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CALORIMETRIC ANALYSIS OF THE CURING BEHAVIOR OF AN UNSATURATED POLYESTER RESIN USING DIFFERENT CATALYTIC SYSTEMS

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ABSTRACT

Differential scanning calorimetry (DSC) has been used to study the thermodependency and thermodynamics of curing behavior of unsaturated polyester resins with different catalytic systems.

The curing reaction of a thermoset resin like unsaturated polyesters with styrene as a crosslinking agent at room temperature, involves the presence of an organic peroxide initiator and a promoter that induces by chemical reduction of the peroxide, free radical production at low temperatures.

Dynamic and isothermal runs were performed for each initiator/promoter combination in order to study its influence in gel and curing times, exothermic heat and cure reaction kinetics.

In this paper we will present the results obtained from dynamic calorimetric experiments that show the great effect of the kind of catalytic system in the curing behavior of the resin. For a particular initiator/promoter ratio the presence of more than one exothermic peak reveals different kinetic processes that we attribute to decomposition of initiator by two different processes: chemical reduction provoked by the promoter and thermal decomposition.

INTRODUCTION

Organic peroxides are the most common initiators in unsaturated polyester applications. Heat and temperature would be used to induce decomposition. Many applications call for room-temperature cure, in this case, an accelerator or promoter is needed to induce free radical production by chemical reduction of the peroxide. Different initiator/promoter ratios produces different gel and curing times and influences also the crosslinking nature of cured resin and their glassy state (1)(2).

By means of DSC isothermal and dynamic experiences it is possible to know gel and curing times, exothermic effects and kinetic parameters (3)(4). In this paper

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we want to show and discuss the results obtained from dynamic experiments in the process of curing two unsaturated polyester resins with styrene as crosslinking agent with two kinds of catalytic systems. The presence of more than one exothermic peak typifies the complex kinetic process of curing and reflects the importance that the catalytic system has not only on the rate of cure but in the final reaction extent, the presence of residual monomer in cured materials and the structure of network formed.

EXPERIMENTAL

Materials

Two commercially available general purpose unsaturated polyester resins supplied by Rio Rodano (Spain) with commercial names Estratil A-228 and Estratil A-100 were used for the study. The base polyester of both consist of phthalic anhydride, maleic anhidride and propilene glycol with a mole ratio of 3:2:5: and 3:1:4 respectively obtained by NMR. They were supplied with 35 wt% and 33 wt% respectively of styrene as a crosslinking agent. The resins contained a proprietary inhibitor and were used without removing it.

In curing the resins we used two different catalytic systems: Benzoyl peroxide (BP) as 50% dispersion and N,N-dimethylaniline (DMA) as promoter and a 50% solution of methyl ethyl ketone peroxide (MEKP) in dibutyl phthalate with a 6% cobalt octoate (CoC) solution in phthalate. All these materials were supplied by Akzo Chimie.

Calorimetric instrumentation and procedure

The calorimetric measurements were carried out using a Mettler DSC equipped with a control and programming unit (microprocessor TC10 and calorimetric cell DSC 20 arranged to permit temperature scans to -10 to 600 °C). In order to store the calorimetric results and normalize the calorimetric signal per unit of weight, the experimental DSC data were transferred and stored into a IBM-XT computer using a serial data interface (EIA RS232C). With the help of our own and commercial software the data were avaluated and plotted.

A standard sample was prepared by mixing 10 g resin with the different proportions of initiator and promoter for about 1 minute. The required amount of sample (10-12 mg) was weighed into a previously weighed sample pan, sealed and placed in the DSC cell for each measurement. The dynamic scans were performed from 0 °C to 250 °C, using a programed heating rate of 10 °C/min and a nitrogen atmosphere. Table 1 shows the different mixing proportions ob base resin, styrene, initiator and promoter used.

TABLE 1

Mixing proportions of resin, styrene, initiator and promoter.

No ref	Wt% resin		Wt% styrene	Wt% initiator *		Wt% promoter **	
	A-223	A-100		BP	MEKP	1±n	C_oO
1	65		35	2			
2		67	33	2			
3	65		35		1		
4		67	33		1		
5	65		35	2		0.10	
5	65		35	2		0.17	
7	65		35	2		0.25	
8	65		35	2		0.50	
9	65		35	2		1.50	
10	65		35		1		0.2
11	65		35		1		2.5
12	65		35		1		5.0
13	65		35		1		10.0
14	65		35	0.03			
15	65		35	0.50			
16	65		35	1.00			
17	65		35	3.00			

* parts per hundred (resin + styrene) ** parts per hundred (resin + styrene)

RESULTS AND DISCUSSION

Figs. 1 and 2 show dynamical exothermical peaks obtained from curing the two resins with BP and MEKP initiators without promoters. For each initiator system only one peak appears approximately at the same temperature. The exothermal heat varies with the kind of resin but it is approximately the same for each initiator system. (See Table 2). According to the literature (5) we assume that the heat generated during the cure is proportional to the number of reactive double bonds present in the polyester. As can be expected, resin A-228 is more reactive than resin A-100.

TABLE 2

Overall exothermic heat and peak temperatures for the resin A-228 and resin A-100. (Table 1, Refs. 1,2,3 and 4)

RESIN	INITIATOR	H (J g^{-1})	T_p (°C)	T_i (°C)	T_e (°C)
A-228	BP	342	115	85	165
	MEKP	357	125	80	200
A-100	BP	295	119	85	165
	MEKP	308	129	80	200

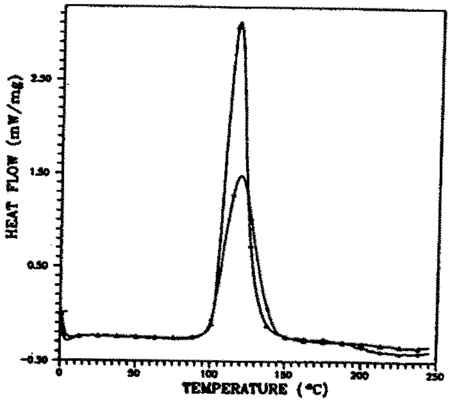

Fig. 1. Heat flow versus temperature for the resin (Δ) A-228 and (●) A-100 activated with BP (Table 1, Ref.1 and Ref.2).

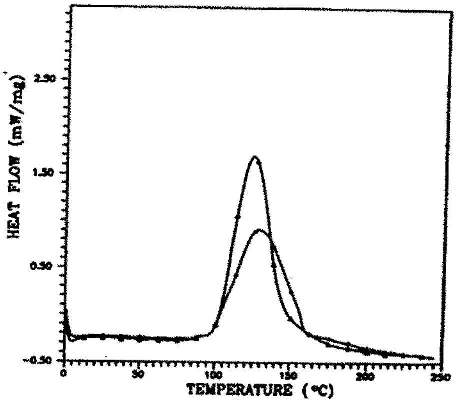

Fig. 2. Heat flow versus temperature for the resin (Δ) A-228 and (●) A-100 activated with Mekp. (Table 1, Ref.3 and Ref.4).

In the range of temperatures that the exothermic peak appears, without initiator no reactive process has been detected for the resins studied. It can be concluded that the temperature at which the exothermic peak appears must be attributed to thermal decomposition of initiator and production of free radicals. In our case the peak temperature of curing process coincides with the temperature reported in the literature for thermal decomposition of BP initiator (6)(7).

This result is also confirmed when the initiator/resin ratio is changed (see Fig. 3). Samples initiated with BP from 0.5 to 3 wt% show a single peak temperature ranging from 129 to 114 °C. The differences in the overall exothermic heat can be attributed to the decomposition heat of the initiator. With a small amount

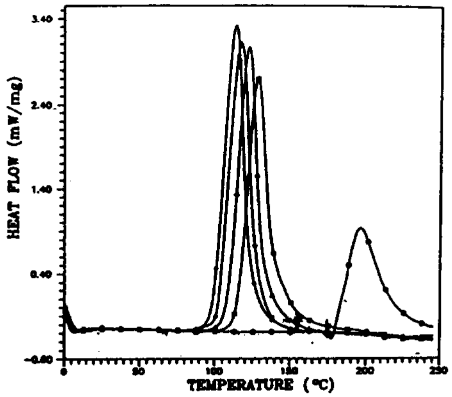

Fig. 3. Heat flow versus temperature for the resin A-228 with different BP proportions. (Table 1, (★) Ref.1, (O) Ref.14, (□) Ref. 15, (Δ) Ref.16 and (●) Ref.17).

of initiator, (in our case <0.05 wt%) the curing process appears in a very different temperature range with an important exothermic heat reduction that may be a consequence of a poorly crosslinking reaction although the possible styrene vaporization can mask the exothermic effect.

From figs. 1 and 2 and Table 2 it can be seen that the curing process activated by PB is produced in a smoller temperature range than MEKP and it can be concluded that with the proportions used, BP induces a great curing rate than MEKP does.

Figs. 4 and 5 show dynamical exothermic peaks of curing samples of A-228 resin with the same proportion of initiator and different proportions of accelerator for the DMA/BP and CoO MEKP catalytic systems. The position and the form of the first peak varies with the proportion of promoter used. The presence of more than one exothermic peak is frequently reported in the literature for epoxy curing systems (8)(9) and is attributed to different kinetics reactions of their components. For unsaturated polyester resins, Avella and coworkers (10) suggested that the first peak may be related to crosslink processes and the second peak to homopolymerization of the maleic double bonds. In our case, from the experimental results obtained, we attributed the two peaks to the chemical and thermal decomposition of initiator and kinetic competition of these two processes. We suggest that the first peak is the result of the partial decomposition of initiator induced by chemical reduction of the promoter. In consequence, the position and the form of the peak is function of the promoter/initiator ratio. The second peak that takes place approximately at the same temperature in all experiments and coincides with the temperature of the exothermic peak without promoter. It can be assumed that it is related to the termal decomposition of residual initiator.

Peak temperatures of the first exothermal peak and overall exothermic heat for the two catalytic systems used are plotted in fig 6. It can be seen that the peak

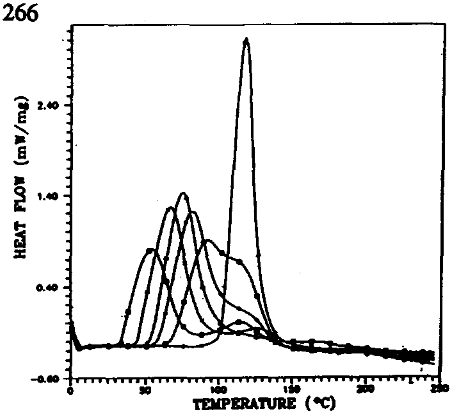

Fig. 4. Heat flow versus temperature for the resin A-228 with BP and different proportions of DMA. (Table 1, (★) Ref.1, (○) Ref.5, (●) Ref.6, (△) Ref.7, (X) Ref.8 and (□) Ref.9).

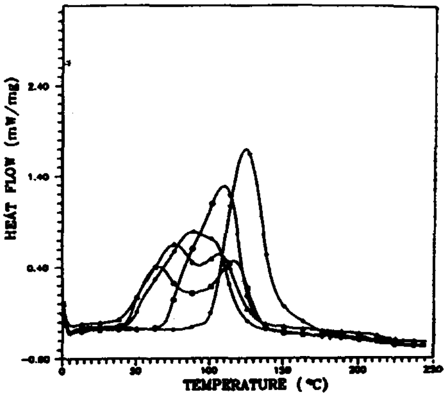

Fig. 5 Heat flow versus temperature for the resin A-228 activated with MEKP and different proportions of CoO. (Table 1, (★) Ref. 3, (○) Ref.10, (●) Ref.11, (△) Ref.12 and (□) Ref.13).

temperature of the first peak diminishes with the increment of promoter/initiator ratio. These results agree with the fact that the promoter accelerates the curing process and enables it to take place at room temperatures. Nevertheless, the kinetic process of chemical reduction and the possibility of a solely partial initiator decomposition imply that the material formed will be partially cured. This can be demonstrated by isothermal runs and by observing the amount of thermal polymerization that can be induced during a post-cure of the sample (11).

On the other hand, the increment of promoter/initiator ratio and the production of faster rates of initiation will produce shorter gel and cure times. The total extent of cure and the structure of the crosslinked matrix formed can be affected by this initiation process. In Fig. 6 it can be seen that the overall heat reaction of samples activated by both catalytic systems diminishes with the increment of amount of promoter used, although after a certain promoter/initiator ratio, the addition of more promoter produces only a slight effect in the chemical decomposition. From these experimental results it can be suggested that the curing of a resin by chemical decomposition of the initiator at low temperatures can make it impossible for the system to reach a certain extent of cure. At higher temperature, the extent of cure would be greater than at lower ones. Geling and partial vitrification induced in the initial curing process could explain why this happen (12). The post cure treatments, that are widely used in industrial processes, will make it possible to obtain a cured material in a state that will be different depending on the first stage of curing process.

CONCLUSIONS

- The catalytic promoter/initiator system plays an important role in the kinetic curing process of unsaturated polyester resins. Dynamycal DSC experiments exhibit

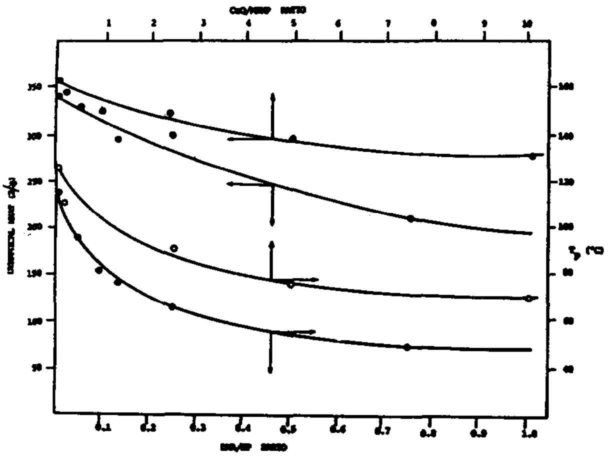

Fig. 6. Overall exothermic heat and peak temperature for the resin A-228 activated with different DMA/BP and CoO/MEKP ratios.

more than one exothermic peak that typifies the complex of curing process.

- Without promoter, a single peak is obtained in dynamic DSC runs. We attribute this peak to the thermal decomposition of the peroxide that produces free radicals and possibilities the crosslinking reation process.
- Varying the amount of initiator used, a slight variation of exothermic peak temperature is produced. At a very slow amount of initiator the curing reaction takes place at a different range of temperatures and produces a poorly crosslinked material.
- When different amounts of promoter/initiator are used we attribute the presence of two exothermal peaks to the chemical and thermical decomposition of the initiator.
- The results obtained agree with the fact that the promoter accelerates the curing process and enables it to take place at low temperatures. Without post-cured thermal treatment, the samples can remain partially cured.
- With a thermal post-cured treatment, a partially crosslinked resin can increase in some degree the extent of cure but the network structure and the properties of the formed matrix will depend on the first stage of curing process.

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