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Application of a probability model for relaxation to the dielectric α - and β -relaxation of amorphous polyethylene terephthalate

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Abstract. A probability model (PM) developed recently, which is an alternative to the conventional Havriliak–Negami (HN) dispersion function for polymer systems, is applied for the first time to the study of the dielectric α - and β -relaxation of amorphous polyethylene terephthalate (PET). It has been found that the temperature dependence of the maxima of the imaginary part of the dielectric function and of the half-width of the distribution in the PM of the α -relaxation exhibit Vogel–Fulcher-type temperature behaviour; the temperature dependence of the maxima of the imaginary part of the dielectric function of the β -relaxation is proportional to the ratio of the *gauche* content to the *trans* content of the ethylene glycol linkages in PET. Finally, the mechanisms of the α - and β -relaxation are elucidated concisely.

Polyethylene terephthalate (PET), the condensation product of terephthalic acid and ethylene glycol, is the first fibre-forming polyester of economic importance. The glass transition temperature T_g is 69 °C. Between the crystallization temperature T_c (90 °C) and the melting temperature T_m (265 °C), PET exhibits a stepwise crystallization [1, 2]. This polymer is easily obtained in different states of order by suitable thermal treatment. The physical and technological properties of PET are determined by the states of order and the molecular motions of the different groups in the long chains. During the past few decades, studies of molecular motions by dielectric [3, 4], dynamic mechanical [5, 6] and nuclear magnetic resonance methods [7, 8] have provided some insight into the internal kinetics of the polymer. The influence of crystallization, orientation and absorbed low-molecular-weight compounds upon the relaxation processes of PET has also been discussed by several authors [3, 9] and reviewed by Illers and Breuer [1]. Although the HN function [10] has been used for representing polymeric dispersion data and Alvarez *et al* [11] discussed the relationship between the time-domain Kohlrausch–Williams–Watts and HN functions, an appropriate decay function for polymer systems has remained lacking. One of the reasons for this absence is that the shapes of the dispersions in the complex plane are seldom the shapes that are observed in the case of simple molecules, making the evaluation of the dispersion parameters impossible [10]. At one time, mode-coupling theory (MCT) seemed to be a

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relatively appropriate candidate [12]. However, Hofmann, Kremer and Fischer have recently obtained broad-band dielectric spectra (10^{-2} – 10^9 Hz) for PET, which makes it possible to analyse the β -relaxation in full detail. By studying the scaling of the α - and β -relaxation in amorphous PET, they have found that low-frequency β -relaxation ($\omega \leq 10^9$ Hz) cannot be interpreted in the framework of the idealized MCT [13]. A probability model (PM) for relaxation has been developed recently and the relaxation function and internal friction of disordered structural networks has been interpreted well with it [14, 15]. The object of this work is to apply the PM to study the dielectric function of PET, to calculate dispersion parameters and to discuss the mechanisms of the α - and β -relaxation. Meanwhile, the generality of the PM is tested further.

First, we analyse the dielectric function data for of amorphous polyethylene terephthalate. According to the PM, no matter what the relaxation (α or β etc) is, the structural relaxation function $\phi(t)$ can be written as [14]

$$\phi(t) = \frac{\phi_0}{2} \operatorname{erfc}\left(\frac{\lg(t/\tau)}{\sqrt{2}\sigma^2}\right) \quad (1)$$

where the erfc is the complementary error function; ϕ_0 is the nonergodicity level; σ is the half-width of the distribution on a $\lg t$ abscissa; τ is the relaxation time. The imaginary part of the dielectric function is represented by

$$\epsilon''/\epsilon''_{\max} = \int_0^\infty (-d\phi/dt) \sin \omega t \, dt \quad (2)$$

where ϵ''_{\max} is the maximum value of ϵ'' . From equation (1), the derivative of $\phi(t)$ with respect to t is

$$\frac{d\phi}{dt} = \frac{-\phi_0}{t(\ln 10)\sqrt{2\pi}\sigma^2} \exp\left(-\frac{(\lg(t/\tau))^2}{2\sigma^2}\right). \quad (3)$$

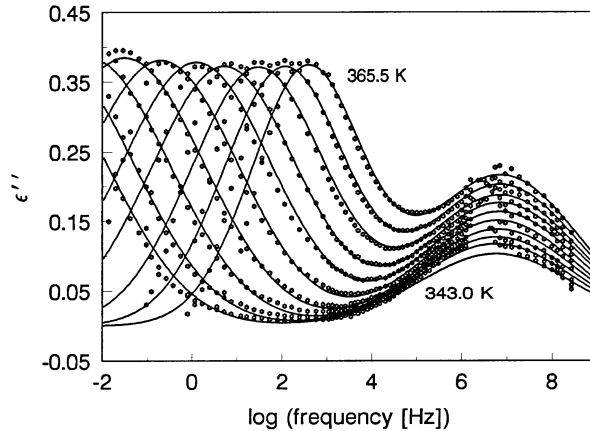


Figure 1. The imaginary part of the dielectric function for different temperatures spaced at 2.5 K intervals. The solid lines indicate the values calculated on the basis of the PM. The symbols represent the experimental data [13].

To describe the ϵ'' -data for α - and β -processes, two relaxation functions ($\phi_\alpha(t)$, $\phi_\beta(t)$) should be used. Like other published results for the mechanical and dielectric α - and β -peaks of amorphous PET [1], the relaxation times of the α - and β -processes obtained by us were also found to obey Arrhenius laws, i.e., $\tau_\alpha \propto \exp(E_\alpha/k_B T)$ and $\tau_\beta \propto \exp(E_\beta/k_B T)$, where

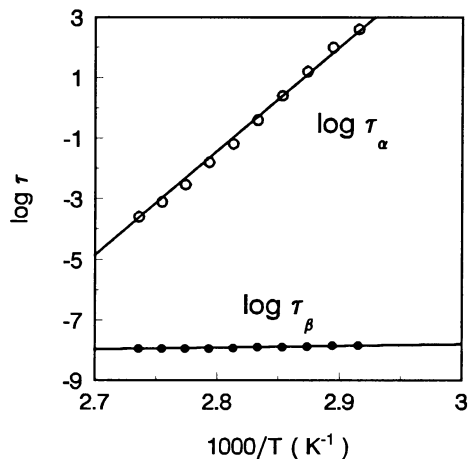


Figure 2. Arrhenius plots of the α - and β -relaxation time of PET. The upper straight line is a plot of the calculated values of the logarithm of τ_α ; the lower one is a plot of the calculated values of the logarithm of τ_β . The symbols represent the fitting values.

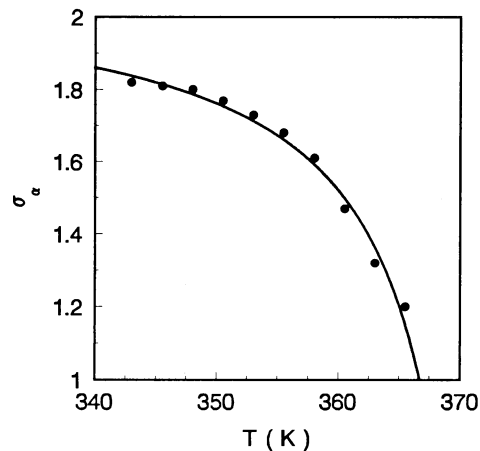


Figure 3. The temperature dependence of the half-width of the distribution (σ_α) in the PM. The symbols represent the fitting values.

the activation energies E_α and E_β are $156.9 \text{ kcal mol}^{-1}$ and $2.5 \text{ kcal mol}^{-1}$, respectively. These activation energies are a little less than those reported by other authors [1]. The magnitude of E_α depends on a lot of factors such as the water content and the crystallinity of the PET. A value of E_α of this magnitude is usually found for α -relaxation processes for other amorphous polymers [1]. The α -relaxation of amorphous systems is associated with the glass transition [10, 13], at which the temperature dependences of many physical quantities undergo drastic changes and are often represented by empirical Vogel–Fulcher relations. This is considered to be appropriate for the temperature dependence of the maxima of the imaginary part of the dielectric function and of the half-width of the distribution of the α -relaxation, i.e., $(\epsilon''_{\max})_\alpha \propto \exp[D/(T - T_0)]$ and $\sigma_\alpha \propto \exp[D/(T - T_0)]$, where $D = 2.9$, $T_0 = 372.5 \text{ K}$. So, how should the $(\epsilon''_{\max})_\beta$ and σ_β be assigned values for different

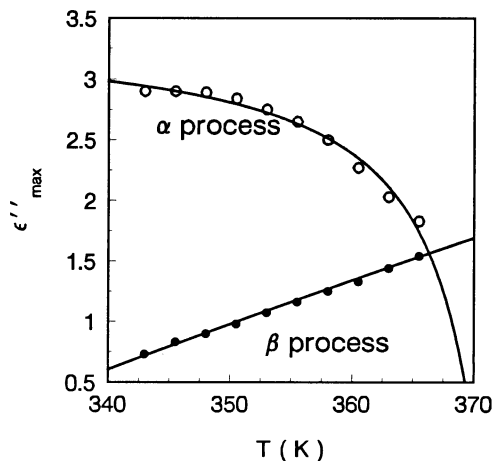


Figure 4. The temperature dependence of the maxima of the imaginary part of the dielectric function for the α - and β -relaxation of PET, $(\epsilon''_{\max})_{\alpha}$ and $(\epsilon''_{\max})_{\beta}$. The symbols represent the fitting values.

temperatures? Using polarized infrared radiation, Schmidt [16] has shown that the ethylene glycol linkage of the amorphous PET molecule exists in either of two forms—the *gauche* form or the *trans* form. These forms are rotational isomers. The *trans* isomer occurs in both the crystalline and amorphous regions of the polymer, but the *gauche* isomer occurs only in the amorphous regions. The energy (E_g) of the *gauche* configuration is higher than that (E_t) of the *trans* configuration. As the temperature rises, *gauche*-polyethylene terephthalate is transformed into *trans*-polyethylene terephthalate and the number (N_g) of *gauche* forms decreases, and the number (N_t) of *trans* forms increases. The transition between the *gauche* form and the *trans* form causes β -type dielectric loss of amorphous PET. Hence the intensity of the β -type dielectric loss should be proportional to the ratio of N_g to N_t , i.e., $(\epsilon''_{\max})_{\beta} \propto N_g/N_t$. It follows from the Boltzmann distribution that $(\epsilon''_{\max})_{\beta} \propto \exp[-(E_g - E_t)/k_B T]$, where $(E_g - E_t)/k_B = 340$ K (0.675 kcal mol $^{-1}$). This is the difference of two minima of the potential energy curve, corresponding to rotation of the methylene group. The expression for $(\epsilon''_{\max})_{\beta}$ shows that the intensity of the β -type dielectric loss will decrease rapidly when the temperature is lower than 340 K, i.e., T_g . It is verified by the NMR experiments of Ward [7] that there are hindered rotations of the methylene groups below T_g . ϵ'' calculated from equation (2) is plotted in figure 1. The temperature dependences of the parameters used are shown in figure 2–figure 4.

Next, we turn to the mechanisms of molecular motions responsible for the α -relaxation. In the crystallites of PET, the repeat unit is substantially planar and centrosymmetric, which is referred to as the *trans* form of ester linkage by Reddish [3]; thus there is no resultant dipole moment [17]. But in the amorphous PET, there is an asymmetric structure (the *cis* form [3]). This kind of repeat unit has a large dipole moment perpendicular to the chain axis and in the plane of the benzene ring. As the temperature rises, free rotation will take place around the bond joining the ester group to the benzene ring. The *cis* forms of the ester group (higher-level states) are transformed into the *trans* forms (lower-level states). The transition between the *cis* and the *trans* configurations of the ester groups is probably the cause of the dielectric α -absorption process.

In summary, the dielectric α - and β -relaxation of amorphous polyethylene terephthalate

has been studied using a probability model for the relaxation. The temperature dependences of the parameters of the PM are derived. The mechanisms of the α - and β -relaxation are elucidated concisely. From the comparisons between the theoretical results and experimental data, it seems that the probability model for the relaxation is also suitable for polymer systems and is more general than other relaxation theories.

Acknowledgments

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