

Analysis of Thermal Curves Obtained during Radiation Curing of Polymeric Films

G. GOZZELINO,* A. PRIOLA, and M. MANTEGNA

Dipartimento di Scienza dei Materiali e Ingegneria Chimica, Politecnico di Torino, Torino, Italy

SYNOPSIS

Thermal curves were obtained during the UV curing process of a film containing reactive oligomers by monitoring in "real time" the temperature of the film surface by means of a high sensitive thermocouple. The system can be reproduced by a mathematical model that allows one, in well-defined conditions, to obtain the thermal curve of the system when the physical parameters of the materials, the polymerization enthalpy, and the kinetics of the double bond conversion are known. By using the kinetic data obtained through real time FTIR analysis, the model allows one to obtain the theoretical thermal curve of the system. The agreement between this curve and that obtained experimentally was found satisfactory, thus confirming the validity of the model proposed. The possible applications of the method are discussed.

INTRODUCTION

Radiation curable systems are known as very fast polymerization processes which involve the use of multifunctional unsaturated oligomers with formation of highly crosslinked polymeric networks.¹ The kinetic investigation of these systems is a very difficult task due to the high polymerization rates and the complexity of the products obtained. Several methods have been proposed to solve this problem, which presents considerable interest either from fundamental or industrial point of view. They include infrared analysis,²⁻⁴ differential thermal analysis,^{5,6} dilatometry,⁷ etc. Because of the rather long response time, they give only a qualitative picture of the curing process.

Recently a "real time" infrared spectroscopy method⁸ and a FT-IR based method⁹ were proposed, which allow one to obtain directly the kinetic curve of polymerization for these systems. One of the problems with IR and FT-IR spectroscopy is that it can be used only on transparent thin films usually coated on a NaCl disk, in conditions far from the usual curing conditions.

From this point of view thermal methods can offer important advantages; therefore, we decided to use these methods to investigate in real time the kinetics of the polymerization process. The technique used was based on the measurement of the actual temperature of the polymeric film during the photopolymerization process.

By means of a suitable modeling of the system, the experimental thermal curve can be reproduced if the thermal parameters of the system and the kinetics of polymerization are known.

In this paper we report the application of this method whose validity is checked by comparing the experimental thermal curve with the theoretical one obtained by using FT-IR kinetic data. Preliminary results of the experimental technique used were reported previously.¹⁰

EXPERIMENTAL

The curing experiments were carried out on a typical UV curable resin based on bisphenol-A-diglycidyl-ether-diacrylate (BGEDA) and a reactive diluent tripropyleneglicol-diacrylate in 75/25 w/w mixture in the presence of 1-5% of 2,2-dimethoxy-2-phenylacetophenone (DMPA) as photoinitiator. We have adopted experimental conditions which allow an

* To whom correspondence should be addressed.

easy modeling of the system. For this reason the resin was coated on thin Al foils (thickness $14\ \mu\text{m}$) by using a calibrated wire wound applicator to obtain films with controlled thickness.

The thickness of the films was measured after the curing reaction by means of a coating thickness gauge Minitest 3000 (Elektro-Physik, Cologne), equipped with a probe for nonmagnetic substrate. The irradiation of the samples was performed with a 500 W medium pressure mercury lamp (Helios Italquartz) equipped with a water jacket, for infrared radiation screening, and with a camera shutter for controlling the UV exposure time.

The sample was put at a distance of about 20 cm from the lamp, in a box with a quartz window which allows one to work under a controlled flow of air or pure nitrogen without reduction of the UV radiation intensity. The UV energy power on the resin film was $5.6\ \text{mW}/\text{cm}^2$ as measured with a Black Ray Meter instrument.

The temperature of the films during the curing reaction was continuously monitored by recording the thermoelectric voltage of an electric circuit, part of which was constituted by an iron and a Cu-Ni (constantan) wire connected with two close points of the aluminum surface. The two junctions were both at the surface temperature of the aluminum foil in contact with the polymer layer, and the thermoelectric voltage, generated by the temperature difference between the Al foil and the two cold junctions at 0°C , was recorded on a x-y recorder. In the adopted conditions the response time of the system was very small ($< 0.1\ \text{s}$). The scheme of the adopted apparatus is reported in Figure 1.

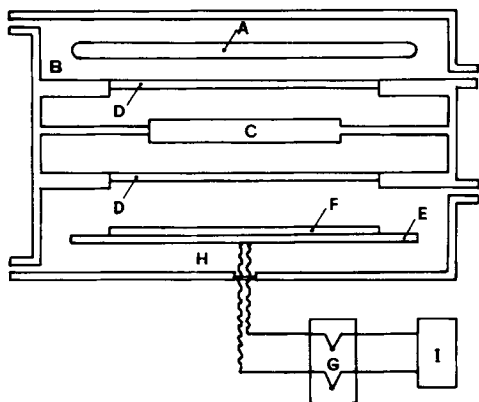


Figure 1 Scheme of the UV curing apparatus: (A) UV lamp; (B) water jacket; (C) shutter; (D) quartz window; (E) aluminum foil; (F) polymer film; (G) cold junctions; (H) box with controlled atmosphere; (I) recorder.

The thermal curves, temperature vs. time, were obtained by conversion point by point of the voltage-time curves through the Seebeck voltage values. The thermal experiments were carried out on polymer films with thickness higher than $15\ \mu\text{m}$. At lower thickness the weak thermal effect causes scattering of thermal measurements.

The kinetic curves of double bond conversion were obtained with a Bruker FTIR 45 instrument properly modified for the purpose. A KBr disk coated with the resin was placed in the FTIR sample holder, and a suitable optical fiber, equipped with a camera shutter, was located in such a way to irradiate the sample without interfering with the analytical IR beam. The other end of the optical fiber was located in the focus of a medium pressure mercury lamp. The distance of the sample was changed in order to have on it the same radiation intensity as in the thermal experiments.

After purging the sample cavity with nitrogen, the scans of IR interferograms were started and the spectra, one every second, were collected through a modified standard Bruker software for gas chromatography-IR and postrun processing. The UV irradiation of the sample was started when a suitable collection of spectra of the initial sample was collected and in this way a real time kinetics of the curing reaction was obtained.⁹

The data reported in Table I are the mean of several FTIR runs, some of them performed with a time delay of 0.5 s in the spectra collection. The double bond concentration was evaluated by computing the area of the IR band at $1636\ \text{cm}^{-1}$ (db stretching band) with reference to the $1510\ \text{cm}^{-1}$ band (aromatic ring band) used as an internal standard.

Reproducible results were obtained for films with thickness values less than $20\ \mu\text{m}$. Thicker films gave a high spectrophotometric error due to the high absorbance value.

RESULTS AND DISCUSSION

A typical thermal curve obtained by using the above-reported apparatus and a sample of $80\ \mu\text{m}$ thickness is shown in Figure 2. The initial high slope of the curve shows the high polymerization rate, which causes a fast increase of the temperature of the system.¹⁰

The shape of the curve is determined by the different factors which influence the temperature of the system, namely, the enthalpy of the polymerization reaction, the heat accumulation, and the heat dissipation of the film by conduction and convection

Table I Physicochemical Parameters¹⁴ and FT-IR Kinetic Data for the UV-Cured System

Parameter	Units	Value	
Al			
Density	Kg m ⁻³	2700	
Thermal conductivity	W m ⁻¹ K ⁻¹	240	
Specific heat	J Kg ⁻¹ K ⁻¹	900	
Polymer			
Density	Kg m ⁻³	1200	
Thermal conductivity	W m ⁻¹ K ⁻¹	0.21	
Specific heat	J Kg ⁻¹ K ⁻¹	1600	
Heat of polymerization	KJ Kg ⁻¹	339	
FT-IR d.b. Conversion			
Time (s)	Conversion (%)	Time (s)	Conversion (%)
0	0	0	55.5
0.5	9.9	3.5	58.2
1	35.5	4	58.7
1.5	45.8	4.5	60.5
2	50.1	5	60.7
2.5	53.2	5.5	60.8

mechanism.¹¹ Moreover, the energy absorption from the UV lamp must be taken into account.

The thermal contribution due to the UV lamp can be evaluated from the curve (b). It is evident that in our conditions an asymptotic T increase of about 2°C only is due to the UV radiation absorption: We have taken into account this effect by using the lamp curve as the baseline for the thermal curve.

The experimental system adopted allows us to elaborate a physical model which can give the ther-

mal curve at the film surfaces during the polymerization reaction when the physicochemical characteristics of the system and the reaction kinetics are known. A discussion of general methods useful for a thermokinetic analysis was reported elsewhere.¹²

In the case of an homogeneous film sufficiently extended, the thermal phenomena at the edge can be neglected, thus simplifying the classical thermokinetic equations. In fact, the thermal behavior of this system can be described through only one dimensional variable.

On the basis of the one dimension heat transfer equation through the polymeric film, the thermal diffusion is equal to the difference between the energy accumulation in the polymer film and the development of energy due to the chemical reaction:

$$\frac{\delta^2 T_p}{\delta z_p^2} = \frac{\rho_p c_{p,p}}{\lambda_p} \frac{\delta T_p}{\delta t} - \frac{\rho_p}{\lambda_p} \phi \quad (1)$$

In the above equation, λ_p is the thermal conductivity of the polymer, T_p the temperature at the time t of the polymer layer at the distance z_p from the surface, ρ_p the density, c_p the specific heat, and ϕ the energy flux due to the exothermic curing reaction.

In the case of the supported polymer film, a similar equation, without the term of energy development, can be written for the support. For the aluminum foil coated with the resin we have

$$\frac{\delta^2 T_s}{\delta z_s^2} = \frac{\rho_s c_{p,s}}{\lambda_s} \frac{\delta T_s}{\delta t} \quad (2)$$

where the symbol s refers to the aluminum layer.

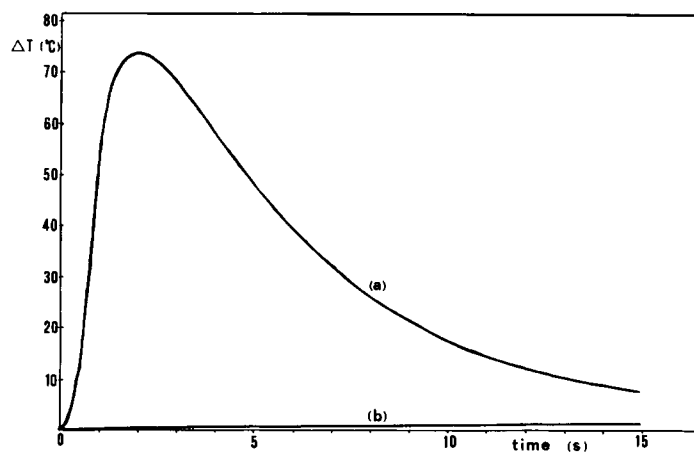


Figure 2 (a) Typical thermal curve obtained during UV curing of a 80 μm film of BGEDA resin. (b) Thermal effect of the UV lamp.

Equations (1) and (2) constitute a rigorous description of the heat diffusion phenomena occurring in our system. In order to solve these equations, it is necessary to specify the boundary conditions and the initial state of the system.

In the initial conditions the polymer–aluminum system is allowed to reach thermal equilibrium with the surrounding gas. When the equilibrium is established, the gas (a), the polymer (p), and the aluminum (s) are at the same temperature:

$$(T_s)_0 = (T_p)_0 = (T_a)_0 \quad (3)$$

The boundary conditions must define the heat exchange at the surface of polymer and aluminum and at the interface between the two materials at the time t .

At the interface (i), because of the continuous contact between the two faces, the heat conduction occurs without thermal resistance:

$$(T_p)_i = (T_s)_i, \quad \lambda_p \frac{\delta T_p}{\delta z} = \lambda_s \frac{\delta T_s}{\delta z} \quad (4)$$

At the surface of the polymer film we have

$$\frac{\delta T_p}{\delta z_p} = \pm \frac{h}{\lambda_p} (T_p - T_a) \quad (5)$$

where h is the convection coefficient for the solid–gas heat exchange.

Analogously for the aluminum, support is

$$\frac{\delta T_s}{\delta z_s} = \pm \frac{h}{\lambda_s} (T_s - T_a) \quad (6)$$

The mathematical system of eqs. (1) and (2) with the conditions (3), (4), (5), and (6) cannot be solved because the ϕ factor changes as a function of time in a complex way (Trommsdorff effect).⁷ This difficulty was surmounted taking into account point by point the experimental kinetic data obtained through FTIR analysis of the film during the curing reaction, and solving the equation by means of a numerical method.

We applied the finite difference approximation method¹³ for solving the aforementioned equations using the parameters values reported in Table I together with the kinetic data obtained by means of FT-IR analysis. In this way the temperature change with time as well as distance from the surface was obtained. The results obtained show that, in the case of a film with thickness in the range 10–200 μm and

with values of the heat transfer convection coefficients between 10 and 20 $\text{J}/(\text{m}^2 \text{s K})$ (respectively referring to still gas and slow convective motion of the gas around the film), there is a temperature difference lower than 1°C between the core and the polymer surface.

This means that, despite the low thermal conductivity of the polymeric film (see Table I), the heat dissipation is controlled by the transport at the solid–gas interfaces: The polymer film can be considered thermally homogeneous, the temperature of each point being dependent on the time but independent of the distance from the surface. On the other hand, this result is confirmed by calculating the ratio of thermal conductance of the film by convection and conduction as expressed through the Biot number¹⁴: A value between 0.05 and 0.2 was evaluated, well below the unity, thus indicating that the heat transfer is dominated by convection phenomena. These results allow one to evaluate from the experimental data the convection coefficient h without arbitrary hypothesis on the fluidynamic behavior of the system.

On the assumption that the films behave as an isothermal body, the films were heated by the Joule effect, in the same conditions of those adopted for recording the thermal curve, and the cooling curve was analyzed. The convection coefficient was evaluated through the equation

$$T - T_a = (T_0 - T_a) \exp(-hSt/mc_p)$$

where T is the temperature of the body at the time t , T_0 the film starting temperature, T_a the flowing gas temperature, S the surface, m the mass, and c_p the specific heat. The experimental values of h , the chemical FTIR kinetic data, and the values of the parameters reported in Table 1 were introduced into eqs. (1)–(6), which were treated with the finite-difference method to obtain the theoretic thermal curve of the system during the curing process.

In Figure 3 the comparison of the calculated and the experimental thermal curve obtained for a film 17 μm thick is reported. The agreement between the two curves is good: The small deviation can be attributed to the different substrate used for IR and thermal experiments.

This agreement can be taken as an indication of the validity of the model proposed to simulate the curing process in the adopted conditions (thickness 15–20 μm). At this moment we do not have other kinetic results capable of checking the validity of the model at higher thickness.

In the same figure, the thermal curves obtained

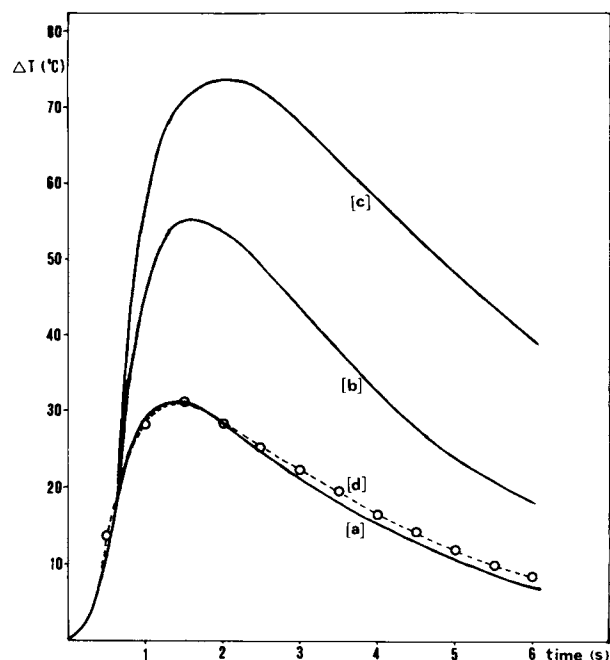


Figure 3 Experimental and calculated thermal curves obtained for the BGEDA resin system: (a) experimental, thickness 17 μm ; (b) experimental, thickness 40 μm ; (c) experimental, thickness 76 μm ; (d) theoretical, thickness 17 μm .

at two higher thickness value (40 and 76 μm) are reported. It can be seen that the shape of all the experimental curves is very similar, although at higher thickness the thermal effect (maximum temperature increase) is considerably higher due to the higher heat evolution during the curing process of thicker films. Moreover, it must be taken into account that a higher temperature increase will induce also a higher final double bond conversion as reported in the literature.⁷

A further development of the mathematical model will allow the determination of the chemical kinetic behavior from the thermal curves obtained by means of this simple experimental system.

CONCLUSIONS

In conclusion, we propose a mathematical model for the curing process of a thin polymeric film which is

able to reproduce the experimental thermal curve when the kinetic data are available.

The validity of the method has been tested by verifying that the experimental and the calculated thermal curves are very close by using thickness of the polymeric film in the range 15–20 μm .

The interest of the method is connected with the possibility of following in real time the curing process and obtaining data directly in the usual curing conditions.

The authors thank the CNR, P. F. Chimica Fine II, for financial support.

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Received December 21, 1990

Accepted May 14, 1991