MICROWAVE DIELECTRIC MEASUREMENTS DURING THERMAL ANALYSIS

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(Received 29 May 1987)

ABSTRACT

A simple, fast and fully automated thermoanalytical method for the measurement of complex permittivities and temperature of solid or liquid samples heated by microwave absorption at 2.4 GHz is described. The technique uses the small perturbations of a resonant cavity by a sample suspended at a maximum of the electric field on the optical fibre of a fluorescence thermometer, non-interfering with standing waves. Microwave power adjustable from some mW to 6 W is applied to the sample at the cavity resonance maximum frequency. During the heating and in order to follow the variable perturbation of the cavity by the sample, this frequency is determined at regular time intervals after an incremental sweeping around the previous maximum resonance frequency.

The method is suitable for the study of dielectrical behaviour of materials as a function of temperature, and physical changes and processes such as drying or chemical reactions occurring during solid or liquid sample heatings. Examples of each kind are given and first results discussed.

INTRODUCTION

Advantages of microwave heating of dielectric materials over conventional heating are evident since energy transfer is direct and homogeneous inside these materials. This leads to a reduced thermal gradient and allows extremely rapid heating. Energy transfer yield depends on the products' dielectric losses, making this form of heating very specific. Low conductivity materials are heated both by their dielectric losses and by the Joule effect. But for most of the materials, and particularly pure dielectrics, these losses are too small to allow self heating by direct irradiation. Electrical resonators, generally cavities in which standing waves develop, must be used to concentrate energy. In these cavities, homogeneous heatings are only obtained when the samples are placed at an electric field maximum and have small dimensions compared to the irradiating guided wavelength. In this way, most materials can be heated by microwave irradiation. This is leading to a rapid development of the use of microwaves, particularly in industrial

heating, and to a need for knowledge of material dielectric behaviour as a function of temperature since the complex permittivity variations determine energy transfer [1]. Therefore, in addition to the advantages brought by the specificity of energy transfer, there is a great interest in developing a thermoanalytical technique able to perform dielectrical measurements during microwave heating [2]. Apart from understanding microwave heating, knowledge of the complex permittivity of materials is also of importance since it gives information on dipole–dipole interactions inside materials. At microwave frequencies it is possible to study polar group freedom, and especially water interactions with materials.

Among the different techniques allowing dielectric measurements, the method known as "small perturbation of a resonant cavity" is probably the most accurate and is widely used [3–7]. In this method, the perturbations caused by a sample to frequency and amplitude of cavity electromagnetic resonance are compared to standards to determine its complex permittivity [8]. Because of the dependence of dielectric constants on temperature, sample temperature is precisely fixed. Few authors tried to carry out microwave heating and dielectric measurements simultaneously. Indeed the power levels required for heating and measurement, which generally differ by several orders of magnitude, respectively W or kW against mW, make these determinations difficult. Two microwave sources or a complex electronic set-up are generally used to overcome this difficulty [2,9–11].

Another difficulty lies in the measurement of temperature since all materials, and especially electrical conductors perturb electromagnetic fields. Temperatures of irradiated samples are indirectly determined either by a thermocouple external to the cavity and measuring an air flow surrounding the sample, or by dilatation [10,11]. Limitations in temperature accuracy or heating rates result. Optical methods, already used to determine temperature or other parameters of irradiated samples [12,13], present advantages over the indirect methods in being less- or non-interfering and/or more accurate.

In this paper, a simple, fast and fully automated thermoanalytical method for the measurement of complex permittivities and temperature of solid or liquid samples heated by microwave absorption at 2.43 GHz is presented. The small perturbation technique is used to perform accurate permittivity determinations. The delicate temperature measurement problem has been solved by using a fluorescence thermometer. Applications and first results are discussed.

METHOD AND APPARATUS

The microwave complex permittivity of a dielectric is temperature dependent. Knowledge of this dependence is one of the aims of this technique and
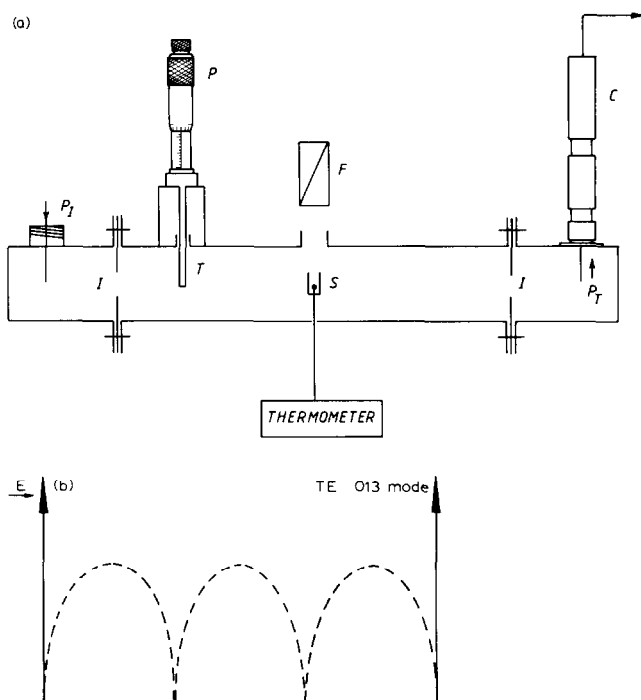
Fig. 1. (a) Schematic drawing of the cavity (S = sample, C = crystal detector, I = iris, P_I = power input, P_T = power output, F = electric furnace, P = piston used to remove the silica tube T when large sample has to be measured). (b) Electric field distribution along the cavity for the TE 0,1,3 mode. Sample is positioned at an electric field maximum.

is necessary to monitor the heating of a dielectric since dielectric losses govern the sample heating. In the method described below, permittivity measurements are used directly to monitor the heating of a sample placed in the centre of a rectangular cavity at a maximum of the electric field (Fig. 1).

The small perturbation technique [5] is used, but the cavity resonant frequency tracking is obtained by frequency tuning instead of the mechanical adjustment generally used. Moreover, permittivity measurements and heating are both performed with the same microwave source (6 W). A microcomputer continuously monitors the microwave frequency applied to the cavity, in the closed loop circuit presented in Fig. 2, by measuring at regular intervals the cavity perturbations with a fast frequency sweep (50 msec) around the resonance maximum. These perturbations are compared to standards (aliphatic alcohols from methanol to decanol, water or more convenient solid standards) to determine the dielectric constants ϵ' and ϵ'' of the sample. A short description of the electronic part of this technique is reported in ref. 14, and more detailed ones are being prepared [15,16].

The temperature is measured inside the sample by a non-perturbing fluorimetric thermometer (Luxtron, Mountain View, CA), with an optical
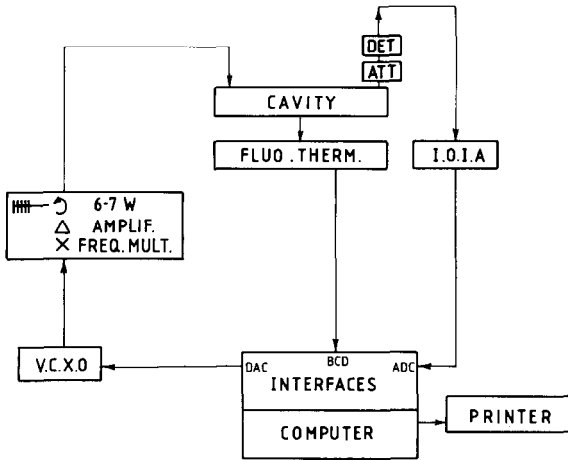
Fig. 2. Electronic set up of the apparatus. The basic closed loop used to monitor the cavity resonance is clockwise: a VCXO voltage controlled Xtal oscillator, an amplifier–frequency multiplier, a cavity, an attenuator, an Xtal detector, an Insulated by Optical coupling Instrumentation Amplifier, a computer and its interfaces. Fluo. therm. is the fluorescence thermometer.

fibre as temperature probe which is in close contact with the sample or the sample holder (made of Teflon, with a very thin wall between the fibre and the sample). This silica fibre is also the only sample support (Fig. 3) in order to minimize conductivity thermal losses. Thermometer resolution is 0.1° C and we believe the temperature accuracy to be better than 1° C during a
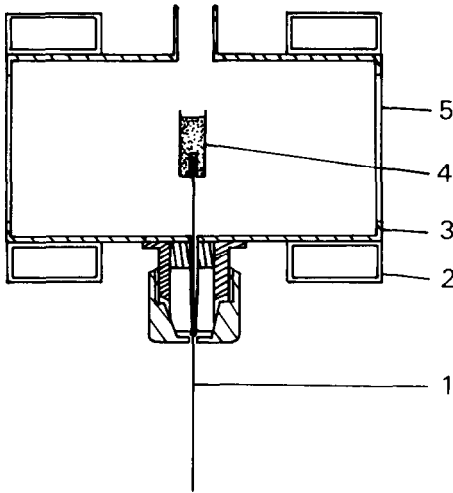

Fig. 3. Cross-section of the cavity. 1, thermometer optical fibre; 2, thermal stabilization tube; 3, cavity; 4, sample, sample-holder; 5, observation slits.

typical 16 min experiment. The thermometer operating range is -50 to $+210\,^{\circ}$C.

Dimensions of the sample, which is generally cylindrical, must be chosen (height as well as diameter) so that its permittivity and losses satisfy the small perturbations conditions. As cavity perturbations are related to cavity size [6], a larger cavity with 11 standing wave arches [1] (TE 0,1,11) has been designed for larger samples or high complex permittivity materials.

RESULTS AND DISCUSSION

Several studies have been undertaken using this method as principal investigation technique [14–17]. Examples discussed below are chosen to illustrate the variety of possible determinations. Solid or liquid samples are cylindrical or placed in a cylindrical sample-holder and heated by micro-wave irradiation according to the material and method section conditions.

Sample heating

The sample is heated and stays chemically unmodified. Initial physical and chemical properties of the product are restored after heating. Screen copy of the heating of a 468 mg cylindrical nylon sample (polyamide PA6) is presented in Fig. 4a. Dielectric constants and temperature are displayed and recorded as a function of time allowing the following of heating kinetics. Dielectric constants can be a posteriori related to temperature (Fig. 4b). As observed in this figure, at 2.43 GHz the nylon dielectric losses increase dramatically over $80\,^{\circ}$C.

Heating involving physical modifications

One or several compounds are heated; no chemical modification takes place but at least one of the physical parameters such as volume, shape, structure, etc. changes irreversibly during the heating. Then the absolute dielectric constant can only be measured up to the transition point; beyond this, measurements are either relative or meaningless. An example of such behaviour, the heating and boiling of hexanol, has already been given in ref. 14.

Heating involving chemical reaction and related process

Various kinetics and even chemical reactions can also be followed by the evolution of the dielectric parameters of a mixture or a material. Because of the complexity of such a process, the method becomes fully effective as described below.
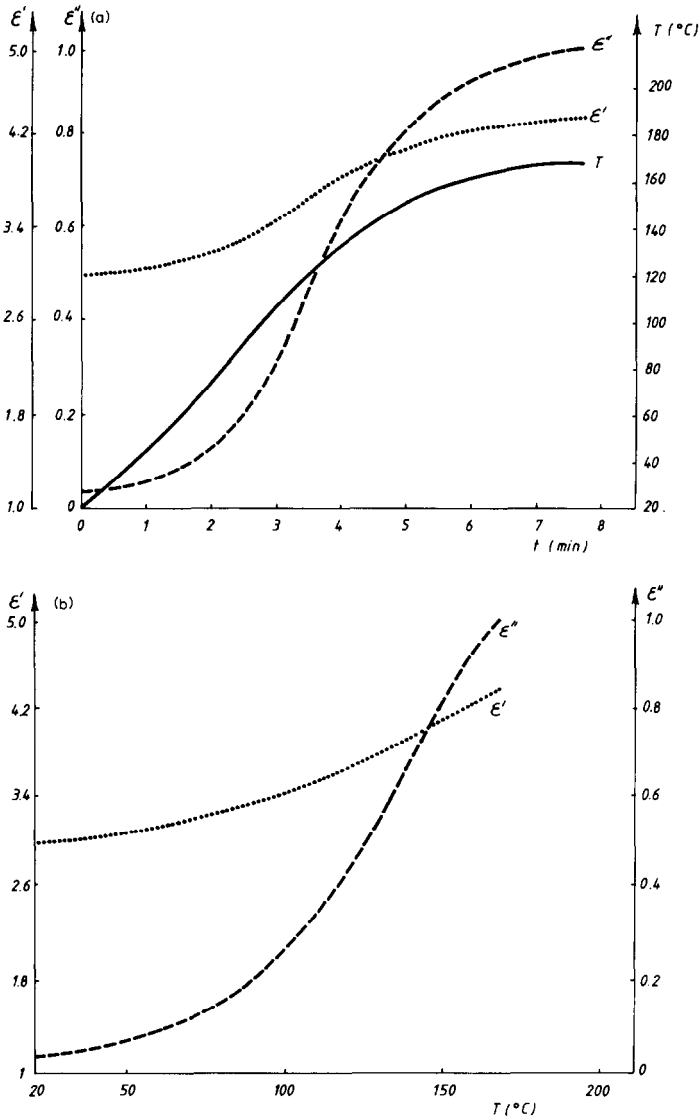
Fig. 4. Nylon sample heating. (a) Dielectric constants ϵ', ϵ'' and temperature of a 468 mg nylon sample heated by 2.43 GHz microwave irradiation as a function of time. (b) Temperature dependence of ϵ' and ϵ'' replotted from Fig 4a.

Composition changes may occur during heating by compound consumption or formation, or both. These changes may be due for instance to adsorption–desorption, decomposition, excursion in a phase diagram or chemical reaction. In these cases, both temperature and species concentrations are changing simultaneously during the experiment. As permittivity and losses of each constituent are varying with temperature during the experiment, there are too many parameter variations for the system be-

haviour to be explained with only one data set. It is necessary to collect more information on the system by varying concentrations or by studying separately the temperature dependence of the dielectric constants of each of the initial components and of the final products. Additivity of the dielectric constants should be verified in domains corresponding to the absence of reaction or composition change and only in these domains. Non-additivity may result from the existence of such processes, which can be verified a posteriori. This can be illustrated by the following examples.

Chemical reaction

Figure 5a shows the progress of curing of a two component epoxy resin sample (500 mg), made of a 1 : 1 diglycidylether of bisphenol A (DGEBA) and diaminodiphenylsulfone (DDS) mixture, during its microwave heating. Figure 5b shows the variation of the dielectric constants of the resin during the polymerization as a function of the temperature. Both figures are typical of a chemical reaction and this throws light on the polymerization mechanism.

First, the relatively high permittivity and losses of the DGEBA–DDS mixture and their rapid increase with temperature lead to rapid heating. Variations of both dielectric constants are attributed to passing through DGEBA maximum relaxation, then to the reduction of polar function contributions to dielectrical values, due to polymerization. The exothermic reaction associated with this period leads to a new rise in temperature. The last step is a general slow decrease of apparent dielectric constants and of the temperature. The slow decrease of the latter and its tendency to reach a plateau are related to the reduction of ϵ'' values. Sample temperature is determined from its energetic balance. Energy exchanged by the system (sample + sample-holder) Q_i is the sum of the energies dissipated from the transfer (dielectric losses Q_{diss}, chemical reaction Q_{chim}, and system thermal losses Q_{loss} due to optical fibre conductivity, radiation and air convection)

$$Q_i = Q_{diss} + Q_{chim} + Q_{loss} \tag{1}$$

When $Q_i \neq 0$, the sample temperature changes according to the sign of Q_i. Thus these changes depend on sample and sample-holder specific heats and masses, respectively c_s and c_h, m_s and m_h. The resulting temperature jump ΔT in $°C$ can be deduced from the energy balance by

$$Q_i = \Delta T (m_s c_s + m_h c_h). \tag{2}$$

However Q_{diss} is related to the electric field strength E_s in $V\ m^{-1}$, the sample volume V in m^3, the time t in seconds and the effective relative loss factor ϵ'' at 2.43 GHz according to eqn. (1)

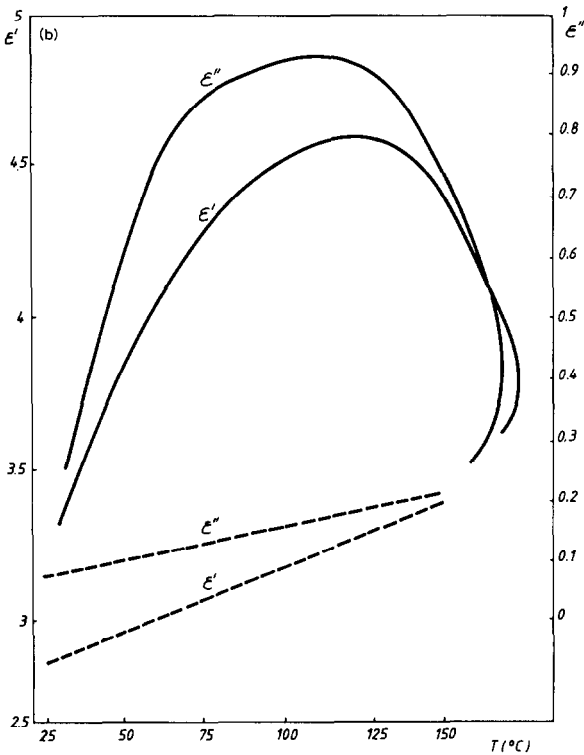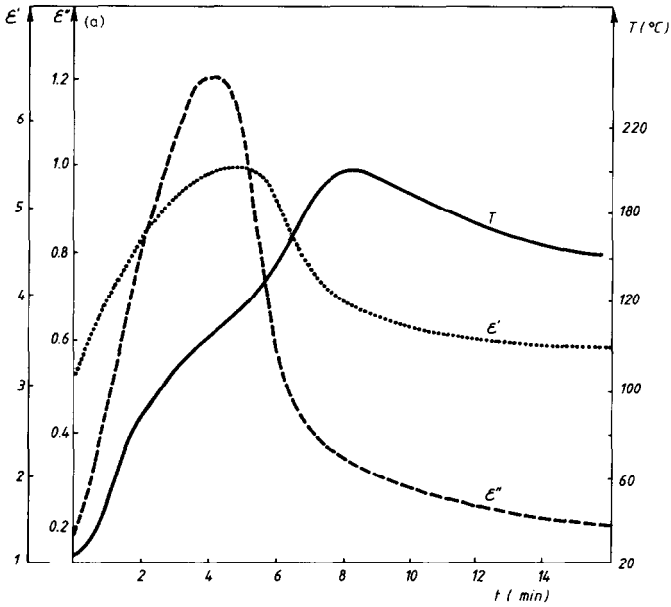$$Q_{diss} = 0.1351\epsilon'' E_s^2 V t \tag{3}$$

Fig. 5. Polymerization reaction of a two component epoxy resin. (a) Evolution of the dielectric constants and temperature of a 500 mg DGEBA–DDS 1 : 1 sample ————, second heating of the same sample, polymerization being assumed complete after the first heating - - - - - -. (b) Variation of the dielectric constants as a function of temperature deduced from Fig. 5a.

As a function of the curing process, the epoxy and amine chemical functions are consumed to a point at which $Q_{diss} + Q_{chim} < Q_{loss}$. When Q_{chim} becomes negligible, the sample temperature drops to a plateau for which the remaining energies involved equilibrate

$$Q_{diss} = Q_{loss} \qquad (4)$$

Decrease of permittivity and losses in the dielectric constants, (compared with their maxima in Fig. 5b) are typical of constituent consumption during the heating process. Moreover, the negative slopes are characteristic of an exothermic process. In such a system, assuming as a first approximation both linear additivity of the complex permittivities of constituents at any temperature and no volume change during the reaction, it is possible to sum their contributions with respect to their proportions in the mixture and determine reaction progress. For instance, in the chemical reaction $mA + nB \rightarrow pC + qD$ additivity of the complex dielectric constants leads to

$$\sum_{i=A}^{D} \epsilon_i^{\star}(T)\phi_i(T) = \epsilon^{\star}(T) \qquad (5)$$

in which $\epsilon_i^{\star}(T)$ is the complex dielectric constant of i at temperature T, $\phi_i(T)$ is the corresponding volume fraction and $\epsilon^{\star}(T)$ is the whole sample complex dielectric constant measured at T. Thus reaction progress can be followed by dielectric constants evolution.

In order to determine the temperature dependence of dielectric constants of each of the constituents, DGEBA and DDS were analysed the same way but independently, sometimes using an external heating furnace prior to recording sample dielectric behaviour during sample cooling (data not shown). After cooling, the polymerized sample was again submitted to microwave heating. The lower curves of Fig. 5b show dielectric constant variations of the cured epoxy resin, measured during this second heating. In this example, studies of the various dielectric contributions to the dielectric balance at different DGEBA/DDS ratios lead to the hypothesis of the formation of a polar intermediate complex [15].

Dehydration process

Starch and cellulose dehydrations are shown in Figs. 6 and 7, respectively, for low water content samples.

Figures 6a and 6b represent two consecutive heatings of the same cornstarch sample. In the first heating (Fig. 6a) the sample (200 mg and 10.5% water) is dehydrated to a humidity less than 0.3%, then reheated in order to measure dielectric behaviour of the dry starch (Fig. 6b). The first heating can be divided in three parts. During the first part, the starch sample is heated to about 110 °C with almost no water losses, as deduced from sample weight. There is a regular ϵ' increase in this domain, however ϵ'' passed through or reached a maximum as seen in Fig. 6c. The slow decrease of both
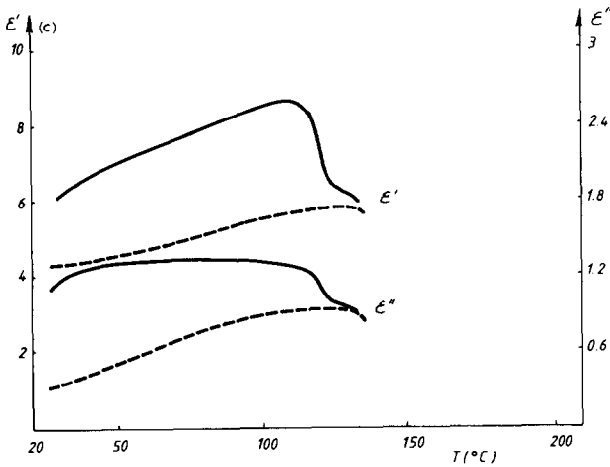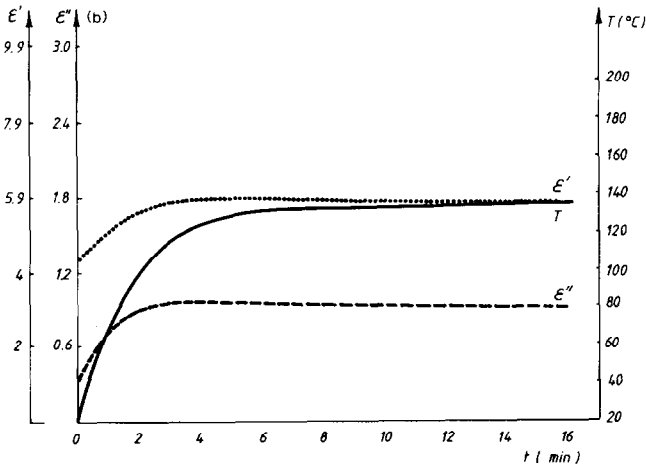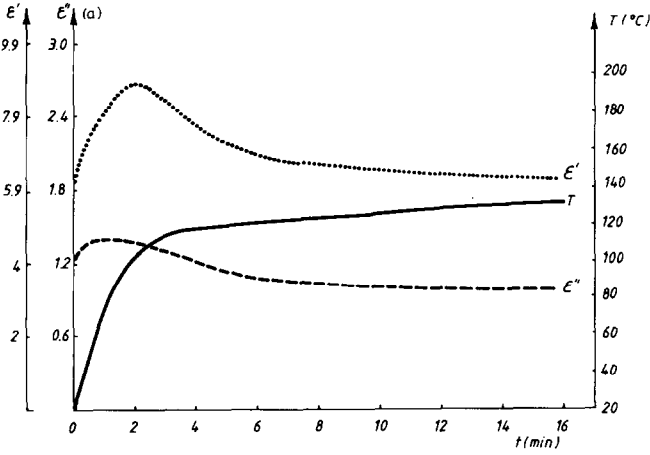
Fig. 6. Dehydration of starch. (a) Dehydration kinetic of a 200 mg cornstarch sample by microwave heating. (b) Reheating of the sample dehydrated in the experiment shown in Fig. 6a. (c) Comparison of the dielectric constants' evolution during experiments corresponding to Fig. 6a, ———; and Fig. 6b, ------.
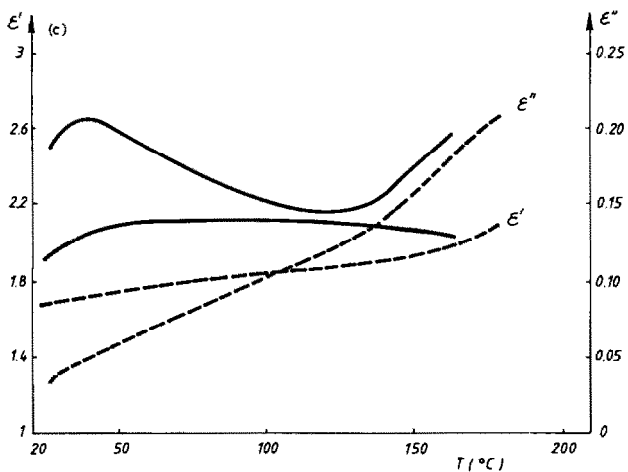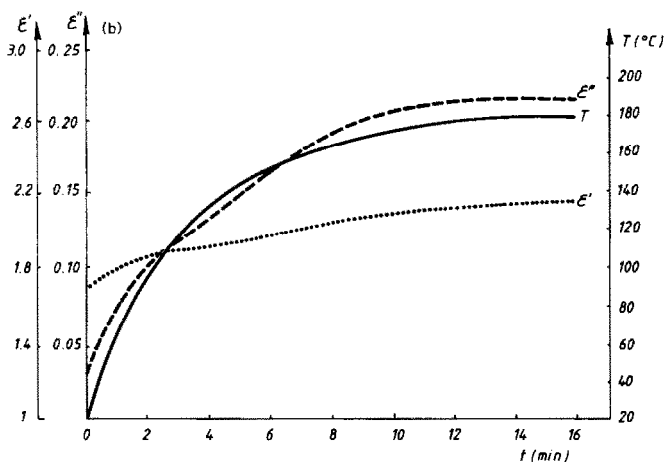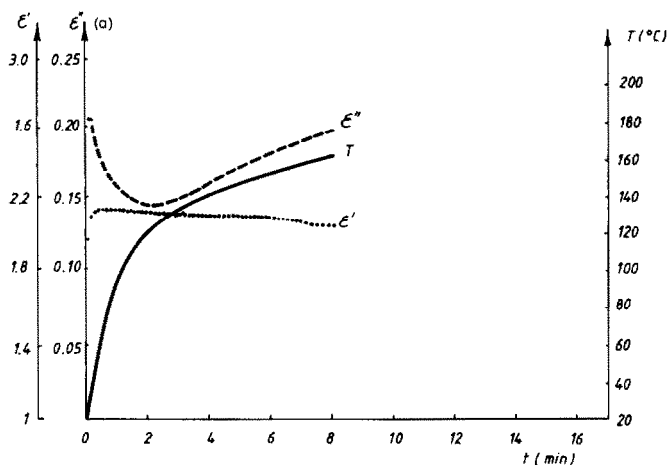
Fig. 7. Dehydration of a 6% water/cellulose sample (110 mg). For (a), (b), (c) see Fig. 6.

ϵ' and ϵ'' in the second domain corresponds to the removal of water from starch. The slow temperature increase in this part, attributed to positive thermal balance is surprising since dielectric losses in the sample are decreasing. The third part of the recording is a temperature plateau not clearly visible in Fig. 6c but clearly visible in Fig. 6b. It corresponds to a completely dried sample, then to constant values of ϵ' and ϵ''. In this domain, as seen before, the sum of the thermal losses of the sample is exactly compensated by microwave-to-thermal energy transformation due to dielectric losses. As already observed with many hydrated materials, microwave heating is a very efficient way to get them dry and the final thermal regulation observed is an insurance against overheating [18].

Comparison of the two dielectrical patterns (Fig. 6c) shows clearly that dehydration occurs mainly at temperatures over $100\,^\circ C$, when dielectric constants decrease to reach a plateau (Figs. 6a and 6c). The difference of the dielectric constant values measured before and after dehydration of the same sample is not necessarily the only contribution of water, since starch matrix dielectric constants are not necessarily identical before and after dehydration. In fact, some starch hydroxyl groups probably interact with water in hydrogen bonds which are progressively broken over $100\,^\circ C$. The hydroxyl group freedom to rotate and relax at microwave frequencies is then different when interacting with water and when not.

The ϵ'' maximum of the hydrated sample (Fig. 6c) is interpreted as relatively weak interactions of water with starch hydroxyl groups. From studies at different levels of hydration it turns out that dielectric constants are monotonically related to the water content at $30\,^\circ C$ [17]. The absence of a crystallization peak in the DSC measurement for 0–15% hydration starch samples shows that this water is unable to freeze (data not shown). Probably the distance between water molecules does not allow sufficient water–water interaction at such concentrations to permit freezing.

Experiments on cellulose (filter paper tightly rolled in a spiral inside a Teflon sample holder) lead to the thermal patterns presented (Fig. 7). As for starch, Figs. 7a and 7b show two consecutive heatings of the same sample (110 mg, 6% water) and Fig. 7c shows the dielectric constant variations as a function of heating and drying. These last, although qualitatively similar to those recorded for starch, are very dependent on the hydration level and cellulose type (data not shown). Careful analysis of the dependence on hydration indicates different degrees of water–cellulose interaction. Attempts to quantify these interactions and comparison of these results with free water DSC measurements are under way.

Relationships and complementarity of this method with more conventional thermoanalytical techniques, like DSC, which are evident from these last two examples, will be treated in more detail in a subsequent paper.

In summary, results reported above show that this method may be helpful for physico-chemical studies mainly in the two following domains. First in

order to improve dielectrical heating by the knowledge of material dielectrical behaviour, second by the fact that the measurement of dielectric properties during heating informs on dipole–dipole interaction variations of temperature dependent processes. Practically, at microwave frequencies these variations are related to polar group interactions. Therefore, the ability of this method to follow complex processes, for instance chemical reactions or water–matrix interactions during adsorption–desorption steps, makes it a relatively powerful tool for thermal investigations.

ACKNOWLEDGEMENTS

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