Thermochimica Acta, 93 (1985) 305-308
Elsevier Science Publishers B.V., Amsterdam

USE OF CONTINUOUS AND PULSED MICROWAVES FOR QUICK POLYMERIZATION OF EPOXY RESINS : STUDY OF SOME THERMOMECHANICAL PROPERTIES

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INTRODUCTION

In the frame of material science studies on polymers and vitreous materials, the use of microwaves has been introduced in the thermal analysis techniques, especially in thermodilatometry and DTA, as published in former papers [1, 2]. Thermal analytical results incite to think a part of the absorbed microwave energy enters the sample under an other form than heat [3]. Polymerization of epoxy resins and microwave absorption studies of polymerist researchers [4, 5, 6] tend to similar conclusions. In this work we study different ways of polymerization using continuous or pulsed microwaves and confront their thermal behaviour to those obtained in a standard furnace. This paper shows that the use of a low energy continuous or pulsed microwave field allows to polymerize in a couple of minutes a commercial epoxy resin, getting at least as good mechanical properties as those obtained by using a standard furnace at 373 K for an hour. Polymerizations are realized in a standard furnace or in a 2.45 GHz wave guide as described in the experimental set so as to compare thermomechanical and some mechanical properties of polymerized samples.

MEASURING METHODS

A commercial epoxy resin AY 103 and the hardener HY 991 are mixed during five minutes with an electric motor. Then, after five minutes of pause, samples are filled in 6 cm high and 1 cm in diameter teflon sample holders. For conventional heat polymerisation the sample holder is put in a 373 K furnace for an hour and for microwave polymerization the sample is put in a 2.45 GHz TE_{10} wave guide at ambiant temperature as shown in figure 1.

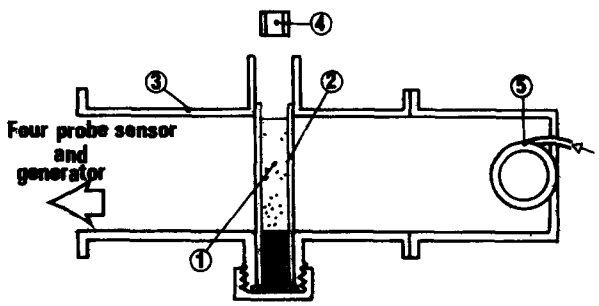

Figure 1 - Cross view of the applicator.
1 : Sample ; 2 : Teflon sample holder ; 3 : Wawe guide ;
4 : Optical pyrometer , 5 : Matched water load.

The microwave generator is a 2.45 GHz pure spectrum, 0 to 5 Kw SAIREM* generator, which delivers a continuous or a pulsed energy from 1 to 10 KHz an adjustable cyclic ratio. Temperature of the sample is measured by an optical

Proceedings of ICTA 85, Bratislava

pyrometer (figure 1) or a thermocouple [2]. Thermomechanical curves are recorded with an optoelectronic thermodilatometer published in a former paper [7].

RESULTS AND DISCUSSION

Figure 2 shows thermodilatometric curves under continuous and pulsed microwave energy. Temperature increases at first slowly,then polymerization begins and increases temperature till a maximum (about 328 K). Under continuous microwave energy a slope change appears (A, curve 1) which we have not observed under 10 Hz pulsed energy. As the cyclic ratio is 50 %, 150 W pulsed energy correspond to 75 W of continuous microwave energy. This fact explains that the peaks maxima are observed at the same time (210 seconds) for both the samples and that the maxima temperatures are also the same (about 343 K). Maximum temperature does not correspond to the end of reticulation, but as this reaction slows down, heat production decreases. It looks that the maximum B of the peaks shows the gel point of the material which reduces the dipolar structures mobility, and consequently absorption of microwave energy. Finally, temperature stabilizes for a value at which all the absorbed energy is dissipated as heat to the environement.

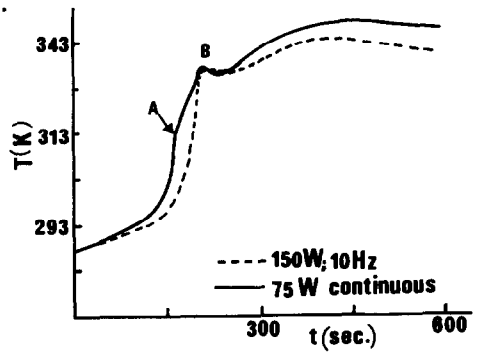

Figure 2 - Temperature versus time curves of an epoxy resin under continuous and pulsed microwave energy.

Thermodilatometric curves shown on figure 3 are got for a continuous 150 W pulsed microwave energy. The shrinkage magnitude increases with frequency : 0.22 % for 100 Hz, 0.60 % for 1 KHz and 0.83 % for 5 KHz ; the level parts length L follows the same order. Finally the expansion coefficients of the last part of the curves are the same ($\alpha = 200.10^{-6}\ K^{-1}$). These considerations incite to think that polymerization and reticulation are at a higher level for a lower frequency. Figure 4 confronts the thermodilatometric curves of the same resin polymerized in a standard furnace at 373 K for an hour (sample 1), in a continuous microwave field of 75 W during 600 seconds (sample 2) and in a 100 Hz pulsed microwave field of the same global energy during 600 seconds (sample 3). It appears that the sample 3 has only 0.22 % of shrinkage, the sample 2 has 0.32 % and the sample 1 has 0.39 %. These curves tend as the former ones to prove that the state of polymerization and reticulation is higher for the sample cured at 100 Hz pulsed microwave energy.

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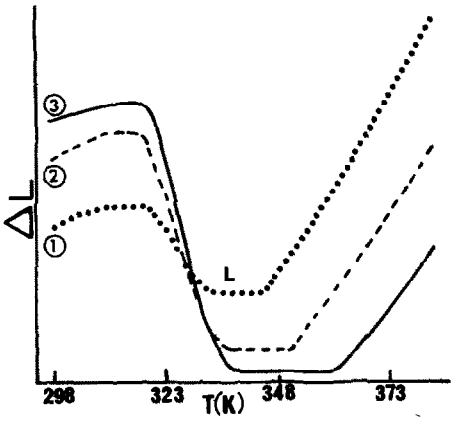

Figure 3 - Thermodilatometric curves of an epoxy resin polymerized in a pulsed microwave field of 150 W. 1 : 100 Hz ; 2 : 1 KHz ; 3 : 5 KHz.

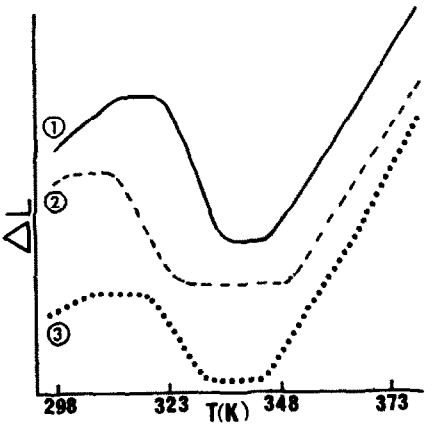

Figure 4 - Thermodilatometric curves of the resin polymerized in a standard furnace at 373 K for one hour (1), in a continuous 75 W microwave field (2), and in a 100 Hz pulsed microwave field (3).

Table I - Comparison of Young modulus and Tg values of an epoxy resin polymerized by different ways.

P(W)	t(sec)	F(Hz)	*E($N.mm^{-2}$)	**Tg(K)
Pulsed microwave field				
150	600	100	502	325
150	600	1000	513	323
150	600	5000	518	326
Continuous microwave field				
75	600	Continuous	567	324
50	600	Continuous	437	312
Standard heating (373 K for an hour)			535	325

* determined with a JJ LOYD APPARATUS ; ** determined with Mettler TMA 40.

According to table I and measurements precision, it looks that the Young Modulus of the samples are all of comparable magnitude. Only the sample polymerized under continuous 50 Watts microwave energy looks to have a lower value for Young Modulus and Tg. The sample polymerized under 75 Watts of continuous microwave, looks to have the highest Young Modulus and the same Tg as the other samples.

CONCLUSION

The use of microwaves for quick polymerization of epoxy resins is valuable. Thermomechanical behaviour of the samples depend of the frequency of pulsed microwave energy. Tg values of the samples are of the same magnitude. Thermodilatometric curves tend to show that the sample polymerized 600 sec. in a 100 Hz pulsed microwave field has the best behaviour. The Young Modulus of the sample polymerized 600 sec. in a 75 W continuous microwave field is more than 10 % higher than the Young Modulus of the same resin polymerized at 373 K during an hour in a conventional resistor furnace. This work is going on to do a systematic study according to microwave pulsed frequencies and cyclic ratio on a great number of samples.

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