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THICKENING AND CURING BEHAVIOR OF UNSATURATED POLYESTER

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Key Words: Curing; DSC; Thickening; Unsaturated polyester

ABSTRACT

An investigation was made of the curing behavior of an unsaturated polyester resin during thickening by magnesium oxide. In this paper the thickening and curing behavior of an unsaturated polyester resin were investigated by using differential scanning calorimetry and viscometry. The acid number during the period of thickening was observed by titration. Based on the results thus obtained, the authors discuss the thickening mechanism and the effects of thickening on the curing behavior of an unsaturated polyester resin.

INTRODUCTION

Sheet molding compounds and bulk molding compounds are chemically thickened molding compositions. Alkaline earth oxides and hydroxides react with the resin in a manner that causes a very large increase in viscosity. This phenomenon has advantages in the preparation of these compounds because relatively low viscosity slurries can be used during compounding, and this allows higher filler and glass levels and less glass fiber degradation. Because of the high viscosities obtained after thickening, segregation of reinforcement during molding is reduced and lower polymerization shrinkages occur, resulting in an improved surface finish [1].

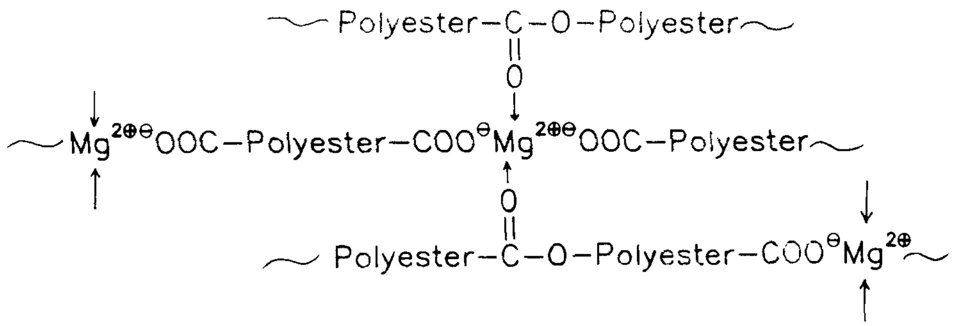

FIG. 1. A two-stage thickening mechanism.

The thickening reaction has been discussed in the past by several investigators [2-8]. Two different theories have been proposed: One postulates a two-stage reaction [2-6] and the other postulates chain extension and chain entanglement [7, 8]. In the two-stage reaction theory (Fig. 1), it is postulated that a higher molecular weight salt is first formed by the reaction between magnesium oxide and carboxylic acid groups on a polyester chain, and then a complex is formed between the salt and carbonyl groups of the ester linkages. In this theory, the second stage of the reaction is considered to be responsible for a large increase in viscosity. In the chain extension/chain entanglement theory (Fig. 2), it is postulated that the dicarboxylic acid groups on a polyester chain react with magnesium oxide to yield a very high molecular weight species (via condensation polymerization) and thus give rise to a large increase in viscosity. A recent report [9] supports the thickening mechanism of a two-stage reaction proposed by Vansco-Szmercsanyi [2-6].

Curing of an unsaturated polyester is highly exothermic because the unsaturated polyester resin has a high concentration of reactive double bonds. Differential scanning calorimetry (DSC) provides a very useful technique for following and analyzing the kinetics of exothermic and endothermic reactions [10]. The heat generated or absorbed in the course of reaction can be measured directly with DSC, and the rate of heat generation or absorption with respect to time or temperature can be obtained from the DSC curve. It is assumed here that the exothermic heat of polyester curing comes from the propagation in free radical crosslinking of a reactive styrene monomer with a reactive double bond of the unsaturated polyester. This makes it possible to follow the degree of curing with respect to time, which allows for the determination of the final degree of curing as well.

Although many reports have been presented on the mechanism of the thickening of unsaturated polyester with magnesium oxide, information regarding the effect of thickening on the curing reaction of unsaturated polyester is almost nil. In the present work, the effect of thickening on the initial stage of curing behavior of an unsaturated polyester was investigated by DSC. O'Driscoll et al. [11] predicted

$$\sim Mg^{2\oplus\ominus}OOC-Polyester-COO^{\ominus}Mg^{2\oplus\ominus}OOC-Polyester\sim$$

FIG. 2. Chain extension/chain entanglement thickening mechanism.

that the termination rate constant (K_t) of the initial stages of free radical polymerization will increase with the polymer molecular weight as long as the polymer concentration (C) is smaller than the overlap concentration (C^*). However, the initial stage termination rate constant (K_t) will be controlled by the diffusion process of the whole polymer chain, and it will decrease with the polymer molecular weight when the polymer concentration (C) is higher than the overlap concentration (C^*). In the present study, O'Driscoll's prediction was used to discuss the effect of thickening on the curing behavior of the unsaturated polyester.

EXPERIMENTAL

Unsaturated Polyester. Unsaturated polyester resin was prepared from isophthalic acid (IPA), fumaric acid (FA), and propylene glycol (PG). The mole ratio of the final composition of the polyester resin determined by NMR was IPA/FA/PG = 1.0/1.67/3.23. The acid value of the solid resin was 30.0 mg KOH/g. The mole ratio of OH/COOH was 1.21. The number-average molecular weight of the polyester as determined by gel permeation chromatography was 1800, and $M_w/M_n = 4.3$. The weight ratio of styrene to polyester was 33/67.

Initiator. The initiator was *tert*-butyl peroxybenzoate from Akzo Chemie Co. with a purity of 98% and an active oxygen content of 8.07%.

Thickening Agent. The thickening agent was Starmag-U (from Konoshima Co.). It is magnesium oxide with a particle size of 0.35 μm and a density of 0.43 g/mL.

Differential Scanning Calorimetry. A Du Pont 910 DSC was used to measure the exothermic curing reaction. Hermetic DSC pans were used to minimize losses of volatile materials (such as styrene monomer) during heating of the sample in the DSC cell. The size of the sample used ranged from 6 to 10 mg. A small sample size was required in order to achieve isothermal operation during cure.

Viscosity. A Brookfield DV II Digital HBT viscometer was used to measure the viscosity of the thickened unsaturated polyester resin.

Acid Number. A titration method was used to determine the acid number of the sample. The method was the same as that described by Han et al. [9]. Approximately 2 g of the sample was weighed to the nearest milligram into a 125-mL Erlenmeyer flask. Several drops of 0.5 wt% phenolphthalein solution were added to a solvent mixture consisting of toluene, isopropyl alcohol, and *N,N*-dimethylformamide (DMF). Thirty milliliters of the solvent mixture was used to dissolve the resin sample. After the resin was dissolved, the mixture was titrated with 0.1 N potassium hydroxide solution to the phenolphthalein end point. The acid number was calculated directly from the amount of titer.

To study the thickening behavior, we added 6 g magnesium oxide and 1 g initiator for each 100 g unsaturated polyester resin. The mixture was then trans-

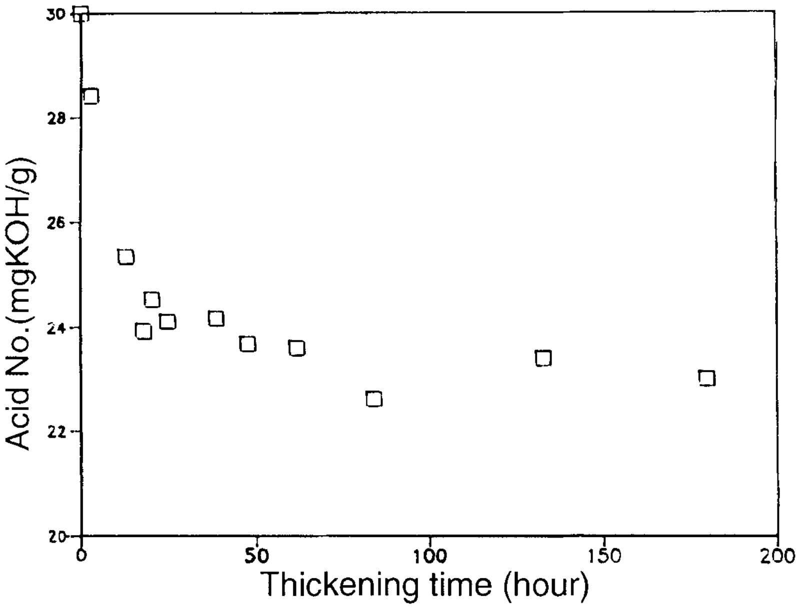

FIG. 3. Plot of acid number vs thickening time.

ferred into a 500-mL wide-neck glass bottle with a glass stopper to prevent the evaporation of styrene monomer. The stoppered bottle was placed in a thermostated bath maintained at 30 ± 0.5°C for the entire period of thickening (about 4 days). During thickening, we conducted the following measurements: 1) determination of the acid number by titration, 2) determination of the viscosity of the thickened resin with a Brookfield viscometer, and 3) determination of the isothermal curing reaction by DSC.

RESULTS AND DISCUSSION

Figure 3 plots acid number vs thickening time for the unsaturated polyester resin. In our study the acid number is expressed by mg KOH/g solid resin. Figure 4 gives a plot of viscosity vs thickening time for the polyester resin. During the initial period of thickening, the viscosity increased and the acid number decreased rapidly versus the thickening time. After 50 hours of thickening, the viscosity increased slowly and the acid number changed only slightly. The polyester resin has —OH and —COOH terminal functional groups. Three possible polyester structures are: (1) HOOC∼∼COOH, (2) HO∼∼COOH, and (3) HO∼∼OH. Only Structure (1) will give a high molecular weight polymer through the chain extension/chain entanglement thickening mechanism. Structure (2) will give a molecular weight twice that of the original polymer if the chain extension/chain entanglement thickening mechanism is followed. Structure (3) will not be thickened through a chain extension/chain entanglement mechanism. Since the resin we used has an —OH/—COOH mole ratio of 1.21, it is not possible for the viscosity of the thickened

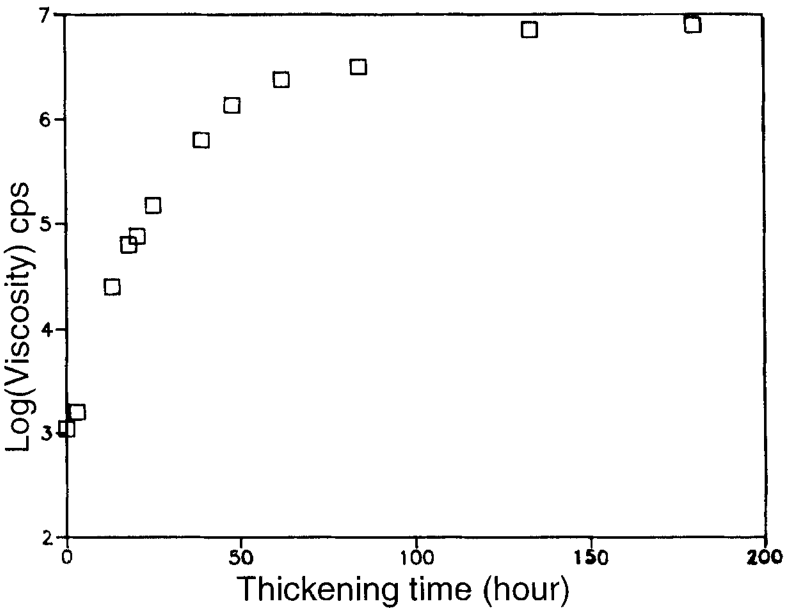

FIG. 4. Plot of viscosity vs thickening time.

resin to increase from 10^3 to 10^6 cPs if the thickening reaction follows the chain extension/chain entanglement mechanism. Hence, our results support a two-stage reaction mechanism.

In the use of DSC for studying the isothermal curing kinetics of thermosetting resins, one assumes that the amount of heat generated due to the curing reaction is directly proportional to the degree of curing (or the extent of reaction) of the sample at that time, and then one relates the rate of cure, $d\alpha/dt$, to the rate of heat generated, dQ/dt, by

$$\frac{d\alpha}{dt} = \frac{1}{Q_{\text{tot}}} \frac{dQ}{dt} \tag{1}$$

From the integration of Eq. (1) with respect to time, one obtains the relative degree of cure, α:

$$\alpha = \frac{1}{Q_{\text{tot}}} \int_{t_i}^{t} \frac{dQ}{dt}\, dt \tag{2}$$

In Eqs. (1) and (2), the total heat of the curing reaction (Q_{tot}) is given by

$$Q_{\text{tot}} = Q_t + Q_r \tag{3}$$

where Q_t is the heat generated during the isothermal 110°C DSC runs and Q_r is the residual heat released when the sample is heated to 200°C at a rate of 5°C/min after completion of the isothermal curing reaction.

Figure 5 is plots of $d\alpha/dt$ vs cure time for different degrees of thickening of unsaturated polyester resins. Figure 6 is plots of conversion α vs cure time t for

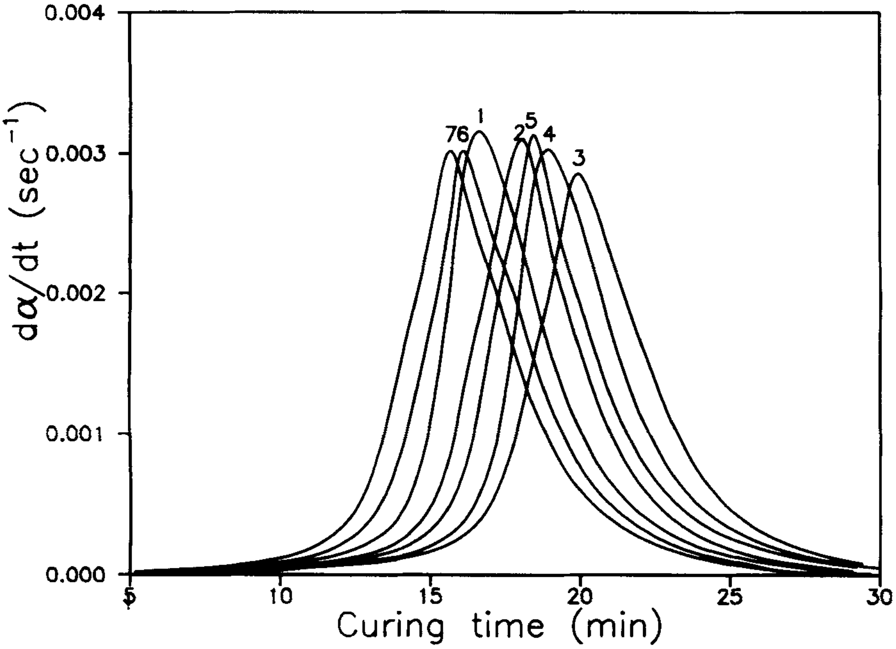

FIG. 5. Plots of $d\alpha/dt$ vs curing time at 110°C for different degrees of thickened unsaturated polyester resins. (1) Thickened 4 hours. (2) Thickened 8 hours. (3) Thickened 14 hours. (4) Thickened 22 hours. (5) Thickened 36 hours. (6) Thickened 46 hours. (7) Thickened 84 hours.

different degrees of thickening of unsaturated polyester resins. The curing temperature was 110°C. Table 1 shows data of the onset cure time t(onset), peak cure time t(peak), heat generated during isothermal curing at 110°C, Q_t, and residual heat Q_r at different degrees of thickening. In the initial period of thickening, we found that t(onset) and t(peak) increase as the degree of thickening increases. However, after 22 hours of thickening, the t(onset) and t(peak) decrease as the degree of thickening increases. From Fig. 5 and Fig. 6 we find that the initial stage of polymerization rate of the curing reaction decreases as the degree of thickening increases in the initial period of thickening reaction. After 22 hours of thickening, the initial stage of polymerization rate increases as the degree of thickening increases.

Mahabadi and O'Driscoll [11] discussed the polymer concentration and molecular weight dependence of the termination rate constant in the initial stages of free radical polymerization. From their prediction, the termination rate constant K_t in the initial stages of polymerization has the following relation with polymer concentration C and polymer molecular weight M:

$$K_t/K_{t0} = 1 + qC, \qquad \text{if } C < C^* \tag{4}$$

where

$$q = B(<h>^2/M)^{3/2}M^{1/2}Z \tag{5}$$

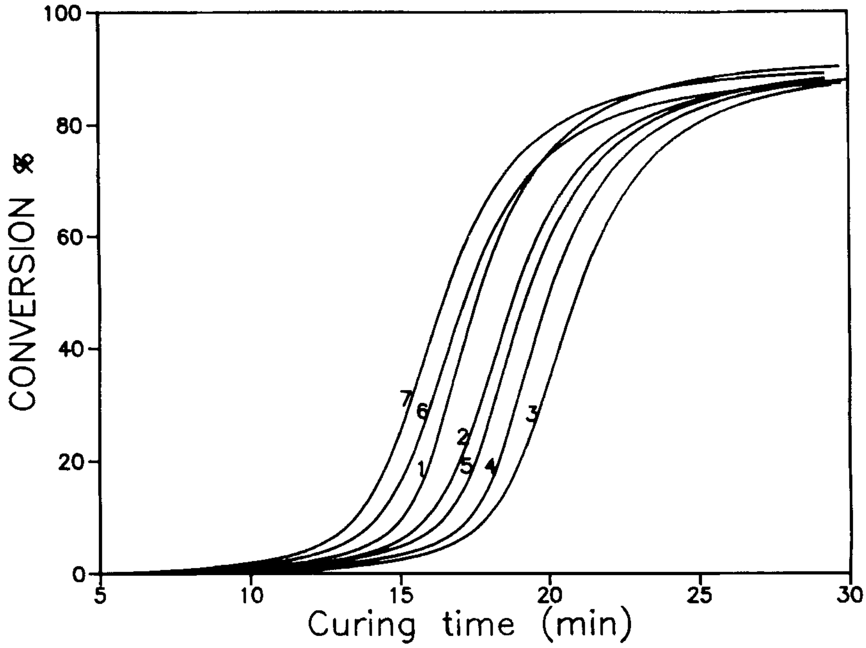

FIG. 6. Plots of conversion vs curing time at 110°C for different degrees of thickened unsaturated polyester resins. (1) Thickened 4 hours. (2) Thickened 8 hours. (3) Thickened 14 hours. (4) Thickened 22 hours. (5) Thickened 36 hours. (6) Thickened 46 hours. (7) Thickened 84 hours.

and K_{t0} is the termination rate constant when the polymer concentration is zero. In Eq. (5), B is a constant for a given polymer–solvent system, $<h>^2$ is the mean square end-to-end distance of a polymer chain, Z is the polymer–solvent interaction parameter, and C^* is the polymer overlap concentration which has the following relationship with the polymer molecular weight M:

TABLE 1. Isothermal DSC Curing at 110°C for Unsaturated Polyester Resin

Sample no.	Thickening time, h	Viscosity $\times 10^{-3}$ cP	t(onset), min	t(peak), min	Q_t, cal/g	Q_r, cal/g
1	4	6.45	14.49	16.65	58.34	6.13
2	8	9.90	14.76	18.19	56.81	6.88
3	14	32.80	14.78	20.17	57.34	7.10
4	22	97.00	16.77	18.97	55.28	6.87
5	36	550.00	15.90	18.28	60.79	6.91
6	46	1240.00	13.24	16.24	57.79	8.02
7	84	3200.00	12.48	15.58	57.12	6.76

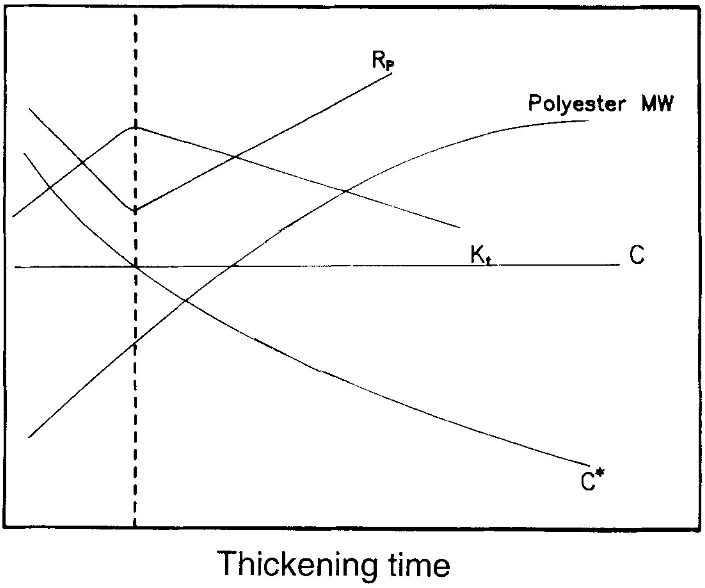

FIG. 7. Qualitative plots of thickened polyester MW, overlap concentration C^*, initial stage termination rate constant K_t of the curing reaction, and the initial stage of polymerization rate R_p of curing reaction vs thickening time for unsaturated polyester resin.

$$C^* = \frac{K^*}{(<h>^2/M)^{3/2}M^{1/2}} \tag{6}$$

In Eq. (6), K^* is a constant for a given polymer–solvent system. Since the mean square end-to-end distance of a polymer chain is proportional to the first power of the degree of polymerization, hence $<h>^2 \propto M$, $C^* \propto M^{-1/2}$, and $q \propto M^{1/2}$. From Eq. (4) we know that the initial stage termination rate constant K_t will increase as the molecular weight M of the thickened polyester chain increases with the degree of thickening if the polyester concentration $C < C^*$. Thus, the initial stage of polymerization rate of a curing reaction will decrease with the degree of thickening if the polyester concentration $C < C^*$. However, the overlap concentration C^* will decrease as the molecular weight M of the thickening polyester chain increases. Thus, C^* decreases as the degree of thickening increases. Once the overlap concentration C^* is lower than the polyester concentration C, the initial stage termination rate constant K_t of the curing reaction will be controlled by the diffusion process of the whole polymer chain, and K_t will decrease as the degree of thickening increases if the polyester concentration $C > C^*$. Hence, the initial stage of polymerization rate of a curing reaction will increase with the degree of thickening if $C > C^*$.

A qualitative picture of the thickened polyester molecular weight, overlap concentration C^*, initial stage termination rate constant K_t, and initial stage of polymerization rate R_p of the curing reaction vs the thickening time is shown in Fig. 7.

CONCLUSIONS

Our viscosity and acid number data support a two-stage thickening mechanism for unsaturated polyester resin. In the initial period of thickening, the onset curing time [*t*(onset)] and the peak curing time [*t*(peak)] in an isothermal DSC study are proportional to the degree of thickening. The initial stage of polymerization rate of the curing reaction decreases as the degree of thickening increases during the initial period of thickening reaction. However, in the latter period of the thickening reaction, *t*(onset) and *t*(peak) decrease, and the initial stage of polymerization rate of the curing reaction increases as the degree of thickening increases. The effect of thickening on the curing behavior of an unsaturated polyester can be explained by the O'Driscoll theory of polymer concentration and molecular weight dependence of the termination rate constant K_t during the initial stage of the free radical curing reaction.

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