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INFLUENCE OF FUNCTIONAL RUBBERS ON THE CURING PROCESS OF UNSATURATED POLYESTER RESINS

M. Avella, E. Martuscelli and *M. G. Volpe*

ISTITUTO DI RICERCHE SU TECNOLOGIA DEI POLIMERI E REOLOGIA
DEL C.N.R. VIA TOIANO 6,800 72 ARCO FELICE, NAPOLI, ITALY

The influence of an elastomeric second-phase on the kinetics of the curing reaction and the gel-time of a standard unsaturated polyester resin, by using the isothermal and dynamic techniques of differential scanning calorimetry (DSC) and a thermocouple was investigated. In particular we examined two different rubbers (polybutadiene hydroxyl-terminated and polybutadiene isocyanate-terminated), that, in the presence of polyester resins, affect the overall curing reaction kinetics in two ways: the former reduces the rate of reaction whilst the latter increases it.

Unsaturated polyester resins, formed by a free radical reaction of an α, β unsaturated acid in a polyester with a vinyl monomer, show poor properties when thoughness and high impact strength are required [1].

It is known that the impact resistance of such resins can be improved by incorporating inclusions of liquid reactive rubbers in the resins [2]. These rubbers must be mixed with the base resin before the curing process and then made to precipitate in a second phase, during the cure, from the solution to give the rigid matrix the desired toughening action [3].

Of course, it is very important to know the influence of the rubber phase on the curing process of the polyester resins.

The cure of thermoset resins, in general, is the overall transformation from liquid to gel, to rubber, to glass that occurs as a result of a reaction of curing which produces a measurable exothermic effect [4, 5].

In this paper the results of studies on the curing kinetics and the gelation time of rubber-modified polyester resins are reported. In particular two sets of blends were investigated, consisting of the same unsaturated polyester matrix and two elastomers having the following terminal functional groups:

i) low molecular weight hydroxyl terminated polybutadiene;
ii) low molecular weight isocyanate terminated polybutadiene.

The two different terminal groups of the elastomer interact with the matrix in

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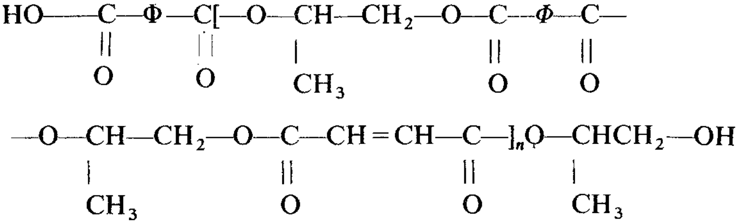
different ways: the hydroxyl terminal groups do not react chemically with the functional groups present in the polyester, whereas the isocyanate terminal groups react with the terminal groups of the polyester matrix, in the usual temperature range used for the curing process. This different reactivity of the terminal groups of polybutadiene with the matrix strongly influences the kinetic parameter and the gel-time of the base resin.

Experimental

Materials

The uncured unsaturated starting polyester resin (code: PER), supplied by SNIAL–Colleferro–Roma, is constituted by a solution containing about 68% of a polyester prepolymer dissolved in a solution of a styrene monomer. The prepolymer is formed by the reaction of a mixture of phthalic and maleic anhydride with a saturated glycol, propylene glycol (mole ratios 0.7 : 0.3 : 1). The molecular structure of such a prepolymer may be schematically represented as follows:



$$HO{-}\underset{\underset{O}{\|}}{C}{-}\Phi{-}\underset{\underset{O}{\|}}{C}[{-}O{-}\underset{\underset{CH_3}{|}}{CH}{-}CH_2{-}O{-}\underset{\underset{O}{\|}}{C}{-}\Phi{-}\underset{\underset{O}{\|}}{C}{-}$$

$${-}O{-}\underset{\underset{CH_3}{|}}{CH}{-}CH_2{-}O{-}\underset{\underset{O}{\|}}{C}{-}CH{=}CH{-}\underset{\underset{O}{\|}}{C}{-}]_nO{-}\underset{\underset{CH_3}{|}}{CH}CH_2{-}OH$$

Φ = phenyl ring

The acid number of the prepolymer was maintained around 40÷45 (this value represents the milligrams of KOH used for the titration of 1 g of resin). Methyl ethyl ketone peroxide (Butanox, 1 wt%) and Co-octoate (0.25 wt%) were used as catalyst and accelerator respectively (the first is available as 50 wt% solution in dimethyl-phthalate while the second was already present in the starting formulation, as naphthenate solution).

Hydroxyl terminated polybutadiene (HTPB) $\overline{Mn} = 1350$, supplied by Polysciences, was used as starting rubber. The molecular structure of HTPB was determined by analyzing the 270 Mz ^{1}H-NMR spectrum in $CDCl_3$ solution, using TMS as the internal standard. It was found that about 70% of the units are arranged in a 1.2 enchainment and 30% in a 1.4 cis/trans enchainment. The hydroxyl number was determined by the following procedure: first the hydroxyl end groups were quantitatively converted into isocyanate end groups, then an excess of dibutylamine was added and finally the amine excess was titrated with 0.03 N HCl solution in *o*-dichlorobenzene/isopropanol 9/1 by volume. The resulting number of hydroxyl groups was 1.2 meq/g.

The isocyanate terminated polybutadiene (PBNCO) was obtained by reaction of HTPB 1350 with toluene di-isocyanate (TDI). HTPB and TDI (molar ratio TDI/HTPB slightly exceeding 2:1), were mixed for 10 minutes at 70° under nitrogen atmosphere and mechanical stirring. The TDI, supplied by Fluka, was a 80/20 mixture of 2.4 and 2.6 isomers; it was used without further purification. The details of such reaction are reported in a previous paper [6].

Experimental techniques

A Mettler TA–3000 apparatus, equipped with a control and programming unit (microprocessor Tc–10) and a calorimetric cell DSC 30, that allows a temperature scan from −170 to 600°, was used to study the kinetics of the curing process.

The gel-time (Gt) of all the samples was determined by the following procedure [7]: 25 g of uncured sample were placed in a 25 mm diameter sample tube in a temperature-controlled bath ($T = 40° \pm 0.1$ deg). When all the components have reached the test temperature, 1% by weight of Butanox catalyst was added and mixed virogously for a few seconds; at this point a thermocouple was inserted into the geometric center of the reacting mass and the temperature changes following the cure reaction recorded. The inside temperature increase of the system recorded as a function of time, generated a trace shown in Fig. 1. From this curve the following times relative to the cure reaction are determined:

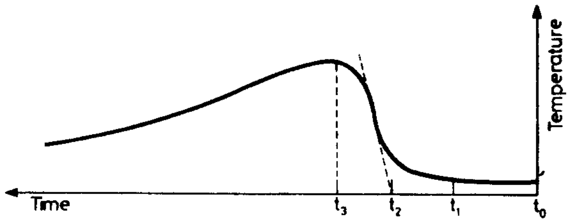


Fig. 1 Typical curve temperature/time for the gel-time determination

i) t_0, the time corresponding to the addition of the catalyst;
ii) t_1, the time corresponding to the starting of exothermic reaction;
iii) t_2 (the flex point) corresponding to the gel time;
iv) t_3, the time corresponding to the maximum temperature reached by by the system.

Preparation of rubber modified polyester resins

Rubber modified polyester resins were prepared in the following manner: initially 10 g of HTPB or PBNCO rubbers were dispersed in 90 g of the styrene solution containing the polyester prepolymer by mechanically stirring for 30 minutes at 80°. A polymerization reaction flask, capacity 250 cm^3, equipped with a mechanical stirrer and a vacuum outlet was used. The mixture was then cooled to room temperature and air bubbles were removed under reduced pressure. At this point the catalyst was added under stirring; the mixture was poured into a mould consisting of either glass or metal glazing plates, separated by a flexible rubber gasket held by springs and finally cured at 80° for three hours. Methyl ethyl ketone peroxide (Butanox) and Co-octoate (0.25% wt) were used as catalyst and accelerator respectively (the first is available as 50% solution in dimethylphthalate, while the second is already present in the starting (PER) formulation as naphthate solution).

The code and the composition of the rubber-modified polyester resin materials investigated are given in Table 1.

Table 1 Codes and compositions of samples examined

Code	Elastomer, %	Resin, %
PER	0	100
PER/HTPB 5	5	95
PER/HTPB 10	10	90
PER/HTPB 15	15	85
PER/HTPB 20	20	80
PER/PBNCO 5	5	95
PER/PBNCO 10	10	90
PER/PBNCO 15	15	85
PER/PBNCO 20	20	80

Results and discussion

The curing process of an unsaturated polyester resin is an exothermic free radical reaction characterized by the fact that a reactive diluent (styrene) is able, in the presence of a suitable catalyst, to act as crosslinking agent by reaction with the unsaturated double bonds of the α, β acid residues present along the repeat unit of the polyester chains [8]. This conversion of double bond to a single bond is accompanied by an evolution of heat:

$$\text{reactant} \xrightarrow{Q} \text{products}$$

where Q is the exothermic heat per gram of reactive mass. This heat emission (Q) can be easily measured by DSC technique. Moreover it is assumed that the reaction rate is directly proportional to the rate of heat generation dH, which is true, providing the cure reaction is the only thermal event. Note that dH is also the ordinate of a DSC trace (see Fig. 2).

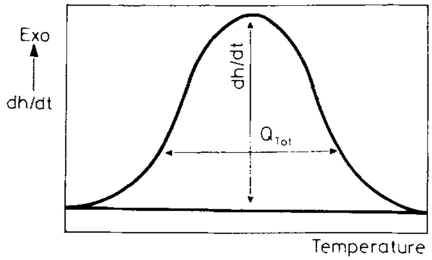


Fig. 2 Example of curing reaction exotherm for a standard polyester resin

a) Curing kinetics of PER/HTPB blends

In Table 2 the values of curing reaction heats for PER and for PER/HTPB blends obtained during the cure process are reported. Such heats have been obtained by heating the samples from room temperature to 230° using a scan rate of 20 deg/min (Q_{TOT}) (see Fig. 3) and by isothermal treatment at T = 40° (Q_{T} = 40°) (see Fig. 4a–c). The values in joule of Q_{TOT} and $Q_{\text{T}=40°}$ are referred to 1 g of blend. From these values it follows that the presence of the rubber phase does not significantly influence on the heat generated during the curing process of polyester resin.

Table 2 Values of heats and times of curing reaction for blends PER/HTPB

Sample	Q_{TOT}, J/g	$Q_{\text{T}=40°}$, J/g	t^*_{start}, min	t^*_{max}, min	t^*_{end}, min
PER	335	173	5	13	34
PER/HTPB 10	310	157	8	15	46
PER/HTPB 20	260	136	11	17	48

* The start, max and end curing times are referred to isothermal treatment at T = 40°.

Moreover Table 2 also shows the time of starting of the reaction (t_s), the time corresponding to the maximum of isothermal peak (t_m) and the time of ending of the reaction (t_e); these values are obtained from the thermal curve of the isothermal curing process at T = 40°. These findings indicate that the presence of rubber produces a slowing down of the overall curing kinetics. This fact is probably to be chiefly attributed to the low matrix viscosity due to the inert rubbery additive that

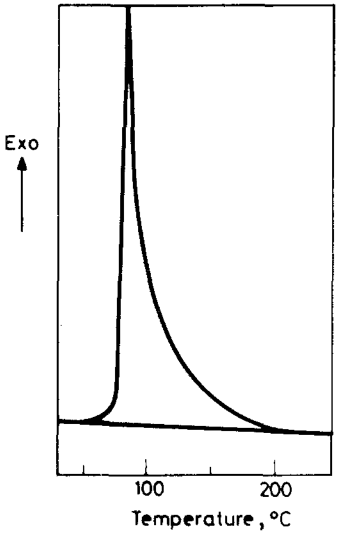


Fig. 3 Experimental curve for the curing reaction obtained in dynamic scan from 25° to 230° for PER sample

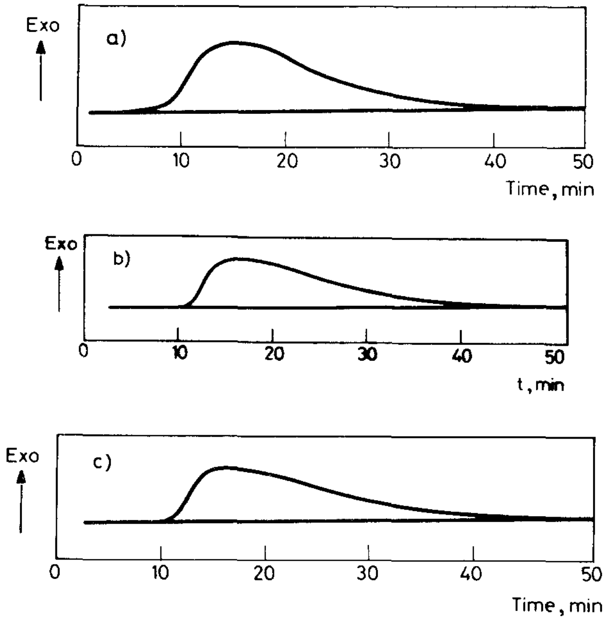


Fig. 4 Experimental curves for the curing reaction obtained in isothermal scan (t = 40°) for the following samples: a) PER, b) PER/HTPB 10, c) PER/HTPB 20

does not participate in the curing reaction and reduces the rate of curing reaction. In fact the DSC curve of PER/HTPB blends before the curing process is flat indicating that no reaction occurs, at least under our experimental conditions.

b) Experimental determination of cure kinetics of PER/PBNCO blends

The preparation of the PER/PBNCO blends, as described in another paper [6], is carried out in two steps involving the endcapping of the hydroxyl terminated polybutadiene by a condensation reaction with toluene di-isocyanate to obtain PBNCO and the subsequent reaction of the latter with the terminal groups of the unsaturated polyester prepolymer, which leads to the formation of urethane $(-O-\underset{\underset{O}{\|}}{C}-\underset{\underset{N}{|}}{N}-)$ links. Initially in the course of the reaction di-block and tri-block copolymers may form according to the following scheme:

OCN—R—NH—CO—O—PB—O—CO—NH—R—NCO + 2HO—PER—COOH →

HO—CO—PER—O—CO—NH—R—NH—CO—O—PB—O—CO—NH—R—NH—CO—O—PER—CO—OH

(A—B—A TRIBLOCK COPOLYMER FORMATION)

OCN—R—NH—CO—O—PB—O—CO—NH—R—NCO + HO—PER—COOH →

OCN—R—NH—CO—O—PB—O—CO—NH—R—NH—CO—O—PER—COOH

(A—B DIBLOCK COPOLYMER FORMATION).

At this point with the introduction of the catalyst into the system the normal curing reaction takes place.

In Table 3 the Q_{TOT}, $Q_{T=40°}$, time of starting, time relative to maximum of the peak and ending time of the cure reaction for the PER/PBNCO blends are reported (see also Fig. 5a–b).

Table 3 Values of heats and times of curing reaction for blends PER/PBNCO

Sample	Q_{TOT}, J/g	$Q_{T=40°}$, J/g	t^*_{start}, min	t^*_{max}, min	t^*_{end}, min
PER	335	173	5	13	34
PER/PBNCO 10	305	149	3	8	22
PER/PBNCO 20	280	120	1.5	5	20

* The start, max and end curing times are referred to isothermal treatment at $T = 40°$.

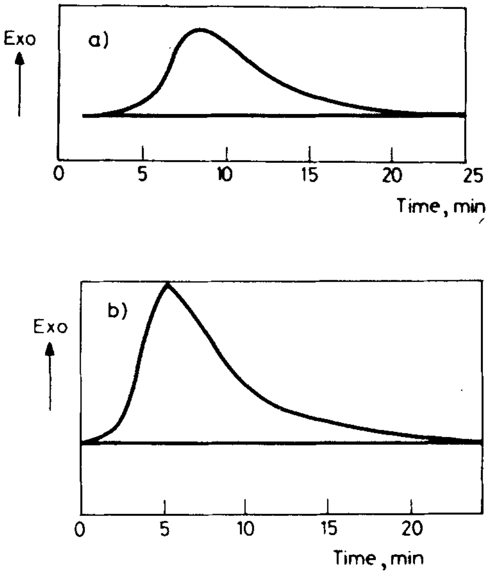


Fig. 5 Experimental curves for the curing reaction obtained in isothermal scan (T=40°) for the following samples: a) PER/PBNCO 10, b) PER/PBNCO 20

The Q_{TOT} and $Q_{\mathrm{T}=40^\circ}$ of the polyester matrix, as in the case of the PER/HTPB blends, do not seem to be affected by the previous formation of the ABA and AB copolymers; on the contrary, the curing times (t_s, t_m and t_e) show a great decrease as compared to the times observed for PER. This effect is due to the increase in the initial viscosity of the system generated by previous copolymer formation, which leads to the formation of macromolecules having higher molecular weight as it is clear also from the determination of the gel time.

c) Gel-time determination for the PER/HTPB and PER/PBNCO blends

The gel effect is a macroscopic phenomenon that occurs during the cure at a fixed chemical conversion that can be predicted if the functionality of the reactants is known [9].

The gel-time marks the first appearance of an infinite molecular weight network, where the transformation from a viscous liquid to an elastic gel is sudden and irreversible [4].

InTable 4 the gel-times (t_1, t_2, t_3) (in minutes) calculated for all the investigated blends are summarized. The gel-time findings show the same trend as those of the cure times described above. In fact the gel-times (measured at the start, at the flex point and the end of the exotherm curve of gelation) of the PER/HTPB blends

Table 4 Gel times (t_1, t_2, t_3) of the base resin and of the blends at $T = 40°$. t_1, t_2 and t_3 are respectively the starting, the flex point and the maximum of the gel curve (see Fig. 2)

Sample	t_1	t_2	t_3
PER	0.78	1.05	1.24
PER/HTPB 5	0.80	1.08	1.32
PER/HTPB 10	0.83	1.16	1.47
PER/HTPB 15	0.90	1.25	1.56
PER/HTPB 20	0.92	1.32	1.70
PER/PBNCO 5	0.72	0.98	1.19
PER/PBNCO 10	0.68	1.00	1.17
PER/PBNCO 15	0.47	0.76	0.94
PER/PBNCO 20	0.36	0.62	0.81

increase with the increase in the content of rubber-phase. This slowing down can be attributed to the physical hindrance of the incompatible rubber particles during the radical reaction of the curing process.

On the contrary, the gel-times of the PER/PBNCO blends decrease with the increase in the proportion of rubber-phase. This decrease can be due to the fact that the PBNCO, before the start of the cure reaction, reacts with the hydroxyl terminal groups of polyester matrix resulting in, as previously described, an A—B—A copolymer. Of course this reaction produces an increase in molecular weight and consequently also a higher viscosity ($\eta = \text{kMn}^a$). The gel time is greatly affected by the viscosity of resin and high viscosity leads to a decrease in gel-time [1]. This finding can be easily explained considering that the A—B—A copolymer reaches gel-time more rapidly since it has a higher molecular weight.

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Zusammenfassung — Der Einfluß einer elastomeren Zweitphase auf die Kinetik der Aushärtung und der Gelierungszeit eines als Standard dienenden ungesättigten Polyesterharzes wurden mittels isothermer und dynamischer DSC untersucht. Insbesondere wurden zwei unterschiedliche Gummis (hydroxylendständiges und isocyanatendständiges Polybutadien) untersucht, die die Kinetik der Aushärtung des Polyasterharzes in unterschiedlicher Weise beeinflussen: hydroxylendständiges Polybutadien verringert, isocyanatendständiges dagegen erhöht die Reaktionsgeschwindigkeit.

Резюме — Используя изотермическую и динамическую ДСК, а также термопару, изучено влияние эластомерной вторичной фазы на кинетику реакции отверждения и время гелеобразования обычной ненасыщенной полиэфирной смолы. Добавка полибутадиенового каучука с различными концевыми группами (гидроксильной и изоцианатной) оказывает различное влияние на полную реакцию отверждения полиэфирной смолы: каучук с концевой гидроксильной группой понижает скорость реакции, а каучук с изотиоцианатной группой — увеличивает.