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Dielectric properties of PET below its glass transition temperature

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Abstract

Dielectric relaxation measurements on poly(ethylene terephthalate) (PET) samples of different microstructures (semi-crystalline, amorphous, amorphous oriented), between 80 and 300 K for frequencies ranging from 10^2 to 10^5 Hz have been performed. The data pertaining to the β relaxation of PET could be fitted to the Cole–Cole (CC) phenomenological equations, from which the relaxation strength, the average activation energies, and the temperature-dependent distribution functions of relaxation times were obtained. On the basis of these results, we discuss briefly the origin of the β relaxation and the degree of cooperativity of the β motions.

Keywords: Dielectric spectroscopy; Poly(ethylene terephthalate) (PET); β relaxation

1. Introduction

Numerous studies have already been devoted to the molecular origin of the sub-glass relaxations of poly(ethylene terephthalate) (PET) [1–5]. However, due to the complexity of the question and to the technical importance of the polymer, further research seems desirable at the present time. In this paper, we will concentrate on time-dependent polarization studies in the β relaxation range to get information on the local chain dynamics of PET.

Whatever the technique used to characterize the β relaxation of PET, dielectric spectrometry [3], NMR [4], or thermally stimulated depolarization current method [5], the main features of the relaxation are maintained: the relaxation time always displays an Arrhenius-type dependence on temperature, and the relaxation peak is quite broad. The exact temperature location of the maximum of the β relaxation depends on the characteristic frequency of each probing technique.

It is known that the relaxation originates from main chain motions, since hydroxyl chain ends have been experimentally shown not to play any role in the relaxation [2]. The contribution of methylene units to the relaxation is also minor, because bis-phenol-A polycarbonate, which contains no methylene, and poly(tetramethylene terephthalate) or poly(butylene terephthalate) (PBT), which contains more methylene units, display basically the same relaxation patterns as PET [2]. The fact that

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the uniaxial stress does not change the shape of the relaxation suggests that the movement of the glycol units, *cis* or *trans*, is not relevant for the β relaxation of PET.

2. Experimental section

The samples are commercial sheets of PET, in semi-crystalline form (43% crystallinity), PETC, in amorphous form, PETA, and in amorphous uniaxially-oriented form, PETU. Thin Gold–Palladium electrodes were PVD-deposited on both sides of the samples. On one of the sample faces, a guard electrode was also deposited. The variation of the real and imaginary part of the complex permittivity (ϵ^*) was measured among 77 and 295 K in the frequency range from 200 Hz to 100 kHz with a General Radio type 1615 capacitance bridge fitted to a cryostatic system described elsewhere [6]. Typical relative precisions are ~2% on ϵ_i and better then 0.01% on ϵ_r.

3. Results

Fig. 1 shows the evolution of ϵ_i vs. frequency for different temperatures. With increasing temperature, the absolute values of ϵ_i increase and are shifted to higher frequencies. The temperature dependence of ϵ_i is stronger than the frequency dependence. This has been also found for similar polymers like poly(ether ether ketone) (PEEK) [7]. PETC has the lowest relaxation temperature and the smallest relaxation peak of all three samples, while PETU has the strongest signal.

The shape of the relaxations was studied by fitting the experimental data to the Cole–Cole phenomenological equation [8]

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + (i\omega\tau)^\beta}$$

ϵ_0 and ϵ_∞ are the limiting values of the real part of the permittivity at very low and very high frequencies, respectively. τ_p is the characteristic or principal relaxation time, β ($0<\beta<1$) is an empirical parameter which is related to the width of the relaxation peak, and ω is the angular frequency.

In Table 1 the resulting values for the C-C parameters and the relative standard deviations of the fitted values relative to the experimental ones (perc, in percent), are presented for all samples. In general, the relative standard deviations are smaller than the expected experimental accuracy (of about 1.4%), which indicates that our data are in good correlation with the C-C phenomenological equation. The C-C parameters depend roughly linearly on the temperature, as reported previously, [8], and, furthermore, their evolutions with temperature are comparable, independent of sample morphology.

3.1. *Relaxation strength*

The relaxation strength, $\epsilon_0 - \epsilon_\infty$, has been calculated from the fit results (Table 1). For all samples, the relaxation strength decreases with increasing temperature, according to results previously published [3]. By computing the ratio between the relaxation strengths of the semi-crystalline and amorphous samples

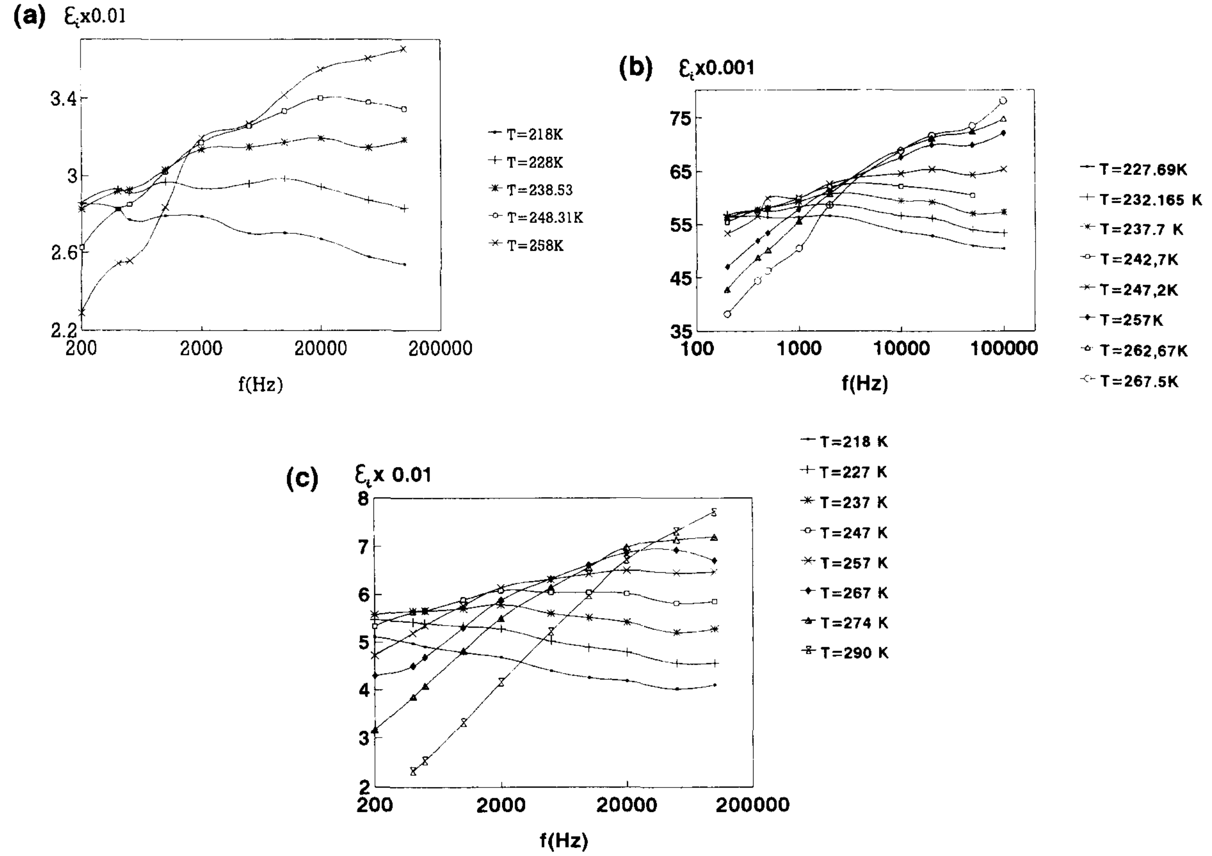

Fig. 1. Evolution of the imaginary part of the dielectric permittivity, ϵ_i vs. frequency for various temperatures. (a) PETC sample (b) PETA sample (c) PETU sample.

$$r=\frac{\Delta\epsilon_c}{\Delta\epsilon_a}$$

an approximation for the proportion of dipoles participating in the relaxation in the semi-crystalline sample can be obtained, neglecting changes in the correlation factors between amorphous and semi-crystalline samples [9]. We found that $r=55\%$, 62% and 57% at respectively $T=228$ K, 238 K and 248 K. These values are very close to the fraction of amorphous phase in the crystalline samples (about 57%), which clearly indicates that the β relaxation originates from the amorphous phase.

The proportionality between the amorphous proportion of a semi-crystalline sample and the β relaxation strength also suggests that the motions responsible for this relaxation are only sensitive to their local environment. If this were not the case, a simple two-phase model would not be able to predict the β relaxation strength. It should be noted, that the strength of the α-relaxation of PET, which comprises large-scale motions related to the glass transition, does not depend linearly on the amorphous content [3]. The β motions may be dependent on external potentials resulting from nearby local chain packing and on internal potentials resulting from torsion angles. The weak dependence of the dielectric losses with frequency, which was experimentally observed in this study may result from

Table 1
Best-fit values for the Cole–Cole parameters of different PET samples at different temperatures

Sample	T [K]	ϵ_0	ϵ_∞	α	β	τ[ms]	Perc [%]
PETC	198.8	3.128	2.605	0.523	0.1115	1.741	1.722
PETC	218.75	3.209	2.536	0.754	0.0955	1.742	0.43
PETC	228	3.165	2.575	0.59	0.1278	0.0046	0.43
PETC	238.5	3.121	2.581	0.54	0.15	0.0072	0.51
PETC	248.31	3.074	2.652	0.422	0.2	0.0054	0.34
PETA	227.8	3.994	2.922	1.072	0.1305	2.8745	0.36
PETA	237.9	3.821	2.967	0.854	0.1694	0.1241	0.41
PETA	247.9	3.744	3.014	0.73	0.2107	0.0258	0.41
PETA	257.9	3.7	3.062	0.698	0.2571	0.0096	0.61
PETA	267.05	3.688	3.082	0.606	0.2848	0.0044	0.41
PETA	274	3.684	3.086	0.598	0.3006	0.0023	0.49
PETA	290.4	3.676	3.141	0.534	0.3593	0.0009	0.39
PETU	227.07	3.924	2.787	1.137	0.1317	0.4491	0.41
PETU	232.65	3.933	2.705	1.228	0.1232	0.0886	0.32
PETU	237.7	3.757	2.868	0.889	0.179	0.0406	0.45
PETU	242.7	3.743	2.869	0.874	0.1885	0.01973	0.34
PETU	247.2	3.723	2.859	0.864	0.1965	0.0088	0.34
PETU	257.6	3.684	2.924	0.76	0.2414	0.0041	0.36
PETU	262.7	3.668	2.962	0.706	0.2669	0.0033	0.82
PETU	267.5	3.655	2.998	0.657	0.2921	0.0026	0.71

the large distribution of activation energies reflecting the disorder of the amorphous regions (see below). The existence of a broad distribution function of activation energies has been confirmed by TSDC measurements [5].

The local nature of the β motions is further sustained by the experimental observation [2] that poly(ethylene isophthalate), PEI, where the phenyl ring substituents are connected in *meta* positions instead of *para* positions, shows a secondary relaxation in the same range of temperature as PET, although with lower values of loss maxima [2]. Thus, the β motions are practically unaffected by isomeric changes introduced regularly along the chain, pointing to the local nature of the β relaxation. This is in marked contrast to the cooperative motions excited at the glass transition, which is located for PEI 20°C below the glass transition of PET [2].

3.2. Activation energies

The activation energy of the relaxations, W_{fit}, has been computed from the values of characteristic relaxation times obtained by the fit using an Arrhenius plot (Table 2). These values can also be obtained from the temperature dependence of the frequency at the point where the loss curve presents a maximum (isothermal representations), or from the frequency dependence of the temperature at the point where the loss curve presents a maximum (isochronal representations) (Table 2). The values obtained from isothermal representations are smaller than those from isochronal ones. This simply results from changes in the relaxation shape with temperature, as signalled by the variation of the shape parameter, β, of the Cole–Cole equation. A similar observation was made for the sub-glass relaxation of polyethylene and other polymers [10]. The relatively small values of activation energy,

Table 2

Values of average activation energy for the three PET samples of this study, obtained from an isothermal representation of the data, from an isochronal representation of the data, and from a fit of the Cole–Cole equation to the data

Sample	W(isothermal)(kJ/mol)	W(isochronal)(kJ/mol)	W(fit)(kJ/mol)
PETA	48.71	55.97	54.05
PETC	43.23	53.27	52.43
PETU	68.32	6836	61.30

which is typical for secondary relaxation processes in polymers [10], reflects again the local-scale character of the β relaxation process, whose occurrence requires the rearrangement of the chain packing only in a small volume.

A third argument for the local-scale nature of the β motions can be given under the hypothesis of zero activation entropy, which is typical for local non-cooperative relaxations. The temperature T' corresponding to a characteristic relaxation frequency of 1 Hz can be expressed as [16,17]

$$W_0 = RT'(\ln T' + 22.922),$$

where W_0 is the activation energy of the relaxation. From the values of T' obtained using the Arrhenius relationship between temperatures and frequencies, W_0 of 43.37 kJ/mol and 43.85 kJ/mol are calculated for PETA and PETU samples. For PETA, the computed W_0 is in good accordance with the 54.97 kJ/mol found experimentally for the activation energy (Table 2), which is a good evidence for the local nature of the β relaxation with limited cooperativity. For PETU, however, the discrepancy between W_0 and the experimental activation energy is more severe, indicating that more cooperativity is required to initialize the β motions in the oriented polymer. In other words, the activation entropy of the β relaxation in oriented PET is significantly larger than zero.

As expected from the temperature dependence of the C-C shape parameter (β), the reduction of the data in the complex plane (ϵ_r, ϵ_i) cannot provide a single curve (Fig. 2). This can be due to a temperature-dependent distribution of relaxation times [12], or, alternatively, to a distribution of the activation energies with zero activation entropy (reflecting the local character of the relaxation). The distribution of activation energies can be computed by [11]

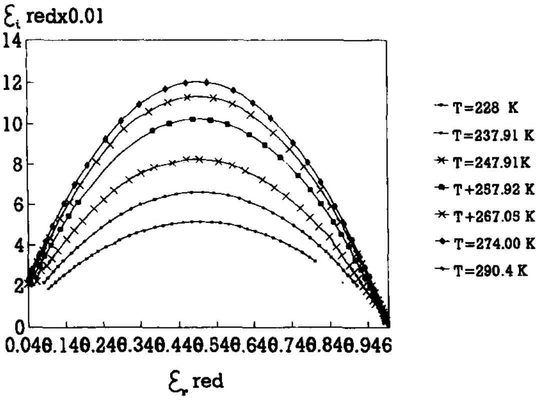

Fig. 2. Complex plane plots of reduced dielectric permittivity at different temperatures (PETA sample).

$$F(W) = \frac{1}{2\pi RT} \frac{\sin(\beta\pi)}{\cosh\left[\frac{\beta(W-W_p)}{RT}\right] + \cos(\beta\pi)}$$

where $W(\tau)$ is the activation energy associated with each relaxation time, R is the gas constant, and the values of W_p are derived from the fit. The values of the distribution functions obtained are presented in Fig. 3 for PETU. For all three samples, the distribution functions are temperature-dependent. The narrowing with temperature of the distribution functions results directly from the experimental variation of the C-C β parameter with temperature. Therefore the time–temperature superposition method for obtaining master curves cannot be used. The temperature variation of $F(W)$ necessarily results from a change in the distribution of the local potentials affecting the β motions. This could be due to a change in the chain packing density with temperature, as sustained by the variations of the coefficient of linear thermal expansion of various types of samples in the temperature range of their secondary dielectric relaxation [13]. This would support our previous model for the molecular motions at the origin of the secondary dielectric relaxation of PET [5].

3.3. Characteristics of the molecular motions responsible for the β relaxation

An important clue to understand the nature of the β motions in PET comes from the observation that the degree of cooperativity of these motions increases by orienting the sample. This results from the denser chain packing promoted by the orientation of the chains, with a consequent increase of the interchain potential barriers and a larger volume of cooperation needed for these motions. Similarly, the width of the distribution of relaxation energy in the amorphous unoriented polymer may reflect the local variation of the interchain packing for the amorphous state. Evidences from various experimental techniques suggest that a short-range order may exist in glassy PET [8,15], while a long-range order is clearly absent. Local parallelization of the chains in small volumes containing a few repeating units is

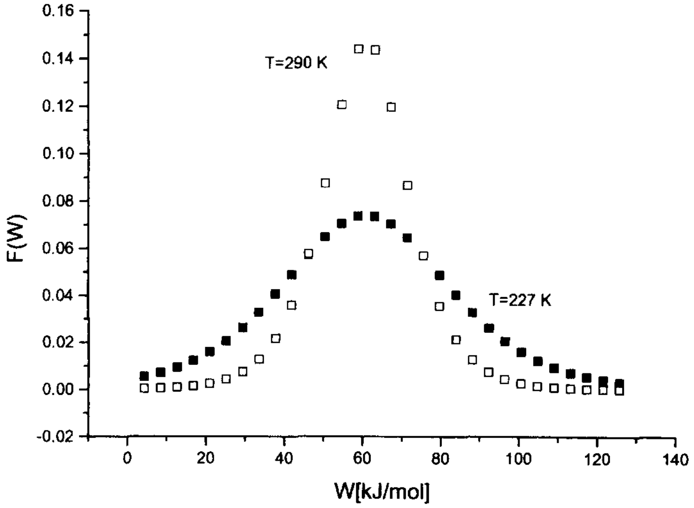

Fig. 3. Distribution function of activation energies, $F(W)$, for the β relaxation of amorphous PET (PETU sample). Plotted are the distribution functions corresponding to the highest and to the lowest temperature used in our experiments.

possible, and would explain the high energy tail of the distribution of activation energies of amorphous PET. In this model, the β relaxation of pure amorphous PET would have a composite cooperative character. Less dense regions relax more easily in a local non-cooperative way, and denser regions require at least some cooperativity to relax, as in oriented PET. The non-cooperative character of the β relaxation, which was deducted in a previous section of this paper results most probably from the dominance of the less dense regions in the recorded signal, either because they are more numerous, or because the amplitude of the active molecular motions is larger in these regions.

The partial cooperative feature of the β relaxation is also compatible with the influence of water on this relaxation. With increasing water content the loss peak is shifted towards lower temperatures, the average activation energy decreases, and the dielectric loss maximum increases in height [1]. Similar effects have been observed for other aromatic polymers like PEEK [6]. In our description, this would result from penetration of water in the less dense regions. Therefore the weight of these regions in the relaxation pattern increases due to the enhancing effect of the water dipole on the relaxation strength, or due to an increase of the amplitude of the β motions in these regions because of a further decrease of the local chain packing density.

As for the detailed trajectory between the amorphous and crystalline phases of the molecular segments during relaxation, our data alone cannot solve this question. Phenyl flipping has been suggested to occur in the β-relaxation range on the basis of NMR measurements [11]; it has also been proposed as an important parameter to explain the β relaxation of bisphenol-A polycarbonate [14] and PEEK [7].

4. Conclusions

The analysis of the relaxation strength, of the mean activation energies and of the distribution function of the relaxation times for the sub-glass relaxation in PET reveals its complex character.

A local movement of the entities participating at the relaxation is suggested by the following: the Cole–Cole parameters of the relaxation are independent of the morphology of the samples; the proportionality between the amorphous portion of a semi-crystalline sample and the strength of β relaxation; the isomeric changes do not affect the localization of the relaxation; the low values for the activation energies; the relaxation is dependent on the local potential which are temperature dependent; the small amount of the activation entropy variation in the amorphous samples.

The degree of cooperation of the molecular motion is increased by orienting the films and by water presence.

More experimental work on the influence of various swelling agents and of aging on the PET β relaxation, together with detailed theoretical studies based on conformational energy maps, are clearly required to progress this question.

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