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USE OF LOW- AND HIGH-POWER MICROWAVE ENERGY FOR THERMAL ANALYSIS

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ABSTRACT

The possibilities of using low- and high-power microwave energy for thermal analysis are described as follows: the use of conventional heating to study the dielectric loss factor $tg\delta$ or thermal evolution of ϵ'' to characterize physico-chemical transformations; the use of microwave heating with conventional thermal analysis techniques; and the use of microwave heating and transmitted microwave power data by the loaded applicator to characterize physico-chemical transformations.

An apparatus is described and the experimental results are compared with conventional thermal analysis results. The advantages of the microwave techniques are discussed.

INTRODUCTION

When discussing less common methods of thermal analysis, it is valuable to consider the use of microwaves. Microwaves, commonly used for signal transmission in radar devices, are being increasingly used as a heating agent in industry and electric domestic appliances, hardly at all in thermal analysis.

The use of microwaves in thermal analysis methods may be considered essentially in three respects: the first consists in using a very low-power microwave source and to record the dielectric loss factor $tg\ \delta$ and/or ϵ'' versus temperature; the second is to use microwave energy as a heating agent to generate heat uniformly inside the sample and to follow any conventional thermal analysis parameter versus temperature; and the third consists in using microwave energy as a heating agent but simultaneously to follow the level of transmitted microwave power by the loaded applicator to characterize physico-chemical transformations.

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USE OF MICROWAVE TECHNIQUES WITH CONVENTIONAL HEATING FOR THERMAL ANALYSIS

The variation of the dielectric loss factor, $tg\ \delta$, or the dielectric constant, ϵ, versus temperature is studied by physicists working on electric isolators and by polymer chemists working on macromolecules. These parameters are studied over a wide frequency range, from audiofrequencies to microwaves. The thermograms show a number of dielectric relaxations which may be correlated with the structure of a polymer, the glass transition of which may be determined by this technique as with thermomechanical analysis [1,2].

Figure 1 is a typical curve showing the dielectric loss factor versus temperature. These curves may be recorded at low or high frequencies, going beyond 2.45 GHz. The evolution of the dielectric loss factor with temperature may be used to study physico-chemical transformations and to acquire valuable data that may be correlated with the structure of the sample.

USE OF MICROWAVE HEATING TECHNOLOGY WITH CONVENTIONAL THERMAL ANALYSIS METHODS

Conventional heating is efficient with good heat conductors such as metallic compounds in which thermal gradients are not very important. For bad heat conductors such as ceramics or polymers, thermal gradients are important and are proportional to the sample size. The thermal analysis

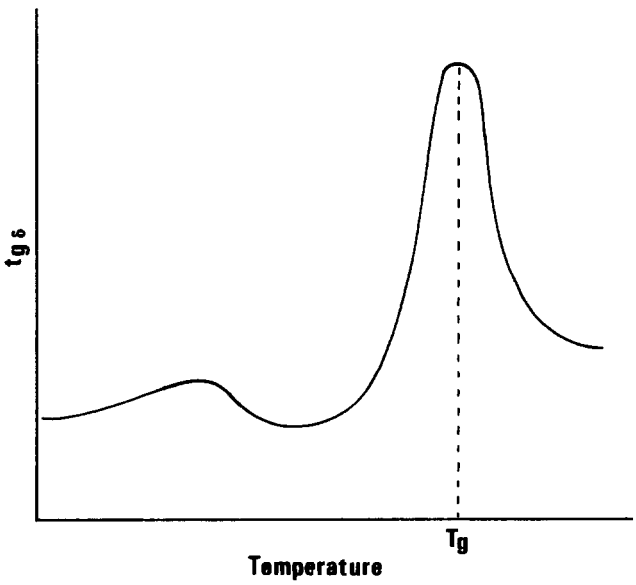

Fig. 1. Typical graph of dielectric loss factor versus temperature.

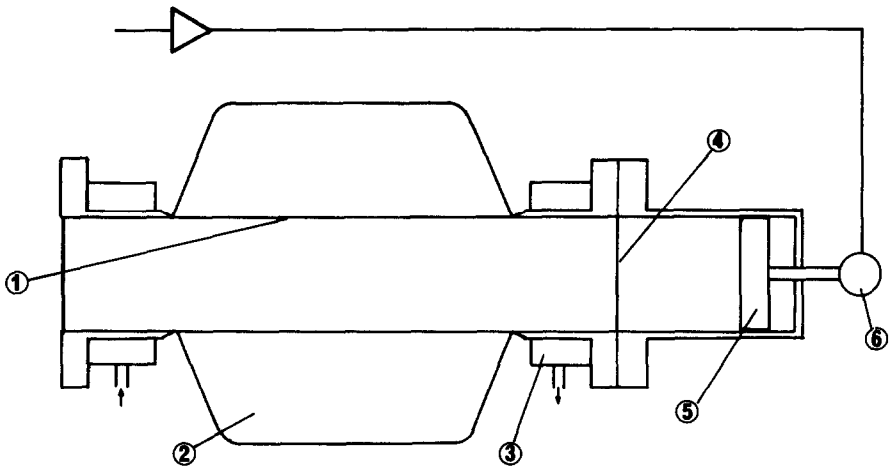

Fig. 2. Cross-section of the microwave applicator for thermal analysis. 1 = Thin stainless-steel layer; 2 = resistor furnace; 3 = water jacket; 4 = PTFE diaphragm; 5 = short circuit; 6 = micrometric motor for automatic tuning.

signals or peaks are wide because each part of the sample must reach in its turn the transformation temperature. The use of a very small sample and a high electronic amplification does not resolve the problem because, on the one hand, a very low electric signal requires a treatment that alters the information given by the signal, and on the other, too small a sample may be not representative of the material being studied.

Generating heat uniformly inside the sample may abolish conventional thermal gradients. The reverse thermal gradient due to a warm sample in a cold environment may easily be removed by controlling the waveguide temperature around the sample with a resistor heating system as shown in Fig. 2. As the waveguide temperature is the same as the sample temperature, no heat exchange by radiation or convection can occur.

THE MICROWAVE APPLICATOR FOR THERMAL ANALYSIS AT 2.45 GHz

Figure 2 shows a cross-section of a microwave applicator designed for thermal analysis. As the penetration of microwaves does not exceed 10 μm in a metal, metallization on a refractory material may be sufficient, or a very thin stainless-steel layer around the sample holder (1) (Fig. 2).

A resistor may be wound around the waveguide as a conventional furnace with its control thermocouple. Two water jackets prevent the ends of the applicator from acquiring too high a temperature and protect the PTFE or silica diaphragms (4), which simultaneously protect the power control system from sample degradation products and permit operation under a vacuum or controlled atmosphere.

Tuning of the cavity is effected continuously with a short circuit moved by a servomechanism and controlled by a microcomputer. Automatic tuning is very valuable because it ensures optimal adaptation of the cavity to the load, even if the absorption coefficient changes with temperature.

The temperature control device was described previously [3]. It allows linear heating rates, the programme being controlled by the microcomputer, which ensures data acquisition.

USE OF MICROWAVE HEATING TECHNOLOGY WITH SPECIFIC MICROWAVE THERMAL ANALYSIS TECHNIQUES

It is possible to follow the dielectric loss factor, $tg\ \delta$, or the evolution of ϵ' or ϵ'' with temperature when the sample is heated with microwaves. This may be achieved simultaneously by the same apparatus, the Dielecmetre, which is a computerized system (Sairem S.A., 22, Avenue Albert Einstein, B.P. 6043, 69604 Villeurbanne Cedex, France). This apparatus records $tg\ \delta$, ϵ' and ϵ'' from room temperature to 523 K. The heating programme and data acquisition is controlled by an Apple II microcomputer. A schematic diagram of the apparatus is shown in Fig. 3.

To study physico-chemical transformations, when the sample is heated by microwaves it is possible to follow any physical parameter versus temperature, so TG, TMA, thermodilatometry, etc., can be used, but it is also possible to follow an electrical factor, e.g., the energy transmitted by the loaded applicator. In that case, physico-chemical transformations will be indicated by very steep peaks characterizing the transformation. These peaks may be vertical and allow one to determine very precisely the physico-chemical transition temperatures.

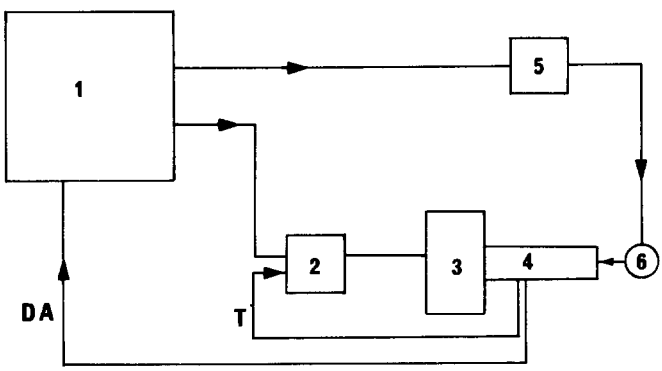

Fig. 3. Schematic diagram of the system. 1 = Apple IIe microcomputer; 2 = digital temperature comparator; 3 = microwave generator [6]; 4 = microwave applicator with circulator and power checking device; 5 = servomechanism amplifier; 6 = automatic tuning servomotor.

Following a thermal parameter, even with microwave heating, may not give so steep a peak because, although the whole sample is at the transformation temperature at the same time, there is a certain heat inertia. This phenomenon does not occur with power absorption peaks.

EXPERIMENTAL RESULTS

Results have already been published in previous papers [3–5], especially using thermodilatometry and DTA. Thermal curves were obtained on the same apparatus and at the same heating rate with conventional and microwave heating. Thermograms were compared and the advantages of microwave heating technology were discussed.

In this work only one curve will be presented for each method.

Figure 4 shows the thermodilatometric curves of a polyester resin; on the first part of the thermal curve realized with conventional heating thermal expansion is less important because only part of the material participates in expansion. This explains the shortness of the level part on the curve. With microwave heating, as the whole sample is at the same temperature, the first part of the curve shows a strong expansion, then a long level portion and a very steep fall, because the whole sample participates in shrinkage.

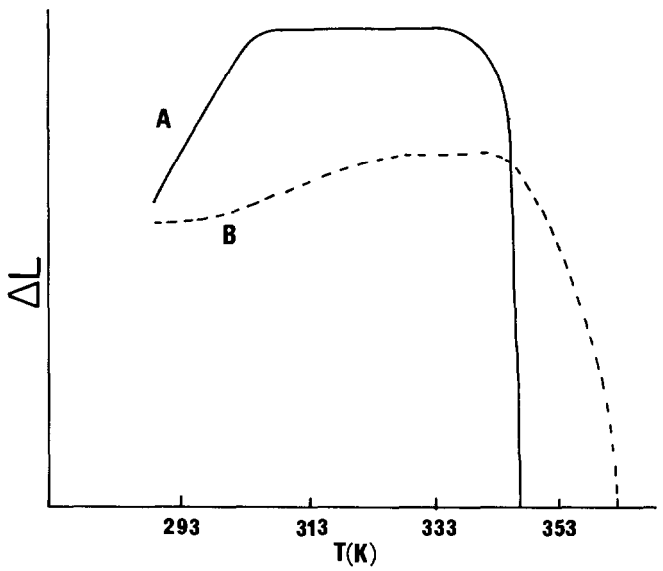

Fig. 4. Thermodilatometric curves given by an industrial polyester resin (A) with microwave heating and (B) with conventional heating, obtained with the same thermodilatometer. Heating rate, 5 K min^{-1}.

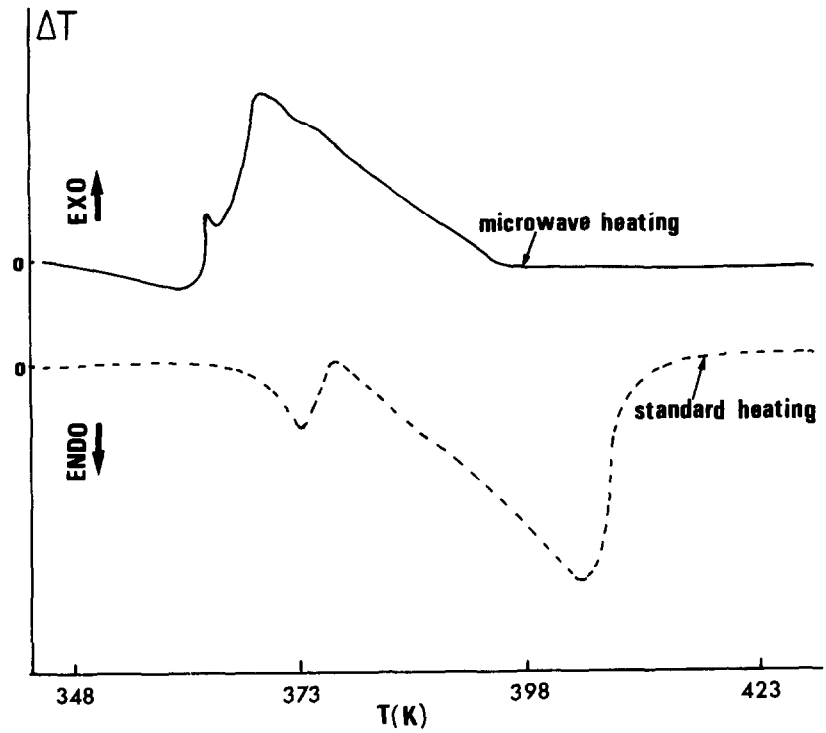

Fig. 5. Conventional and microwave heating DTA curves for $CaHPO_4 \cdot 2H_2O$. Heating rate, 5 K min^{-1}.

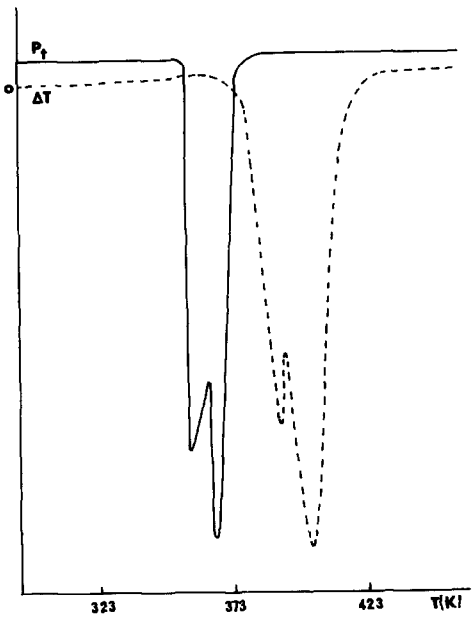

Fig. 6. Conventional DTA and microwave transmitted power curves for $(CH_3COO)_2Zn \cdot 2H_2O$.

Figure 5 shows DTA curves for $CaHPO_4 \cdot 2H_2O$. The fact that dehydration appears as an exothermic reaction means that water, after leaving the crystal, was for some time in an adsorbed liquid form before vaporization (water vapour does not absorb microwaves). Using microwaves, the dehydration peak begins more steeply and appears at a lower temperature because the whole sample is at the same temperature. The end of the dehydration peak is not steep because of thermal inertia of the sample.

Figure 6 shows the thermal curves for $(CH_3COO)_2Zn \cdot 2H_2O$ recorded by DTA with conventional heating and transmitted power versus temperature. In the latter technique, the dehydration phenomenon is indicated by a vertical peak that ends as steeply as it began, because there is no inertia in power absorption. The transformation temperature can be easily and very precisely determined without any extrapolation. A comparable precision cannot be obtained with thermal measurements.

CONCLUSIONS

The use of microwave techniques is very valuable for thermal analysis. To follow the dielectric loss factor, $tg\ \delta$, or the permittivity constants, ϵ' or ϵ'', at various frequencies versus temperature may be valuable in determining physico-chemical transformations of the sample; glass transitions may be determined by such a technique.

The use of microwave heating technology with conventional thermal analysis methods allows one to work without thermal gradients even on large samples that are perfectly representative of the studied material.

Comparison of thermodilatometric curves obtained with the same apparatus and at the same heating rates using conventional and microwave heating indicates that the apparent expansion coefficients measured with conventional heating are considerably affected by thermal gradients, and some points may be hidden. The DTA curves show that the thermal peaks are steeper and appear at lower temperatures with the same heating rate using microwave heating, and give more precise transition temperatures.

A specific microwave technique such as recording of transmitted power by the loaded cavity may give vertical peaks and allow a very precise characterization of physico-chemical transformations, which are indicated without any thermal inertia.

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