

Polyurethane curing by a pulsed microwave field

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The complete study of the crosslinking of polyurethane resins by means of a pulsed microwave field has been made, in order to describe the energy transfer processes in polymer films and to optimize the transfer efficiency. Experimental data show the energy transfer can be strongly enhanced by using specific pulse repetition frequencies which correspond to dielectric relaxation of polar structural elements in polymers. Moreover, the hardness of cured films can be also correlated with this pulse frequency specificity.

(Keywords: dielectric heating; curing; microwave; polyurethane coatings; pulsed microwaves)

INTRODUCTION

Few fundamental data are available on the polycondensation and the hardening of thermosetting polymers by microwaves. Some papers only report on the crosslinking of epoxy resins, unsaturated polyesters or polyurethane systems under 2.45 GHz electromagnetic radiations.

Gourdenne and coworkers¹ studied the crosslinking of the diglycidyl ether of bisphenol A (DGEBA) with 4,4'-diaminodiphenylmethane (DDM), and of a maleic anhydride-phthalic anhydride-propyleneglycol polyester with styrene. They proposed a quantitative interpretation for the variations of temperature *versus* time, which led to simulated curves that fit reasonably with the experimental curves. These authors showed that the same crosslinking process is also convenient for polyurethane systems² and epoxy-glass fibre composites³. A further step in this approach was made by analysing the time dependence of the electrical power degraded as heat by dielectric losses inside the samples, in DGEBA-DDM epoxy resins⁴ and in epoxy-glass fibre composite systems⁵.

At the same time, we described the formation of glass-supported polyurethane films^{6,7} when exposed to a 2.45 GHz microwave electric field, in a wave guide, studying temperature *versus* time variations recorded by means of an infra-red pyrometer. However, in the complete estimation of the film formation process, the thermal contribution of both solvent and substrate had to be considered, as well as the exothermicity of the polycondensation reaction. The study of the thermal behaviour of poly(vinyl acetate) or styrene solutions in polar or non-polar solvents, settled in PTFE plates (as a non-polar material, without dielectric losses, and thus thermally inert in a microwave field) showed that in such conditions the nature of polymers was the dominant parameter for the thermal evolution of polymer solutions. Thus, the dielectric relaxation losses of structural elements in

polymers were the main parameters in the heating process.

Considering thermosetting prepolymer mixtures, such as epoxy resins or polyurethane systems before hardening, the dielectric losses are partly or totally brought about by the polar functional groups which operate the crosslinking reaction. Thus we now have to examine whether, in addition to the thermal effect of microwaves, the oscillating electric field intensity has a specific influence upon the polar functional groups, and thus upon the chemical reaction itself. To investigate this phenomenon, it is necessary to compare the effects of microwaves with a variable electric field intensity as a parameter, but with a constant mean power level, so that the electrical energy transferred to the material remains constant. Thus the differences which occur in the thermal behaviour and for the final qualities of cured materials can be attributed to the influence of electric field variations on the chemical reaction.

An experimental mean to obtain this result consists of using pulsed microwaves with different pulse regimes, but with a constant average power: thus the electric field intensity is a function of the peak power, which is determined by the pulse procedure which is explained in *Figure 1*. Procedure 1 is a continuous wave, the microwave power of which is fixed at a unit level 1; procedures 2 and 3 are typical pulsed regimes, both with the same period, and also the same average power as the continuous wave 1.

When the average power is fixed at a given value, there is an infinite number of pulse regime possibilities, which are only limited by the maximum power of the generator (3 kW). The results can then be presented in two ways: as a function of pulse period, and as a function of peak pulse power.

Two different series of experiments are reported here. Firstly, we studied the thermal behaviour of polyurethane resin formation from a polyisocyanate-polyalcohol mix-

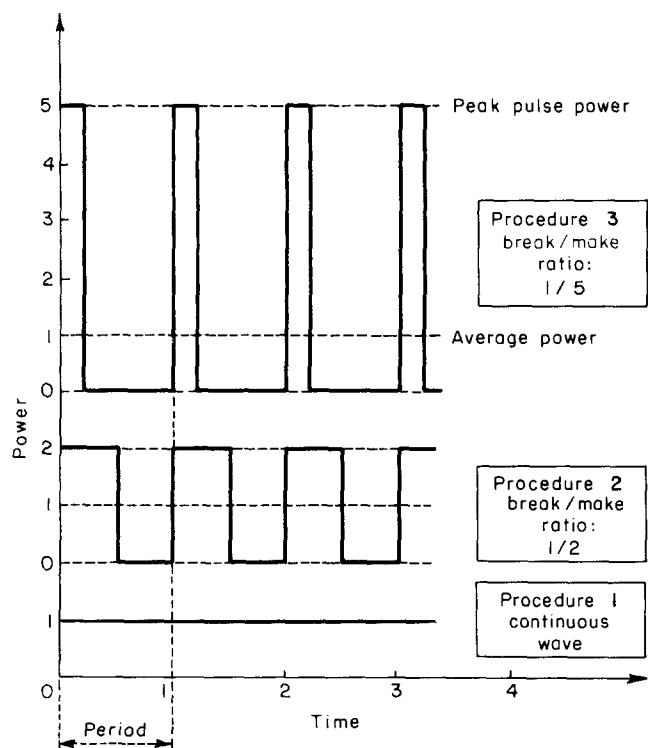


Figure 1 An example of 3 pulse procedures with the same average microwave power transferred to materials

ture; then we examined the formation of polyurethane coatings from the same mixture, studying the film hardness as a function of different pulse regimes.

EXPERIMENTAL

Polyurethane resin formation

The material studied was an ethyl acetate 75% solution of the stoichiometric mixture of two prepolymers: a triisocyanate Desmodur L75, and a polyester-polyalcohol Desmophen 800.

In order to cancel the substrate effect, the prepolymer solution was poured in hollowed PTFE plates. PTFE is a non-polar material without dielectric losses, so that its contribution to microwave heating is negligible. Every sample bearer was the same size, including the hollow in the PTFE plate, and the amount of solution was weighed (1.4 g). Thus all the samples were identical in shape and volume, so that the microwave cavity filling factor only varied as a function of the complex dielectric constant in the evolved material.

As shown in Figure 2, the experimental set-up included:

- (i) a microwave generator (2.45 GHz, 3 kW), provided with an auxiliary pulse generator and a d.c. generator for power level adjustment;
- (ii) a circulator to protect the microwave generator from reflected waves;
- (iii) a crystal detector associated to an oscilloscope in order to control pulse time and period;
- (iv) a tunable resonant cavity with, just above the sample bearer, an aperture through which a non-interferent fluorescence temperature sensor was settled. The cavity was closed with an adjustable short-circuit, in order to transfer the maximum of microwave energy to materials.

By means of an optical fibre, the temperature sensor

transmitted the information to a digital thermometer (Luxtron Fluoroptic 1000 A), connected to a recorder which was run at the same time as the microwave generator, in order to draw temperature versus time curves.

In these series of experiments, the microwave average power was 30 watts; the peak pulse power was varied from 200 to 2500 W, the pulse period from 2 to 200 ms so that the pulse time was varying from 50 μs to 30 ms.

Microwave cured film hardness

In order to correlate our results with a physical property of the microwave cured materials, another sort of experimental procedure was necessary, in which the same prepolymer mixture was used. The procedure consists of spreading 300 μm thick films over 75 × 25 mm quartz plates, and to cure the films in the same resonant cavity as above. However, the experimental set-up was modified as shown in Figure 3. The fluorescence temperature sensor failed to measure the temperature inside a film, so the surface temperature of the film was measured using an infra-red pyrometer.

The volume of organic materials being very small, it was necessary to increase the average microwave power to 150 W to attain a similar temperature range. Every sample has been cured for the same time, i.e. 5 min. The peak pulse power was varied from 250 to 2500 W, the pulse period from 2 to 200 ms, so that the pulse time was varying from 0.15 to 120 ms.

Film hardness was measured by means of a Persoz pendulum. Two identical samples were necessary to do

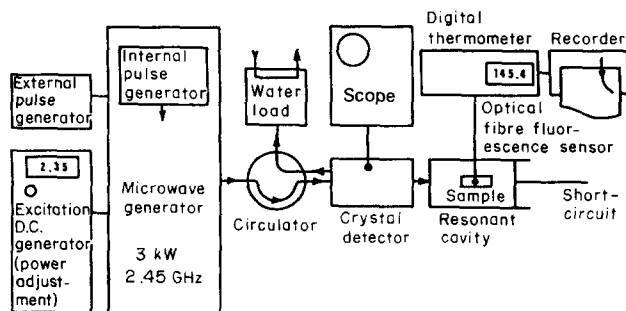


Figure 2 Scheme of the experimental set-up. Optic fibre thermometer

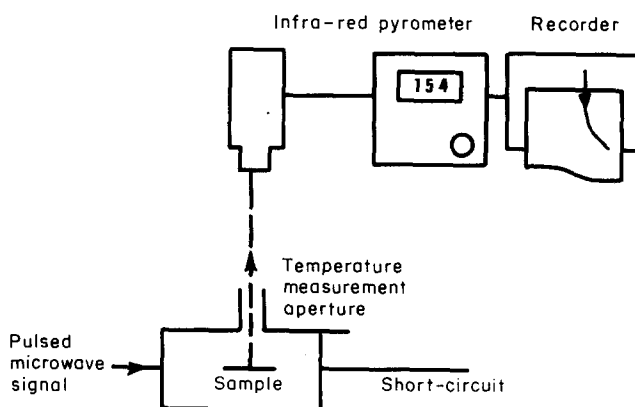


Figure 3 Modification of the experimental set-up for film hardening: infra-red pyrometer

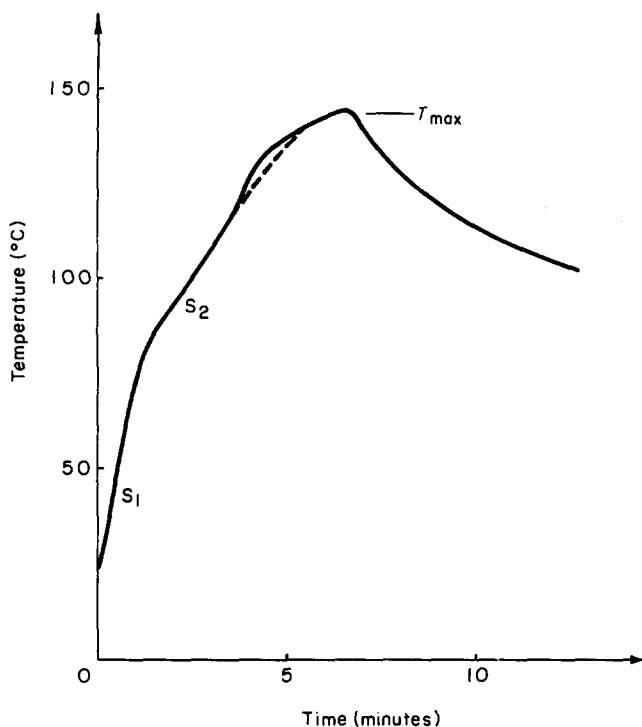


Figure 4 Typical diagram of the time dependence of temperature in pulsed microwave cured polyurethane samples

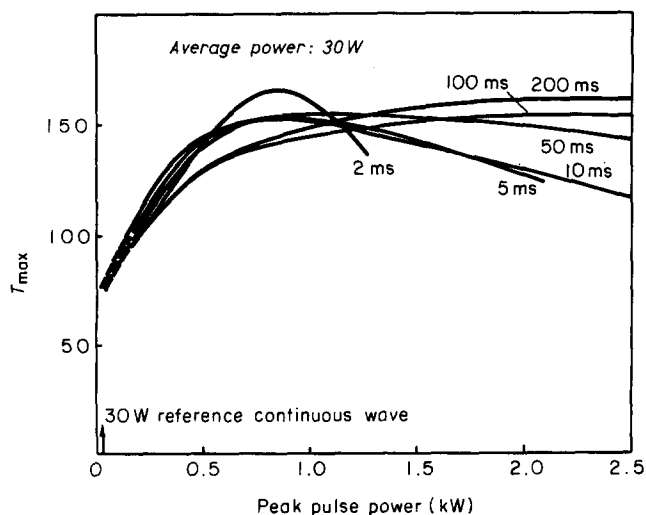


Figure 5 Peak pulse power dependence of the maximum temperature T_{max} . Second parameter: pulse period

one measurement. Hardness is given as the pendulum damping time from a 12° to a 4° oscillation amplitude.

RESULTS AND DISCUSSION

Thermal behaviour

In Figure 4, a typical diagram of the sample temperature time dependence is shown. The first and second phases, S1 and S2 respectively, are quite linear variations, mainly associated with sample heating and solvent evaporation. The perturbation which appears near 120°C–140°C is due to the initiation of the exothermic polycondensation reaction. The reaction consumes the polar functional groups and the dielectric losses in sample are therefore decreasing, so that a maximum temperature T_{max}

is observed. Then the crosslinking reaction is completed while the temperature slowly decreases.

As parameters such as T_{max} , S1 and S2 vary similarly with peak microwave field intensity or pulse repetition time, we decided to keep the parameter T_{max} as the main thermal characteristic of the interaction between field and material.

In Figure 5, the variations of the maximum temperature T_{max} with peak power are reported where each curve is related to a pulse period. All the curves are issued from the same point (on the left side), corresponding to the reference continuous wave: power 30 W, T_{max} 70°C. Starting from this point, T_{max} always increases with pulse power. It can already be concluded that the energy transfer by pulsed microwaves is more efficient than by an energy equivalent continuous wave value (in degrees Celsius).

Nevertheless, related to pulse period, two possibilities are observed. For long periods (100 and 200 ms) also corresponding to long pulse times, T_{max} is continuously increasing with peak power; for shorter periods (≤ 50 ms), an optimum value, about 800 W, appears for peak power, so that an optimum value also exists for the electric field intensity (which varies as the square root of power). The thermal effect is then at a maximum, whatever the pulse period and pulse time are. Pulse time only controls thermal effect amplitude, particularly for the 2 ms period which corresponds to the optimum value of T_{max} in this peak power region.

The pulse period dependence of T_{max} is represented in Figure 6, where each curve is related to a peak pulse power value as a second parameter. For high pulse periods, for instance 200 ms, microwave thermal effect regularly increases with electric field intensity. When pulse period is decreased, a particular type of behaviour occurs: over the critical value of 800 W (already noted as a critical value in Figure 5), all the curves intersect at the same point (pulse period 70 ms, T_{max} near 150°C), at which the microwave thermal effect is identical whatever the peak power values (i.e. of electric field intensity) and pulse time. This is characteristic of a low frequency dielectric relaxation, which could be associated with an α relaxation, related to the movements of chain segments in the macromolecular network. Such a relaxation, observed in polymers by

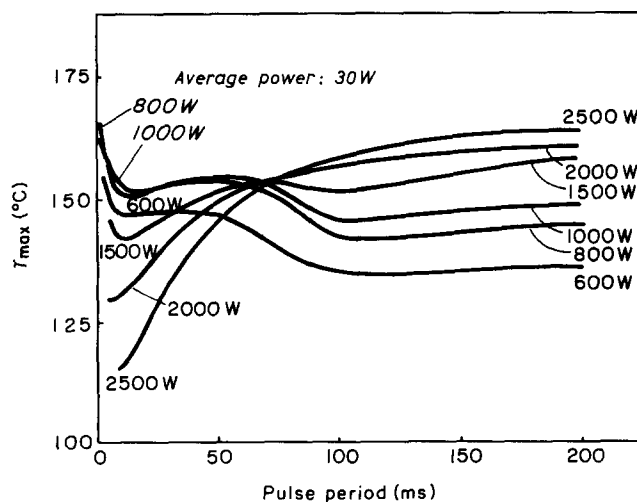


Figure 6 Pulse period dependence of the maximum temperature T_{max} . Second parameter: peak pulse power

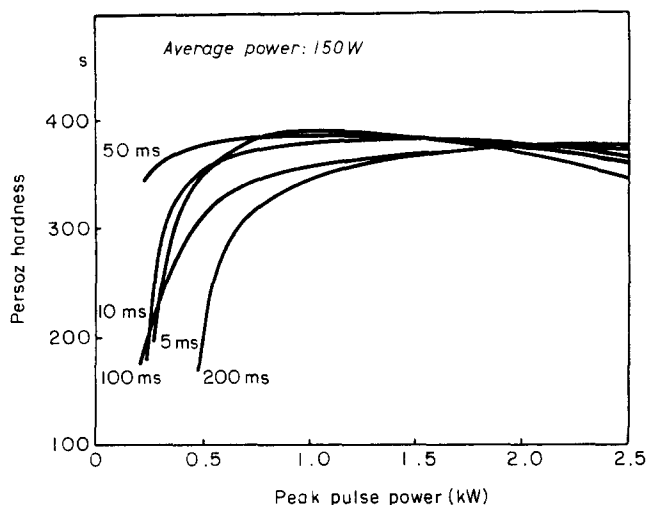


Figure 7 Variations of the Persoz hardness of polyurethane films with peak pulse power. Second parameter: pulse period

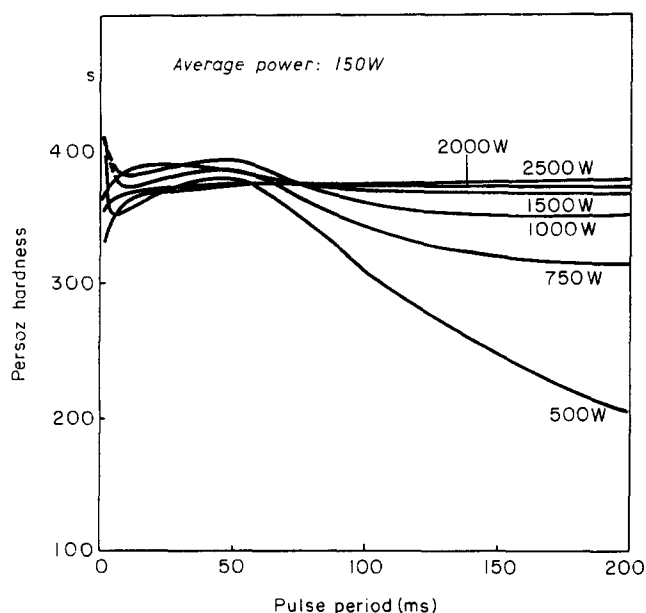


Figure 8 Variations of the Persoz hardness of polyurethane films with pulse period. Second parameter: peak pulse period

many authors⁹, excited by low frequency oscillating fields, would be excited by the microwave pulse modulation.

Moreover, for pulse repetition under 10 ms, almost every curve is raised up and a second relaxation may be expected at very low periods. These high frequency relaxations could then be related to the movements of small macromolecular regions, as functional groups for instance (β relaxation). The experimental device does not allow us to attain this fast pulse region.

Film hardness

Similar diagrams were drawn showing the variations of Persoz hardness in pulsed microwave cured polyurethane coatings with peak pulse power (Figure 7) and with pulse period (Figure 8). In Figure 7, it appears, as in Figure 5 for T_{max} , that hardness is an increasing function of peak pulse power, without a maximum for high pulse period (100 and 200 ms) and with a maximum for 5, 10 and 50 ms. However, the peak power value corresponding to this maximum is near 1200 W, rather than 800 mW. That

means the applied electric field at this point is somewhat higher than for the T_{max} curves. However, considering that we have already mentioned that the film thickness for the hardness experiments is lower than for thermal experiments, it is necessary to apply a larger electric field for thinner films to have the same internal field in both hardness and thermal experiments. In other words, if we were able to present data as a function of the internal microwave field, both curve maxima should be very similar.

In Figure 8 (as for T_{max} in Figure 6, for high pulse period values) hardness is found to increase with electric field intensity for peak pulse powers over 750 W. All the curves also intersect at the same point (pulse period 75 ms, hardness 375 s) which is very close to the same point for T_{max} versus pulse period. For lower pulse periods than 75 ms, the most efficient peak power values are 1500 W and then 1000 W. Lastly, for very low pulse period values, hardness and T_{max} are again raised, and the most efficient peak pulse power value would be about 750–1000 W. But the temperature is then too greatly increased, so destroying the coatings.

Moreover, we generally observe that microwave cured films are harder (370–380 s) than oven-cured films (generally 340–360 s). In the most efficient conditions (1000 W–50 ms, or 500 W–2 ms for instance), very high hardness of about 400 s can even be obtained. In Figure 9, hardness values are reported versus T_{max} . Although film hardness is generally an increasing function of temperature, nevertheless it is clear that there is no direct correlation between hardness and temperature, and this was confirmed by linear or quadratic regression computerized calculations. Some pulse regimes clearly appear to give very hard films, though they are cured at middle temperatures of 130°C–175°C, while, inversely, curing temperatures over 175°C give middle hardened films (near 360 s).

It is now clear that, using pulsed microwaves, two parameters have a particular effect on polyurethane hardening reactions. Peak pulse power has an optimal value of about 750–1200 W, which depends on the geometrical shape of samples, so that there is also an optimum value for the electric field, which is proportional

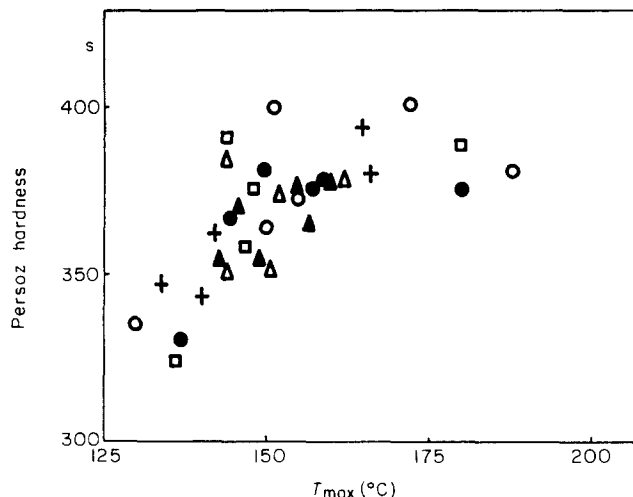


Figure 9 Temperature dependence of the Persoz hardness of pulsed microwave cured polyurethane films. No correlation is found. (Peak pulse power: +, 500W; □, 750W; △, 1000W; ○, 1500W; ▲, 2000W; ●, 2500W). Average power 150W

to the square root of the peak power. This value is a threshold used to obtain a particular dielectric relaxation for the period 70–75 ms (13.3–14.3 Hz), which can be interpreted as a low frequency relaxation related to the movements of macromolecular chain segments. The pulse period is the other parameter influencing the polymer thermal behaviour, and *Figure 8* shows that, for lower values of pulse period, high film hardnesses can be obtained with the optimal peak pulse powers of 750–1000 W.

Moreover, high curing temperatures and high film hardnesses can also be obtained for very low pulse periods, close to our experimental limits (2 ms and under). Further experiments are now in progress to investigate this domain.

CONCLUSION

Under precise experimental conditions for peak pulse power and pulse period, we have clearly shown that a pulsed microwave electric field acts upon the hardening reaction of polyurethanes. Thermal kinetics, film hardness and thus macromolecular networks are influenced, so that microwave cured polyurethane films, which are very much harder than oven cured materials, can be obtained. However, another important question is: is the resulting hardness only due to a farther completion of the hardening reaction, or to a different structure for polymer? At the moment, no answer can be given to this fundamental

question, however, work is in progress which may enable us to do so.

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