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MICROWAVES AND THERMODILATOMETRY

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ABSTRACT

In the frame of microwave studies in the thermoanalytical field, an original microwave thermodilatometer has been set up. The apparatus is described. Experimental curves recorded under conventional and microwave heating are compared for several organic compounds. It appears that transformation temperatures are evidenced generally at much lower values under microwave heating and more accurately. The example of an epoxy resin shows that Tg may be determined more quickly and more accurately under microwave heating. The example of a P.V.C. shows that some transformations which almost do not appear under conventional heating are clearly evidenced.

INTRODUCTION

In thermodilatometry, temperature gradients get very strong internal tensions in the sample, especially for bad heat conductor materials as ceramics, polymers and glassy materials. For this technique, increasing sensitivity and accuracy may be quite unprofitable above a certain level, if problems caused by thermal gradient are not solved.

In most cases, uniform generation of heat inside the material by a microwave heating, may solve the problems, and large samples quite representative of the material may be studied.

The microwave thermodilatometer set up in our laboratory provides the sample with a constant and well defined heating rate allowing very accurate measurements (ref.1).

EXPERIMENTAL SET

Sample S lies between the rear part of a silica tube and a pushrod P as shown in figure 1. An optoelectronic system (ref.2) fitted in body B is used as displacement transducer. Once the mechanical zero is adjusted with the micrometer-gauge M, the apparatus enters the wave guide, moving on slide A, till the sample is in the middle of the wave guide at a propagation distance of $\lambda/4$ (fig.1). Tuning of the wave guide is realized by a short circuit moved by the micrometer-gauge M'.

The wave guide is suited for a H(1,0) propagation mode so as to introduce a thermocouple T along the X axis as shown in figure 2.

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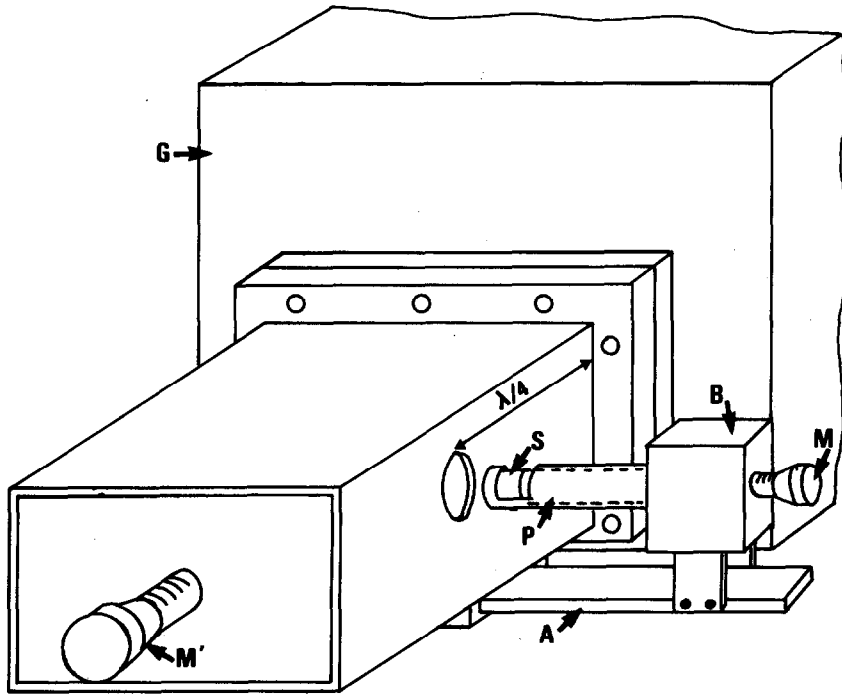

Fig. 1. External view of the microwave thermodilatometer (ref.1). A : slide ; B : body ; G : microwave generator ; M : micrometer-gauge ; M' : tuning micrometer-gauge ; P : pushrod ; S : sample.

This thermocouple is in close contact with the sample and works quite normally as published in previous papers (ref.3,4). The thermocouple T is simultaneously used to measure the sample temperature and to control the 1.2 KW microwave generator G.

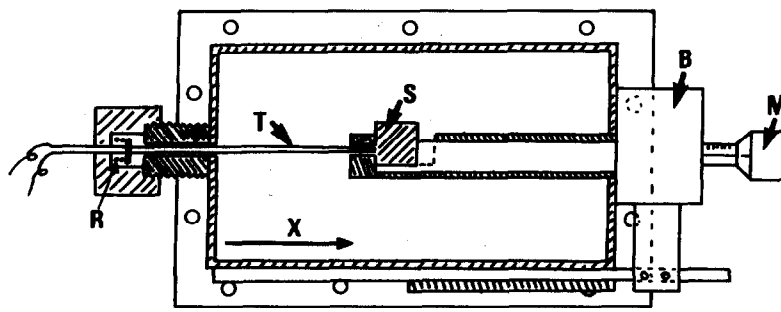

Fig. 2. Cross view of the thermodilatometer. B : body ; M : micrometer-gauge ; R : spring ; S : sample ; T : thermocouple.

A microcomputer (Apple II E) is simultaneously used to collect the thermodilatometric information, and to program the heating cycle which is submitted to the microwave power generator, by means of an electronic regulator. This apparatus provides the sample with a constant and well defined heating rate.

EXPERIMENTAL RESULTS

For each sample, thermograms are recorded with the same apparatus under conventional and microwave heating, using the same heating rates and the same heating cycles. Samples length is between a fraction of a millimeter and a centimeter (ref. 5).

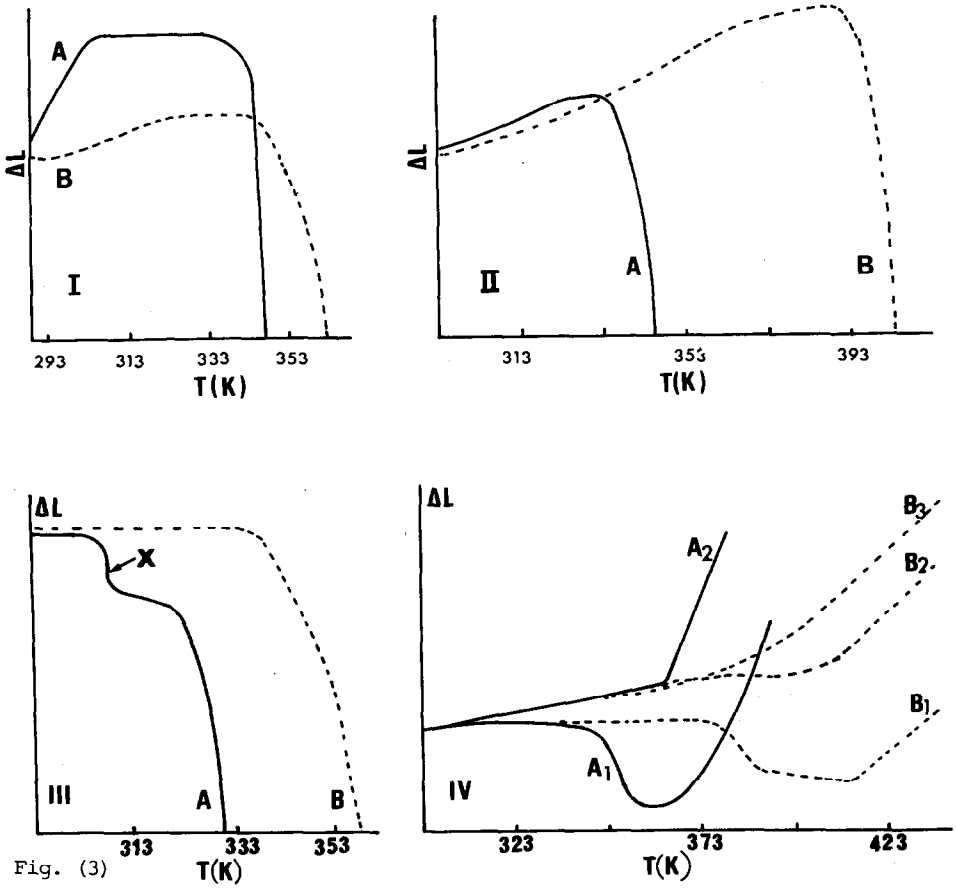

Fig. (3)

Thermodilatometric curves given by an industrial polyester resin (diagram I), a plexiglass sample (diagram II), an industrial PVC (diagram III) and by an industrial epoxy resin (diagram IV); microwave heating : curve A ; conventional heating : curve B.
I, II, III (heating rate 3.5 $K.min^{-1}$), IV (heating rate 5 $K.min^{-1}$).

Figure 3 shows the thermograms given by an industrial polyester resin. It appears that under conventional heating (curve B), this sample presents a weak expansion till 323 K, then a stable area and shrinks progressively after 340 K. Under microwave heating (curve A), the first expansion coefficient is five times higher till 300 K, then the stable area is very long and shrinkage, which begins at a lower temperature (338 K) is very fast.

Thermograms given by a commercial plexiglass (fig. 3) show roughly the same expansion coefficients but under microwave heating (curve A) shrinkage begins very early (330 K) instead of at 390 K.

Figure 3 presents the thermograms given by an industrial epoxy resin for several heating cycles at 5 $K.mn^{-1}$. It appears that for the first heating cycle (curve A_1) the shrinkage appears at much lower temperature (330 K in stead of 370 K) and this area is short.

On the second cycle under microwave heating (curve A_2) Tg is clearly evidenced at 365 K. Under conventional heating, it is necessary to realize at least three heating cycles to determine the Tg temperature, and this determination is less accurate.

Thermograms given by an industrial PVC (fig. 3) show a very long mechanically stable area (till 330 K) followed by a progressive shrinkage. Under microwave heating, the mechanically stable area is short (till 300 K) and a transformation appears clearly at 306 K (point X, curve A) when it was not discernible under a conventional heating.

CONCLUSIONS

The use of microwaves is very valuable in thermodilatometry. It appears that some specimen as polyester may have a different behaviour under a microwave heating. Generally transformation temperatures are much lower under microwave heating and better evidenced. The example of PVC shows that some transformations which almost do not appear with a conventional heating are clearly evidenced. As no error was done on transformation temperature measurements, which are much lower under microwave heating, it is not exclued that a part of the absorbed microwave energy enters under another form than heat. A work is done at the present time, considering activation energies.

REFERENCES

1. Apparatus patented by CNRS France (1984) n° 8408819
2. E. Karmazsin, P. Satre and M. Romand, Thermal Analysis, vol. 1, Proc. 7th Int. Conf. Therm. Anal., Ontario, John Wiley, New York, 1982, p. 337.
3. E. Karmazsin, R. Barhoumi, P. Satre and F. Gaillard, A.F.C.A.T. Bruxelles, Vol. X, 1984, pp. 1-10.
4. E. Karmazsin, R. Barhoumi, P. Satre and F. Gaillard, World Conference on Thermal Analysis, Amsterdam, Hollande, 4-5 juin 1984.
5. R. Barhoumi, Thesis, Lyon, France, 1984.