Measurement of the absorption spectrum of polytetrafluoroethylene in the near millimetre region by an untuned cavity

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The absorption spectrum of polytetrafluoroethylene has been measured between 3 and 15 cm^{-1}, a region which until now has been virtually unexplored. Absorption was found to arise almost entirely from amorphous regions of the sample and absorption in crystalline regions is small. A novel feature of the investigation is that measurements are made in an untuned cavity which has the advantage for low loss materials, that losses from reflection, scatter, and diffraction become unimportant. Loss measurements can be made on samples even when they are in the form of fine powder.

INTRODUCTION

The absorption spectra of synthetic polymers have been well explored and interpreted in the wavenumber region between the visible and 30 cm^{-1}. In this interval absorption bands are narrow, having widths of about 1% of peak frequency value. At the upper end of this frequency region absorption is ascribed to the stretching and deformation of covalent bonds, while below 200 cm^{-1} it more frequently comes from bond torsion. The peak frequency value of all these internal modes is relatively insensitive to temperature. At wavenumbers below about 100 cm^{-1}, absorption may also arise from intermolecular modes[1]. For crystalline regions of a polymer intermolecular distances are precisely defined, so that the intermolecular or crystal modes appear as sharp lines which are superficially similar to those due to internal molecular modes. However, since the crystal lattice contracts with decreasing temperature, intermolecular distances shorten and crystal mode frequency values usually rise, by up to about 10%, in going from room temperature to 100K. Observation of such a frequency increase is therefore useful in distinguishing lattice modes from internal modes of the polymer molecules.

Absorption also arises from intermolecular motions in amorphous regions of polymers but these intermolecular distances are not well defined and the corresponding absorption is broad: it is seen as a band near 100 cm^{-1} with a half band width of up to 50 cm^{-1} and the description 'liquid lattice' modes[2] has been given to these features.

The spectra observed at frequencies below about 3 cm^{-1} are of a different origin. Bands are characteristically broad, often extending over a decade of frequency and have been ascribed to relaxation processes. These are attributed to cooperative motion of a number of adjacent atoms and their pendant groups in the polymer backbone. Such modes would be expected to be strongly temperature dependent, and it is found that the frequency of their absorption maxima falls as the sample temperature decreases[3]. The region on either side of 10 cm^{-1} is therefore of particular interest since it is the overlap where losses may arise from intramolecular torsional modes, intermolecular modes or relaxation processes. However, there has been comparatively little spectroscopy of polymers in this region by traditional methods. One reason for this is the difficulty in distinguishing between losses due to true absorption by the polymer and apparent losses from reflection, scatter and diffraction in the sample[1]. Another consideration is that true absorption losses will often be affected by the procedures necessary to prepare the sample in the physical form (e.g. film, disc or rod) required for measuring the spectrum by traditional methods. This is particularly the case when heat treatment is involved in its preparation. This may cause oxidation of the polymer, or change in the morphology, especially orientation. It may also change the crystalline to amorphous ratio. Apparent losses may also be affected by refractive index discontinuities, including voids, within the sample. All of these have made it difficult to measure true loss levels in this frequency region by conventional spectroscopic techniques.

The basic quantity of interest in these investigations is the molar absorption coefficient, i.e. the absorption cross-section of the molecule, or, in the case of a polymer, the molecular repeat unit. This quantity can be determined by measuring the mass absorption coefficient α/ρ, where α is the absorption coefficient and ρ the density of the material. In the untuned cavity technique the sample is immersed in a uniform isotropic radiation field so that it can be in the form of powder or chip, of which a known weight is placed in the cavity. The mass absorption coefficient is measured directly and this can be compared with the value measured on the sample after fabrication. In this way any effects resulting from fabrication may be detected. To verify these ideas, and to find if the loss processes of synthetic polymers are intrinsic to the

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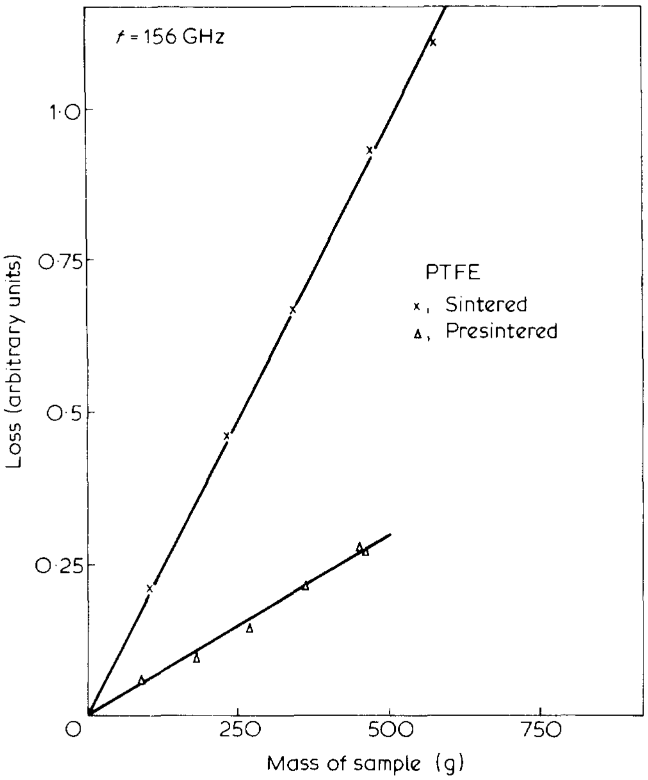

Figure 1 Linear relationship between measured loss and the amount of material in the cavity. Measurements made at a wavenumber of 5.2 cm^{-1} on sintered and presintered blocks of various shapes

material as manufactured or are introduced during processing, we have investigated the absorption spectrum of polytetrafluoroethylene (PTFE). This loss material is well suited to study by the new method since it is available in a variety of physical forms. Also losses are small so that relatively large blocks of the material, with dimensions of several centimetres, do not show saturation effects. With this material it is also possible to change the crystalline/amorphous ratio in a well defined way.

EXPERIMENTAL

Samples

PTFE can be prepared as a powder with a range of particle sizes. Samples of 20 μm, 200 μm diameter were examined, and some 1000 μm powder lightly pressed into cubes of 10 × 10 × 10 mm. Preform blocks were examined, which had been made by compressing the powder at room temperature under 1 ton/sq. in. pressure into discs 100 mm diameter and 100 mm long. A series of sintered samples were also examined. These were preformed at 1 ton/sq. in., heated at 380°C for 2 h, and cooled at 30°C h^{-1} to room temperature. They were in the form of several irregular portions cut from a single disc 14 cm diameter × 2 cm.

Technique

The untuned cavity technique, which originated in acoustics, can also be used for making microwave measurements of low values of loss in gases[4]. Recently, the technique has been adapted[5] for making measurements of loss in solid dielectrics for which it offers several important advantages; namely, the sensitivity of a high-Q resonator, little dependence upon the shape, size, and position of the sample, and the fact that, as the resonator is closed, all radiation reflected and scattered from the sample is contained within the measuring system and not confused with true absorption losses.

The cavity used for these measurements was an approximately cylindrical enclosure with highly reflecting walls, and a length and diameter of about 30 cm or 100 wavelengths at 3 cm^{-1}, which was the lowest frequency at which measurements were made. This ensured that the cavity was an overmoded resonator of which the diversity of resonant modes was greatly increased by the presence of a rotating reflector inside the cavity which acted as a mode scrambler. As a result of this, the cavity was resonant at all frequencies within its operating range. It was excited by harmonic power at 5.2 cm^{-1} from an IMPATT oscillator for single frequency observations and by the black body radiation from a high pressure mercury arc lamp for wide bandwidth observations, in which case the cavity output passed through a Fourier spectrometer.

In each case, radiation was detected by wide bandwidth far infra-red detectors. The cavity was calibrated by the established method of opening an aperture of known area in the walls which is analysed by Lamb[6]. A full account of the application of this technique to dielectric measurements is given in ref 5.

The linear relationship between absorption measured in the cavity and the weight of the sample, independent of its shape, is illustrated by the data shown in *Figure 1*. The results of a series of such measurements made with a single frequency source at a wavenumber value of 5.2 cm^{-1} are summarized in *Table 1*.

A series of spectroscopic measurements over the range 3 to 15 cm^{-1} were also made in the untuned cavity, using a black-body source, and a two-beam interferometer. Comparison of results for presintered (cold compressed) block, and a sintered sample are shown in *Figure 2*. Data in adjacent frequency ranges from the work of Reddish[7], Fleming and Chantry[8] and Cook[9] are given for comparison.

DISCUSSION

The results on the highly crystalline powders are all similar, and are found to be independent of particle size over a 100-fold change of particle diameter. In each case the measured loss is directly proportional to the weight of sample placed in the cavity, which confirms that there are no measurable losses from reflection, scatter or diffraction. The measurements made on cold compressed blocks in the form of discs and cylinders also gave the same value of absorption coefficient.

The crystallinity of PTFE before sintering cannot be readily measured on the powder, but various methods (e.g. X-ray diffraction, i.r. absorption and differential scanning calorimetry) can be applied to the cold compressed samples. The results obtained depend upon the assumptions made, but it is generally agreed that the crystallinity of such samples is in the range 90–95%[7]. By similar methods, the crystallinity of fully sintered samples is approximately 65%, which implies that the amorphous content is about 4 times that of cold compressed blocks. The losses at 5.2 cm^{-1} rise by the same factor, and so we may say with confidence that the loss of PTFE at this frequency arises mainly from amorphous material, and that the contribution from the crystalline regions is small.

Table 1 Results of loss measurements at 5.2 cm^{-1} on various PTFE samples are given and individual samples are characterized by their particle size. Measured mass absorption coefficients are listed together with values of absorption coefficient and loss tangent which are characteristic of a density of 2.1 g cm^{-3} and a refractive index of 1.37[10]

Nature of sample	Particle size	Mass absorption coefficient ($cm^2 g^{-1} \times 10^{-3}$)	Molar absorption coefficient ($cm^{-1} \times 10^{-3}$)	Loss tangent (μ radians)
Unsintered	20 μm	2.2 ± 0.2	4.7 ± 0.5	105 ± 11
	200 μm	1.8 ± 0.2	3.8 ± 0.4	85 ± 9
	2000 μm	1.9 ± 0.1	4.0 ± 0.1	89 ± 2
	1000 μm Pressed into 1 cm^3 blocks	1.9 ± 0.2	4.0 ± 0.4	89 ± 9
Average		1.95 ± 0.30	4.1 ± 0.4	91 ± 9
Presintered	Bulk	2.2 ± 0.1	4.6 ± 0.3	103 ± 7
Sintered	Bulk	8.4 ± 0.6	17.7 ± 1.3	395 ± 29

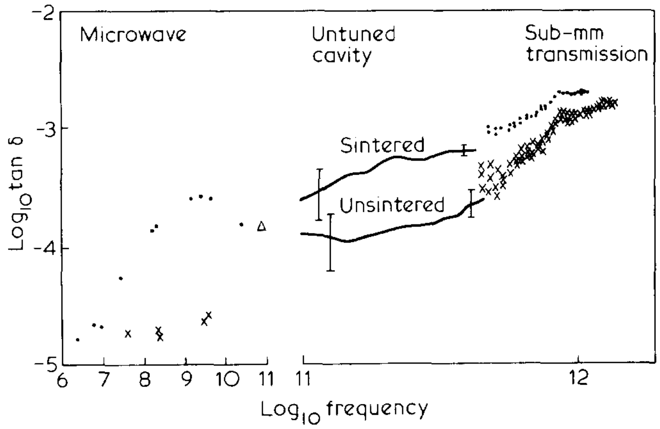

Figure 2 Results of spectroscopic measurements of dielectric loss in the untuned cavity in sintered and unsintered PTFE are shown and compared with conventional spectroscopic measurements[8] at the higher frequencies and microwave measurements[7] at the lower frequencies. The triangular symbol represents the results from ref 9. The new measurements span the wavenumber range 3 to 15 cm^{-1}. The error bars represent one standard deviation

This result is not unexpected, since both Reddish[7] and Fleming and Chantry[8] considered that the losses both at higher and lower frequencies were mainly due to amorphous material. The measurements over a range of frequencies, given in *Figure 2*, for cold compressed PTFE and sintered PTFE show that the present results are consistent with earlier work.

The special significance of the present results is that the measurements were made in a region of the spectrum previously accessible only with difficulty and with samples in physical forms on which spectroscopic measurements have not been possible. This is of considerable practical importance, since it enables samples to be measured without preparation such as cold compression, which is not only time consuming, but may well of itself influence the loss level measured in some cases. We visualize that applying this technique to polymer samples as manufactured might be adaptable to continuous online operations.

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