Measurement of dielectric properties of polymers using Fourier analysis

Angéline Bizet [a],*, Nobutaka Nakamura [a], Yoshihiko Teramoto[a] and Tatsuko Hatakeyama[b]

[a] *Seiko Instruments Inc., Oyama Plant, 36-1 Takenoshita, Oyama-Cho, Sunto-Gun, Shizuoka 410-13, Japan*
[b] *National Institute of Materials and Chemical Research, Higashi 1-1, Tsukuba, Ibaraki 305, Japan*

Abstract

A dielectric spectrometer has been developed which employs Fourier analysis methods for an accurate, straightforward determination of the complex dielectric constants of solid and liquid polymeric materials in the frequency range $10-10^5$ Hz between 120 and 770 K. On application of an electric field to the sample, the response of the sample is the electric displacement which is collected by the current detector circuit. The amplitude and phase relation between the applied electric field and the collected current is analysed using a Fourier transformation circuit and output as the complex dielectric constant.

The structure and performance of the apparatus are described in detail. An example of a dielectric measurement using Nylon 6 films, where the effect of moisture on the dielectric relaxations has been studied, is presented. The activation energy of the observed α-relaxation has been calculated using commercial software.

INTRODUCTION

The methods used to measure dielectric properties of solids can be classified into two groups [1, 2]. Lumped circuits are applied for frequencies ranging from 10^{-4} to 10^8 Hz, where the apparatus is designed to measure the equivalent capacitance and resistance of a sample at a given frequency. At higher frequencies, a large error in the measurement is introduced by the residual inductance of the apparatus. Therefore, in the frequency range 10^8 to 3×10^{10} Hz, the technique used is a distributed circuit. In this case, the attenuation factor α and the phase factor β of the electric field are determined at a given frequency.

In the frequency range $10-10^7$ Hz, the most commonly used apparatus are the Scherring bridge, whose principle is based on the Wheatstone bridge,

---

* Corresponding author at The National Institute of Materials and Chemical Research, Higashi 1-1-4, Tsukuba, Ibaraki 305, Japan.

and the transformer bridge in which the introduction of transformers allows the elimination of the residual impedance and the guard circuit impedance, giving very accurate values of the complex dielectric constant [1].

A dielectric spectrometer (DES 100) has been developed which employs Fourier analysis methods to make an accurate and simple determination of the complex dielectric constants of solid and liquid polymeric materials in the frequency range 10–10^5 Hz between 120 and 770 K. Fourier analysis of the applied electric field and electric displacement functions as a high-performance band-pass filter which reduces the error in the determination of the operating frequency and, therefore, significantly improves the accuracy of the measurement of the complex dielectric constant. A simple consideration of the relationship between the complex applied voltage, the complex capacitance and the complex charge shows that the measured current is proportional to frequency. Therefore at low frequency, the current signal is small. This signal is amplified and, using Fourier analysis, the appropriate frequency component is extracted, leading to an accurate determination of the measured current.

In this study, the dielectric properties of polycaprolactam (Nylon 6) have been investigated in the dry and wet state using the DES 100. The effect of water on the hydrogen bond network in polycaprolactam and its subsequent effect on the dielectric relaxations of the polymer are considered.

MATHEMATICAL BACKGROUND

The dielectric spectrometer DES 100 measures the complex dielectric constant of polymeric materials using Fourier analysis. When an electric field is applied to the sample, the response of the sample is the electric displacement. The sample reaction is proportional to the electric field, but the response lags behind the electric field. This physical phenomenon may be described by

$$D(t) - D^{eq} = X^\infty E(t) + \int_{-\infty}^{t} \phi(t - t')E(t')\,\mathrm{d}t' \tag{1}$$

where t, t' represent the time, $D(t)$ is the electric displacement (which is measured as the displacement current $I = \mathrm{d}D/\mathrm{d}t$), D^{eq} is the displacement at equilibrium, $E(t)$ is the applied electric field, $X(t)$ is the complex capacitance, X^∞ is $X(t)$ at $t = \infty$, and $\phi(t)$ is a retardation function; $\phi(t - t')$ reduces to zero when $t - t'$ becomes large.

The Fourier transformation of the electric field and the electric displacement can be written

$$E(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} E(t)e^{i\omega t}\,\mathrm{d}t \tag{2}$$

$$D(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} [D(t) - D^{\text{eq}}]e^{i\omega t}\, dt \tag{3}$$

where $i = \sqrt{-1}$. Using eqns. (1)–(3)

$$D(\omega) = X^{\infty}E(\omega) + \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \left[\int_{-\infty}^{t} \phi(t - t')E(t')\, dt'\right]e^{i\omega t}\, dt \tag{4}$$

The following variable change, $\tau = t - t'$, allows eqn. (4) to be written

$$D(\omega) = X^{\infty}E(\omega) + \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} e^{i\omega t}\, dt \int_{0}^{+\infty} \phi(\tau)E(t - \tau)\, d\tau \tag{5}$$

With a second variable change, $T = t - \tau$, eqn. (5) becomes

$$D(\omega) = X^{\infty}E(\omega) + \frac{1}{\sqrt{2\pi}} \int_{0}^{+\infty} \phi(\tau)e^{i\omega\tau}\, d\tau \int_{-\infty}^{+\infty} E(T)e^{i\omega T}\, dT \tag{6}$$

Therefore, if we define

$$X(\omega) = X^{\infty} + \int_{0}^{+\infty} \phi(t)e^{i\omega t}\, dt \tag{7}$$

Eqn. (6) can be written in the simple form

$$D(\omega) = X(\omega)E(\omega) \tag{8}$$

If the applied electric field is a periodic function with the period $2\pi/\omega_0$, $D(t)$ is also a periodic function with the same period because of the linearity between $E(t)$ and $D(t)$. In the case of an electric field having the form

$$E(t) = E_0 \sin \omega_0 t \tag{9}$$

and considering the orthogonality of $\{e^{i\omega t}\}$, eqn. (8) becomes

$$X(\omega_0) = \frac{\int D(t) \cos(\omega_0 t)\, dt + i \int D(t) \sin(\omega_0 t)\, dt}{\int E(t) \cos(\omega_0 t)\, dt + i \int E(t) \sin(\omega_0 t)\, dt} \tag{10}$$

where $\int$ denotes the periodic integration.

This method allows calculation of the complex capacitance at a given frequency, for a measured electric field and electric displacement.

Equation (10) shows how Fourier analysis can be used to determine the complex capacitance as a function of the frequency of the applied electric field. The relationship between $X(\omega)$ and the complex dielectric constant ε^* is

$$X(\omega) = \varepsilon^* \varepsilon_0 \frac{S}{L} \tag{11}$$

where $\varepsilon^* = \varepsilon' - i\varepsilon''$, S is the surface area of the electrode and L is the distance between the electrodes. According to the usual relation

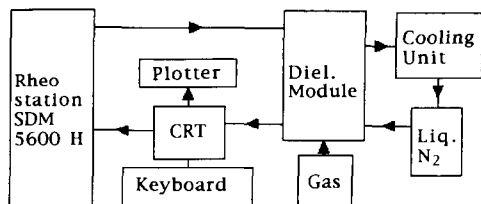$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} \tag{12}$$

Fig. 1. Schematic representation of the dielectric spectrometer DES 100.

DESCRIPTION OF THE APPARATUS

Figure 1 is a schematic description of the dielectric spectrometer DES 100. The experimental parameters of sample thickness, temperature program, and frequency program are set using the keybord. A cooling unit allows automatic control of the temperature of the furnace and an inert atmosphere is maintained using a nitrogen gas flow.

The configuration of the DES 100 dielectric module is shown in Fig. 2. A voltage from the sine-wave generator is applied to the V electrode and the electrical charge that appears in the I electrode is collected by the current detector circuit. The amplitude and phase relation between voltage and current is detected in the Fourier transformation circuit and output as the complex dielectric constant. The thermocouple embedded in electrode G accurately measures the sample temperature.

The sample holder, whose configuration is shown in Fig. 3, is placed in a furnace. The ambient atmosphere in the furnace can be replaced by an
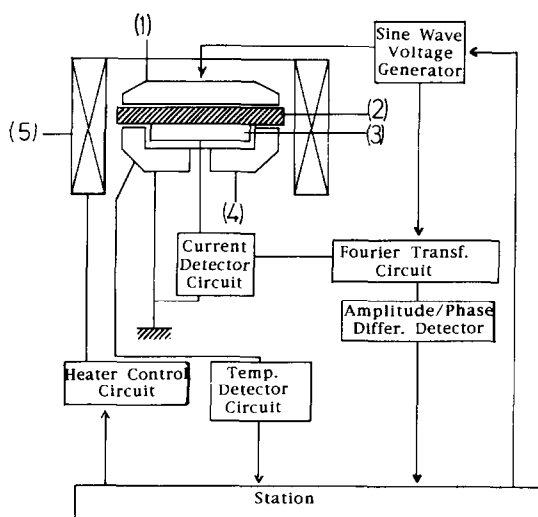

Fig. 2. Configuration of the dielectric module DES 100: (1), excitation electrode (V electrode); (2), sample; (3), response electrode (I electrode); (4), ground electrode (G electrode); (5), heater.
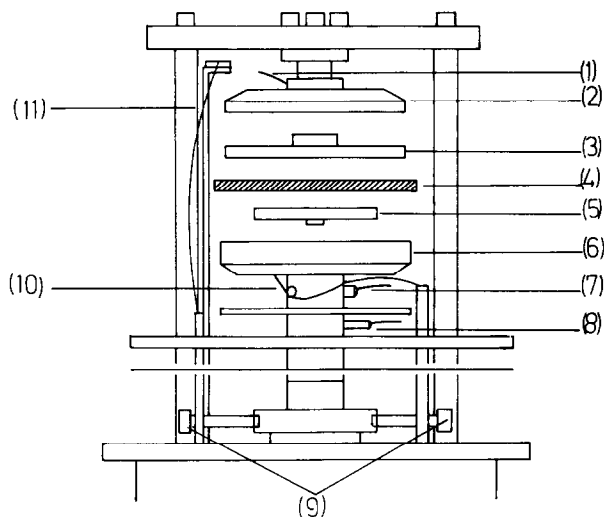
Fig. 3. The sample holder assembly of the DES 100: (1), terminal (connection with the wire going to the V electrode; (2), V electrode (excitation electrode); (3), V electrode plate (quick-release plate to prevent the sample from melting to the V electrode); (4), sample; (5), I electrode plate (quick-release plate to prevent the sample from melting to the I electrode); (6), G electrode (this electrode acts as a guard ring); (7), G terminal (connection with the wire going to the G electrode); (8), I terminal (connection with the wire going to the I electrode); (9), lever (installation or release of the sample by lowering the I and G electrodes to create a space between the V electrode and the other electrodes); (10), sample thermocouple (hidden in the G electrode, it is used to measure the sample temperature); (11), control thermocouple (measure of the temperature of the heater).

inert atmosphere, e.g. nitrogen, thereby removing all moisture from the furnace chamber and, by insulating the sample from the ambient atmosphere, facilitating high precision control of the sample temperature. The temperature program is set through the keyboard where the following options are available: the type of measurement (step mode or ramp mode), the starting and ending temperature, and the heating/cooling rate. The temperature is controlled through two thermocouples: the sample thermocouple, which is embedded in the ground electrode, measures the sample temperature, and the thermocouple, which is inserted inside the furnace, determines the temperature of the heater and provides feedback to control accurately the sample temperature. The cooling unit which connnects the dielectric module and the liquid nitrogen dewar allows automatic control of the temperature variation. It is also possible to control automatically the gas flow (nitrogen gas or air) by means of a gas controller.

The sample, a disc 45 mm in diameter a 45-mm-diameter assembly for liquid samples, is placed between the excitation and response electrode plates and does not need to be sputtered with a metal film before measurement. The response electrode is a disc 35.6 mm in diameter. Figure 4 is a detailed representation of the electrodes and sample configuration.
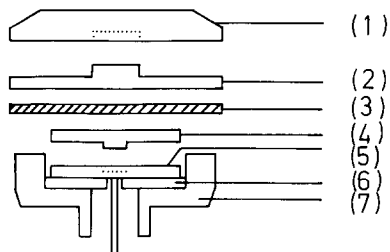
Fig. 4. Detailed view of the electrodes and the sample: (1), V electrode; (2), electrode plate; (3), sample; (4), I electrode plate; (5), I electrode; (6), insulator; (7), G electrode.

The measurement is started using keyboard commands and is terminated when the limit temperature, set in the temperature program, is reached.

The data measured with the DES 100 can be plotted as a function of time, temperature or frequency on the horizontal axis and with ε', ε'', $|\varepsilon^*|$, tan δ, σ, G' or C' on the vertical axis, where σ, G' and C' are the ionic conductivity, conductance and capacitance, respectively, and are calculated using standard formulae [3]. Recently developed software allows an accurate analysis of the data, where scales are simple to set and peaks positions accurately determined. The operator can obtain master curves from the original data and calculate the activation energies related to each dielectric transition from the temperature and frequency dispersion data.

The technical specifications of the DES 100 are presented in Table 1.

In order to measure the dielectric properties of liquid samples, the following method has been developed. The liquid sample is placed between two Teflon films and Teflon rings as shown in Fig. 5. The complex dielectric constants of the whole assembly and of the Teflon film are measured separately under identical experimental conditions. The software subtracts the data obtained for the Teflon film from those obtained for the assembly and the result is the complex dielectric constant of the liquid sample alone.

PERFORMANCE OF THE APPARATUS

The accuracy of the measurement of the sample temperature was tested by measuring the melting temperature of a 5 mg indium sample placed between two circular Teflon films, the whole assembly then being placed inside the DES 100. In order to determine the temperature distribution inside a polymeric sample, the indium sample was first placed in the centre of the Teflon films, and then at the edge. The melting of the indium was observed as a step-like variation of the dielectric constant due to a decrease in the distance between the electrodes following the melting of the indium sample (Fig. 6). In order to investigate the influence of the heating rate on the temperature distribution inside a sample, heating rates of 10 and 2 K min^{-1} were used. These results are summarized in Table 2, and show that in the DES 100 a uniform sample temperature ± 1 K is maintained.

TABLE 1

Specifications of the DES 100

Electrode type	Three-terminal parallel plate with guard ring
Response electrode area	995.38 mm^2
Frequency range	10, 20, 50, 100, 200, 500, 1k, 2k, 5k, 10k, 20k, 50k, 100k Hz
Temperature range	120–770 K
Effective heating rate	−5–10 K min^{-1} (divided into 0.01 K min^{-1})
Heat distribution in sample	Within 1 K for a 0.1-mm-thick sample
Sample shape	Rigid 45 mm i.d. disc
	Liquid Held in Teflon ring and film assembly, 45 mm i.d.
Sample thickness	10 μm to 5 mm
Excitation voltage	10 V
Current amplitude	15 nA to 6 mA
Capacitance measurement	3 pF to 0.1 μF
Dielectric constant range	ε' 1–2 × 10^5 ε'' 0–10^8
Measurement resolution	ε' 10^{-3} tan δ 10^{-4}
Measurement accuracy	ε' ±3% tan δ ±(5% + 0.005)
Output signals	Temperature
	Frequency
	Time
	ε' (Storage dielectric constant)
	ε'' (Loss dielectric constant)
	tan δ (Loss tangent)
	$|\varepsilon^*|$ (Magnitude of the complex dielectric constant)
	σ (Ionic conductivity)
	G' (Conductance)
	C' (Capacitance)

In order to demonstrate the reproducibility of the DES 100, two polymethylmethacrylate (PMMA) samples were measured under the same conditions from 220 to 450 K, between 10 and 10^5 Hz. The heating rate was 1 K min^{-1}. Both samples were kept over silica gel prior to the measurements. The thickness of the films was 0.2 mm. The diameter of the samples
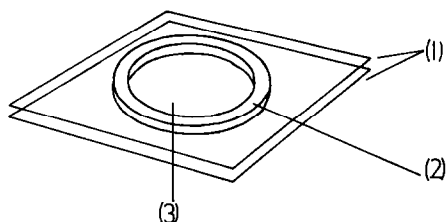

Fig. 5. The assembly Teflon film–Teflon ring–liquid sample, used for the determination of the complex dielectric constants of liquid sample: (1), Teflon films; (2), Teflon rings; (3), liquid sample.
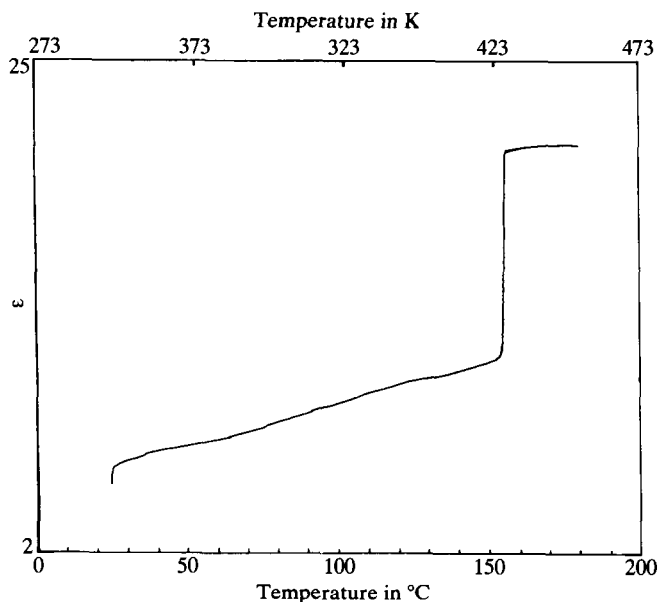
Temperature in K

Fig. 6. Dielectric constant ε' for a 2.6 mg indium sample.

was 45 mm. The difference between the measured values of ε' and ε'' was found to be 2.5% and 5.5%, respectively.

THE INFLUENCE OF WATER ON THE DIELECTRIC PROPERTIES OF NYLON 6 FILMS

The complex dielectric constant $\varepsilon^* = \varepsilon' - i\varepsilon''$ of polycaprolactam (Nylon 6) was measured using the DES 100 dielectric spectrometer equipped with a SDM 5600H Rheological Station over the frequency range $10-10^5$ Hz, between 240 and 450 K. Two relaxation phenomena were observed. The Nylon film used was produced from Nylon granules by simultaneously pressing them at 100 kg cm^{-2} and melting at 520 K between two sheets of Teflon. The granules were manufactured by Unitika Co. Ltd. Two samples were cut from the film thus produced. The first sample was maintained for one week in a 81%RH environment; the second sample was stored for one

TABLE 2

Apparent melting temperatures of indium

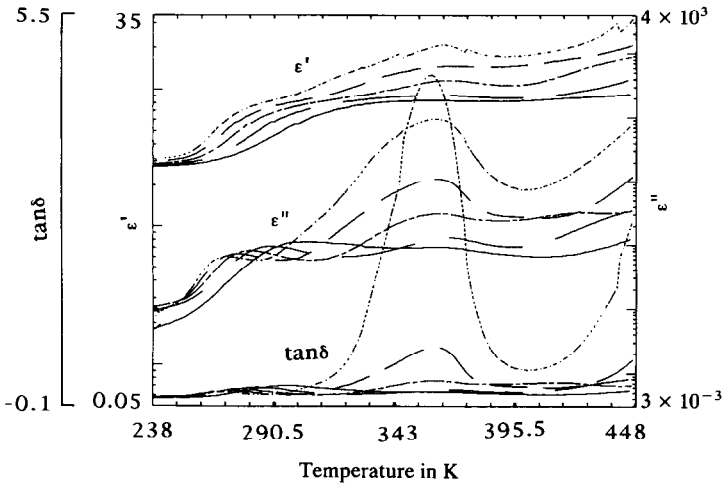|	Indium placed at the centre of the Teflon films	Indium placed at the edge of the Teflon films
10 K min^{-1}	428.5 K	429.6 K
2 K min^{-1}	429.4 K	429.1 K

Fig. 7. Dielectric constant ε', dielectric loss ε'' and tan δ for wet Nylon versus temperature.

week over diphosphorous pentaoxide. A scanning rate of 1 K min^{-1} was used. An inert atmosphere was maintained using a nitrogen gas flow. The wet film was 0.156 mm thick and the dry one was 0.103 mm thick. The diameter of both films was 45 mm.

Figures 7 and 8 show the dielectric constant ε', the dielectric loss ε'' and tan δ of the wet and dry samples, respectively. Two relaxation processes were observed. The high-temperature or α-transition is ascribed to segmental motions in the amorphous regions of the polymer [4] and the low-temperature transition, or β-relaxation, is the result of unbonded or weakly bonded amides in amorphous regions [5, 6].
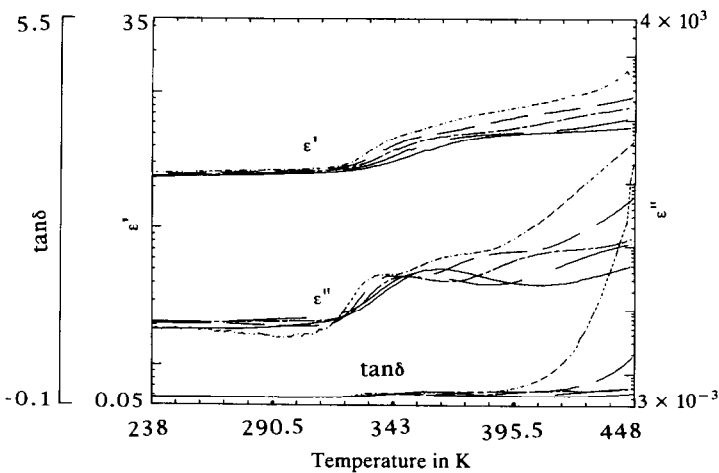

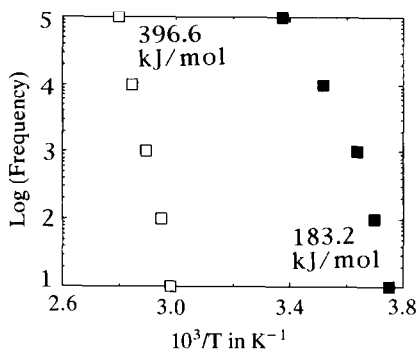Fig. 8. Dielectric constant ε', dielectric loss ε'' and tan δ for dry Nylon versus temperature.

Fig. 9. Logarithm of the relaxation angular frequency versus the reciprocal of the absolute temperature for the α-relaxation of dry and wet Nylon: □, dry Nylon; ■, wet Nylon.

A comparison between Figs. 7 and 8 reveals that the presence of water dramatically changes the dielectric behaviour of Nylon 6. In the dry sample, the α- and β-relaxations are distinct and clearly resolvable, whereas in the wet sample, both relaxations overlap and are shifted to lower temperatures. The intensities of the loss peaks for the α-relaxation are increased in the presence of water. Furthermore, the activation energy for the α-relaxation is halved: in the dry sample the activation energy was found to be 396.6 kJ mol^{-1} and for the wet sample the measured activation energy was 183.2 kJ mol^{-1}, as shown in Fig. 9.

The introduction of water in Nylon 6 strongly influences its dielectric behaviour because, at low temperatures water is considered to form mechanically stable bridges between amide groups [7] (anti-plasticizing effect) and, at higher temperatures, water facilitates motion in the amorphous regions [7] (plasticizing effect).

In the α-transition, plasticization may be thought of as a result of two effects: the reduction of interchain bonding due to replacement of amide–amide hydrogen bonds by water–amide interactions; and the increase in segmental mobility with dilution [5]. The introduction of water increases the number of free amides and increases their mobility [5], resulting in the observation of the β-relaxation at lower temperatures.

In a similar study on the effect of water on the dielectric properties of aromatic polyesters [8], the symmetric peak is ascribed to water in the sample. This conclusion is based on the relatively small temperature shift in the peak position with frequency and the symmetric shape of the peak. In this study of water in Nylon 6, the change in position of the high-temperature peak is only 8 K over the entire frequency range. Also, the peak does display a high degree of symmetry. Therefore, while a definitive assignment of this peak cannot be made at this time, it may be tentatively suggested that this peak is due to water in the sample.

Clearly then, the influence of water on the dielectric behaviour of Nylon 6 can be monitored with the DES 100. A large range of polymeric materials have been similarly investigated using this apparatus.

CONCLUSIONS

A new dielectric spectrometer, whose principle is based on Fourier analysis, has been developed. The measuring stage consists of a three-terminal cell, including a guard ring, an exciting electrode and a response electrode, and is placed in a furnace for temperature variation. Following temperature calibration of the spectrometer with an indium sample, evaluation of the sample temperature distribution gave satisfactory results. Fourier analysis makes it possible and straightforward to obtain accurate results for the complex dielectric constants of solid and liquid samples. The effect of moisture on the dielectric properties of Nylon 6 has been studied. The presence of water facilitates molecular motion of the polymer, enhancing the α- and β-relaxations. This enhancement of molecular motion was clearly observable using the DES 100. In general, variations in the dielectric behaviour of a broad range of polymeric materials may be conveniently probed over a large temperature range in a controlled atmosphere using this instrument.

REFERENCES

1 N.G. McCrum, B.E. Read and G. Williams, Anelastic and Dielectric Effects in Polymeric Solids, Wiley, London, 1991, Chapter 7.
2 A.R. Blythe, Electrical Properties of Polymers, Cambridge University Press, Cambridge, 1979, Chapter 4.
3 C. Kittel, Introduction to Solid State Physics, Wiley, New York, 1956, Chapter 7.
4 S. Hirota, S. Saito and T. Nakajima, Kolloid Z. Z. Polym., 213 (1966) 109.
5 R.H. Boyd, J. Chem. Phys., 30 (1959) 1276.
6 M.N. Stein, R.G. Lauttman, J.A. Sauer and A.E. Woodward, J. Appl. Phys., 32 (1961) 2352.
7 H.W. Starkweather, Jr., Water in Polymers, ACS Symposium Series 127, 1980, Chapter 25.
8 T. Tatsumi, H. Ezure and E. Ito, Kobunshi Ronbunshu, 49 (1992) 521.