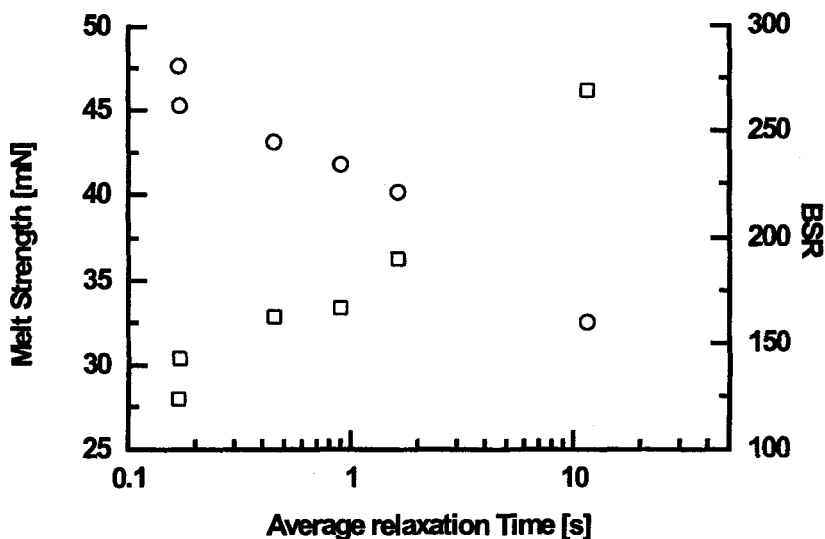


FIGURE 9 Extensional parameters versus average relaxation time.

influence of η_0 and λ_w/λ_n and in turn the influence of the molecular weight and of the polydispersity. Figure 9 shows such a correlation between the melt spinning parameters and the average relaxation time.

4. CONCLUSION

A previous paper has reported empirical relationships between the molecular weight distribution and the parameters of models such as the Cole–Cole or Carreau–Yasuda equations describing the rheological behaviour of PVDF in the molten state. Because of the limitations of such models, the analysis of the continuous relaxation spectrum (using a log normal distribution) and of a discrete relaxation spectrum (with adjustable relaxation modes) obtained from oscillatory data in the melt was performed. The interdependence between both the spectra was also carefully examined. The parameters and properties of the spectra were investigated in view of the molecular weight distribution of various PVDF samples and this leads to the following conclusions:

- The broadness of the relaxation spectrum is related to the polydispersity of the materials.
- In the limit of monodisperse species, values of 2.6 to 4.8 were found for the broadness of the relaxation spectrum in agreement with data from the literature on monodisperse samples with other polymers.

- The average relaxation time of the log-normal spectrum $(\lambda_w \lambda_n)^{1/2}$ is equivalent to the characteristic relaxation time of the Cole–Cole equation.
- The Newtonian viscosity being related mainly to the weight average molecular weight as shown in a previous paper, a relation between the average relaxation time, plateau modulus, polydispersity, and molecular weight is proposed.
- Using this relation, reduced relaxation spectra show the influence of the polydispersity.
- Alternatively, an estimate of the plateau modulus of PVDF (0.6 MPa) can be obtained.
- Since the relative influence of the MWD parameters on the extensional behavior is strong but can hardly be separated, a correlation between the melt strength and breaking stretch ratio and the average relaxation time can be inferred.

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