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Polymer 40 (1999) 2675–2679

polymer

Comparing dielectric measurements on poly(ethylene terephthalate) at constant heating rates with isothermal measurements

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Received 20 October 1997; revised 6 February 1998; accepted 5 March 1998

Abstract

In this study, dielectric relaxation spectroscopy experiments were carried out during heating in the α relaxation region of PET. The results for low heating rates were consistent with isothermal measurements. Moreover, the results expressed as a function of temperature were much clearer than those expressed as a function of frequency. However, the loss peaks obtained in these non-isothermal experiments showed a systematic shift on the temperature axis when the heating rate increased. A significant but nearly constant thermal lag was observed in experiments with heating at 1 K min^{-1} when using different equipment. It appears that isothermal data obtained in a well calibrated apparatus can be used to adjust the temperature axis of dielectric results obtained in ramp temperature experiments. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(ethylene terephthalate); α relaxation; Heating mode experiments

1. Introduction

Dielectric relaxation spectroscopy (or dielectric thermal analysis—DETA) has been widely used to investigate the segmental mobility of the chains and the phase transitions in polymers [1, 2]. This technique also provides some relevant dielectric/electrical information that may be important in specific applications.

Most of the DETA experiments are performed in isothermal conditions, where the complex permittivity ($\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$) is measured over a frequency scan. In this case, the data manipulation and the theoretical interpretation of the results is relatively simple. However, similar experiments can be performed in a heating mode run experiment at a specific frequency, measuring the complex permittivity as a function of temperature ($\varepsilon^*(T)$). In this way, characterization of the material is less time consuming, which is an advantage. Moreover, in some cases the various relaxation regions detected in a polymer may become more evident when the results are expressed as a function of the temperature, relative to those obtained in isothermal conditions and expressed as a function of frequency.

The dielectric study of polymer blends, for instance, illustrates the advantage of the non-isothermal method, where the location of the relaxation regions in the temperature axis, relatively to the location of the pure components, acts as a miscibility criterion [3]. Even for pure polymers, the representation of the permittivity as a function of temperature is used to illustrate the influence of some substitutes [4], or to visualize the different relaxation regions [5]. Also, as we will see later in this paper, some materials exhibit poorly defined relaxation spectra in frequency caused by overlapping processes or by crystallization, but on using a temperature axis representation the ε' or ε'' curves are more easily revealed. Nevertheless, it must be pointed out that in the non-isothermal method the sample is not in thermal equilibrium and the existence of a thermal lag between the mean sample temperature and the temperature of the thermocouple must be considered. In fact, this has been a major problem of many thermal analysis techniques because the thermocouple which measures the temperature of the sample is seldom in direct contact with the sample [6].

In this paper isothermal and isochronal experiments are confronted to investigate the differences and to assess the validity of performing DETA tests in non-isothermal mode. These experiments were carried out on poly(ethylene terephthalate) (PET) which is a main-chain polymer extensively studied by DETA [1, 7–12]. Two main relaxations, α and β, can be detected by means of this technique and result

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PII: S0032-3861(98)00203-1

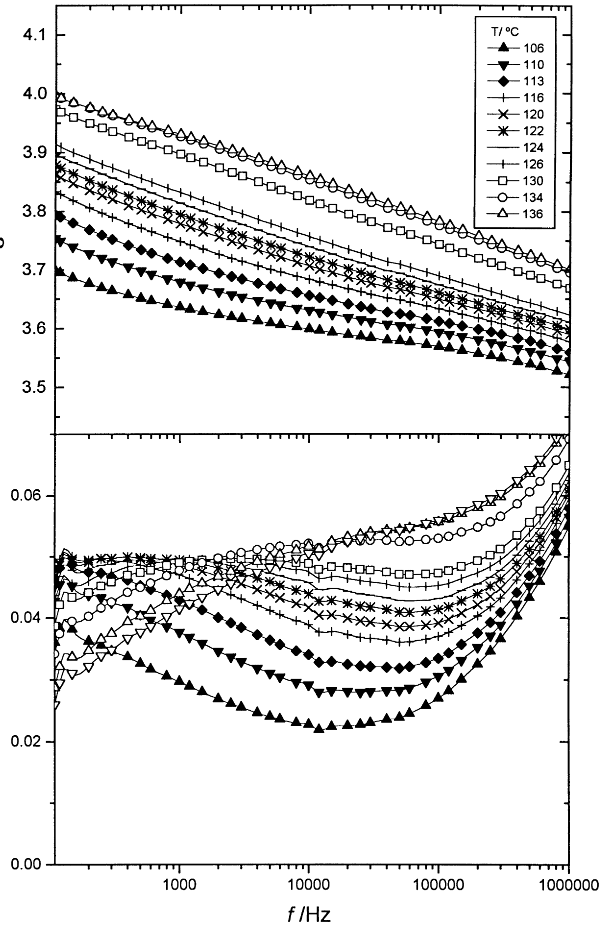

Fig. 1. Real and imaginary components of permittivity (frequency range: 100 Hz to 1 MHz) in the temperature region of the α relaxation of PET. Data from isothermal experiments using the NC equipment.

from different dipolar motions within the amorphous phase of this polymer. The dielectric loss factor ε'' of the α relaxation of PET, ascribed to the cooperative segmental motion of the polymeric chain, will be used as a probe assuming that the general characteristics of that relaxation do not depend on the two modes of testing: isothermal and isochronal.

2. Experimental

The poly(ethylene terephthalate) (PET) film, 125 mm thick, was supplied by Goodfellow.

The dielectric relaxation experiments were carried out with two different apparatus.

2.1. NC equipment

This equipment consists of a Hewlett-Packard impedance analyser HP 4284A, covering a frequency range from 20 Hz to 1 MHz, a BDS 1200 sample cell, and a temperature control module (QUATRO Cryosystem from Novocontrol GmbH) which allows for isothermal and ramp temperature experiments.

For the experiments in the NC equipment, the PET film was sputtered on both sides with a gold layer to enhance the electrical contact. The film was kept between two gold-plated stainless steel electrodes (diameter 20 mm) of the sample cell, which is mounted into a BDS 1100 cryostat and exposed to a heated gas stream evaporated from a liquid nitrogen dewar. The temperature in the cryostat is measured by a platinum PT100-type sensor mounted inside the lower electrode.

The parallel capacitance (proportional to the real part of the dielectric constant, (ε') and the loss tangent ($\tan \delta = \varepsilon''/\varepsilon'$) were measured both in isothermal and ramp temperature tests, within a temperature range of 50–180°C. Before each frequency scan during the isothermal analysis the sample was kept at the set temperature for at least 15 min, making sure that the temperature was maintained constant to within ± 0.02 K. In the ramp temperature analysis, four different heating rates were used: 1, 2, 4 and 8 K min^{-1}. After the test at 1 K min^{-1} the sample was allowed to stabilize overnight, before the 2 K min^{-1} ramp-test was performed. Between the 4 and 8 K min^{-1} experiments an interval of 2 h was guaranteed.

2.2. PL equipment

The Polymer Laboratories DETA apparatus consists of a General Radio 1693 digital RLC bridge, a dielectric spectrometer head, a temperature controller unit (Model 706) and a controlling computer with PL software. The two components of permittivity (ε' and ε'') are measurable as purely capacitative and purely conductive terms on the DETA bridge.

The dielectric spectrometer cell consists of a lower base unit, with provision for mounting the sample, and a demountable temperature enclosure (internal dimensions: 6 cm diameter and 6 cm high). The sample, without any surface treatment, was kept between two condenser plates (33 mm diameter). The temperature is measured by a small platinum resistance thermocouple placed at approx. 5 mm below the bottom electrode.

Measurements were performed over the range 100 Hz–100 kHz in constant heating mode (1 and 2 K min^{-1}) in the temperature range 50–180°C. Prior to the experiments the usual calibration routines of internal reference resistors and removal of stray effects due to leads and cell were accomplished.

3. Results and discussion

PET can crystallize partially and the segmental motions are strongly affected by the presence of crystalline domains [8, 13]. This effect was verified by dynamic mechanical analysis in an as-received sample, during two consecutive heating runs, from below to above T_g. These experiments

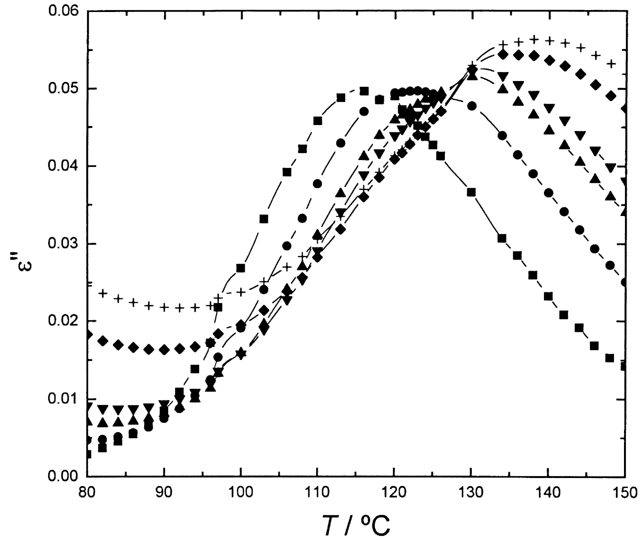

Fig. 2. Imaginary part of permittivity, collected from isothermal experiments in the α relaxation region of PET, expressed as a function of temperature for six frequencies: ■, 100 Hz; ●, 1 kHz; ▲, 5 kHz; ▼, 10 kHz; ◆, 50 kHz; +, 100 kHz.

showed differences both in the intensity of the elastic modulus, and in the position of the loss modulus peak. In order to stabilize the crystallinity of PET, the samples were kept at *ca*. 160°C for about 8 h. Two identical DETA experiments in the NC apparatus using the same treated sample spaced in time for several weeks, have shown no significant changes in ε', as well as in ε''. This assured that the thermal treatment led to the exhaustion of the crystallization process and to the release of the mechanical stress that could result from processing.

The isothermal measurements were carried out using the NC equipment. Fig. 1 shows the overall behaviour of the permittivity (ε' and ε''), from 100 Hz to 1 MHz, in the temperature range 106–136°C. In this range the α relaxation can be identified. Nevertheless, as the figure illustrates, this relaxation provides neither a well defined loss peak nor a clear step of ε'. The tail observed in ε'' at high frequencies corresponds to the low frequency side of the β relaxation.

The isothermal results were treated in order to allow the representation of the data as a function of temperature, at a fixed frequency. In Fig. 2 the loss permittivity is shown against the temperature, in the range 80–150°C, for six different frequencies. These results correspond to true experimental values and not to interpolations of isothermal results.

A review of the mathematical description of the temperature dependence of the dielectric permitivitty at a fixed frequency ($\varepsilon^*(T)$) in polymeric relaxations is given by Schlosser et al. [14] who also proposed a new method to predict $\varepsilon'(T)$ and $\varepsilon''(T)$ curves using fitted parameters from $\varepsilon^*(\omega)$ data at various temperatures. Thus, theoretical curves compatible with the results shown in Fig. 2 could be obtained from the isothermal results (shown in Fig. 1) with the advantage that less isothermal curves are required for calculations, compared with those necessary to construct Fig. 2. In a future work we intend to explore this possibility.

Upon comparison of Figs 1 and 2, it is clear that the α relaxation is much better defined in the temperature representation (Fig. 2). Thus, the determination of the temperature of the loss peak maximum, and its dependence on the frequency can be used to investigate more precisely the dynamic behaviour of the relaxation. The intensity of the loss peak above 1 kHz increases with frequency due to the overlapping of the β process. Part of this secondary relaxation is visible at the lower temperature side, by an increment of the ε'' tail that is moving to higher temperatures at a faster rate than the α relaxation, owing to its lower activation energy.

The α relaxation of PET was also investigated in the NC equipment, at 1 kHz, during an heating mode run of $\mathrm{d}T/\mathrm{d}t = 1\ \mathrm{K\ min}^{-1}$. It is known that for a given $\mathrm{d}T/\mathrm{d}t$, the frequency of the measurement, ω, must be high enough such that the temperature dependence of the response is not significantly smeared out by the heating process [15]. Therefore, for a given $\mathrm{d}T/\mathrm{d}t$, if the temperature dependence of the complex permittivity needs to be resolved within temperature intervals ΔT, one must have $\omega \gg (\mathrm{d}T/\mathrm{d}t)/\Delta T$. Obviously, for the frequency used, it can be considered that the heating process will not interfere with the dynamic measurements.

In Fig. 3, the open symbols represent the loss permittivity and the loss factor (squares and circles, respectively) obtained in the heating mode experiment. The same variables resulting from the isothermal experiments at the same frequency are also shown (solid symbols). The comparison of both experiments is useful because it can be said that the temperature in the isothermal results is assigned to the true temperature of the sample, within an error of 0.02 K, whereas in a non-isothermal experiment the temperature is assigned to the temperature measured by the thermocouple during the heating mode run. The agreement between both tests in respect of the temperature location, the maximum intensity and even the shape of both the loss peaks and the

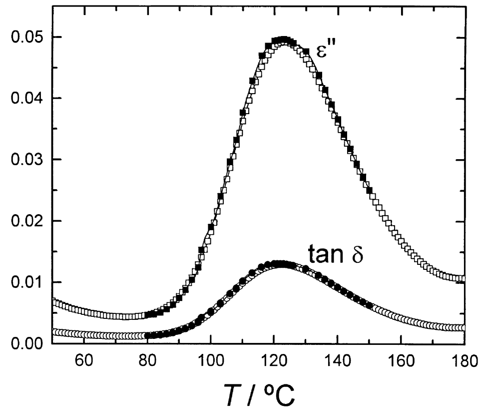

Fig. 3. ε'' (squares) and tan δ (circles) as a function of temperature for the α relaxation of PET at 1 kHz. Solid symbols correspond to isothermal experiments and open symbols correspond to the heating mode run experiment ($1\ \mathrm{K\ min}^{-1}$).

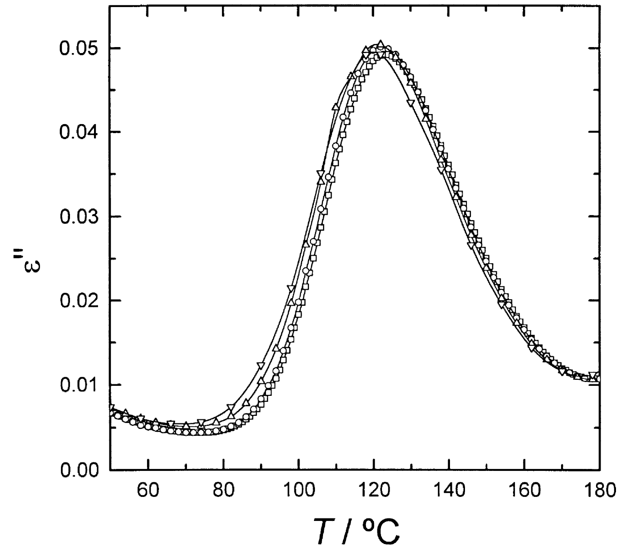

Fig. 4. Isochronal experiments (1 kHz) in the α relaxation region of PET obtained at different heating rates: □, 1 K min^{-1}; ○, 2 K min^{-1}; △, 4 K min^{-1}; ▽, 8 K min^{-1}.

tan δ peaks is very satisfactory. The storage permitivitty curves, $\varepsilon'(T)$, observed in the two methods, were also found to be very similar; this should be expected because $\varepsilon' = \varepsilon''/\tan\delta$. However, to be more precise, Fig. 3 shows that the loss peak obtained in the heating mode experiment is shifted to higher temperatures by a small value: the maxima of the loss peaks for the isothermal case and for the heating experiment case occur at about 122.6°C and 123.4°C, respectively. In spite of being close to experimental errors (note that in this temperature region the isothermal experiments were carried out at every 1 K), this small positive thermal lag (less than 1 K) was found to be reproducible when the same experiments were repeated. It is well known that polymers are good thermal insulators and this difference can be ascribed to the high thermal resistance of the sample.

The influence of the heating rate on the results was also investigated. The loss peaks at 1 kHz obtained at different heating rates (1, 2, 4 and 8 K min^{-1}) are shown in Fig. 4. Observation of all the peaks in Fig. 4 shows a small shift to lower temperatures as the heating rate is increased. Due to the thermal inertia of the sample we should expect a reversal effect, i.e., an increment on the heating rate should lead to larger (and positive) differences between the temperatures of the thermocouple and the sample. The opposite tendency may be attributed to the specific design of the cell, namely the location of the heater and cooler supplies relative to the temperature sensor and the sample holder.

The data in Fig. 4 also suggest that the width of the loss peaks is very similar for the experiments at 1 and 2 K min^{-1}. However, for higher heating rates (4 and 8 K min^{-1}) the loss peaks slightly broaden with the increase in heating rate. This behaviour can be attributed to a more complex response of the sample with increasing heating rate, resulting from a larger temperature heterogeneity within the sample area. Thus, it can be concluded that this kind of experiment should be carried out at relatively slow heating rates in order to minimize this effect.

Further DETA experiments were performed in the PL equipment. This system is equipped with furnace, electrodes and heating and cooler supplies of different types. However, we may predict that the behaviour of the same sample in both NC and PL equipments, at a given sample temperature, must be similar provided the temperature axis corresponds to the true temperature of the sample. Nevertheless, it is not surprising to see differences in the intensity of the loss peaks: in the PL equipment we used samples without any surface treatment, whereas in the NC equipment both sample-free surfaces were previously sputtered with a gold layer. In the latter case higher capacitance values were recorded due to the better electrical contact which avoids air gaps and increases the effective area of the electrodes. Therefore, a comparison of the loss peaks measured in both equipments must be made in terms of normalized values.

The experiments in the PL equipment were carried out at 1 K min^{-1} and at several selected frequencies. In Fig. 5 the normalized loss peaks ($\varepsilon''/\varepsilon''_{\text{max}}$) obtained using this method are compared with the isothermal data from the NC equipment at four frequencies: 100 Hz, 1, 10 and 50 kHz. The loss curves from the PL equipment were shifted on the temperature axis by a fixed factor until the best overlap with the loss curves of the α relaxation obtained from isothermal measurements was achieved. In this case, the temperature shift was + 5.0°C, i.e., the temperature measured by the thermocouple during the heating mode experiments is 5°C lower than the temperature of the sample given by the isothermal curves.

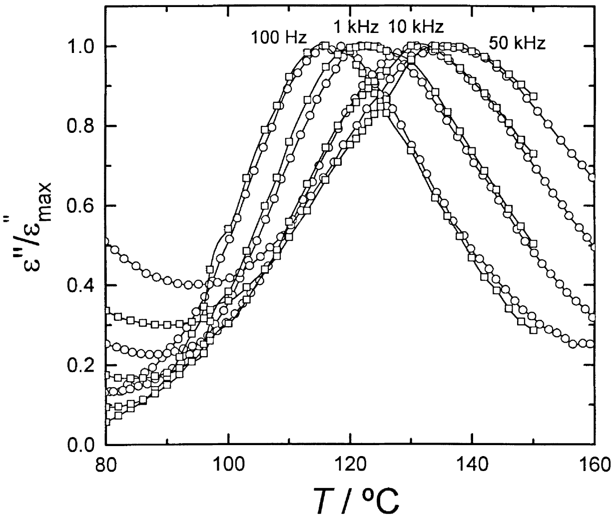

Fig. 5. Normalized ε'' as a function of temperature for four different frequencies in the α relaxation region of PET. Squares: isothermal data obtained in the NC equipment. Circles: non-isothermal experiments (1 K min^{-1}) on the PL equipment. These curves were shifted to higher temperature (5 K) to get the overlap with the isothermal data.

It can be seen that the temperatures corresponding to the maxima of the corrected loss peaks are very close to the isothermal ones (differences below 1°C). Moreover, a satisfactory agreement over all the range of the a peaks at all frequencies can be observed. It must be added that experiments at $2\ \mathrm{K\,min}^{-1}$ with the PL equipment showed loss peaks very similar to those obtained at $1\ \mathrm{K\,min}^{-1}$. This suggests that the 5°C difference between the sample and the thermocouple temperatures arises principally from the poor calibration of the thermocouple. This was confirmed by comparison of static and dynamic measurements performed with this thermocouple and with a previously calibrated one. In any case, as the temperature lag factor has been calculated, from now on experiments can be performed in other materials using the PL equipment provided the same temperature range is used.

4. Conclusions

It is apparent that dynamic dielectric studies carried out during heating are a useful tool to study systems whose relaxations are not well defined on the frequency axis. In the case of PET and for a specific dielectric equipment it was demonstrated that this kind of measurement led to a good agreement with isothermal experiments, with the advantage of less time-consuming testing. However, some precautions must be taken, namely, the dT/dt gradient must be relatively low ($< 2\ \mathrm{K\,min}^{-1}$). When the heating rate is raised a systematic shift of the α relaxation of PET to lower temperatures was observed.

Isothermal measurements on PET were compared with results from heating experiments using other equipment: a significant thermal lag between the mean sample temperature and the temperature measured by the sensor is observed. As this deviation is nearly constant over the frequencies and temperature range studied, a correction of the results with other materials will be possible provided that the same temperature range is used.

In a future study, we intend to investigate other materials, namely, complete amorphous polymers, with different glass transition temperature, in order to confirm our observations in an extended temperature range.

Acknowledgements

The authors sincerely acknowledge Dr. C. Dias and Dr. A. Schönhals for helpful discussions and Prof. A. Pouzada for the critical reading of the manuscript. This work was supported by Junta Nacional de Investigação Científica in the aim of the project PBIC/C/QUI/2158/95.

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