

Curing Behavior of Unsaturated Polyester Resin with Mixed Initiators

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Synopsis

The curing behavior of unsaturated polyester resin with mixed initiators was investigated both experimentally and theoretically. For the experimental investigation, we used various combinations of low- and high-temperature initiators to cure a general-purpose unsaturated polyester resin and determined the rate of cure and the degree of cure, using differential scanning calorimetry and infrared spectroscopy. For the theoretical investigation, we used the mechanistic kinetic model described in our previous paper. It has been demonstrated that the mechanistic model is very useful for predicting the curing behavior of unsaturated polyester resin with mixed initiators, using information on the rate constants of the individual initiators and the concentration of the initiator. Such an approach will help reduce, if not eliminating completely, the number of tedious and time-consuming curing experiments that would otherwise have to be performed.

INTRODUCTION

Various organic peroxides and azo compounds have been introduced as initiators for free radical polymerization. Decomposition of initiators by heat or irradiation generates free radicals which can initiate polymerization reactions. Sheppard and Kamath¹ reviewed the selection and use of these initiators. A kinetic treatment of the polymerization of styrene with mixed initiators was discussed by Lowell and Price.² They pointed out that the rate of polymerization is not merely additive but is given by the square root of the sum of the squares of the individual rates of polymerization. It may be surmised that fundamental information concerning the performance of an initiator is very important for determining optimum combinations of mixed initiators.

In the processing of unsaturated polyester resin (for instance, pultrusion and compression molding), it has been the common industrial practice to use mixed initiator systems, consisting of two initiators. One of them would be a low-temperature initiator and the other a high-temperature one. The reason is very simple. Upon charging the mold cavity (in the compression molding) or entering the die (in pultrusion), the resin begins to cure immediately with the help of the low-temperature initiator and then completes the curing reaction with the help of the high-temperature initiator.

With a high-temperature initiator alone (that may decompose, say, at 90°C), part of the cure time needed will be lost until the initiator reaches its decomposition temperature. Thus one tends to use a little extra initiator, in order to ensure that the resin will be cured completely. In doing so, because of the exothermic curing reaction, too much heat may be generated locally, in too short a time, giving rise to a nonuniform degree of cure in the stock. On

the other hand, with a low-temperature initiator alone (that may decompose, say, at 50°C), the curing reaction may not go far enough. After the initiator completes its decomposition during the initial stage of cure, there will be no free radicals available at temperatures, say above 90°C, that would help complete the curing of the material for the remaining cure time available.

In spite of the practical importance of mixed initiators for curing unsaturated polyester resins, little information has been published, either theoretical or experimental, that discusses the curing behavior of such systems. In this paper, we report our recent investigation, both experimental and theoretical, on the curing behavior of unsaturated polyester resin with mixed initiators.

EXPERIMENTAL

A commercial grade of unsaturated polyester resin (OC-E701, Owens-Corning Fiberglas), containing a proprietary inhibitor, was used for the study. The resin consists of propylene glycol, fumarates, and isophthalates, and contains 43 wt % of styrene. We used the following mixed initiator systems: (1) mixtures of PERCADOX 16N (P16N) (Noury Chemical Corp.) and benzoyl peroxide (BPO) (Noury Chemical Corp.), and (2) mixtures of P16N and *tert*-butyl perbenzoate (TBPB) (Pennwalt Chemical Corp.). Table I gives a summary of the various combinations of resin and initiator used in the present investigation. In all formulations used for curing, the samples contained one part of initiator to 100 parts of resin, by weight. It should be noted that TBPB may be considered to be a high-temperature initiator, BPO a medium-temperature initiator, and P16N a low-temperature initiator. The use of these mixed initiator systems is a very common practice in industrial processing operations, such as pultrusion and compression molding, in order to minimize the residence time in pultrusion and the cycle time in compression molding.

The experimental procedure employed for investigating the curing reaction and the method used for analyzing the experimental data are the same as those described in our previous paper.³

RESULTS

For comparison purposes later, we will first present the curing behavior of the resin with a single initiator. Figure 1 gives plots of the rate of cure (da/dt) vs. cure time for the initiator P16N, Figure 2 for the initiator BPO,

TABLE I
Mixed Initiator Systems Used in the Experiment

Materials	Composition (wt)
Resin/P16/BPO	100/0.10/0.90
Resin/P16/BPO	100/0.25/0.75
Resin/P16/BPO	100/0.50/0.50
Resin/P16/TBPB	100/0.25/0.75
Resin/P16/TBPB	100/0.50/0.50
Resin/P16/TBPB	100/0.75/0.25

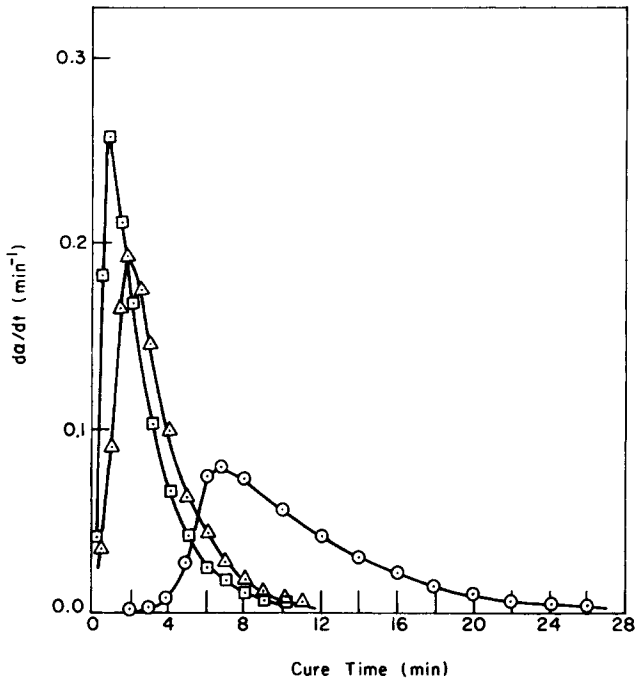


Fig. 1. da/dt vs. cure time for the resin/P16N system at different isothermal temperatures ($^{\circ}\text{C}$): (○) 70; (△) 80; (□) 90.

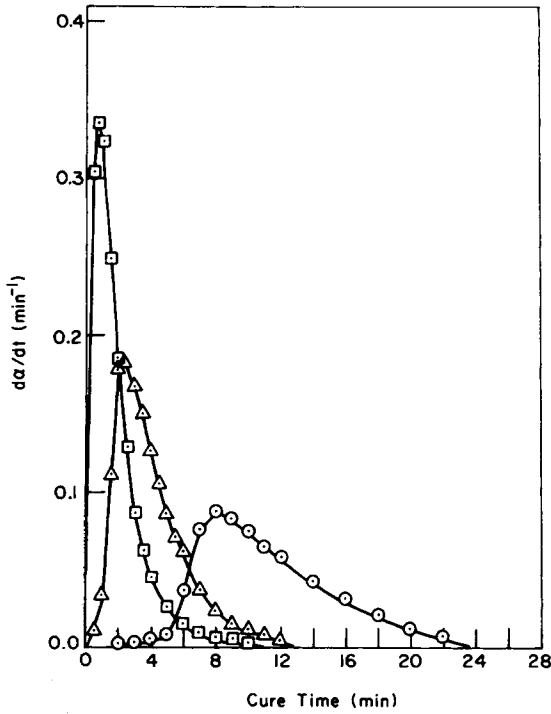


Fig. 2. da/dt vs. cure time for the resin/BPO system at different isothermal temperatures ($^{\circ}\text{C}$): (○) 90; (△) 100; (□) 110.

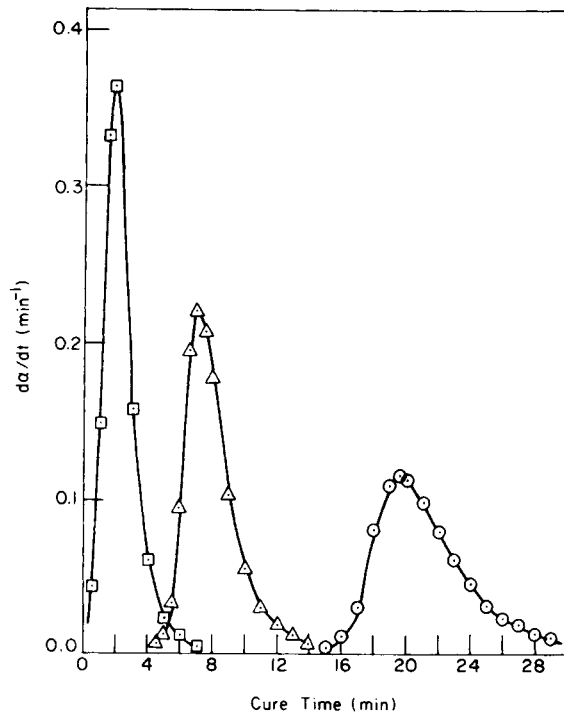


Fig. 3. $d\alpha/dt$ vs. cure time for the resin/TBPB system at different isothermal temperatures ($^{\circ}\text{C}$): (○) 110; (△) 120; (□) 130.

and Figure 3 for the initiator TBPB, at various isothermal cure temperatures. As may be seen in Figures 1–3, the decomposition temperatures of these initiators are such that there exists an optimum range of cure temperature recommended for each of them. Figure 4 gives plots of the degree of cure (α) vs. cure time for the initiator P16N, Figure 5 for the initiator BPO, and Figure 6 for the initiator TBPB, at various isothermal cure temperatures. It is clear from Figures 4–6 that the cure of this resin with the initiator TBPB at temperatures lower than 110°C , for instance, is not effective because TBPB decomposes very slowly, while the cure of this resin with the initiator P16N at temperatures higher than 90°C is not practical because P16N will decompose completely by the time the system reaches 90°C .

Figure 7 gives plots of $d\alpha/dt$ vs. cure time for the resin cured at 90°C , using different compositions of P16N/BPO mixed initiators. It is seen in Figure 7 that, as the amount of P16N in a P16N/BPO mixture increases, the peak value of $d\alpha/dt$ occurs earlier. This indicates that the cure reaction progresses faster as the amount of P16N is increased in a P16N/BPO mixture. But, with the 75/25 P16N/BPO mixture, the peak value of $d\alpha/dt$ occurs at a cure time almost the same as for pure P16N, suggesting that too much P16N in a P16N/BPO mixture is not effective either. How the degree of cure progresses with different P16N/BPO ratios is shown in Figure 8.

Figure 9 gives plots of $d\alpha/dt$ vs. cure time for the resin cured at 90°C , and Figure 10 plots of α vs. cure time, using different compositions of P16N/TBPB mixed initiators. It is seen in Figures 9 and 10 that the use of a P16N/TBPB

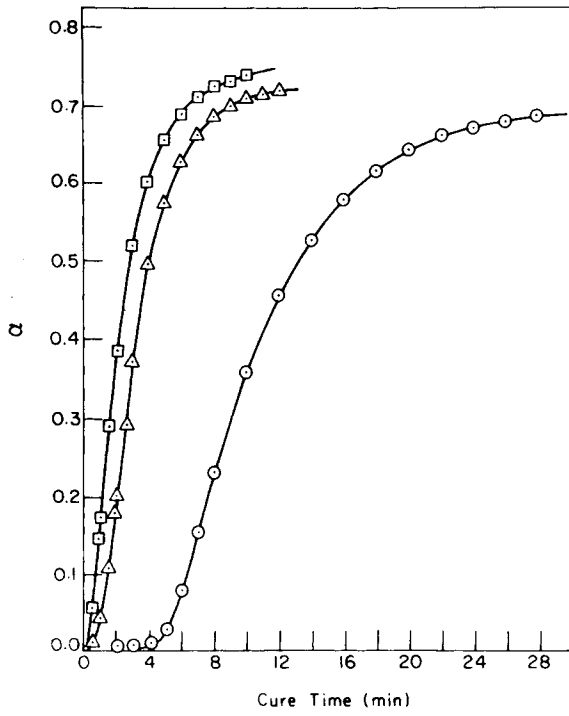


Fig. 4. α vs. cure time for the resin/P16N system. Symbols are the same as in Figure 1.

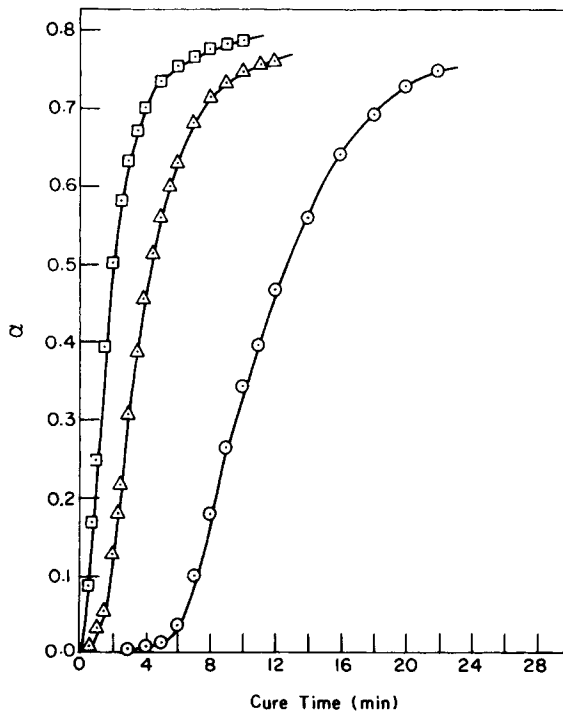


Fig. 5. α vs. cure time for the resin/BPO system. Symbols are the same as in Figure 2.

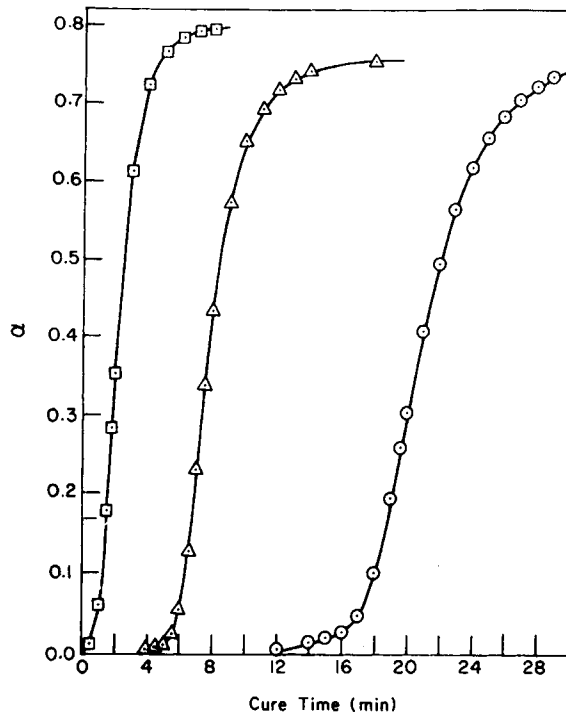


Fig. 6. α vs. cure time for the resin/TBPP system. Symbols are the same as in Figure 3.

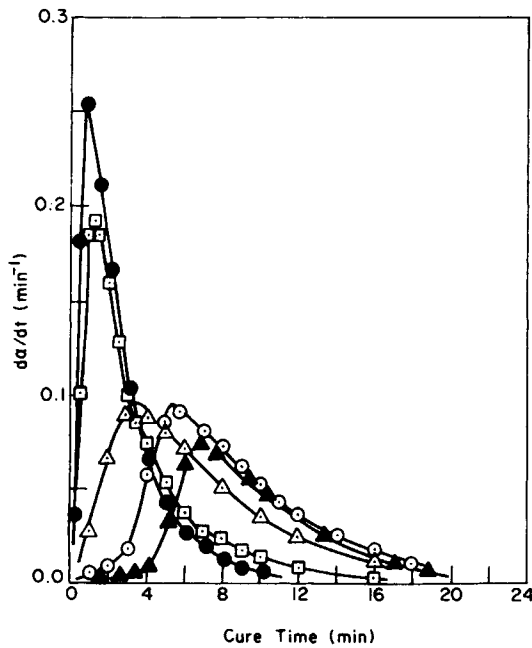


Fig. 7. $d\alpha/dt$ vs. cure time at 90°C for: (●) 100/1 resin/P16N system; (▲) 100/1 resin/BPO system; (○) 100/0.1/0.9 resin/P16N/BPO system; (△) 100/0.25/0.75 resin/P16N/BPO system; (◻) 100/0.5/0.5 resin/P16N/BPO system.

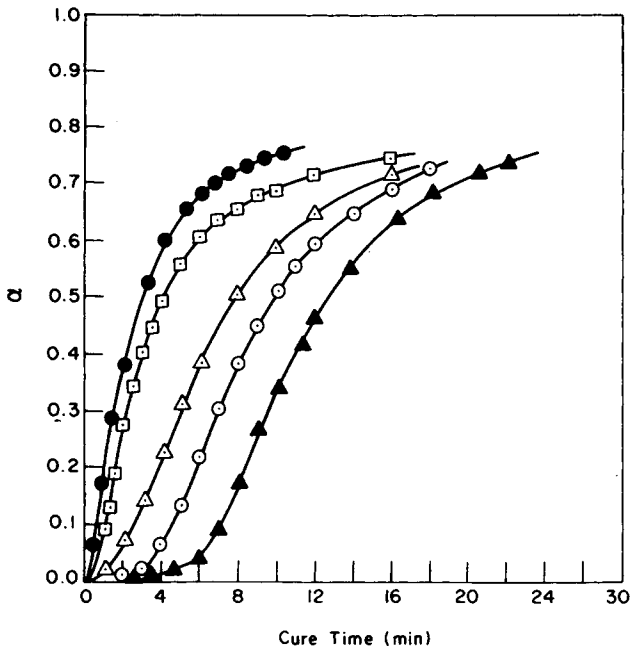


Fig. 8. α vs. cure time at 90°C for polyester resin with P16N/BPO mixed initiators. Symbols are the same as in Figure 7.

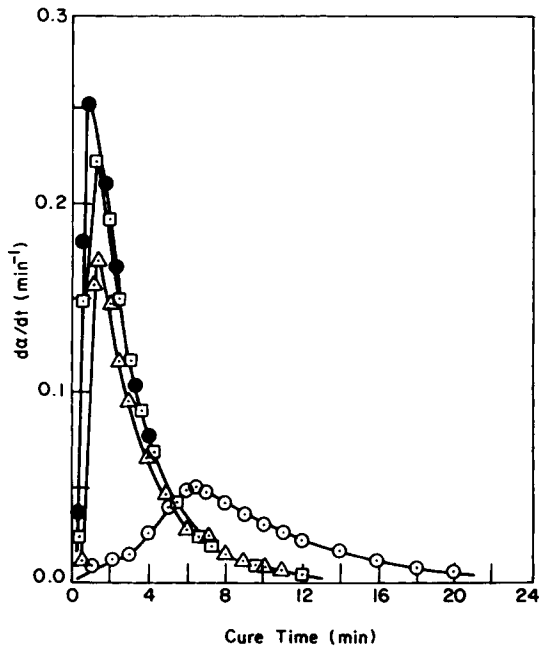


Fig. 9. da/dt vs. cure time for polyester resin with P16N/TBPP mixed initiators: (●) 100/1 resin/P16N system; (○) 100/0.25/0.75 resin/P16N/TBPP system; (△) 100/0.5/0.5 resin/P16N/TBPP system; (◻) 100/0.75/0.25 resin/P16N/TBPP system.

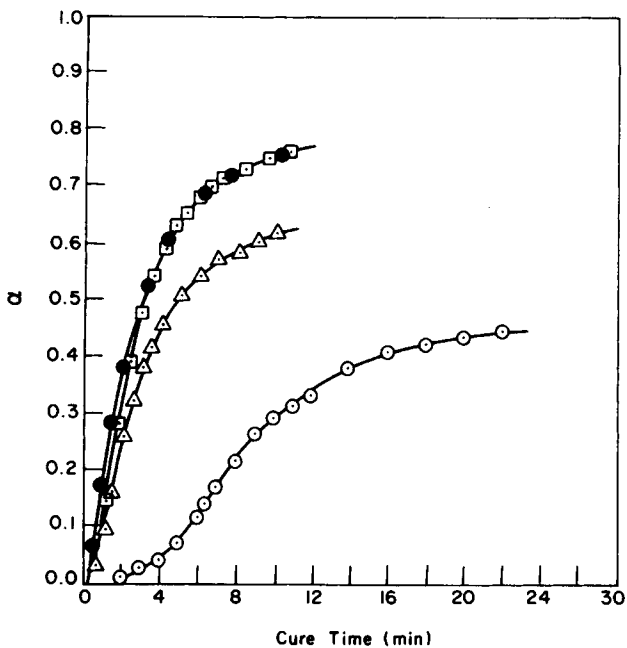


Fig. 10. α vs. cure time for polyester resin with P16N/TBPB mixed initiators. Symbols are the same as in Figure 9.

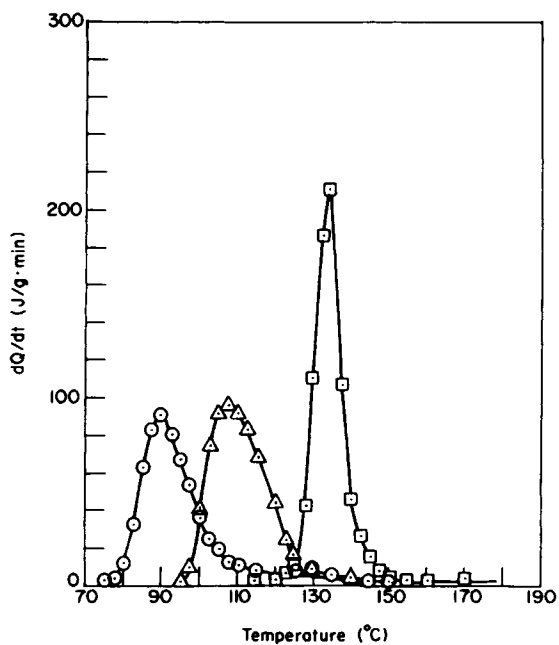


Fig. 11. Nonisothermal DSC thermograms for: (○) resin/P16N system; (△) resin/BPO system; (□) resin/TBPB system. The heating rate was 5°C/min.

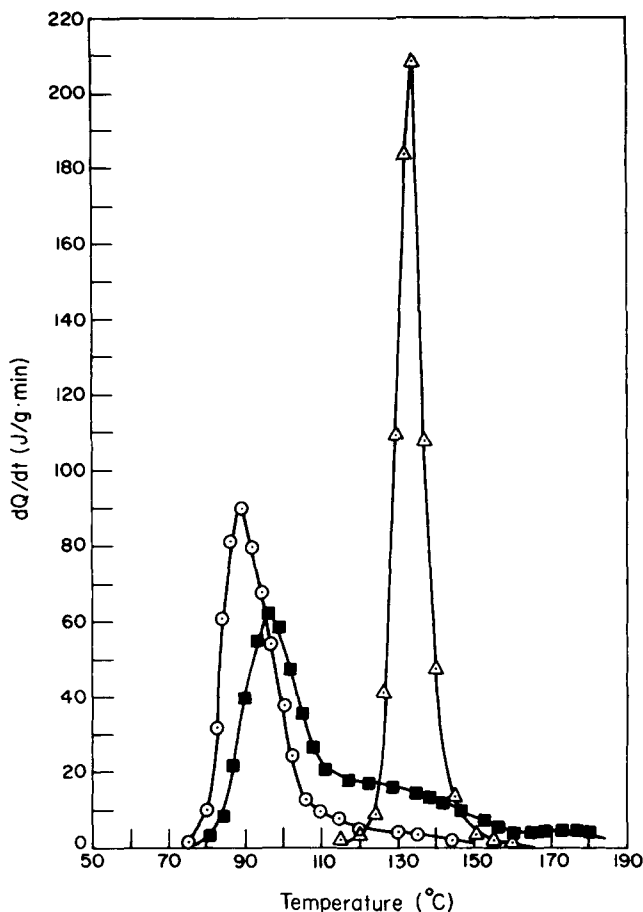


Fig. 12. Nonisothermal DSC thermograms for: (○) 100/1 resin/P16N system; (△) 100/1 resin/TBPB system; (■) 100/0.1/0.9 resin/P16N/TBPB system. The heating rate was 5°C/min.

mixture is not effective for curing the resin at 90°C, and what is observed in these figures is merely the dilution effect of P16N as the amount of P16N in the P16N/TBPB blend is decreased.

The effectiveness of the mixed initiators employed in the present study with respect to cure temperature may be illustrated best with nonisothermal DSC thermograms, shown in Figures 11 and 12. It is quite clear from Figure 11 that there exists a certain range of temperature where the thermogram of the P16N overlaps with that of BPO, whereas there is no overlap in temperature between the thermogram of P16N and the thermogram of TBPB. What is interesting, however, is that the 10/90 P16N/TBPB mixture, as may be seen in Figure 12, increases the peak temperature of P16N from 90 to 100°C (or decreases the peak temperature of TBPB from 135 to 100°C). Since a nonisothermal scanning of a DSC run begins from a low temperature, the low-temperature initiator P16N generates radicals (and thus crosslinking reactions) before the initiator TBPB begins to generate radicals. As the curing reaction proceeds, and the temperature consequently rises above a certain

temperature due to the exothermic chemical reaction, then the high-temperature initiator TBPB participates in the crosslinking reactions. It is of interest to observe in Figure 12 that the role that a mixed initiator plays in controlling the curing reaction is not additive with respect to its composition. There can be many reasons for this observation, but it is very difficult to speculate on this, from the strictly experimental point of view. Further discussion of this subject will be deferred until we present theoretical predictions later.

THEORETICAL PREDICTIONS AND DISCUSSION

In the present investigation, we have used the mechanistic kinetic model that was developed in our previous investigation,³ in order to predict the curing behavior of mixed initiator systems (i.e., resin/P16N/BPO and resin/P16N/TBPB systems). For this, we first had to determine the rate constants and other parameters that are associated with the system equations, using the experimental data obtained for single initiator systems (i.e., resin/P16N, resin/BPO, and resin/TBPB systems). We shall first present system equations for the single initiator systems, and then system equations for the mixed initiator systems.

Single Initiator Systems

On the basis of the kinetic model developed in our previous investigation,³ we have the following system equations:

$$d[Z]/dt = -k_z[Z][R \cdot] \quad (1)$$

$$d[I]/dt = -k_d[I] \quad (2)$$

$$d[R \cdot]/dt = 2fk_d[I] - k_z[Z][R \cdot] \quad (3)$$

$$d\alpha/dt = k_p(1 - \alpha)[R \cdot] \quad (4)$$

in which $[Z]$ is the inhibitor concentration, $[I]$ is the initiator concentration, $[R \cdot]$ is the radical concentration (which is assumed to be the sum of the concentrations of polyester radical $[E \cdot]$, styrene radical $[S \cdot]$, and initiator radical $[I \cdot]$ (i.e., $[R \cdot] = [E \cdot] + [S \cdot] + [I \cdot]$)), α is the degree of cure, k_z is the rate constant of inhibitor, f is the efficiency of initiator, k_d is the rate constant of the initiator decomposition reaction, and k_p is the rate constant of the propagation reaction. In order to incorporate a diffusion-controlled propagation reaction into k_p , we used the following expression³:

$$k_p = k_{p0} \left[1 - (\alpha/\alpha_f) \right]^m \quad (5)$$

in which α_f denotes the final degree of conversion. In deriving eqs. (1)–(4), based on our previous investigation,³ we have assumed that the termination reaction is negligibly small compared to the propagation reaction.

Equations (1)–(5) must be solved for $[Z]$, $[I]$, $[R \cdot]$, and α with the given initial conditions, i.e., $[Z(0)] = [Z]_0$, $[I(0)] = [I]_0$, $[R \cdot(0)] = 0$, and $\alpha(0) = 0$. However, before eqs. (1)–(5) are solved, one must specify the rate constants

k_z , k_d , and k_{p0} , the parameter m , and the efficiency of initiator, f . Following the argument presented in our previous paper,³ f is assumed to have the following form:

$$f = \frac{f_0^2 [1 - (\alpha/\alpha_f)]^2}{2(1 - f_0)([I]/[I]_0)} \left\{ \left[1 + \frac{4(1 - f_0)([I]/[I]_0)}{f_0^2 [1 - (\alpha/\alpha_f)]^2} \right]^{1/2} - 1 \right\} \quad (6)$$

where f_0 is the initial value of the initiator efficiency and $[I]_0$ is the initial concentration of initiator. Note that eq. (6) indicates that f decreases with increasing α .

In carrying out the computation, on the basis of the experimental results presented above, we have used the following numerical values: (a) the initial concentration of the inhibitor $[Z]_0 = 5.09 \times 10^{-4}$ M/L; (b) the initial concentration of the initiator $[I]_0 = 2.561 \times 10^{-2}$ M/L for P16N, $[I]_0 = 3.619 \times 10^{-2}$ M/L for BPO, and $[I]_0 = 5.716 \times 10^{-2}$ M/L for TBPB; and (c) the rate constant of the initiator decomposition reaction k_d was estimated using the following expression:

$$k_d = k_{d0} \exp(-E_d/T) \quad (7)$$

in which $k_{d0} = 2.205 \times 10^{19}$ and $E_d = 1.615 \times 10^4$ for P16N, $k_{d0} = 2.928 \times 10^{16}$ and $E_d = 1.546 \times 10^4$ for BPO, and $k_{d0} = 8.524 \times 10^{15}$ and $E_d = 1.632 \times 10^4$ for TBPB.

In solving the system equations, eqs. (1)–(6), we had to specify numerical values for the following parameters, k_z , k_{p0} , m , and f_0 . Since these values were not known to us, we used the experimentally obtained values of $d\alpha/dt$ and α as a function of cure time t , presented above in Figures 1–6, to determine the numerical values of k_z , k_{p0} , m , and f_0 , using the computational algorithms described in our previous paper.³

Figures 13 and 14 give comparisons of the experimental results with the theoretically predicted values of $d\alpha/dt$ during the entire period of the cure reaction, for three single initiator systems at various isothermal cure temperatures. Table II gives a summary of the numerical values of the parameters k_z , k_{p0} , m , and f_0 , which were obtained from the numerical simulation. It should be emphasized that the values of f_0 and m were determined as part of the solution of the system equations, by using the criterion that the sum of the squares of the differences between the computed values of $d\alpha/dt$ and α and the experimentally measured ones be a minimum.

Figure 15 gives plots of the propagation rate constant k_{p0} vs. the reciprocal of absolute temperature for the unsaturated polyester resin (OC-E701, Owens-Corning Fiberglas) with three different initiators (P16N, BPO, and TBPB). Using least-squares analysis, we have obtained the following expression:

$$k_{p0} = 3.440 \times 10^{14} \exp(-9993/T) \quad (8)$$

As may be seen in Table II, the values of f_0 for P16N are smaller than those for BPO and TBPB. It should be mentioned that the values of k_d , repre-

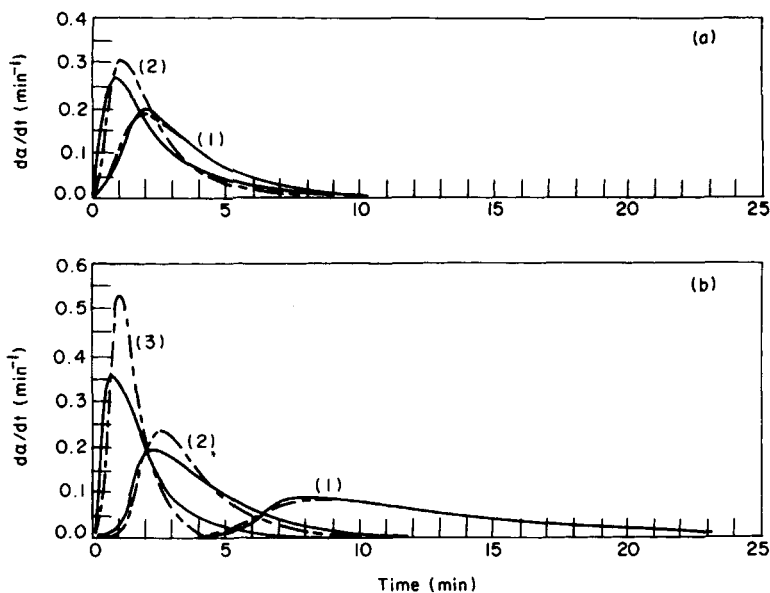


Fig. 13. Comparison of the experimental results (—) with the theoretically predicted profiles (---) of $d\alpha/dt$. (a) resin/P16N system: curve 1 at 80°C and curve 2 at 90°C . (b) resin/BPO: curve 1 at 90°C ; curve 2 at 100°C ; curve 3 at 110°C .

sented by eq. (7), were determined using information on the half-life ($t_{1/2}$) of the initiator in the concentration range 0.1–0.2 M/L at various temperatures,^{4,5} whereas the concentration of P16N used in our experiment was 0.025 M/L. It is generally known that peroxydicarbonates, such as PERCADOX 16N, decompose rapidly as the concentration increases.¹ Therefore, it is entirely possible that the low values of f_0 for P16N, obtained in the course of the numerical simulation, may be due to the low concentration of P16N used, which is an order of magnitude lower than that based on which the values of k_d were estimated.

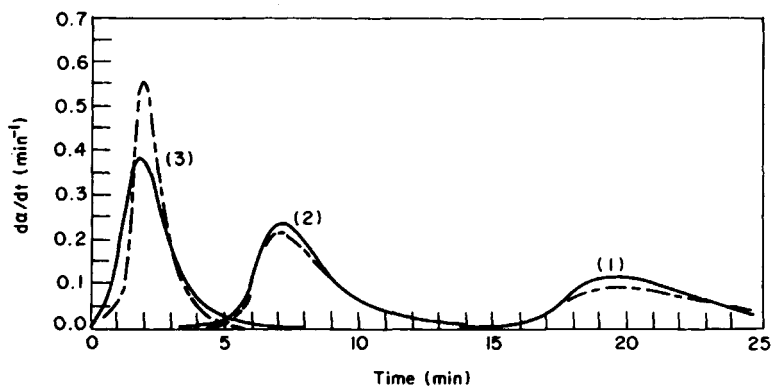


Fig. 14. Comparison of the experimental results (—) with the theoretically predicted profiles (---) of $d\alpha/dt$ for the resin/TBPP system: curve 1 at 110°C ; curve 2 at 120°C ; curve 3 at 130°C .

TABLE II
Summary of the Kinetic Parameters Determined from Computations

Temp (°C)	k_z (L/g mol min)	k_{p0} (L/g mol min)	m	f_0
(a) P16N				
70	1.597×10^4	7.652×10^1	0.65	0.07
80	3.798×10^4	1.747×10^2	0.65	0.09
90	8.609×10^4	3.810×10^2	0.65	0.04
(b) BPO				
90	8.609×10^4	3.810×10^2	0.65	0.16
100	1.868×10^5	7.969×10^2	0.65	0.20
110	3.891×10^5	1.604×10^3	0.65	0.18
(c) TBPB				
110	3.891×10^5	1.604×10^3	0.65	0.13
120	7.809×10^5	3.116×10^3	0.65	0.12
130	1.514×10^6	5.856×10^3	0.65	0.16

In order to gain an insight into the curing behavior of unsaturated polyester resin with a single initiator, let us examine theoretically the predicted profiles of the inhibitor concentration $[Z]$ and the degree of cure α displayed in Figure 16 for the resin/P16N system, and in Figure 17 for the resin/BPO system. It is of great interest to observe in Figures 16 and 17 that, at all isothermal cure temperatures employed, the inhibitor disappears completely before any significant curing takes place.

Figure 18 gives theoretically predicted profiles of the radical concentration $[R \cdot]$ for the resin/BPO system during the entire period of the cure reaction. It is seen in Figure 18 that $[R \cdot]$ reaches a constant value after a certain cure time and that the $[R \cdot]$ remaining in the system (i.e., unreacted radicals)

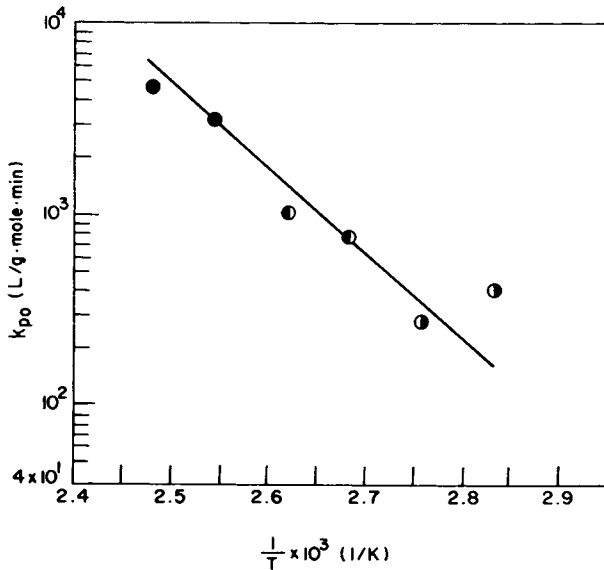


Fig. 15. Arrhenius plots of k_{p0} for polyester resin with the initiator: (●) P16N; (◐) BPO; (◑) TBPB.

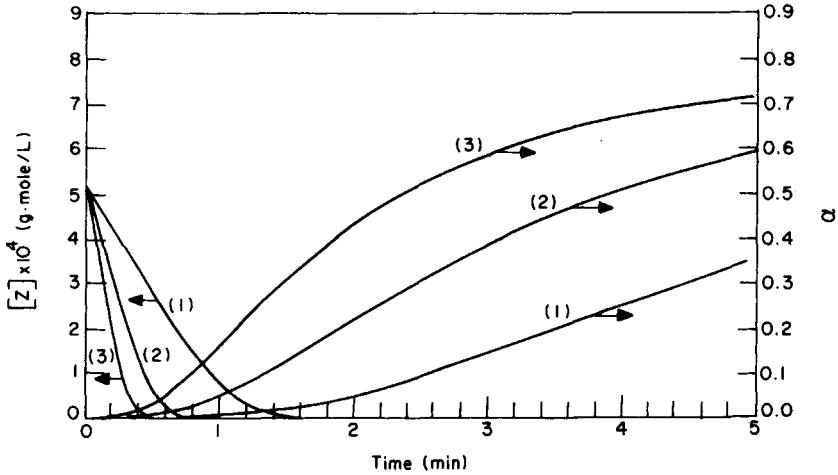


Fig. 16. Inhibitor concentration vs. cure time for the resin/P16N system at different isothermal cure temperatures ($^{\circ}\text{C}$): (1) 70; (2) 80; (3) 90.

becomes larger as the cure temperature is increased. This may be due to the fact that, as cure temperature is increased, the crosslinking reaction proceeds at a faster rate and thus the chances of radicals being entrapped in the networks also increase, leaving a greater amount of unreacted radicals in the system when the cure reaction ceases. Earlier, Slupkowski et al.⁶ studied the curing reaction of unsaturated polyester resin using electron spinning resonance spectroscopy, and observed that the amount of unreacted radicals remaining in the system increased very rapidly as the cure temperature increased. This observation appears to support our computational results displayed in Figure 18.

Figure 19 gives theoretically predicted profiles of the initiator concentration [I] for the resin/BPO system for the entire period of the cure reaction. It is

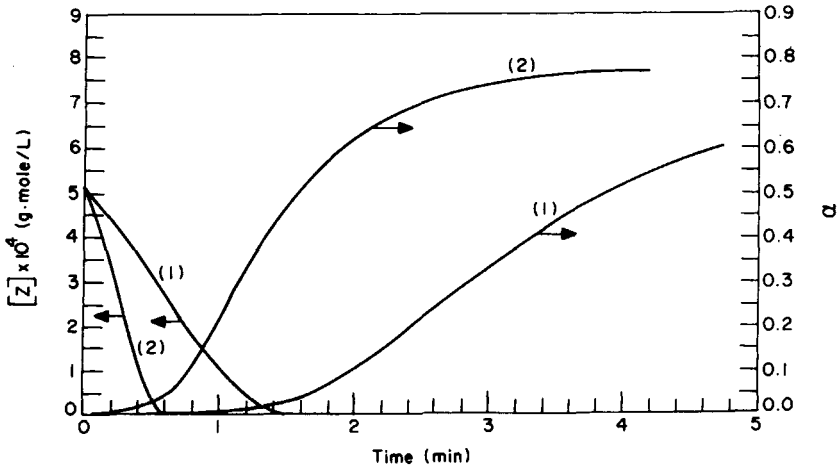


Fig. 17. Inhibitor concentration vs. cure time for the resin/BPO system at different isothermal cure temperatures ($^{\circ}\text{C}$): (1) 100; (2) 110.

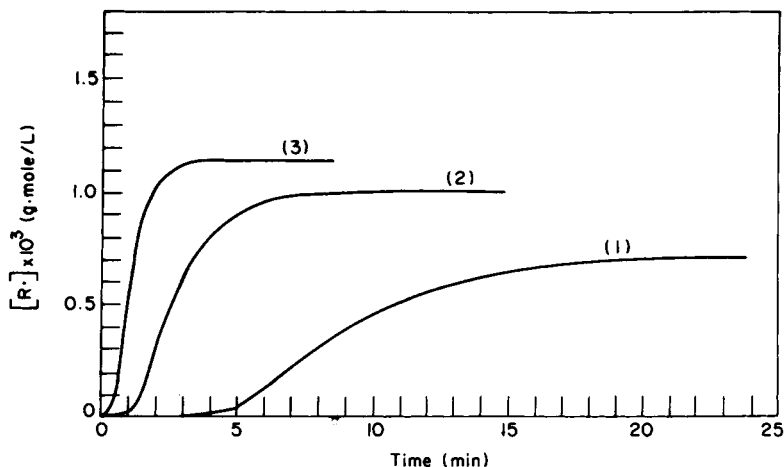


Fig. 18. Radical concentration vs. cure time for the resin/BPO system at different isothermal cure temperatures ($^{\circ}\text{C}$): (1) 90; (2) 100; (3) 110.

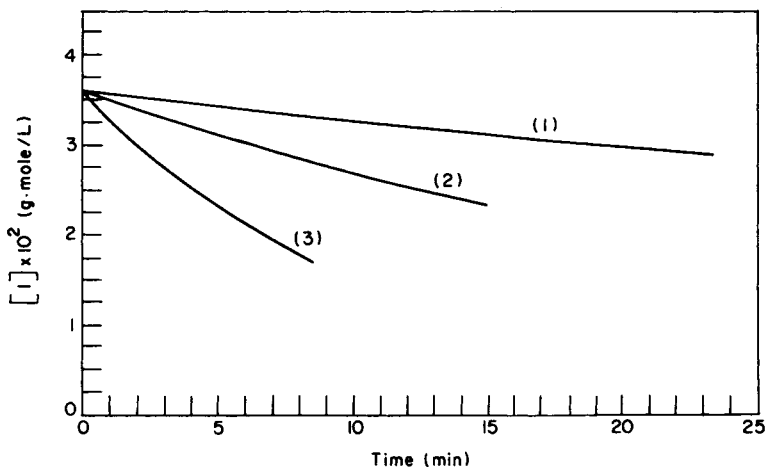


Fig. 19. Initiator concentration vs. cure time for the resin/BPO system at different isothermal cure temperatures ($^{\circ}\text{C}$): (1) 90; (2) 100; (3) 110.

seen in Figure 19 that $[I]$ decreases rapidly with cure time as cure temperature increases. This is due to the fact that, as the cure temperature is increased, the rate of cure is increased (see, for instance, Figs. 1–3) and thus initiator will be consumed at a faster rate. Note that, as the cure temperature is increased, the decomposition of initiator proceeds at a faster rate, also. Space limitations here do not permit us to present computational results for the resin/P16N and resin/TBPB systems investigated.

Mixed Initiator Systems

Once the rate constants k_z and k_{p0} , the parameter m , and the initial efficiency of initiator f_0 for single initiator systems are determined, one can

then proceed to predict the curing behavior of mixed initiator systems. However, one must first modify the system equations presented above.

Since our experimental study used mixed initiator systems consisting of two initiators, we must replace eq. (2) with the following expressions:

$$d[I_1]/dt = -k_{d1}[I_1] \quad (9)$$

and

$$d[I_2]/dt = -k_{d2}[I_2] \quad (10)$$

where $[I_1]$ and $[I_2]$ are the concentrations and k_{d1} and k_{d2} the decomposition rate constants, of initiators 1 and 2, respectively. Also, eq. (3) must be replaced by

$$d[R \cdot]/dt = 2(f_1 k_{d1}[I_1] + f_2 k_{d2}[I_2]) - k_z[Z][R \cdot] \quad (11)$$

and eq. (6) by

$$f_1 = \frac{f_{10}^2 [1 - (\alpha/\alpha_f)]^2}{2(1 - f_{10})([I_1]/[I_1]_0)} \left\{ \left[1 + \frac{4(1 - f_{10})([I_1]/[I_1]_0)}{f_{10}^2 [1 - (\alpha/\alpha_f)]^2} \right]^{1/2} - 1 \right\} \quad (12)$$

and

$$f_2 = \frac{f_{20}^2 [1 - (\alpha/\alpha_f)]^2}{2(1 - f_{20})([I_2]/[I_2]_0)} \left\{ \left[1 + \frac{4(1 - f_{20})([I_2]/[I_2]_0)}{f_{20}^2 [1 - (\alpha/\alpha_f)]^2} \right]^{1/2} - 1 \right\} \quad (13)$$

where $[I_1]_0$ and $[I_2]_0$ are the initial concentrations, and f_{10} and f_{20} the initial efficiencies, of initiators 1 and 2, respectively.

In carrying out computations to predict the curing behavior of mixed initiator systems, we had to solve eqs. (1), (4), (5), and (9)–(12), with the given initial conditions. For this, on the basis of the experimental results presented above, we have used the following numerical values: (a) the initial concentration of inhibitor $[Z]_0 = 5.09 \times 10^{-4}$ M/L; (b) the initial concentrations of initiators, $[I_1]_0$ and $[I_2]_0$, given in Table III; (c) the decomposition rate constants of initiators, k_{d1} and k_{d2} , as evaluated from eq. (7) for the three initiators P16N, BPO, and TBPB; (d) the rate constants k_z and k_{p0} , the

TABLE III
Initial Concentration of the Mixed Initiators Used

Materials	$[I_1]_0$ (M/L)	$[I_2]_0$ (M/L)
Resin/P16N/BPO = 100/0.10/0.90	2.561×10^{-3}	3.257×10^{-2}
Resin/P16N/BPO = 100/0.25/0.75	6.403×10^{-3}	2.714×10^{-2}
Resin/P16N/BPO = 100/0.50/0.50	1.281×10^{-2}	1.809×10^{-2}
Resin/P16N/TBPB = 100/0.25/0.75	6.403×10^{-3}	4.287×10^{-2}
Resin/P16N/TBPB = 100/0.50/0.50	1.282×10^{-2}	2.858×10^{-2}
Resin/P16N/TBPB = 100/0.75/0.25	1.921×10^{-2}	1.429×10^{-2}

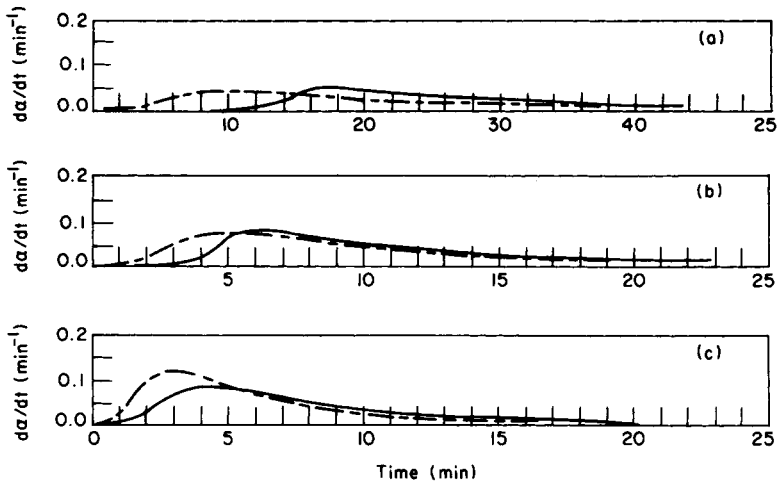


Fig. 20. Comparison of the experimental results (—) with the theoretically predicted profiles (---) of $d\alpha/dt$ at 80°C: (a) 100/0.1/0.9 resin/P16N/BPO system; (b) 100/0.25/0.75 resin/P16N/BPO system; (c) 100/0.5/0.5 resin/P16N/BPO system. $f_{10} = 0.07$ for P16N and $f_{20} = 0.16$ for BPO.

parameter m , and the initial efficiency of initiator f_{j0} ($j = 1, 2$) listed in Table II.

Figures 20–22 give comparisons of the experimental results with the theoretically predicted profiles of the rate of cure $d\alpha/dt$ during the entire period of cure, for the resin/P16N/BPO system at 80, 90, and 100°C, respectively. It is of great interest to note that in Figure 20 (i.e., at 80°C) the peak of $d\alpha/dt$ predicted by the kinetic model occurs sooner than that observed from the

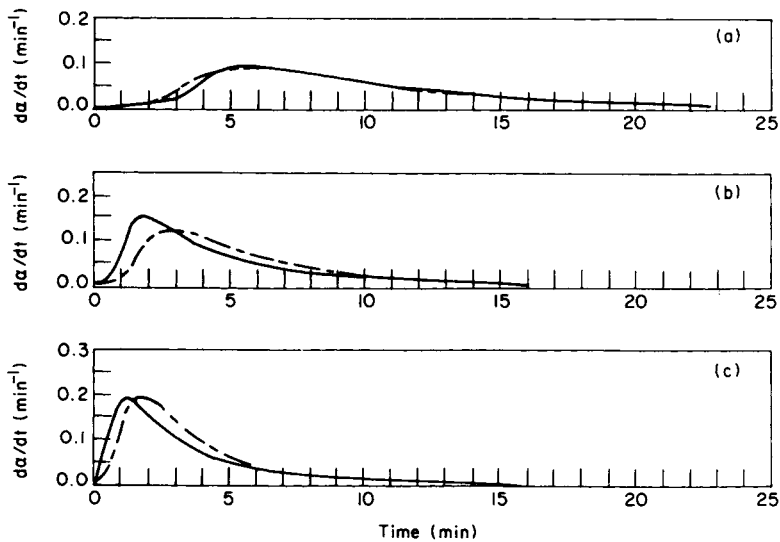


Fig. 21. Comparison of the experimental results (—) with the theoretically predicted profiles (---) of $d\alpha/dt$ at 90°C for the resin/P16N/BPO system: (a) 100/0.1/0.9; (b) 100/0.25/0.75; (c) 100/0.5/0.5. $f_{10} = 0.09$ for P16N and $f_{20} = 0.16$ for BPO.

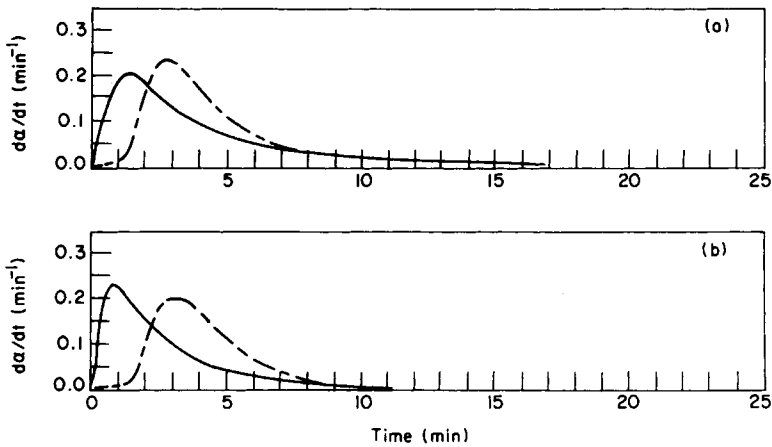


Fig. 22. Comparison of the experimental results (—) with the theoretically predicted profiles (---) of $d\alpha/dt$ at 100°C for the resin/P16N/BPO system: (a) 100/0.1/0.9; (b) 100/0.25/0.75. $f_{10} = 0.09$ for P16N and $f_{20} = 0.20$ for BPO.

experiment, whereas in Figure 22 (i.e., at 100°C) the opposite trend is seen, for all three compositions of mixed initiators.

Since temperature greatly influences the availability of inhibitor in the system, as demonstrated in Figures 16 and 17, we have attempted to adjust the value of $[Z]_0$ to investigate whether or not any improvement in the theoretical predictions of $d\alpha/dt$ can be achieved. Indeed we have observed some improvement in the theoretical prediction of $d\alpha/dt$ when the value of $[Z]_0$ was decreased as cure temperature was increased. This is displayed in Figure 23. We believe that the observed trend is in the right direction. However, agreement between the theoretical predictions and the experimental results is not quite satisfactory.

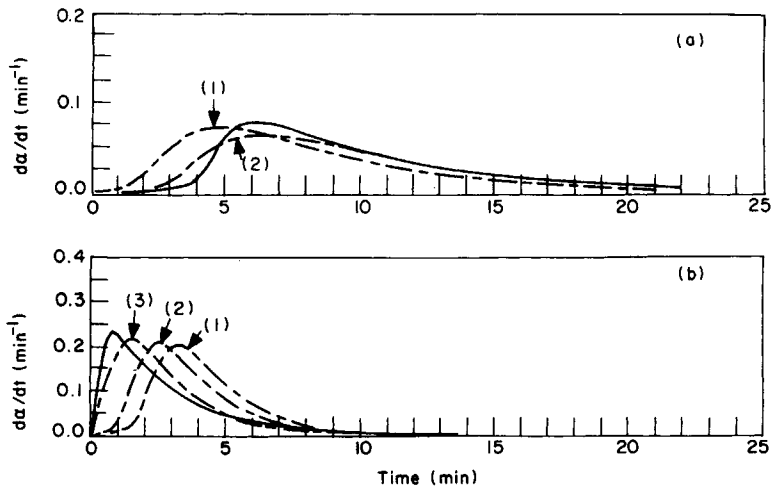


Fig. 23. Comparison of the experimental results (—) with the theoretically predicted profiles (---) of $d\alpha/dt$ for the 100/0.25/0.75 resin/P16N/BPO system. (a) At 80°C for $[Z]_0$ (M/L): (1) 5.09×10^{-4} ; (2) 8.0×10^{-4} . (b) At 100°C for $[Z]_0$ (M/L): (1) 5.09×10^{-4} ; (2) 3.0×10^{-4} ; (3) 0.

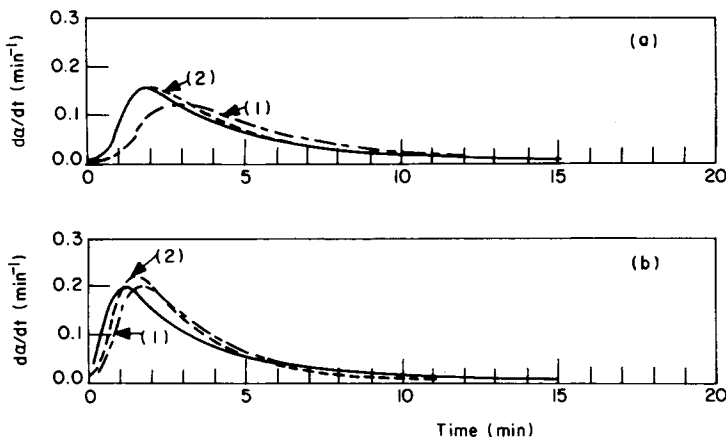


Fig. 24. Comparison of the experimental results (—) with the theoretically predicted profiles (---) of $d\alpha/dt$ at 90°C . (a) 100/0.25/0.75 resin/P16N/BPO system: (1) curve 1 for f_{10} (P16N) = 0.04 and f_{20} (BPO) = 0.16; (2) curve 2 for $f_{10} = 0.07$ and $f_{20} = 0$. (b) 100/0.5/0.5 resin/P16N/BPO system: (1) curve 1 for $f_{10} = 0.04$ and $f_{20} = 0.16$; (2) curve 2 for $f_{10} = 0.05$ and $f_{20} = 0$.

Note in Figure 21 that at 90°C the agreement between the theoretically predicted profiles of $d\alpha/dt$ and the experimental results is very good for the 100/0.1/0.9 resin/P16N/BPO system but not satisfactory for the 100/0.25/0.75 resin/P16N/BPO and 100/0.5/0.5 resin/P16N/BPO systems. It should be remembered that, in obtaining the theoretical predictions of $d\alpha/dt$ displayed in Figure 21, we used the values of f_{j0} ($j = 1, 2$) that had been obtained when simulating the cure reaction of single initiator systems (see Table II). In other words, we assumed that the efficiencies of the individual initiators did not change when two initiators were mixed together. There is no theoretical reason why such an assumption should be valid. As a matter of fact, the nonisothermal DSC thermograms given in Figure 12 appear to indicate that such an assumption is not valid. This has prompted us to investigate whether or not an adjustment of the values of f_{j0} ($j = 1, 2$) can improve the theoretical predictions of the curing behavior of mixed initiator systems. Figure 24 displays the results of such an attempt for the 100/0.25/0.75 resin/P16N/BPO and 100/0.5/0.5 resin/P16N/BPO systems, in which values of f_{10} and f_{20} were determined during computation while searching for the best fitting of the theoretical predictions of $d\alpha/dt$ to the experimental results, using optimization computational algorithms. The computational techniques used are described in our previous paper.³

It is seen in Figure 24 that satisfactory agreement is obtained between the experimental results and the theoretical predictions for the 100/0.25/0.75 resin/P16N/BPO system when the value of f_{10} for the P16N was increased from 0.04 to 0.07 while the value of f_{20} for the BPO was decreased from 0.16 to 0. For the 100/0.5/0.5 resin/P16N/BPO system, satisfactory agreement was obtained when the value of f_{10} was increased from 0.04 to 0.05 while the value of f_{20} was decreased from 0.16 to 0. This result then indicates that, for the particular combinations of the two initiators considered, the BPO apparently has participated *little* in the curing reaction. This can be explained when we examine the curing behavior of the single initiator systems, displayed

in Figures 1 and 4 for the resin/P16N system and in Figures 2 and 5 for the resin/BPO system. It is seen in Figure 4 that at 90°C, for the first 4 min of cure time, the resin/P16N system has already achieved about 60% conversion but virtually no cure reaction has taken place in the resin/BPO system. Note that, of the two initiators, the P16N may be considered to be a low-temperature initiator and the BPO a high-temperature initiator. It appears therefore that, when the concentration of the P16N is sufficiently high in a mixture of P16N and BPO, the cure reaction is controlled predominantly by the P16N. On the other hand, as may be seen in Figure 21(a) for the 100/0.1/0.9 resin/P16N/BPO system, both initiators, P16N and BPO, appear to have participated in the curing reaction when the concentration of the P16N is rather low. It can be concluded, therefore, from the above observation that the mechanistic kinetic model employed here is capable of determining whether a particular choice of mixed initiator system is effective or not.

CONCLUDING REMARKS

It is demonstrated in this paper that mixed initiators can be much more effective than a single initiator for achieving a uniform quality of cured unsaturated polyester composites. This is because a judicious choice of mixtures of two or more initiators can avoid excessively large exothermic heats of reaction. Of particular importance is the composition of mixtures of two or more initiators, which in turn depends on the decomposition temperature of the constituent initiators. This is illustrated in Figure 12 for the 100/0.1/0.9 resin/P16N/TBPB system. It is seen in Figure 12 that, compared to the single initiator system (i.e., 100/1 resin/P16N system), the peak exotherm of the mixed initiator system is reduced while its heat of reaction is increased from 348 to 407 J/g. This implies that, in the beginning of cure, the cure reaction due primarily to the P16N is slowed down by the TBPB present in the mixture (i.e., due to the dilution of P16N by TBPB), thus reducing the peak exotherm. Then, in the later stage of cure (i.e., after all the P16N has been decomposed), the TBPB in the mixture sustains the cure reaction, increasing the total degree of conversion when the reaction is completed.

It is shown in this paper that the mechanistic kinetic model employed describes reasonably well the curing behavior of unsaturated polyester resin with mixed initiators. The advantage of having such a kinetic model lies in that, without having to conduct time-consuming and costly experiments, it allows one to investigate the effectiveness of various combinations of many different initiators that are available in the market today, for various applications, such as in compression molding and pultrusion processes. What is needed now is to develop mathematical models simulating such processes and then to incorporate the kinetic model into the process model. In a future publication, we shall report our investigation on the applications of the kinetic model to the processing operations of unsaturated polyester resin and its composites.

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