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SYNTHESIS UNDER MICROWAVES (2.45 GHz) OF POLYURETHANE POLYMERS—I

MODEL STUDY FROM DIISOCYANATE AND POLYETHERTRIOL PREPOLYMERS

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Abstract—Microwave (2.45 GHz) activation of crosslinking reactions of polyurethane resin, including diisocyanate and polyethertriol prepolymers, is described. All samples of polymerizable material are placed inside a wave guide where the waves propagate in a progressive TE_{01} mode. Step-growth reactions are followed through variations with time of the temperature and dielectric loss. A complete model study at given electrical power (P_o) is presented; liquid–liquid (fluidification) and sol–gel transitions are found. The P_o dependence of the rate of conversion is also discussed.

INTRODUCTION

It has been reported [1] that polyurethane prepolymer resins in bulk can be polymerized under microwaves at 2.45 GHz: the conversion to heat of the dielectric loss due to dipolar relaxation of the chemical species is used to thermally activate the cross-linking reaction. Three steps were found in the process, viz. preheating, exothermal conversion and cooling. The electrical power dependence of the rate of conversion was presented: as the power increases, the condensation is faster just as the intensity of the maximum is the highest. More recently, a systematic study of curing of polyurethane films by a pulsed microwave field has been published [2]; such an electromagnetic treatment shows itself more efficient towards the rate of crosslinking. No reference to the variations of the associated dielectric loss was presented in this work, as in the previous work. In this publication, our aim is to correlate the variations of the temperature to those of the dielectric loss which is better connected to the chemical and physical structures of the polymerizing medium, more especially as we have a quantitative microwave bench which provides data on the temperature and the dielectric loss at the same time [3].

EXPERIMENTAL

The microwave apparatus used for this study has been previously described [3] but a few details will be given here. The propagation model of the waves is TE_{01} where the electrical field is polarized in a direction parallel to the small side of the waveguide where they are forced to propagate. All samples of liquid polymerizable matter are poured into small Pyrex-glass pill-boxes which are placed inside the guide for electromagnetic treatment. The average temperature (T) of the samples is determined with a thermocouple perpendicular to the electrical field and various electrical powers are measured along the line through wattmeters viz. initial (P_o), transmitted (P_t), reflected (P_r) and absorbed by the pill-boxes and the walls (P_a). The dielectric loss (P_u) inside the samples is easily deduced:

$$P_u = P_o - (P_t + P_r + P_a)$$

No stationary wave system takes place since (P_t) and (P_r) are absorbed with load charges.

The variations with time of $T = T(t)$ and $P_u = P_u(t)$ are stored in a computer, and the derivatives $(T)' = dT/dt$, $(P_u)' = dP_u/dt$ are then calculated.

Some measurements of the viscosity at different temperatures of the prepolymer are carried out with a Brookfield viscometer—Mode RVJ—with calibrated spindles. The viscosity values are given in centipoises (Cp).

The resin mixtures consist of two components: the first, called Desmodur VL from Bayer, is a diisocyanate derived from diphenyl 4,4′-methane diisocyanate homologues with a weight percentage of $-N{=}C{=}O$ functions of 31% (our experimental value = 31.4%); the second is a low viscosity polyethertriol commercialized by Shell Chemicals as Caradol 555-1 containing 17% of hydroxyl groups and with an average molecular weight of 300 g/mol. The mixing of the two components does not present any problem: the polyethertriol is added in stoichiometric ratio 1:1 at room temperature with no phase separation. No catalyst is used. All samples are then degassed under primary vacuum, and stored at −15° for up to a day before microwave treatment.

RESULTS AND DISCUSSION

Figure 1 collects the four curves $T = T(t)$, $P_u = P_u(t)$, $(T)' = dT/dt$ and $(P_u)' = dP_u/dt$ for a sample of 20 g of polymerizable material submitted to an average electrical power P_o of 50 W. The recording of the temperature (Curve 1) and power (Curve 2) parameters starts as soon as T reaches the zero value which is used for reference.

The T curve can be divided in three parts, each corresponding to a step of a condensation reaction, viz. preheating of the resin, exothermal conversion and cooling period. Its shape is very similar to that of the temperature curve for thermally activated

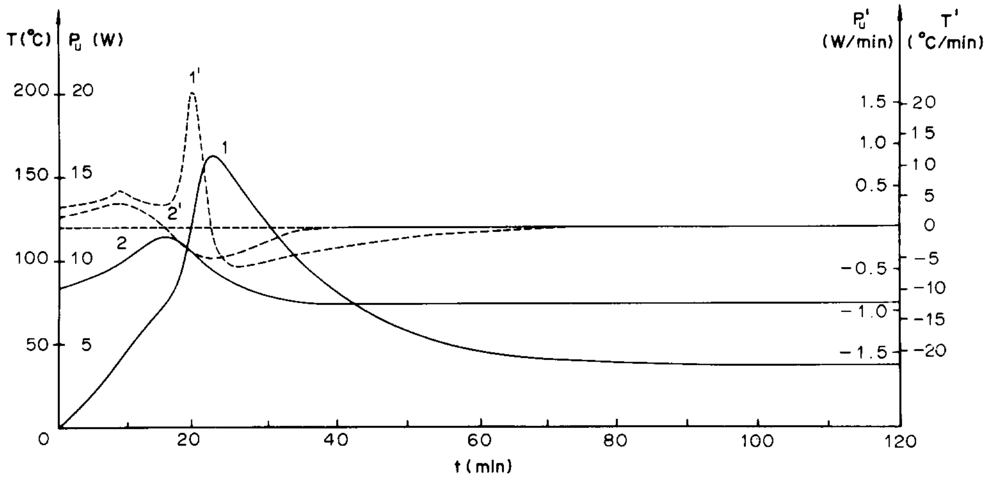

Fig. 1. Model study of the crosslinking reaction of the polyurethane resin at $P_o = 50$ W. (1) $T = T(t)$; (1′) $(T)' = dT/dt$; (2) $P_u = P_u(t)$; (2′) $(P_u)' = dP_u/dt$.

curing of polyurethane in an oven at 60° (Fig. 2). The microwave *T* curve can be described at lower level by analyzing its progress little by little and resorting to the variations of the $(T)'$, P_u and $(P_u)'$ functions. The temperature goes up from zero because of the conversion to heat of the dielectric loss due to dipolar relaxation. Now, since the Brownian motion is increased, P_u is enlarged and more and more heat is produced leading to acceleration of dipolar relaxation, and so on. $(T)'$ and $(P_u)'$ are proportional to the rates of heating of the samples and of dissipation of electrical energy with short intervals of time and the sense of their variations provides information on the structural changes in the organic mixture. Always inside the first step, *T* grows with time, but whereas *T* undergoes an inflexion point (8.5 min; 40.5°), $(T)'$ passes through a maximum, just as $(P_u)'$ at the same time. Beyond that transition, *T* and P_u continue to increase, but before long, at $t = 14.6$ min, P_u becomes maximum while *T* continues its rise until a second inflexion point (15.4 min; 76°) which marks the end of preheating period. The interpretation of the transitions linked to both preceding inflexions in *T* curve is easily deduced from our results on curing of epoxy resins [4] and viscosity measurements carried out in this work. During the crosslinking process under microwaves of epoxy resins, the maximum of P_u corresponds to the sol–gel transition with formation of a soft chemically crosslinked network which induces a strong viscosity effect in the medium and consequently hinders or slows down the dipolar relaxation i.e. the dielectric loss. The same conclusion can be drawn for our polyurethane resin, more especially as the condition that the abcissa of the gel point must be very near to that of the second inflexion point is observed, respectively 14.6 min and 15.4 min. The later decrease of P_u, in spite of the rise of *T*, is due to the exothermal spread of the crosslinking reaction which even tends to immobilize the polymeric segments. The transition corresponds to the first inflexion point has to be attributed, as in the case of epoxy resin prepolymer, to a liquid–liquid transition (or fluidification) between a viscous state where the various components of the prepolymer are associated through Van der Waals bonding and a fluid state with limited interactions; some micro-

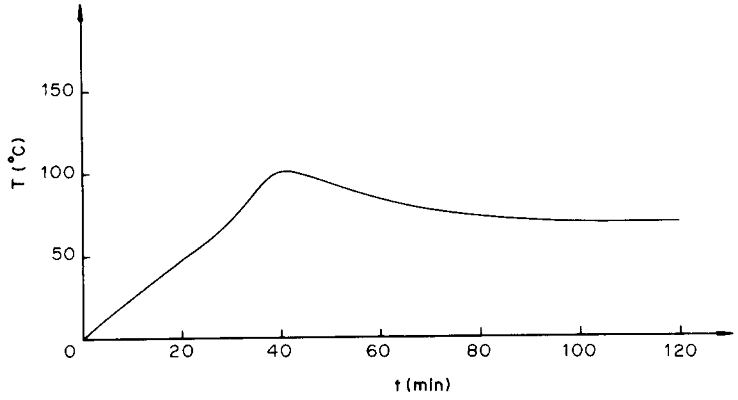

Fig. 2. Thermal activation of the crosslinking reaction of the polyurethane resin in an oven at 60° [Curve $T = T(t)$].

syneresis could be considered owing to the fact that the samples remain for some time at $-15°$. These two transitions are revealed by viscosity measurements from a prepolymer resin standing in a silicon oil bath with a temperature programme as shown in Fig. 3: (1) is a single point at 23°C giving the viscosity of the mixture just after its fabrication; (2) presents the temperature dependence of the viscosity which first drops from 16.8×10^3 Cp at 11° to 0.2×10^3 Cp at 56°, and then climbs before being unmeasurable at the gel point (79°). The fact that the viscosity decreases with rising temperature for a sample aged at low temperature indicates an aggregated structural organization inside the polyurethane prepolymer which does not lack chemical species for temperature sensitive physical bonding. When the organic medium undergoes the fluidification transition in the case of the electromagnetic activation, $(T)'$ and $(P_u)'$ take maximum values. Their later decrease indicates that the condensation reaction starts, proceeding to the gel transition with formation of covalent linkages with some viscosity effect and progressive change of dipolar species due to the addition of hydroxyl groups to isocyanate functions.

When one leaves the preheating period, i.e. when T passes the second inflexion point which is located as the first minimum in $(T)'$ curve (Fig. 1), the exothermal reaction takes place with a fast and strong thermal effect up to a maximum (21.7 min; 165°) and heat is produced in large excess, whereas P_u still continues to decrease. The rate of heating is maximum at the inflexion point of the exothermal segment (18.9 min; 125°) and equal to zero when T is maximum.

Beyond the maximum of temperature, the cooling step takes place. The interpretation of the thermal decay can be understood by referring to results from epoxy resin curing [4] where exchanges of energy between the sample and the external medium are considered. At any time of the electromagnetic treatment, the chemical medium receives energy from the microwave beam (dielectric loss) and loses energy by heat transfer (convection) towards the external medium. Moreover, when the curing occurs, chemical heat is produced; that amounts to saying that during the step-growth polymerization, the sample receives from outside an energy $+|\Delta H_p|$ if the heat of reaction is ΔH_p. The rise of temperature during the exothermal step expresses the fact that heating of the sample (microwaves + chemical heat) overcomes the convection loss which is proportional to the thermal gradient $(T - T_0)$ where T_0 is the temperature of the surrounding air ($\sim 20°$). But, when the curing reaction is ended, no more chemical heat is produced whereas P_u continues to drop down from the sol–gel transition. The time of end of conversion is probably in the vicinity of the maximum of temperature and cannot be defined more precisely because the resin system is thermodynamically opened, and that the T curve is more or less shifted in time. However, it is certain that the decrease of T results from the stopping of the curing process since the production of chemical heat is hindered. After 40 min, P_u stabilizes while T continues to fall. Such an observation means that the system still stores much chemical heat when the cooling period occurs, and that it needs a long time (until the thermal plateau) to remove it. Moreover the fact that T and P_u keep final plateau values indicates that the corresponding material has a permanent chemical and physical structure.

The P_0 dependence of $T = T(t)$, $(T)' = dT/dt$, $P_u = P_u(t)$ and $(P_u)' = P_u/dt$ are successively presented in Figs 4–7, where the curves are labelled 1, 2, 3, 4, 5 and 6 when P_0 takes values 10, 20, 30, 40, 50 and 60 W.

In Fig. 4, the series of T curves is shown: except for Curve 1, all curves exhibit the same shape with three classical steps of the condensation reaction. When P_0 increases from 10 to 60 W, the exothermal peaks tend to be narrower whereas their maximum is shifted to lower times (59.1, 51.0, 35.0, 30.7, 21.7 and 19.8 min), and their intensity becomes higher and higher (51, 87, 126, 137, 165 and 173°). This type of change is in accordance with the principle of microwave heating: the more P_0 keeps high values, the more the heating effect is intense and the activation is strong. Curve (2′) corresponds to a second treatment at the same P_0 value of 20 W; it quickly takes the previous plateau value (25°) reached with a single heating. This result has the merit of also estabishing the good running of our microwave bench and of the accomplishment of the curing at the end of the first electromagnetic treatment. The $(T)'$ series (Fig. 5) confirms the existence of the fluidification transition (first peak) which is faster and better underlined with increasing P_0; by another way, the maximum of the heating rate (second peak) varies as P_0. As for $P_u = P_u(t)$ (Curve 6), it obeys the same type of law as encountered for $T = T(t)$, and all samples undergo the sol–gel transition after 33.1 min at $P_0 = 20$ W and 12.3 min

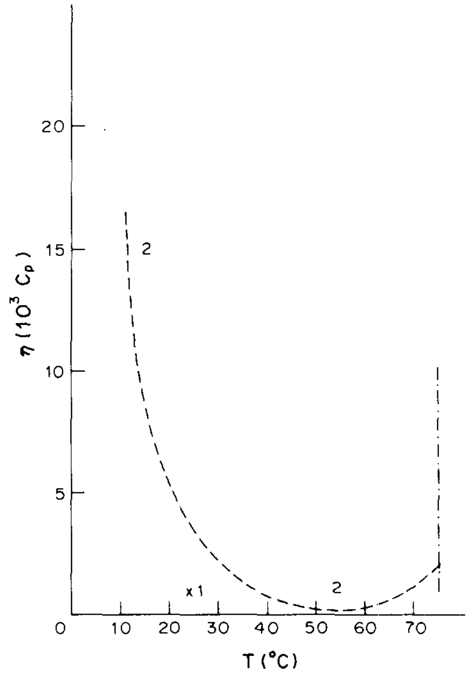

Fig. 3. Temperature dependence of the viscosity (in centipoises) of the polyurethane resin. (1) Viscosity after mixing (23°); (2) temperature dependence of the viscosity in a bath at 60°.

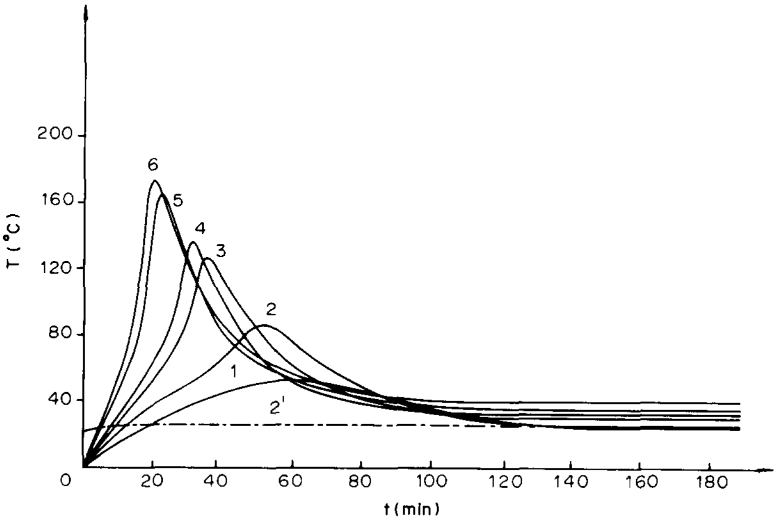

Fig. 4. P_0 power dependence of the temperature $T = T(t)$ (1) 10 W; (2) 20 W; (3) 30 W; (4) 40 W; (5) 50 W; (6) 60 W.

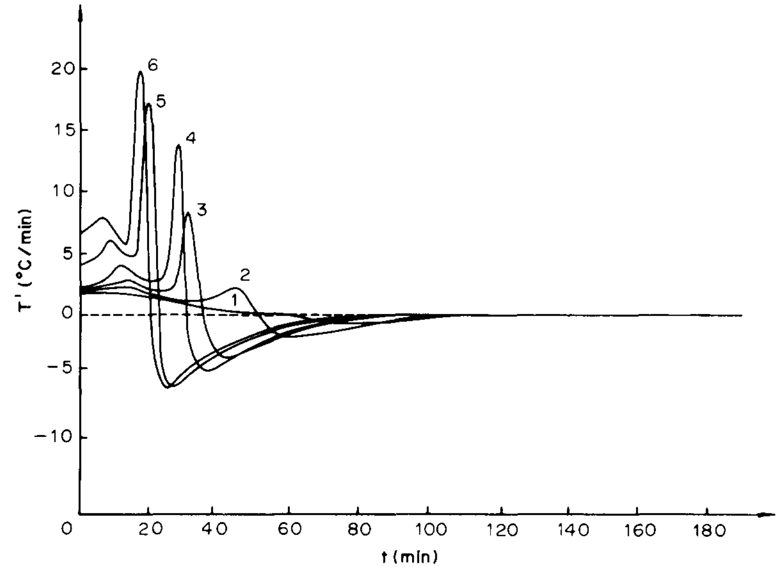

Fig. 5. P_0 power dependence of the derivative $(T)' = dT/dt$ (1) 10 W; (2) 20 W; (3) 30 W; (4) 40 W; (5) 50 W; (6) 60 W.

at $P_0 = 60$ W. Moreover, the final values of P_{u_p} are distinctly classified according to values of P_0, as in the case of initial P_u which corresponds to an average energetic yield of 18–20% when just P_0 is considered. The series $(P_u)' = dP_u/dt$ (Fig. 7) does not bring much, but that it confirms the regular behaviour of the samples submitted to the microwaves in the considered P_0 power bracket.

The curing of the resin samples irradiated at P_0 values from 10 to 60 W leads to final networks with mechanical properties of quality at least equivalent to those prepared in an oven. For example, the average elasticity modulus determined from uniaxial compression with samples ($h = 25$ mm; $\phi = 12.5$ mm) is equal to 3120 MPa for curing under microwaves at $P_0 = 20$ W during 1 hr and to 2810 MPa for curing in an oven at 60° for 8 hr.

CONCLUSION

The results which have been presented and discussed have been obtained during a preliminary study of the activation of the crosslinking reactions of polyurethane prepolymers. They show that the electromagnetic curing process works for such resins and gives final networks with a regular structure. The overall mechanism of energetic exchanges is now well-known, but many problems still remain, such as

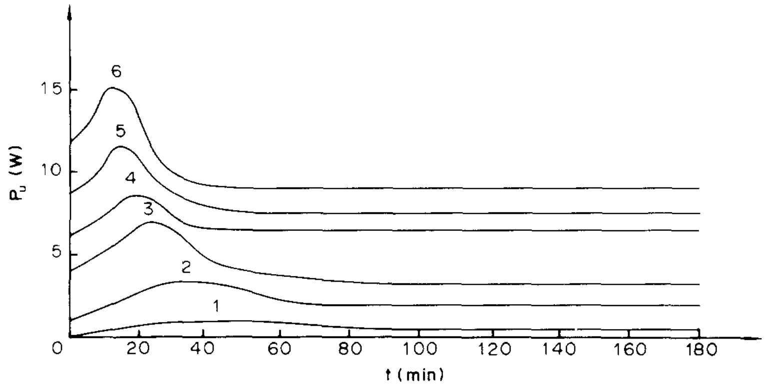

Fig. 6. P_0 power dependence of the power $P_u = P_u(t)$ (1) 10 W; (2) 20 W; (3) 30 W; (4) 40 W; (5) 50 W; (6) 60 W.

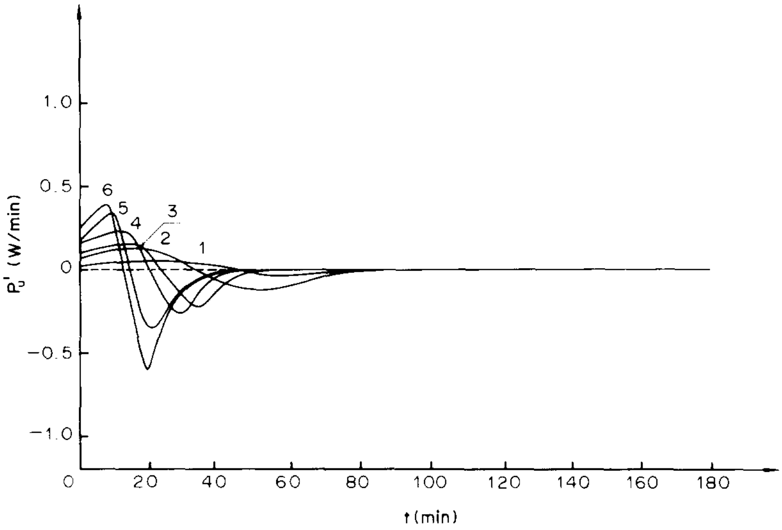

Fig. 7. P_0 power dependence of the derivative $(P_u)' = dP_u/dt$ (1) 10 W; (2) 20 W; (3) 30 W; (4) 40 W; (5) 50 W; (6) 60 W.

the shape and quality of the electrical signal before entering and inside the polymerizable matter, the nature of the modes of dipolar relaxation and the conversion of the dielectric loss as heat which is not complete. Later papers of this series will concern (a) the effect of formulation on the behaviour of the resins under pure continuous microwaves—the commercial M.O. generators which are currently used, do not deliver a continuous signal of power, but rather discontinuous and complicated, the average electrical power being nevertheless maintained constant (b) the curing of the resin in pulsed microwave regime and (c) the mechanical properties of the final networks in relation to the mode of irradiation (continuous or pulsed).

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