High temperature dielectric loss of poly(ethylene terephthalate) films at microwave frequency

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An apparatus developed for microwave dielectric measurements at high temperatures was used to determine the dielectric loss ε'' at 4.0 GHz between 20 and 105°C for biaxially stretched and unstretched poly(ethylene terephthalate) (PET) films that had crystallinities of 35 and 5% at room temperature, respectively. The ε'' for the former increased slightly with increasing temperature, whereas that for the latter showed a gradual increase up to 50°C followed by a sharp upswing with further increase in temperature. These temperature changes in ε'' are attributable to the shift of the dielectric β relaxation to higher frequency with increasing temperature. Time dependence studies on ε'' at 4.0 GHz and fixed high temperatures for the unstretched PET film showed a significant decrease in ε'' with time only above 75°C. This phenomenon may be ascribed to the crystallization of PET in the amorphous region. The microwave method described in this paper is useful in that it allows dielectric behaviour at high temperature to be measured quickly with a sample in the contact-free state.

(Keywords: dielectric loss; microwave frequency; high temperature)

INTRODUCTION

Both basically and practically important is the high temperature dielectric behaviour of polymer films at microwave frequencies. For example, high temperature data for the microwave dielectric constant ε' and loss ε'' of polymer films are useful for elucidating the dielectric β relaxation due to the local motions of molecular chains and also for evaluating high temperature characteristics of sheet materials in the microwave oven[1]. Few such data are available, though many reports exist of dielectric measurements on polymer samples in the audio frequency region[2,3], where the β relaxation usually appears at low temperatures. This situation reflects the lack of an apparatus relevant for high temperature dielectric measurements.

In previous papers[1,4–14] we reported the use of a new apparatus consisting of a cavity resonator system that allows contact-free dielectric measurements at microwave frequencies to be made on sheet materials such as polymer films. The temperature range covered by our apparatus, however, has so far been restricted to room temperature[1,4–14] because of the thermal expansion of the waveguides, the poor heat resistance of the parts, and the difficulties in controlling the temperature of the cavity system.

We have recently overcome these instrumental problems by modifying the previous apparatus and have made it possible to measure the complex dielectric constant for polymer films up to 100°C.

In this paper, we report an experimental study performed with the new apparatus. We determined the temperature dependence of ε'' at 4.0 GHz for poly(ethylene terephthalate) (PET) films from room temperature to a maximum temperature of 90°C and also the time dependence of ε'' at 4.0 GHz in the range from 20 to 105°C.

EXPERIMENTAL

The samples used were commercial, biaxially stretched and unstretched PET films which were supplied by Teijin Co.; room temperature crystallinities were estimated to be 35% for the former and 5% for the latter. The former was annealed at 140°C for 2 h in order to minimize the crystallinity change during the dielectric measurements at high temperature. The anisotropic properties of the samples have been described elsewhere[13]. When dielectric measurements were completed on the unstretched PET films kept for ca. 100 min at 60, 70, 85, and 105°C, the samples were quenched to room temperature and their crystallinities were found to be 5, 8, 18, and 32%, respectively. The ε'' showed no appreciable change when the samples were kept standing for more than 100 min at these temperatures. The room temperature crystallinity χ was evaluated from the density measured at 20°C by the flotation method using aqueous KI solutions and also from the empirical formula[7] $\varepsilon''=2.33\times10^{-2}-(1.36\times10^{-4})\chi$ at 4.0 GHz and 20°C. The glass transition temperature of the unstretched PET estimated by differential scanning calorimetry (d.s.c.) was 75°C.

In the dielectric measurements using our 'high temperature dielectric analyser', polarized microwaves were incident perpendicularly onto a given film held in a sample holder after the sample and holder assembly had been inserted into a narrow gap between a pair of rectangular waveguides in the cavity resonator system.

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The system was completely surrounded by an oven consisting of heat-resistant, adiabatic sheet materials covered with stainless steel sheets.

The cavity resonator system was heated by blowing hot air into it, with the temperature variation regulated to within 0.3°C. Effects due to the thermal expansion of the waveguides were corrected by use of the temperature-dependence data for the resonance frequency in the cavity system containing no sample. Heat-resistant connectors and cable were used. The sample holder was made of stainless steel sheets with a circular opening of 80 mm diameter that prevented microwave reflection. Hot air blowing into the system minimized temperature fluctuations in the oven. The temperature was measured by a thermocouple placed near the sample. Warming the cavity system up to ca. 100°C took a long time. If the sample film had first been mounted in the system and then heated to high temperature, the PET would have crystallized before the dielectric measurement was taken. Therefore, the sample was always inserted into a system preheated to the temperature of the measurement. This method quickly brought the sample to the desired temperature.

To study the time dependence of ε'' at 4.0 GHz the measurements were made as a function of time for a sample kept standing after insertion into the system. In determining the temperature dependence of ε'' the sample was removed from the system soon after the measurement at a particular temperature was complete. The time needed for a single dielectric measurement was 30 s at any temperature. The cavity system was operated in a transverse electric wave (TE) of type TE_{10L}[15], with the frequency adjusted continuously between 3.6 and 4.2 GHz. The sample size was 100 x 100 mm for biaxially stretched and unstretched PET films, with the film thickness being 100 μm for the former and 150 μm for the latter.

The dielectric loss of the sample at temperature T can be calculated from[7,15]

$$\varepsilon''(T)=B'[c(T)/2t(T)][1/Q_2(T)-1/Q_1(T)] \quad (1)$$

Here, t is the sample thickness, c is a parameter relating to the depth of the waveguide, B' is an instrumental constant, and Q_1 and Q_2 are the Q values reflecting the sharpness of the resonance curve, with the subscripts 1 and 2 indicating before and after insertion of the sample into the cavity system.

RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of the dielectric loss ε'' at 4.0 GHz for the biaxially stretched and unstretched PET films. We can see that the increase in ε'' with temperature for the stretched film is weak, whereas that for the unstretched film is also weak up to 50°C but becomes steep above 50°C. As mentioned above, the crystallinities were 35% and 8% for the stretched film and unstretched film, respectively, when the samples subjected to the loss measurements up to 90°C were quenched to room temperature. Thus, the crystallinity of the unstretched sample changed only a little during the measurement.

At room temperature the loss peak of the dielectric β relaxation appeared around 100 kHz for both stretched and unstretched samples[7,16]. This peak frequency is far lower than the 4.0 GHz at which the present dielectric measurements were made. Hence, ε'' at 4.0 GHz for PET film at room temperature should be in the high frequency tail of the broad β relaxation that can arise from the amorphous region and the interfacial semicrystalline part[7,16]. As is well known, the dielectric loss due to the β relaxation increases with decreasing crystallinity and the increase is most pronounced at the loss peak of this relaxation[7,16]. The peak shifts towards higher frequency with increasing temperature. Thus, it may be expected that the difference in ε'' at 4.0 GHz between the stretched and unstretched PET is due to the difference in crystallinity and should become more appreciable at higher temperatures. This expectation agrees with what can be seen in *Figure 1*. The marked difference between the two curves at temperatures above 70°C probably indicates that the main part of the β relaxation enters the microwave frequency region.

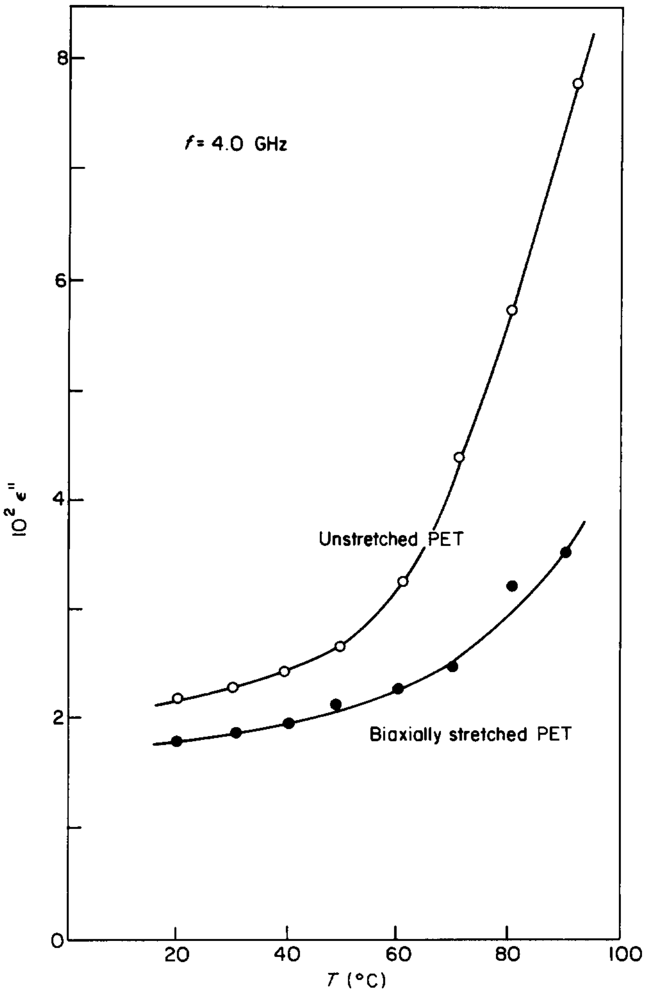

Figure 1 Temperature dependence of ε'' at 4.0 GHz for biaxially stretched and unstretched PET films. The room temperature crystallinity for stretched PET was 35% both before and after the dielectric measurements. For the unstretched PET, the crystallinities were 5% before and 8% after the measurements

Figure 2 shows the time dependence of ε'' at 4.0 GHz over a range of temperatures for the unstretched PET. The ε'' at 105°C is seen to decrease rapidly and then level off. At 85°C the decrease is slow, and below 70°C no substantial change is observed. Thus, the time dependence of ε'' is significant only above the glass transition temperature of the system (75°C) and it becomes stronger as the temperature gets higher.

When the unstretched PET was annealed at 105°C for 100 min and then quenched to room temperature, its crystallinity increased to 32% from the initial value of

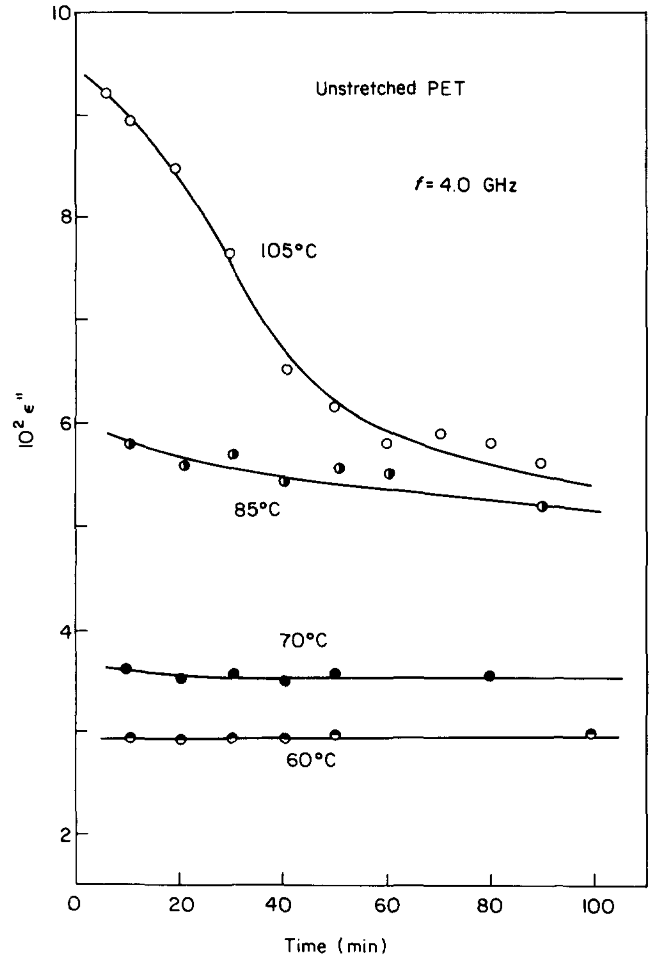

Figure 2 Time dependence of ε'' at 4.0 GHz for unstretched PET films at different fixed temperatures. The room temperature crystallinity was 5% before the dielectric measurements

5%. The crystallinity was 18% when the unstretched PET was annealed at 85°C for 100 min and then quenched to room temperature. Keeping the sample below the glass transition temperature of 75°C gave rise to no appreciable changes in ε'' and crystallinity after quenching to room temperature.

In sum, the dielectric loss of unstretched PET decreases and its crystallinity increases after quenching to room temperature if the film has previously been kept above the glass transition temperature, and the changes are enhanced with increased standing time and temperature of dielectric measurement. These findings suggest that a relationship exists between ε'' and the crystallinity of PET at temperatures above the glass transition point. However, we have to leave the quantitative discussion untouched because we were unable to determine the crystallinity of the sample at such high temperatures. In this connection it is worth noting that at room temperature ε'' of PET has been found to vary linearly with crystallinity[7].

Polymer molecules in the amorphous and interfacial regions tend to crystallize at temperatures above the glass transition point because they can rearrange themselves by the micro-Brownian motion generated at such temperatures[16–19]. Therefore, the observed decrease in ε'' with time above the glass transition temperature may be ascribed to the decrease with time in the number of chain segments responsible for the β relaxation.

The apparatus used in this work allows ε'' at high temperatures to be measured directly. This advantage is useful for studying the dielectric characteristics of plastic containers and packages when used in a microwave oven. In order to enhance the heating efficiencies of polymeric materials in the oven, their high temperature dielectric losses at microwave frequencies should be low.

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