Effect of Particulates and Fiber Reinforcements on the Curing Behavior of Unsaturated Polyester Resin

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Synopsis

The effect of particulates and reinforcement on the curing behavior of unsaturated polyester resin was investigated. Also investigated was the effect of surface treatment of particulates on the curing behavior of unsaturated polyester resin. We have found that (1) an increase in the surface area, by either increasing the loading of particulates for a fixed particle size or decreasing the size of particulates for a fixed loading of particulates, enhanced the rate of cure, and (2) the treatment of glass beads with γ-methacryloxy propyltrimethoxy silane enhanced the rate of cure of unsaturated polyester resin.

INTRODUCTION

In the use of thermosetting resins for composite materials, one invariably uses fibrous materials as reinforcement and particulates as filler. For instance, in the preparation of polyester molding compounds, one uses, for 100 parts of resin, about 300 parts of calcium carbonate as filler, and about 120 parts of chopped glass fiber as reinforcement. The end-use properties of the molded composites are dependent upon the formulations of the molding compounds and the processing conditions employed.

It has long been recognized that the surface characteristics of particulates and fibrous reinforcement greatly influence the curing behavior of thermosetting resins. For instance, the nature of the chemicals, used to treat the surface of glass fibers, greatly influences the curing behavior of polyester resin and consequently the mechanical and physical properties of fabricated products. Ishida and Koeng[1] investigated the characteristics of the interface between E-glass fiber and unsaturated polyester resin matrix using Fourier transform infrared (FTIR) spectroscopy. They found that silane coupling agents participate in the curing reaction of polyester resin, namely at the surface of the resin matrix forming an interphase, and that untreated E-glass inhibits the polymerization of unsaturated polyester resin. The characteristics of the interface between the E-glass fiber and epoxy resin was also investigated by Culler et al.,[2] using FTIR. They reported that chemical reactions of epoxy resin at the interface were affected by the thickness of the interphase and, also, by the extent to which silane coupling agents were condensed.

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Understandably, the type of the chemicals used for the surface treatment of glass fibers, commonly referred to as "sizing chemicals," is a tightly guarded secret by the industry concerned. Therefore, very little information, if any, has been reported in the literature that discusses the effect of particulates or fiber reinforcement on the curing behavior of thermosetting polyester resin and on the mechanical and physical properties of fabricated products.

In the pultrusion process, strands of glass fiber are fed continuously to a resin bath where they are impregnated by the resin. The resin-impregnated strands of glass fibers are then passed through an electrically heated pultrusion die in which curing of the resin takes place. The amount of glass fiber used in pultrusion is 70–80% by weight (50–60% by volume). Therefore, considering the very small diameter of the glass fibers, it can easily be surmised that a very large portion of the surface area is occupied by the glass fibers. This greatly influences the curing behavior of the resin in the pultrusion die. Again, very little, if any, has been reported in the literature that deals with the curing behavior of thermosetting resins containing large amounts of fiber strands.

A better understanding of the curing behavior of thermosetting resins in the presence of particulates and fiber reinforcement is important to optimizing the rate of the curing reaction and to achieving the end-use properties desired. Earlier, Lem and Han[3] have reported that particulates have a profound influence on the curing behavior of unsaturated polyester resin.

We have very recently conducted an experimental investigation on the curing behavior of unsaturated polyester resin in the presence of glass beads with and without surface treatment, in the presence of milled glass with and without surface treatment, and in the presence of glass fibers treated with a proprietary sizing chemical. In this paper, we shall present the highlights of our findings.

EXPERIMENTAL

Two different commercial grades of unsaturated polyester resins, OC-P340 and OC-E701 (Owens-Corning Fiberglas Corp.), were used. Using nuclear magnetic resonance (NMR) spectroscopy and chemical analysis, we have found that the OC-P340 has a mole ratio of 1.0 : 0.83 : 1.0, glycol/styrene/fumarate, and that the OC-E701 resin has a mole ratio of 2.5 : 1.5 : 1.0, glycol/fumarate/isophthalate, and a mole ratio of 2.15 : 1.0, styrene/fumarate. It can be concluded that the OC-P340 is a fairly reactive resin that may be suitable, for instance, for compression and transfer molding processes, and that the OC-E701 is a low-reactivity resin that may be suitable, for instance, for pultrusion and filament winding.

For the curing experiment with the OC-P340, we used (a) glass beads (Cataphote Division, Ferro Corporation, MS-XLX) which have diameters ranging from 5 to 44 μm, and (b) two different sizes of milled glass (Cataphote Division, Ferro Corporation), namely Ferro 661-11-0312, with an average diameter of 0.013 mm and a length of 0.79 mm, and Ferro 665-38-0625, with an average diameter of 0.0228 mm and a length of 1.588 mm. The primary purpose for using these two types of glass was to investigate the effect, if any, of the available surface area on the curing behavior of the resin on an equal

weight basis. We have treated both the glass beads and milled glass with 1 wt% of a silane coupling agent, γ-methacryloxy propyltrimethoxy silane (A174) (Union Carbide Corporation). This coupling agent is one of the many sizing chemicals that are widely used in industry for the treatment of glass fibers used with unsaturated polyester resins. For comparison purposes, we also conducted curing experiments with the resin OC-P340, using glass beads and milled glass without surface treatment. For the curing experiments with the OC-E701, we used strands of glass fibers. The purpose was to investigate the curing behavior of the resin during the pultrusion operation.

For curing experiments with the unsaturated polyester resins, we used the following initiators: (a) t-butyl perbenzoate (TBPB) (Pennwalt Corp.) for OC-P340; (b) benzoyl peroxide (BPO) (Noury Chemical Corp.) for OC-E701.

The curing kinetics of the materials was investigated, using differential scanning calorimetry (DSC). For the study, we used a DuPont 1090 Thermal Analyzer equipped with a 910 DSC Module. The details of the experimental procedures employed are the same as those described in a paper by Han and Lem.[4] Table I gives a summary of sample codes and the materials investigated.

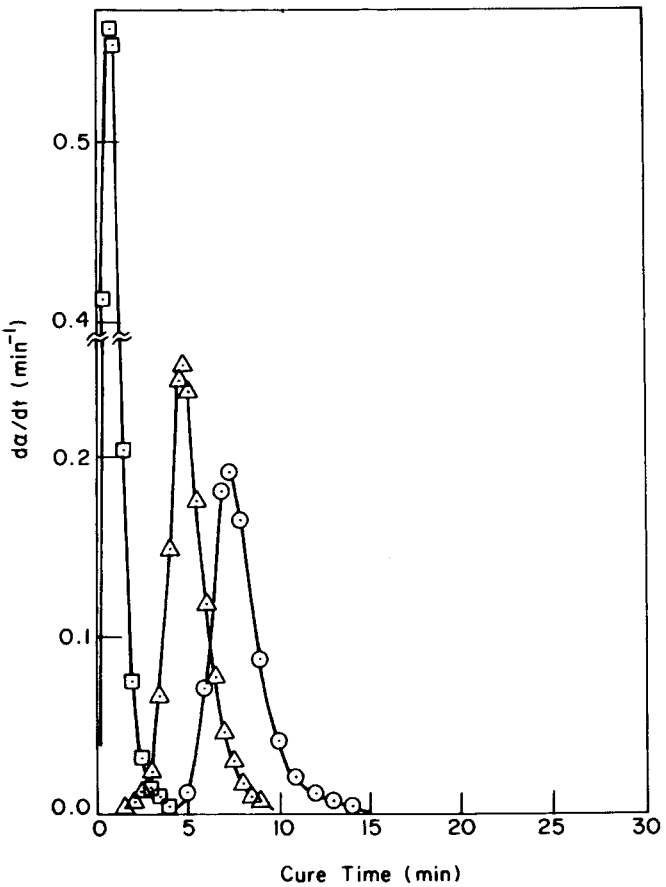

Fig. 1. $d\alpha/dt$ vs. cure time for Fluid 1 under different isothermal cure temperatures (°C): (⊙) 110; (△) 120; (⊡) 130.

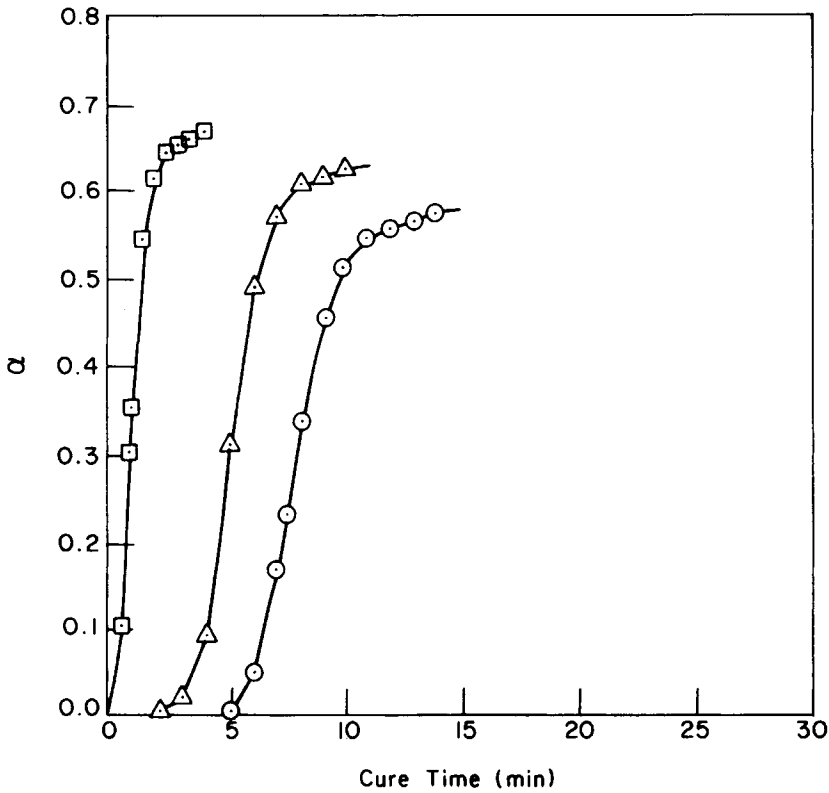

Fig. 2. α vs. cure time for Fluid 1. Symbols are the same as in Fig. 1.

RESULTS AND DISCUSSION

Figure 1 gives plots of the degree of cure ($d\alpha/dt$) versus cure time, and Figure 2 plots of the degree of cure (α) versus cure time, for the neat resin (Fluid 1). These figures are given in order to use them later for comparison purposes. It is seen that both $d\alpha/dt$ and α increase with cure temperature. Note that the values of $d\alpha/dt$ given in Figure 1 were determined from

$$\frac{d\alpha}{dt} = \frac{1}{Q_{UT}}\left(\frac{dQ}{dt}\right)_T \tag{1}$$

where $(dQ/dt)_T$ is the experimentally determined rate of heat generated during cure at constant temperature T, and Q_{UT} is the ultimate heat that is to be generated when complete cure (i.e., 100% conversion) is achieved.

Let Q_T be the heat generated during the isothermal DSC run, and Q_R be the heat released when, upon completion of an isothermal cure reaction, the sample was heated to higher temperatures (say, 250°C) at a fixed scanning rate. Q_{TOT} is then defined as the sum of the two quantities, i.e.,

$$Q_{TOT} = Q_T + Q_R \tag{2}$$

TABLE I
Sample Code and Materials Investigated

Sample code	Materials
Fluid 1	OC-P340/t-BPB[a]
Fluid 2	OC-P340/t-BPB/glass beads[b] (50 wt%).
Fluid 3	OC-P340/t-BPB/glass beads[b] (50 wt%) treated with coupling agent[c]
Fluid 4	OC-P340/t-BPB/glass beads (25 wt%) treated with coupling agent[c]
Fluid 5	OC-P340/t-BPB/milled glass fiber A[d] (50 wt%)
Fluid 6	OC-P340/t-BPB/milled glass fiber B[e] (50 wt%)
Fluid 7	OC-E701/BPO[f]
Fluid 8	OC-E701/BPO/glass fiber[g]

[a] Resin/initiator = 100/1 (by weight).
[b] Resin/initiator/glass beads = 50/1/50 (by weight).
[c] The coupling agent used is γ-methacryloxy propyltrimethoxy silane.
[d] Milled glass A is Ferro 665-38-0625.
[e] Milled glass B is Ferro 661-11-0312.
[f] Resin/initiator = 100/1 (by weight).
[g] Resin/initiator/glass fiber = 25/0.25/75 (by weight).

In earlier studies, Kamal and Sourour,[5] and Han and Lem,[4] have found that Q_{TOT} was constant. Therefore, in their study, Han and Lem[4] used the average value of Q_{TOT}, obtained at various isothermal DSC runs, for the value of ultimate heat Q_{UT} used in determining the $d\alpha/dt$ defined by Eq. (1). Such an approach assumes that complete cure (i.e., $\alpha = 1$) is achieved when a resin is cured isothermally followed by nonisothermal scanning.

We have very recently made an attempt to determine if indeed all the ethylene double bonds, which were originally present in the resin and styrene, reacted to give complete conversion after the resin was subject to this procedure of an isothermal DSC run followed by nonisothermal scanning. Our study has indicated that there are still some unreacted double bonds present in the cured samples, and therefore we have concluded that the assumption of complete cure based on the experimental observation of a constant value of Q_{TOT}, defined by Eq. (2), is not correct. We can intuitively expect that, in the cure reaction of unsaturated polyester resins, 100% conversion would be very difficult, if not impossible, to achieve. This is in view of the fact that gelation begins at a relatively low degree of conversion (say, at $\alpha = 0.1$), and thus a portion of the resin and styrene can be trapped in the networks, and not be able to participate in the curing reaction.

In the present investigation, we therefore used the ultimate heat of reaction Q_{UT} obtained with the aid of the information on the mole fraction of double bonds present in our resin samples before the cure reaction began. We have found that the values of Q_{UT} determined in this way are larger than the values of Q_{TOT} determined from our DSC runs. This implies that the values of $d\alpha/dt$ (and α) based on Q_{UT} will be lower than those based on Q_{TOT}.

Figure 3 gives plots of $d\alpha/dt$ versus cure time, and Figure 4 plots α versus cure time, for Fluids 2 and 3. It is seen in Figure 3 that surface treatment of the glass beads with the coupling agent A174 shortens the time at which the

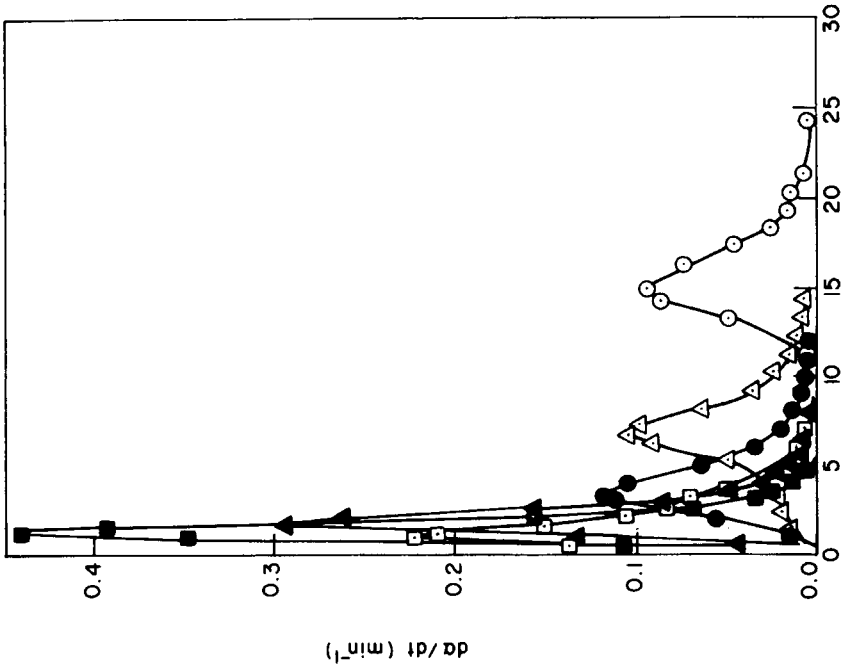

Fig. 3. $d\alpha/dt$ vs. cure time for Fluid 2 (open symbols) and for Fluid 3 (closed symbols) under different isothermal cure temperatures (°C): (⊙, ●) 110; (△, ▲) 120; (⊡, ■) 130.

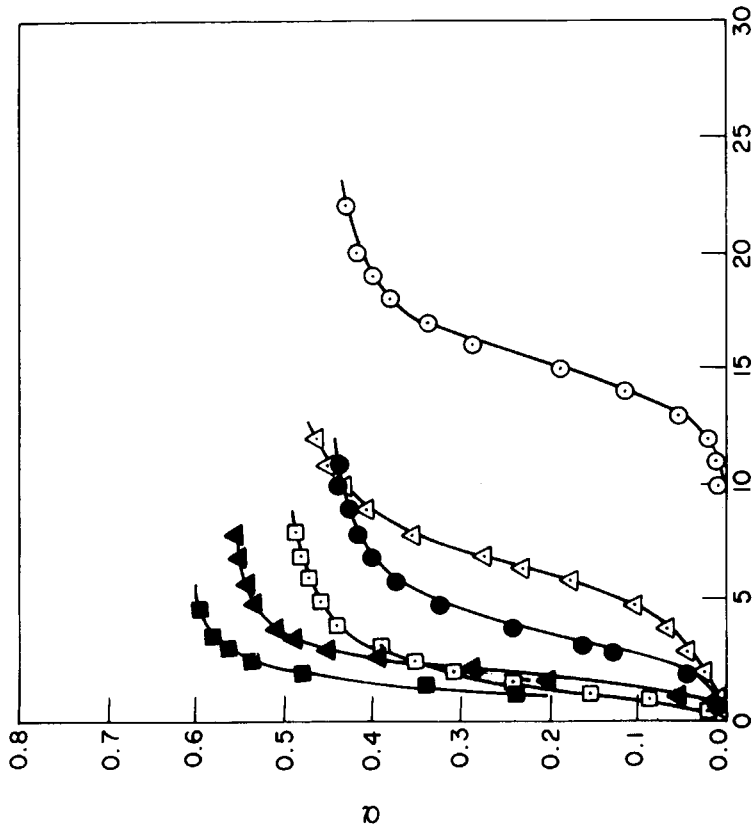

Fig. 4. α vs. cure time for Fluid 2 and Fluid 3. Symbols are the same as in Fig. 3.

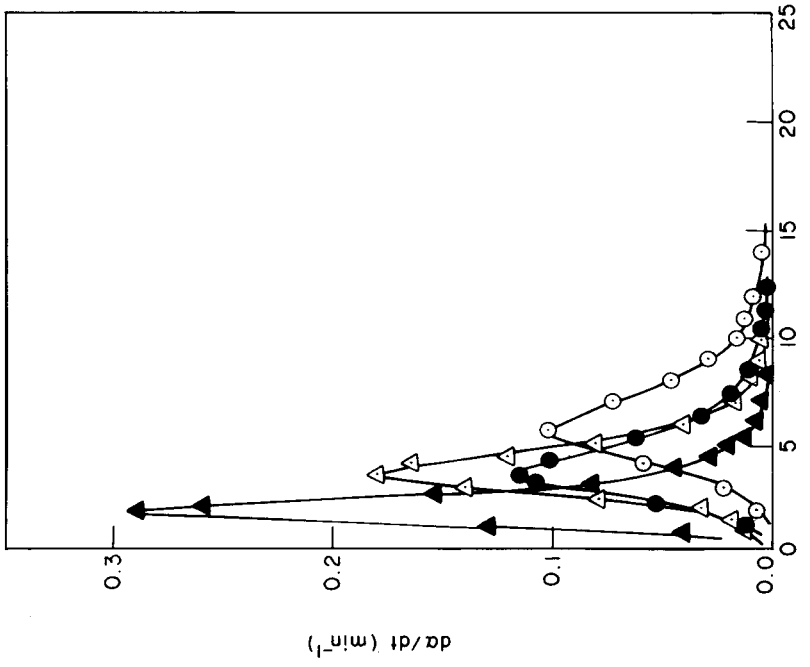

Fig. 5. $d\alpha/dt$ vs. cure time for Fluid 3 (closed symbols) and for Fluid 4 (open symbols) under different cure temperatures (°C): (⊙, ●) 110; (△, ▲) 120; (□, ■) 130.

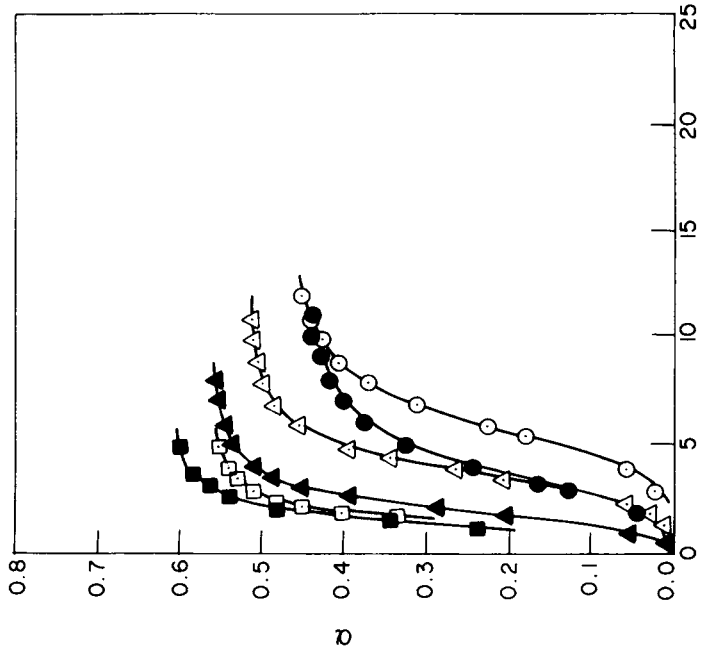

Fig. 6. α vs. cure time for Fluid 3 and Fluid 4. Symbols are the same as in Fig. 5.

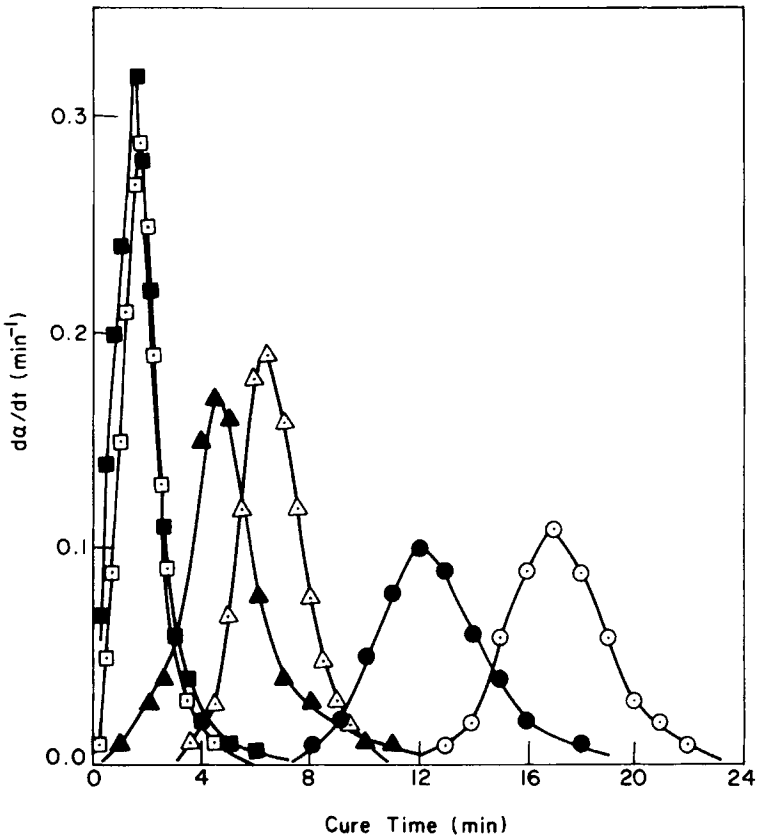

Fig. 7. $d\alpha/dt$ vs. cure time for Fluid 5 (open symbols) and for Fluid 6 (closed symbols) under different isothermal cure temperatures (°C): (⊙, ●) 110; (△, ▲) 120; (⊡, ■) 130.

peak value of $d\alpha/dt$ occurs and also increases the peak value of $d\alpha/dt$, especially at the higher temperatures, 120°C and 130°C. This indicates that the use of the coupling agent A174 to modify the surface of the glass beads has enhanced the curing reaction of the resin OC-P340. It is seen in Figure 4 that the α of the unsaturated polyester resin is increased with surface treatment of the glass beads. According to Ishida and Koenig,[1] free radicals are known to form a charge transfer complex with inorganic oxide on the surface of glasses without treatment, inhibiting the curing reaction. It is speculated that the inhibition of the curing reaction of unsaturated polyester resin would be less, and thus the curing reaction of the resin would be enhanced, if the surface of the glass beads is treated with a coupling agent.

Figure 5 gives plots of $d\alpha/dt$ versus cure time, and Figure 6 plots of α versus cure time, for Fluids 3 and 4. Figure 7 gives plots of $d\alpha/dt$ versus cure time, and Figure 8 α versus cure time, for Fluids 5 and 6. Table II gives the densities and dimensions, and Table III the volume fractions and surface areas, of the particulates and reinforcements employed in the present investigation. It is of interest to note in Figures 5 and 6 that an increase in the quantity of glass beads in the unsaturated polyester resin brings about an increase in both $d\alpha/dt$ and α. This is attributable to the fact that a greater

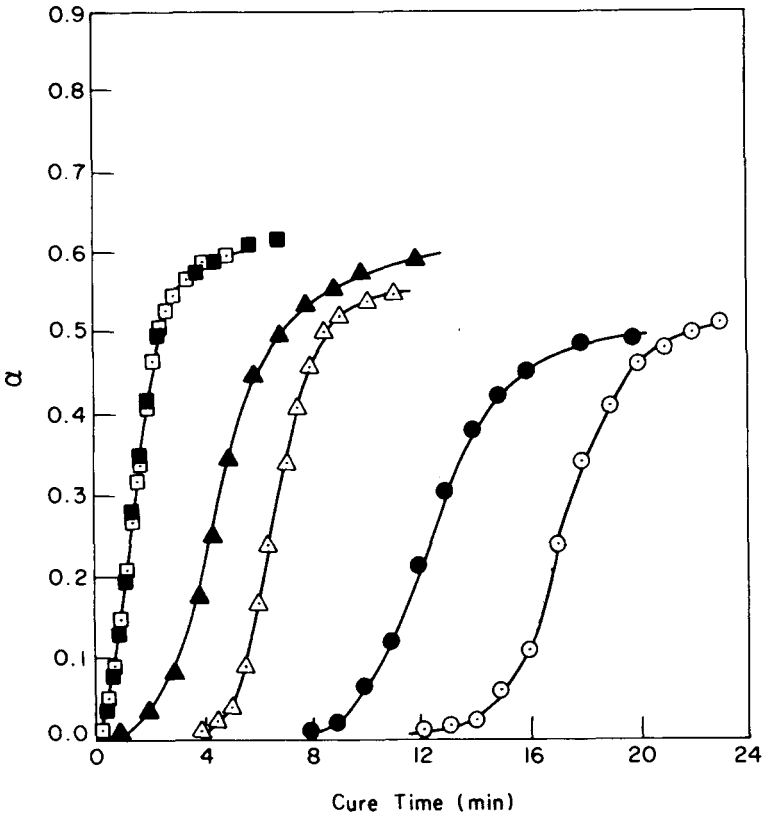

Fig. 8. α vs. cure time for Fluid 5 and Fluid 6. Symbols are the same as in Fig. 7.

TABLE II
The Density and Dimensions of the Particulates and Reinforcement Employed

Material	Density (g/cm^3)	Diameter (cm)	Length (cm)
Glass bead	2.54	2.540×10^{-3}	—
Milled glass A	2.54	2.286×10^{-3}	1.588×10^{-1}
Milled glass B	2.54	1.346×10^{-3}	7.925×10^{-2}
Glass fiber	2.54	2.032×10^{-3}	—

quantity of glass beads in the resin (i.e., Fluid 3) makes a larger surface area available to the curing reaction. It is seen in Figure 7 that the unsaturated polyester resin containing the smaller-sized milled glass (i.e., milled glass B) shows a peak value of $d\alpha/dt$ sooner than the one containing the larger-sized (i.e., milled glass A). This is also attributable to the larger surface area available to the curing reaction, as may be seen in Table III.

Figure 9 gives plots of $d\alpha/dt$ versus cure time, and Figure 10 plots of α versus cure time, for Fluids 7 and 8. It is seen that addition of glass fibers to the resin increased the values of $d\alpha/dt$ but decreased the values of α. It is not

TABLE III
The Volume Fraction and Surface Area of the Particulates and Reinforcement Used

Materials (by wt)	Volume Fraction	Surface area (cm^2/g resin)
Resin/glass bead (75/25)	0.126	3.123×10^2
Resin/glass bead (50/50)	0.302	9.643×10^2
Resin/milled glass A (50/50)	0.302	6.938×10^3
Resin/milled glass B (50/50)	0.302	1.209×10^4
Resin/glass fiber (25/75)	0.565	1.500×10^4

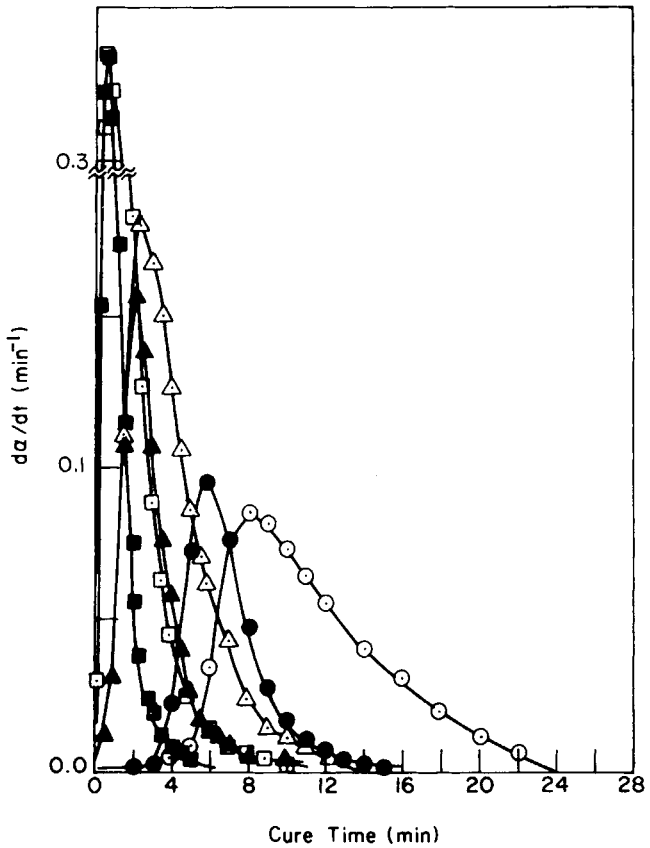

Fig. 9. $d\alpha/dt$ vs. cure time for Fluid 7 (open symbols) and for Fluid 8 (closed symbols) under different isothermal cure temperatures (°C): (⊙, ●) 90; (△, ▲) 100; (⊡, ■) 110.

clear why the ultimate value of α is so low for the resin containing glass fibers compared to that for the neat resin. Further investigation is needed to elucidate the mechanism that may be responsible for this experimental observation.

The present investigation reveals that information on the curing kinetics of resin alone is not sufficient for controlling various processes involving thermosetting composite materials.

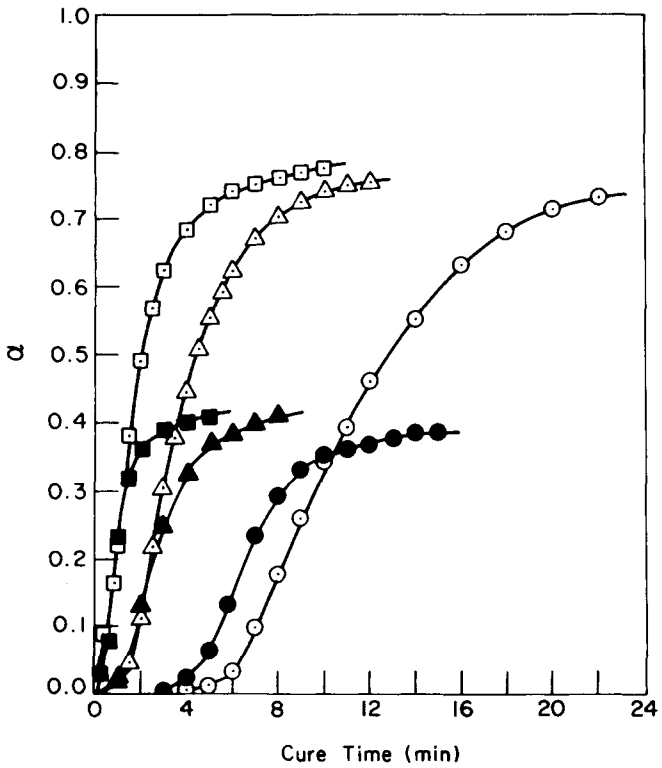

Fig. 10. α vs. cure time for Fluid 7 and Fluid 8. Symbols are the same as in Fig. 9.

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