

The effect of physical ageing on the relaxation time spectrum of amorphous polymers: the fractional calculus approach

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Empirical models corresponding to a constitutive equation with fractional derivatives are proposed for linear viscoelastic polymers. For these models, the relaxation modulus, the dynamic moduli, the relaxation time spectra, and other material functions can be calculated as a function of a few parameters that characterise the behaviour of a viscoelastic polymer. The fractional calculus approach allows us to calculate the relaxation time spectrum $H(\tau)$ via the Stieltjes inversion in the linear viscoelastic zone. Polymethylmethacrylate (PMMA) is chosen as a model amorphous polymer in a temperature range from $T_g - 90^\circ\text{C}$ to $T_g + 25^\circ\text{C}$. This polymer is characterised by a non-equilibrium state between at least the β and α relaxations. The structural recovery of PMMA has been investigated using dynamic mechanical thermal analysis (DMTA) by varying the preparational history. The effect of time and temperature on the model parameters and on the relaxation time spectra are also investigated in the neighbourhood of the glass transition. © 1999 Kluwer Academic Publishers

1. Introduction

Relaxational phenomena in polymers, e.g. the relaxation of mechanical stresses, of the dielectric polarisation, of the enthalpy or of the free volume have been the subject of research for many years. The understanding of the essential processes is still incomplete. Therefore, more and more relaxation models appear in order to complete our knowledge as well as to obtain improved methods for their description. The relaxational phenomena in polymers reveal the existence of a broad distribution of relaxation times which can be determined from experimental data, because the relaxation time spectrum $H(\tau)$ of solid polymers is related to experimental accessible material functions such as, the storage modulus $E'(\omega)$, the loss modulus $E''(\omega)$, or the relaxation modulus $E(t)$ by a specific kind of integral equation [1, 2]:

$$E'(\omega) = E_0 + \int_{-\infty}^{+\infty} H(\tau) \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} d \ln \tau \quad (1)$$

$$E''(\omega) = \int_{-\infty}^{+\infty} H(\tau) \frac{\omega \tau}{1 + \omega^2 \tau^2} d \ln \tau \quad (2)$$

$$E(t) = E_0 + \int_{-\infty}^{+\infty} H(\tau) e^{-t/\tau} d \ln \tau \quad (3)$$

where E_0 is the relaxed modulus.

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Equations 1–3 denote the solid generalised Maxwell model used as an approximation for the study of viscoelastic solids.

Obviously, the determination of the relaxation time spectrum requires the inversion of such an integral equation. This is a degenerate problem, and there are several difficulties connected with the solution of these problems [3, 4].

Several methods have been developed for the calculation of relaxation time spectra from experimental data [1, 5] in the flow and entanglement behaviour of polymers.

In this paper, we attempt to apply these methods between the glass and the glass rubber transition region of amorphous polymers by choosing poly(methyl methacrylate) PMMA as a model amorphous polymer. Our model, based on the fractional calculus method, predicts the viscoelastic behaviour of amorphous polymers and allows us to calculate the relaxation spectrum $H(\tau)$. We shall also analyse the effect of physical ageing on the distribution of relaxation times.

2. Fractional calculus

The application of fractional calculus to the theory of viscoelasticity has been proposed many times and Bagley and Torvik [6, 7] provide a review of attempts

prior to 1980. The origin of these efforts dates back to the observation by Nutting [8], as early as 1921, that relaxation phenomena are often proportional to time or frequency raised to a fractional power and the subsequent suggestion by Gemant [9] in 1938 of the use of derivatives of fractional order to model it. Major advances were made in the 1980s, Bagley and Torvik [6, 7] proposed a general fractional viscoelastic model as:

$$\sigma(t) + \sum_{m=1}^M \tau_m^{a_m} D_t^{a_m} \sigma(t) = E_0 \varepsilon(t) + \sum_{n=1}^N E_n \tau_n^{b_n} D_t^{b_n} \varepsilon(t) \quad (4)$$

where σ is the applied stress, ε is the strain and $D_t^r(f)$ the fractional derivative of order r defined as [10]:

$$D_t^r(f) = \frac{1}{\Gamma(1-r)} \left[\frac{d}{dt} \int_0^t \frac{f(y)}{(t-y)^r} dy \right] \quad \text{for } 0 < r < 1 \quad (5)$$

This approach was first applied to the description of the rheological behaviour of organic glasses [6], elastomers [11], polyurethane [12], polyisobutylene and a monodisperse polybutadiens [13] and even viscoelastic dampers [11, 14] or structures [7, 12], and finally to solid amorphous polymers over a very wide temperature range [15] ($T_g - 190^\circ\text{C}$ and $T_g + 25^\circ\text{C}$).

From Equation 4 if $M = N = 1$; $a_m = b_n = a$, with $0 < a \leq 1$, and $E_1 = E_u$ we can obtain the equation associated to the Fractional Zener Model (FZM) [15] with one spring-pot:

$$\sigma(t) + \tau_1^a D_t^a \sigma(t) = E_0 \varepsilon(t) + E_u \tau_1^a D_t^a \varepsilon(t) \quad (6)$$

where E_u is the unrelaxed modulus, E_0 the relaxed modulus and τ_1 the characteristic material time.

The Laplace transform of the fractional derivative operator $D_t^r f(t)$ can be written as s^r times the Laplace transform of $f(t)$:

$$L[D_t^r f(t)] = s^r L[f(t)] \quad (7)$$

where s is the Laplace variable. This property can be demonstrated by taking the Laplace transform:

$$L[f(t)] = \int_0^{+\infty} f(t) e^{-st} dt \quad (8)$$

of Equation 5. A similar relationship exists in the Fourier transform domain. By taking the Fourier transform,

$$F[f(t)] = \int_0^{+\infty} f(t) e^{-i\omega t} dt \quad (9)$$

of Equation 5, a relationship similar to Equation 7 results:

$$F[D_t^r f(t)] = (i\omega)^r F[f(t)] \quad (10)$$

The Fourier transform of the fractional derivative of order r of $f(t)$ is $(i\omega)^r$ times the Fourier transform of $f(t)$.

Taking the Fourier transform of the FZM Equation 6, yields:

$$\begin{aligned} \sigma^*(i\omega) + \tau_1^a (i\omega)^a \sigma^*(i\omega) &= E_0 \varepsilon^*(i\omega) \\ &+ E_u \tau_1^a (i\omega)^a \varepsilon^*(i\omega) \end{aligned} \quad (11)$$

where $\sigma^*(i\omega)$ and $\varepsilon^*(i\omega)$ are the Fourier transforms of the stress and strain respectively. Factoring and dividing terms in this operation produces:

$$\sigma^*(i\omega) = \frac{E_0 + E_u (i\omega \tau_1)^a}{1 + (i\omega \tau_1)^a} \cdot \varepsilon^*(i\omega) \quad (12)$$

In another way we can use the representation proposed by Tschoegl [5] called the relaxance \bar{Q} in order to obtain a more general description of the Cole-Cole behaviour. The relaxance \bar{Q} is the ratio of the Laplace transformed stress $\bar{\sigma}$ to the Laplace transformed deformation $\bar{\varepsilon}$ and is given as:

$$\bar{Q} = \frac{\bar{\sigma}}{\bar{\varepsilon}} = \frac{L[\sigma]}{L[\varepsilon]} \quad (13)$$

The Laplace transform of FZM Equation 6 yields:

$$\bar{Q}(s) = \frac{E_0 + E_u (s \tau_1)^a}{1 + (s \tau_1)^a} \quad 0 < a \leq 1 \quad (14)$$

The same complex modulus of the Equation 12 can be derived using the following relation:

$$E^*(i\omega) = \bar{Q}(s)|_{s=i\omega} = \frac{E_0 + E_u (i\omega \tau_1)^a}{1 + (i\omega \tau_1)^a} \quad (15)$$

with the Laplace variable ($s = i\omega$).

The real and imaginary parts ($E^* = E' + iE''$) can be calculated by separating the complex function into real and imaginary parts. In the preceding papers [15] we have studied the different cases of the a parameter in the complex plane, then we have shown that FZM cannot be used to model the viscoelastic behaviour of solid amorphous polymers because the Cole-Cole diagram of FZM is symmetrical independently of the value of the a parameter.

From Equation 4 we obtain the equation of FZM with two spring-pots [15] a and b by considering that $0 < a \leq b \leq 1$. The relaxance function $\bar{Q}(s)$ of this model can be written as follows:

$$\bar{Q}(s) = \frac{E_u + E_0 [(s \tau_0)^{-a} + (s \tau_1)^{-b}]}{1 + (s \tau_0)^{-a} + (s \tau_1)^{-b}} \quad (16)$$

It is easy to determine the complex modulus $E^*(\omega)$ as following:

$$\begin{aligned} E^*(i\omega) &= \bar{Q}(s)|_{s=i\omega} \\ &= \frac{E_u + E_0 [(i\omega \tau_0)^{-a} + (i\omega \tau_1)^{-b}]}{1 + (i\omega \tau_0)^{-a} + (i\omega \tau_1)^{-b}} \end{aligned} \quad (17)$$

The real and imaginary parts of the complex modulus can be calculated from Equation (16) as following:

$$\begin{aligned} E' &= E_0 + \frac{(E_u - E_0)(1 + B_1)}{(1 + B_1)^2 + B_2^2} \\ E'' &= \frac{(E_u - E_0)B_2^2}{(1 + B_1)^2 + B_2^2} \end{aligned} \quad (18)$$

where

$$B_1 = D(\omega\tau_1)^{-b} \cos\left(b \frac{\pi}{2}\right) + (\omega\tau_1)^{-a} \cos\left(a \frac{\pi}{2}\right)$$

$$B_2 = D(\omega\tau_1)^{-b} \sin\left(b \frac{\pi}{2}\right) + (\omega\tau_1)^{-a} \sin\left(a \frac{\pi}{2}\right) \quad (19)$$

$$D = \left(\frac{\tau_0}{\tau_1}\right)^{-b}.$$

The variation of E' and E'' with the model parameters has been discussed in a previous paper [15] and the real viscoelastic response of amorphous polymers in the glass transition region can be predicted by this model nevertheless a limit of this model has been observed for temperatures lower than T_g .

The fractional calculus approach allows us to calculate all the viscoelastic functions and in the following we will calculate the relaxation spectra $H(\tau)$ and compare this function with experiments for an amorphous polymer solid in the neighbourhood of the glass transition temperature.

3. Relaxation time spectrum

Linear viscoelastic models are often presented as spectral models. Although direct measurement of the relaxation time spectrum is impossible, the main advantage of this modelling is to ensure consistency with linear viscoelastic theory and to easily solve the problem of converting dynamic data from the frequency domain to the time domain.

The linear viscoelastic theories give the following description of the function $E(t)$ [5]:

$$E(t) = E_0 + \sum_{i=1}^N H_i e^{-t/\tau_i} = E_0 + \sum_{i=1}^N \frac{\eta_i}{\tau_i} e^{-t/\tau_i} \quad (20)$$

where N is the number of relaxation modes, τ_i the relaxation times, H_i the contribution of each time to the modulus and η_i the viscosity associated with each time. The distribution should be considered continuous, however the mathematical treatment of constitutive equations is greatly simplified when a discrete spectrum is used.

Theoretically the characteristic values (τ_i , H_i) can be inferred from the behaviour of the material under oscillations in the linear viscoelastic domain, either in static or in dynamic experiments, provided that both the strain and the rate of strain are low. In a dynamic experiment, where the strain is given by $\varepsilon^*(i\omega) = \varepsilon_0 e^{i\omega t}$, the material response can be described by the use of the complex modulus $E^*(\omega)$ which can be rewritten by using the Fourier transform of relaxation modulus $E(t)$ as follows:

$$E^*(\omega) = i\omega F[E(t), i\omega] \quad (21a)$$

$F[E(t), i\omega]$ is the Fourier transform defined from Equation 9.

From Equations 9 and 20 we obtain:

$$E^*(\omega) = i\omega \int_0^\infty \left[E_0 + \sum_{i=1}^N H_i \cdot e^{-t/\tau_i} \right] e^{-i\omega t} dt \quad (21b)$$

$$= E_0 + \sum_{i=1}^N \frac{i\omega H_i \cdot \tau_i}{1 + i\omega\tau_i}$$

$E^*(\omega)$ can be split into its real and imaginary parts:

$$E'(\omega) = E_0 + \sum_{i=1}^N \frac{H_i(\omega\tau_i)^2}{1 + (\omega\tau_i)^2} \quad (22a)$$

$$E''(\omega) = \sum_{i=1}^N \frac{H_i \cdot \omega\tau_i}{1 + (\omega\tau_i)^2} \quad (22b)$$

However, it must be noted that the results obtained with this method depend strongly on the number N of relaxation times [4]. In addition, there is no unambiguous relation between the discrete relaxation times τ_i , the contribution H_i , and the corresponding continuous relaxation time spectrum $H(\tau)$ [3] Equations 1–3.

Nevertheless, discrete and continuous relaxation time spectra may be compared in the way described by Baumgaertel and Winter [16–18]. A comparison between some of these procedures is presented by Orbey and Dealy [19]. In this paper, we will derive an analytical expression based on the relaxance $\bar{Q}(s)$ Equation 13. Equations 1–3 suggest the use of an inverse Laplace transform in order to obtain $H(\tau)$. However, it is very complicated for most of the different relaxation functions. For this reason, another method—the inverse Stieltjes transform [5]—has been used. In this way, one obtains:

$$H(\tau) = \pm \frac{1}{\pi} \text{Im} \left\{ \bar{Q}(s) \Big|_{s=(1/\tau)e^{\mp i\pi}} \right\} \quad (23)$$

Then, we can calculate the relaxation spectrum of FZM with two spring-pots from Equations 16 and 23 as following:

$$H(\tau) = \frac{E_u - E_0}{\pi} \frac{B_2}{(1 + B_1)^2 + B_2^2} \quad (24)$$

where

$$B_1 = D \left(\frac{\tau}{\tau_1}\right)^a \cos a\pi + \left(\frac{\tau}{\tau_1}\right)^b \cos b\pi$$

$$B_2 = D \left(\frac{\tau}{\tau_1}\right)^a \sin a\pi + \left(\frac{\tau}{\tau_1}\right)^b \sin b\pi$$

$$D = \left(\frac{\tau_0}{\tau_1}\right)^{-b} \quad 0 < a \leq b \leq 1$$

The plot of the logarithm of the normalised relaxation time spectra for Equation 24 is given in Fig. 1 for various values of the parameter b . With $b - a = 0.1 = \text{constant}$, the spectrum becomes broader with decreasing values of b .

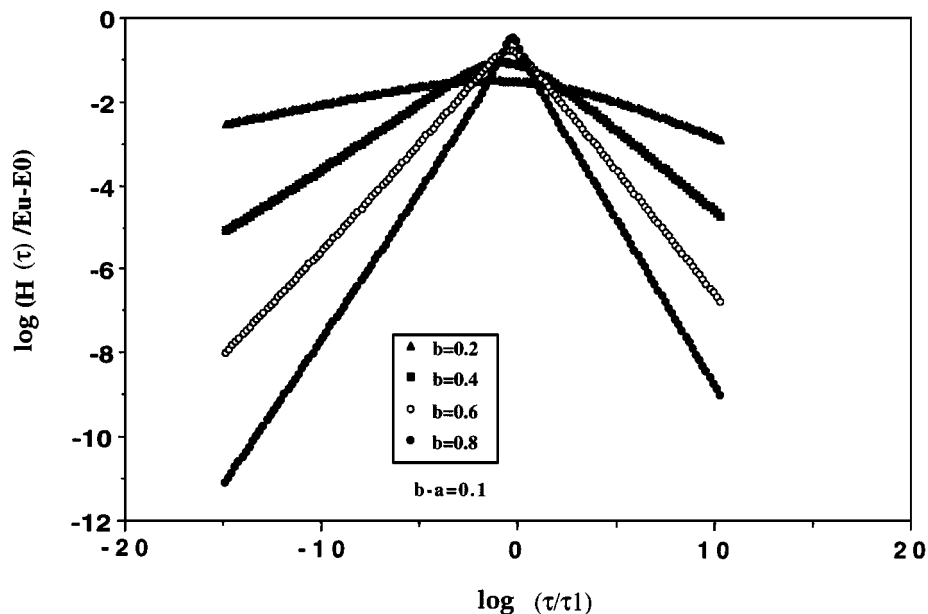


Figure 1 Logarithm of the normalised relaxation spectrum for the FZM with two spring-pots versus the normalised time for various values of a and b with $b - a = 0.1$: \blacktriangle $b = 0.2$; \blacksquare $b = 0.4$; \circ $b = 0.6$; \bullet $b = 0.8$.

4. Experimental

4.1. Material

Samples of PMMA were obtained from ELF, France who prepared and characterised it. Its molecular weight is $3 \cdot 10^6$ g/mol and its polydispersity index is 2.3.

4.2. Dynamic mechanical measurements

Dynamic mechanical measurements were performed by using a DMTA MKIII (Rheometric Scientific) operating in double cantilever bending mode. This instrument provides the real and imaginary parts of the dynamic modulus so called, respectively, the storage modulus E' and the loss modulus E'' . The internal friction or mechanical damping $\delta = (E''/E')$ is also calculated. E'' , E' and δ are displayed as a function of the temperature (under isochronal conditions) or of the frequency (under isothermal conditions).

Rectangular samples ($35 \times 6 \times 2$) mm were used. Before the DMTA run, the samples were dried for 1 hour under vacuum at 80°C . They were next kept for 1 hour at 130°C ($T_g + 15^\circ\text{C}$), always under vacuum, in order to erase thermomechanical history and any water effect. These samples are called the reference samples.

The isochronal scans were recorded from 30 to 130°C at a heating rate of $1^\circ\text{C}/\text{min}$ and at a frequency of 1 Hz.

Physical ageing of PMMA has been studied by DMTA under the same experimental conditions without removing the samples.

After the first DMTA run of the three reference samples up to 130°C ($T_g + 15^\circ\text{C}$), they were kept at this temperature for 20 min. Without removing the sample, they were then cooled down to their ageing temperatures (T_a) of 90 , 70 and 50°C for times (t_a) of 10 , 20 and 96 hours. Next, the samples were cooled to room temperature in an ambient atmosphere and the second DMTA run were made under the same experimental conditions.

Figs 2 and 3 show respectively the DMTA spectra of E'' and $\tan \delta$ versus temperature at 1 Hz of the reference and aged samples for the different times of ageing at 90°C ($T_g - 25^\circ\text{C}$). This set of plots shows that, on the one hand, at temperatures between 120°C and 30°C , the anelastic behaviour of 1 Hz of PMMA is affected by its thermal history (structural recovery). The values of E'' for aged samples depend on the time of ageing and the maximum in E'' vs. temperature of aged samples increases if the time of ageing increases.

Figs 4 and 5 show respectively the variation of E'' and $\tan \delta$ vs. temperature at 1 Hz for the reference and the aged samples of PMMA at different temperatures for an ageing time of 10 hours. This set of plots, show that, at temperature between about 30°C and 120°C , the structural recovery occurs. The viscoelastic behaviour of PMMA between the secondary (T_β) and the main (T_α) relaxations is affected by physical ageing. One may point out in passing that the value of E'' of the sample aged at 90°C decreases sharply between 75°C and 113°C . This behaviour could confirm the existence of two physical ageing kinetics pointed out by micro-creep experiments [20, 22, 23] for temperatures higher and lower than 60°C ($\approx T_g - 55^\circ\text{C}$) in PMMA case.

Cole-Cole diagrams of reference and aged samples of PMMA at 1 Hz are displayed in Fig. 6 for different ageing times at 90°C and for different ageing temperatures and an ageing time of 10 hours. We note that in the high temperature zone, the slopes of the Cole-Cole diagrams are the same. This behaviour is consistent with the fact that physical ageing is not observed in this zone, because amorphous polymers are considered in thermodynamic equilibrium at a temperature well above the glass transition temperature [21]. The difference between Cole-Cole diagrams begins in the vicinity of the E'' maximum ($T_\alpha \approx 122^\circ\text{C}$) and they increase for lower temperatures. Concerning the slopes of Cole-Cole diagrams in the low temperature zone, these slopes are affected by the time of ageing (Fig. 6a) and by the

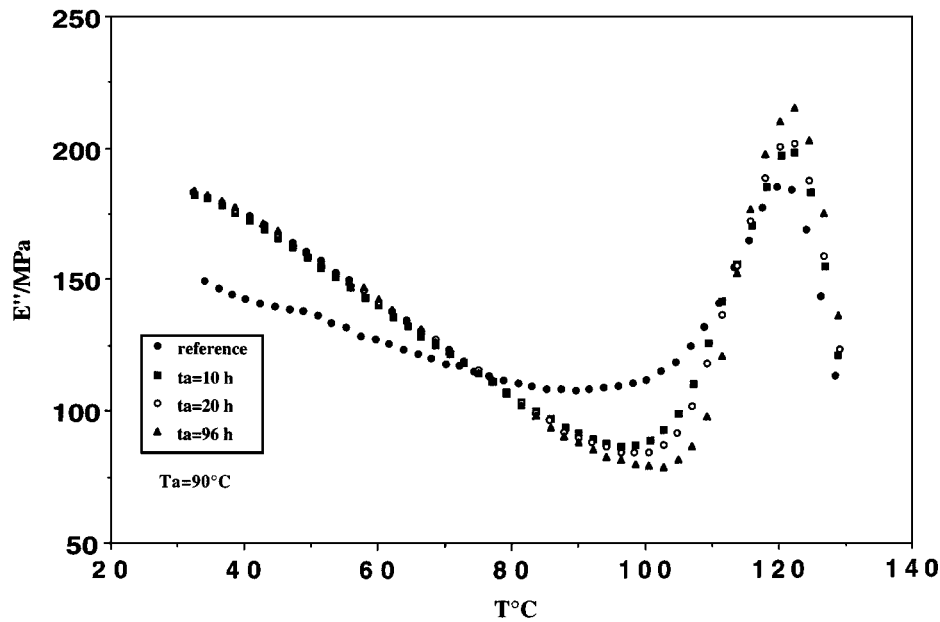


Figure 2 Loss modulus, E'' , versus temperature at 1 Hz for the reference and the aged PMMA samples for different times of ageing t_a at $T_a = 90^\circ\text{C}$: (a) The reference (●) PMMA sample; (b) The aged PMMA samples (■ $t_a = 10$ hours; ○ $t_a = 20$ hours; ▲ $t_a = 96$ hours).

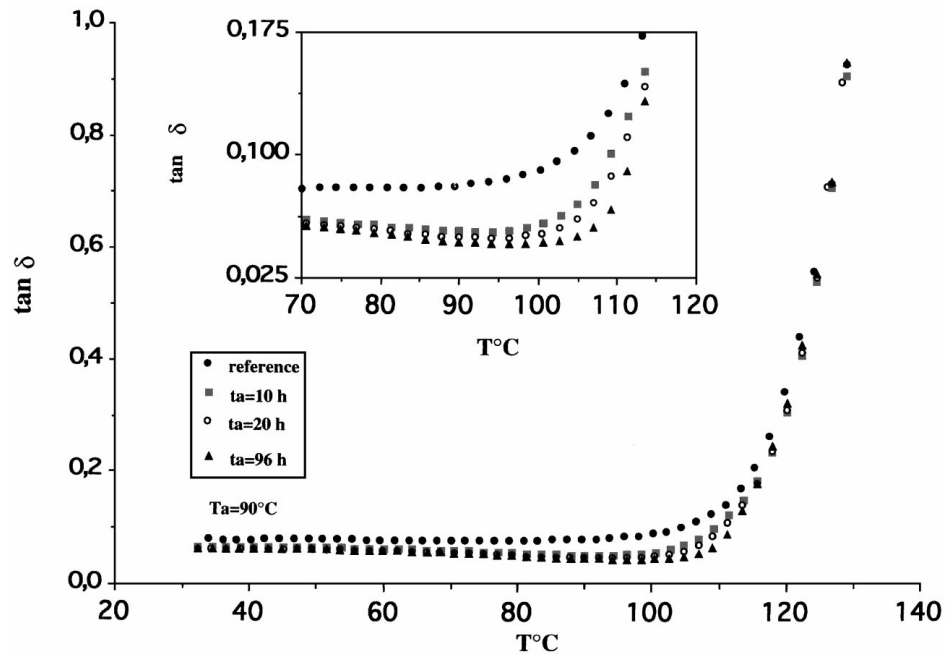


Figure 3 Loss factor, $\tan \delta$, versus temperature at 1 Hz for the reference and aged PMMA samples for different times of ageing t_a at $T_a = 90^\circ\text{C}$: (a) The reference (●) PMMA sample; (b) The aged PMMA samples (■ $t_a = 10$ hours; ○ $t_a = 20$ hours; ▲ $t_a = 96$ hours).

temperature of ageing (Fig. 6b). Therefore, as related in our case to the fractional parameters a and b , these parameters must be affected by the structural recovery or physical ageing.

5. Discussion: model and comparison with experiment

Let us now compare the response of FZM with two spring-pots Equations 18 and 19 with the experimental curves (Cole-Cole diagrams) at 1 Hz. The comparison between the measured and calculated material functions of FZM with two spring-pots is plotted in Fig. 7 for the reference sample of PMMA and in Fig. 8 for the aged sample of PMMA at 90°C during 10 hours. Agreement is excellent except the low temperature zone be-

tween about 30 and $115^\circ\text{C} \approx T_g$, these deviations may be ascribed to the presence of β relaxation and eventually, another relaxation at about 60°C in the case of PMMA [15, 20, 22, 23]. The parameters of the FZM with two spring-pots a and b for all samples are plotted in Table I.

The parameter a is connected with the slope in the glass transition low temperature domain and b is connected with the slope in the high temperature domain.

In order to show the effect of physical ageing on the viscoelastic behaviour of amorphous polymers, the relaxation time spectrum is usually considered because this function can easily be connected with processes on a molecular level [24]. The corresponding density function of the relaxation time spectrum ($H(\tau)/E_u - E_0$) of FZM with two spring-pots calculated from Equation 24

TABLE I The parameters of the FZM with two spring-pots a and b for reference and aged PMMA samples

PMMA	Ref	10 h	20 h	96 h
a_{90}	0.33	0.27	0.26	0.25
a_{70}	0.33	0.3	0.28	0.25
a_{50}	0.33	0.31	0.3	0.26
b_{90}	0.79	0.79	0.79	0.79
b_{70}	0.79	0.79	0.79	0.79
b_{50}	0.79	0.79	0.79	0.79
E_{u-90} (MPa)	1250	1580	1630	1800
E_{u-70} (MPa)	1300	1500	1615	1780
E_{u-50} (MPa)	1200	1400	1550	1650
E_{0-90} (MPa)	30	40	30	20
E_{0-70} (MPa)	20	20	20	20
E_{0-50} (MPa)	20	20	20	20

is plotted in Fig. 9 for the reference and the aged samples of PMMA. The relaxation time spectrum shows a maximum at $\tau = \tau_1$ and the viscoelastic time scale are apparent in the relaxation spectra, the glassy zone to the left of the maximum and the transition zone in which $(H(\tau)/E_u - E_0)$ changes steeply.

The changes observed in the spectra at high time scales (transition zone) e.g., at a high relaxation time, broaden in the aged sample, reflect differences in the modes of motion within the quenched compared with the aged sample. They also reflect the effect of physical ageing on the a parameter which depends on the slope of the Cole-Cole diagram on the low side of the glass transition zone. Fig. 10 shows the relaxation time

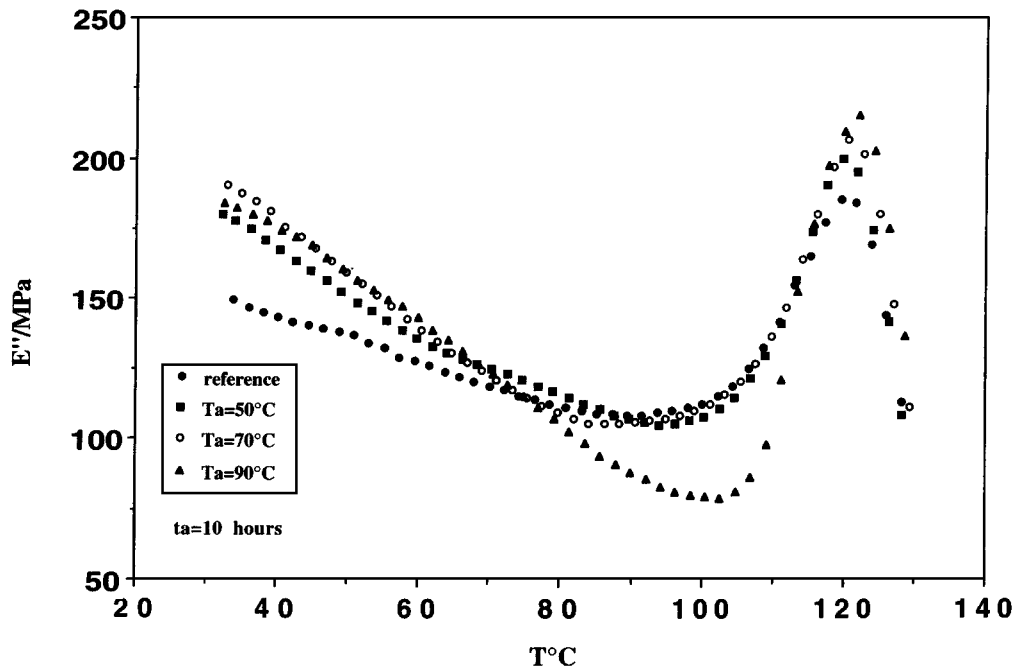


Figure 4 Loss modulus, E'' , versus temperature at 1 Hz for the reference and the aged PMMA samples at different temperatures for an ageing time t_a of 10 hours: (a) The reference (●) PMMA sample; (b) The aged PMMA samples (■ $T_a = 50^\circ\text{C}$; ○ $T_a = 70^\circ\text{C}$; ▲ $T_a = 90^\circ\text{C}$).

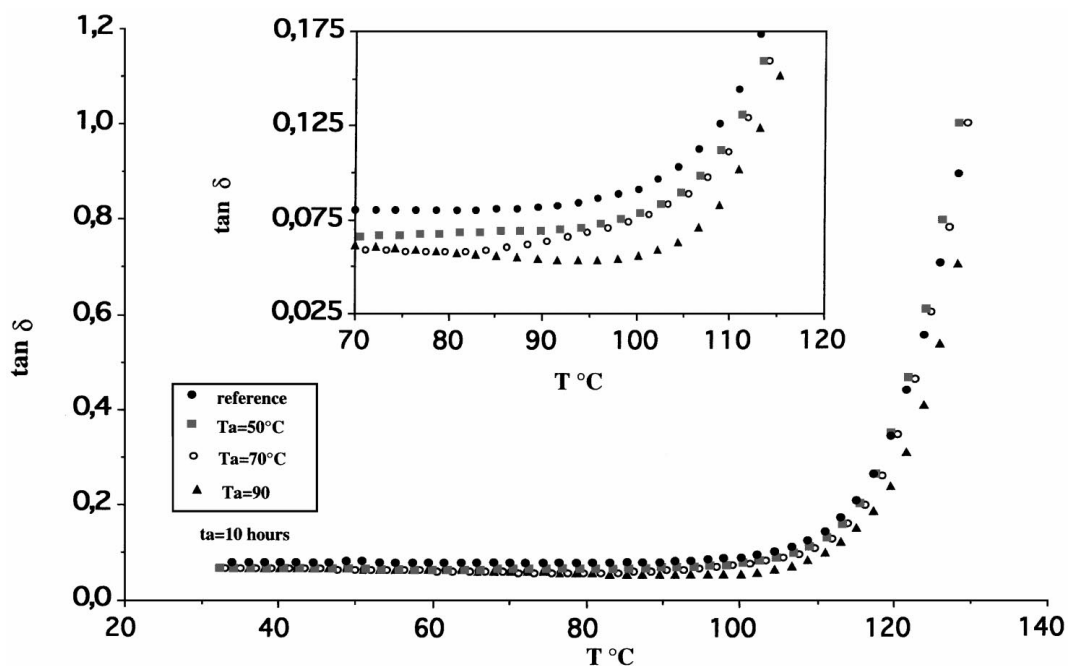


Figure 5 Loss factor, $\tan \delta$, versus temperature at 1 Hz for the reference and aged PMMA samples at different temperatures for an ageing time t_a of 10 hours: (a) ● reference PMMA sample; (b) The aged PMMA samples (■ $T_a = 50^\circ\text{C}$; ○ $T_a = 70^\circ\text{C}$; ▲ $T_a = 90^\circ\text{C}$).

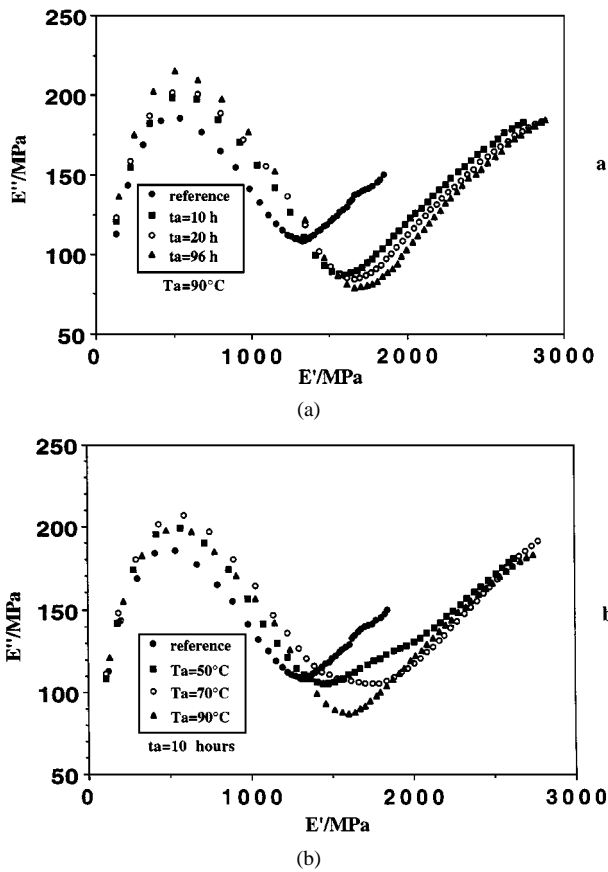


Figure 6 The Cole-Cole diagrams for the reference and the aged PMMA samples for (a) different times of ageing t_a at $T_a = 90^\circ\text{C}$: (a) Reference sample (●), (b) the aged PMMA samples (■ $t_a = 10$ hours; ○ $t_a = 20$ hours; ▲ $t_a = 96$ hours). (b) Different temperatures for an ageing time t_a of 10 hours: (a) The reference (●) PMMA sample; (b) the aged PMMA samples (■ $T_a = 50^\circ\text{C}$; ○ $T_a = 70^\circ\text{C}$; ▲ $T_a = 90^\circ\text{C}$).

spectrum ($H(\tau)/E_u - E_0$) for the other sample studied ($t_a = 10$ hours, $T_a = 50, 70, 90^\circ\text{C}$).

The corresponding parameters used are given in Table I, the b parameter is unaffected by the structural recovery but the a parameter varies from sample to sample. Here, b and a were obtained from the slopes of the

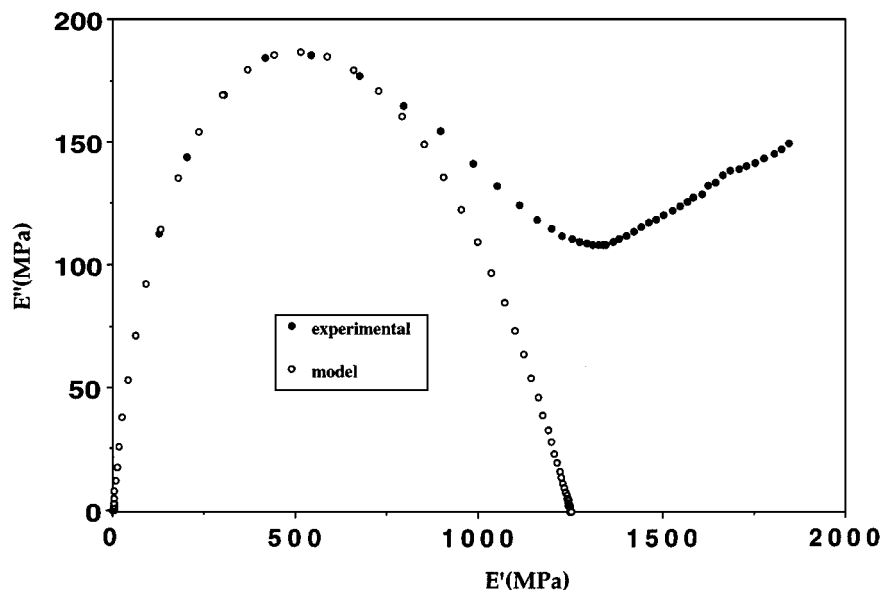


Figure 7 Comparison in the complex plane between the experimental PMMA Cole-Cole diagram at 1 Hz and the corresponding calculated model FZM Equation 18: ● experimental data; ○ model.

model Cole-Cole diagrams. They were obtained from the angles between the tangent and the E' axis. In the same way, the remaining parameters for the glassy and transition zones, E_u and E_0 , were obtained by extending this tangent onto the E' axis to lower and higher temperatures, in the glass transition zone, respectively.

From Figs 9 and 10, we note that the relaxation spectrum is affected by the thermal history of PMMA and depends on the time and the temperature of ageing. The a parameter relates to the broadening of the relaxation spectrum around the glass transition zone. At high time scales, the spectrum is unaffected by the physical ageing so the b parameter is usually constant.

Then, this spectrum gives a clear picture on the molecular mobility of solid amorphous polymers in the neighbourhood of the glass transition zone, but there is a limit of the spectrum in the glassy zone below T_g because the β -relaxation and another relaxation at about 60°C .

We have proposed the Extended Fractional Solid Model [15] (EFSM) to describe the entire viscoelastic behaviour of solid amorphous polymers in the glassy region. This model gives predictions of the entire viscoelastic behaviour of the amorphous polymers in the glassy zone ($T_g - 190^\circ\text{C}$ and $T_g + 25^\circ\text{C}$). The a, b, c parameters can be associated with the relaxation time spectrum $H(\tau)$ of amorphous solid polymers. We will dedicate a future paper to the study of the distribution of relaxation times over a wide range of temperature and frequency to take into account the effect of physical ageing phenomenon on the relaxation spectrum.

6. Conclusion

The examples show that the dynamic moduli of an amorphous polymer (PMMA) can accurately be approximated using the rheological models based on fractional derivatives. The relaxation time spectrum can be derived by the inverse Stieltjes transform (Keeping in mind that the determination of the relaxation time spectrum requires the solution of an ill-posed problem). The

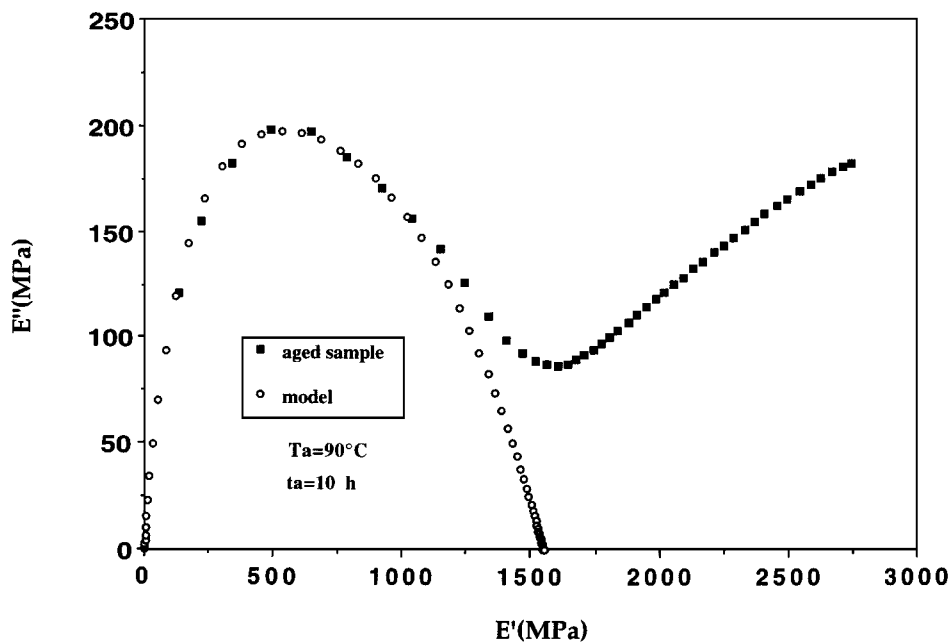


Figure 8 Comparison in the complex plane between the aged experimental PMMA sample at 1 Hz and the FZM model: ■ aged sample; ○ model.

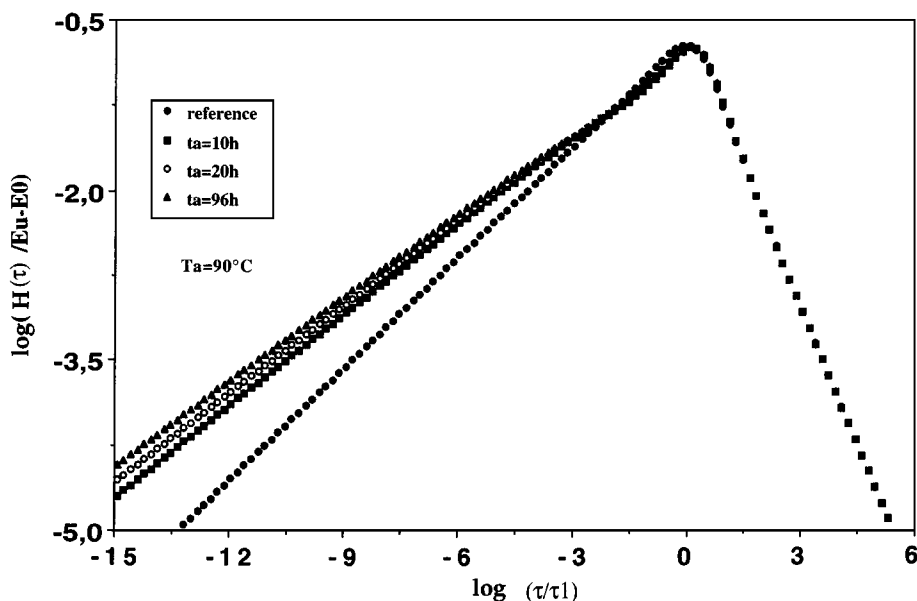


Figure 9 Logarithm of the normalised relaxation spectrum (the density function) versus logarithm of the normalised time for the reference and the aged PMMA samples for different times of ageing t_a at $T_a = 90^\circ\text{C}$: (a) The reference (●) PMMA sample; (b) The aged PMMA samples (■ $t_a = 10$ hours; ○ $t_a = 20$ hours; ▲ $t_a = 96$ hours).

effect of physical ageing (structural recovery) on the model parameters has been investigated in the neighbourhood of the glass transition zone and the distribution of relaxation times is affected by both the time and the temperature of physical ageing.

The models proposed in this paper fit very well, in the vicinity of the glass rubber transition zone. In contrast to their simplicity and their satisfactory fit properties, the physical interpretation has been difficult and insufficient until now. This problem can only be solved if physical explanations are found for the fractional derivatives occurring in the relaxation equation.

But fractal time processes governed by fractional differential or integral equations, as discussed here, seem

to be the natural counterpart to our recent understanding of fractal (geometric) structures [24]. Both concepts are drawing on the same inspiration: the principle of exact or statistical self-similarity. Fractional calculus models should be regarded as tools to describe the behaviour of complex systems in the first instance on a mesoscopic or macroscopic level. Giving an answer to the question for a general connection between the orders of the fractional operators and some sort of fractal (similarity) dimension requires further investigations.

In summary, the models discussed in this paper can be regarded as an interesting generalisation, especially for materials showing cooperative phenomena. Consequently, it should be further developed.

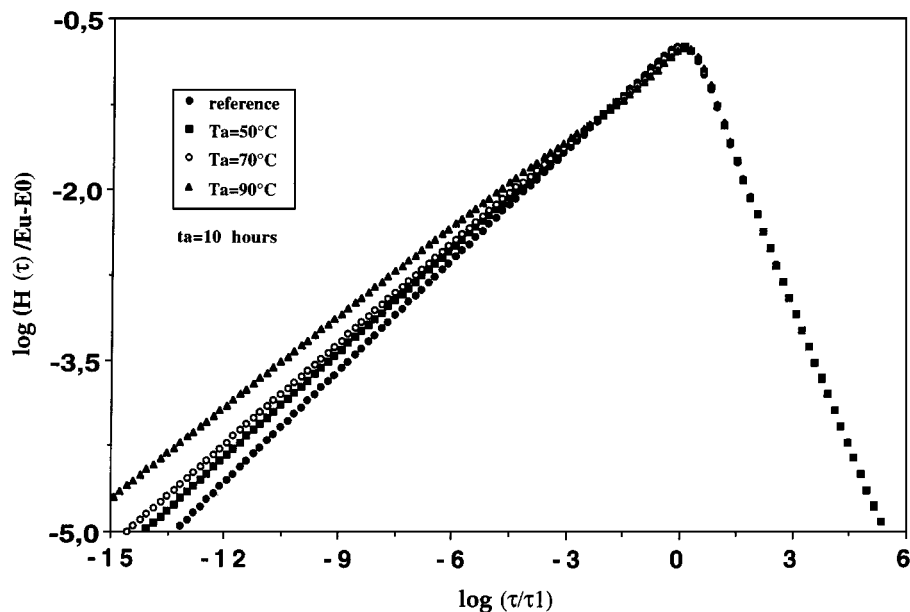


Figure 10 Logarithm of the normalised relaxation spectrum (the density function) versus logarithm of the normalised time for the reference and the aged PMMA samples at different temperatures for an ageing time t_a of 10 hours: (a) The reference (●) PMMA sample; (b) The aged PMMA samples (■ $T_a = 50^\circ\text{C}$; ○ $T_a = 70^\circ\text{C}$; ▲ $T_a = 90^\circ\text{C}$).

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