

Glass Transition Temperature, Free Volume, and Curing Kinetics of Unsaturated Polyester

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ABSTRACT: Variations of glass transition temperature and free volume during the period of curing reaction for unsaturated polyester were calculated respectively from a theoretical equation developed in this work and Shimha-Boyer's free volume equation. The calculated free volume was applied to Huang & Lee's curing kinetic model to predict DSC curing reaction data of unsaturated polyester. Good agreement between the prediction and experimental results was found.

KEY WORDS Unsaturated Polyester / Glass Transition Temperature / Free Volume / Curing Kinetics /

Unsaturated polyester is one of the major resins of polymer composites. However, a theoretical discussion of the glass transition temperature of the crosslinked unsaturated polyester has not yet appeared. In most applications, it is often cured with styrene monomer as a crosslinking agent. In some cases, one may obtain unreacted residual styrene monomer and unreacted ester double bonds in the cured polymer network. The residual styrene monomer acts as a diluent in the system. It is well known that the curing reaction of unsaturated polyester resin is strongly controlled by the diffusion of the polymeric radical from the beginning of the reaction.¹ Hence, the reaction may be controlled by the free volume in the system. In the present paper, we are interested in: (1) the relation of T_g of the crosslinked unsaturated polyester to the crosslinked density, reacted styrene monomer and residual unreacted styrene monomer content; (2) variation of free volume during the period of curing reaction of unsaturated polyester; and (3) applications of

the free volume to the curing kinetics of unsaturated polyesters.

THEORY OF T_g OF CROSSLINKED UNSATURATED POLYESTER

The unsaturated polyester resin is a condensation polymer of diol, dibasic acid and unsaturated dibasic acid, and the copolymer is crosslinked with styrene monomer. We may assume that the crosslinked network is a copolymer of ester and styrene. For a linear copolymer of ester and styrene, the glass transition temperature of the copolymer has the following relation with its composition.²

$$\frac{1}{T_{g,1}} = \frac{W_{PE}}{T_{gPE}^{\infty}} + \frac{W_{PS}}{T_{gPS}^{\infty}} \quad (1)$$

where W_{PE} is the weight fraction of polyester in the crosslinked polymer network, W_{PS} the weight fraction of polystyrene in the crosslinked polymer network, $W_{PE} + W_{PS} = 1$, T_{gPE}^{∞} the glass transition temperature of polyester with an infinite molecular weight, T_{gPS}^{∞} the glass

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transition temperature of polystyrene with an infinite molecular weight, $T_{gPS}^\infty = 373 \text{ K}$,³ $T_{g,1}$ the glass transition temperature of the uncrosslinked linear copolymer of ester and styrene.

The introduction of crosslinks restricts the mobility of polymer segments; hence the glass transition temperature increases. The influence of crosslink on the glass transition, as cited by Nielson,⁴ was developed by DiBenedetto⁵ and given by:

$$T_{g,c} = T_{g,1} \left(1 + K_2 \frac{X_C}{1 - X_C} \right) \quad (2)$$

where $T_{g,c}$ is the glass transition temperature of the crosslinked polymer, $T_{g,1}$ the glass transition temperature of the uncrosslinked linear polymer as a reference, K_2 a constant and X_C the crosslink density expressed as the mole ratio of monomer units present as crosslinks to the total monomer units present in the polymer network.

Owing to impurity, moisture, or the lower curing temperature etc., one may obtain unreacted residual styrene monomer and unreacted ester double bonds in the cured polymer network. The unreacted residual styrene monomer acts as a diluent in the polymer network; hence the glass transition temperature decreases. In the present system, the glass transition temperature of the crosslinked unsaturated polyester with unreacted residual styrene monomer can be expressed by⁶:

$$T_g = \left(\frac{T_{gPS}^\infty T_{gPE}^\infty}{T_{gPS}^\infty W_{PE} + T_{gPE}^\infty W_{PS}} \right) \left(1 + K_2 \frac{X_C}{1 - X_C} \right) \times W_P + T_{g,S} W_S \quad (3)$$

where $T_{g,S}$ is the glass transition temperature of the styrene monomer, $T_{g,S} = 135 \text{ K}$,² W_S the weight fraction of the unreacted residual styrene monomer, and W_P the weight fraction of the polymer network $W_P + W_S = 1$, K_2 a constant. Since the molecular weight of the unsaturated polyester in this system is about

1800, we were not able to get an experimental value of T_{gPE}^∞ . K_2 and T_{gPE}^∞ are parameters obtained by fitting the experimental data to eq 3 as will be shown latter.

FREE VOLUME FRACTION

The free volume fraction V_f is approximate to increase linearly with temperature in accordance with the following relations³:

$$V_f = V_{fg} + \beta_1(T - T_g) \quad \text{for curing temperature } T > T_g \quad (4-1)$$

$$V_f = V_{fg} + \beta_g(T - T_g) \quad \text{for curing temperature } T < T_g \quad (4-2)$$

where V_f is the volume fraction of free volume at temperature T , $V_{fg} = 0.025$ the volume fraction of free volume at T_g , β_1 the thermal expansion coefficient at liquid state, β_g the thermal expansion coefficient at glassy state, and $\Delta\beta = \beta_1 - \beta_g$. According to Simha-Boyer, $\Delta\beta$ and β_1 have the following relations with T_g for many polymers⁷:

$$\beta_1 T_g = 0.164 \quad (5-1)$$

$$\Delta\beta T_g = 0.113 \quad (5-2)$$

In this work, we use eq 4 and 5 to calculate variation of free volume fraction from T_g during the curing reaction of unsaturated polyester.

CURING MODEL OF UNSATURATED POLYESTER

In most studies on curing reactions of unsaturated polyester, researchers⁸⁻¹¹ have used empirical models to fit the reaction profiles.

A typical model is

$$\frac{d\alpha}{dt} = (K_1 + K_2 \alpha^m)(1 - \alpha)^n \quad (6)$$

Where α is the conversion and is defined by the following equation:

$$\alpha = \frac{\left(\begin{array}{c} \text{total number of double} \\ \text{bonds which has been reacted} \end{array} \right)}{\left(\begin{array}{c} \text{total number of double bonds} \\ \text{initially presented in the system} \end{array} \right)}$$

$$\pi_2 = \frac{A_p}{F} \exp\left(\frac{B_p}{V_f}\right) \quad (8)$$

$$\pi_3 = FfI_0k_dk_{p0} \exp\left(-\int_{t_z}^t k_d dt\right) \quad (9)$$

$$\pi_4 = A_M \exp\left(\frac{B_M}{V_f}\right) \quad (10)$$

The above model fits the experimental results well but has little physical meaning.

The other kinetic model is based on the free radical polymerization mechanism. Several authors have proposed methods of incorporating diffusion resistance into free radical reaction kinetics, and have advanced mechanistic interpretations based on the concepts of molecular entanglement,¹²⁻¹⁴ free volume and the glass transition.¹⁵ Chiu *et al.*¹⁶ and Huang *et al.*¹⁷ used film theory in which the diffusion and reaction resistances are combined in series.

By assuming (1) no monomer reacts until the number of initiator radical created is equal to the effective number of inhibitor molecule initially presented (this assumption is valid because that the reaction between the initiator and inhibitor is much faster than the reaction between the initiator and the monomer)^{18,19}; (2) termination is predominated by combination; (3) homopolymerization of unsaturated polyester is negligible; (4) copolymerization of styrene and unsaturated polyester can be expressed by a single average reaction rate constant; (5) termination is totally diffusion controlled; and (6) quasi steady state reaction, Huang *et al.* derived the following curing kinetic model for unsaturated polyester resin¹⁷:

$$\frac{d\alpha}{dt} = \frac{1-\alpha}{1/2\pi_2\pi_3 + \pi_4} \quad (7)$$

In eq 7, π_2 is the parameter related to the diffusion effect on termination; π_3 the parameter related to the kinetic effect on propagation; and π_4 the parameter related to the diffusion effect on propagation.

π_2 , π_3 , and π_4 can be defined by the following equations:

where F is a parameter defined as:

$$F = \frac{\left(\begin{array}{c} \text{free radical concentration assuming that the} \\ \text{termination is totally diffusion controlled} \end{array} \right)}{\left(\begin{array}{c} \text{free radical concentration assuming} \\ \text{no termination} \end{array} \right)} = \frac{k_d A_p \exp(B_p/V_f)}{\exp[k_d(t-t_z)] - 1} \quad (11)$$

and I_0 is the initial initiator concentration; f the initiator efficiency; t_z the induction time for the initiator to consume the inhibitor; k_d , k_i , k_z , k_p , and k_t the rate constants of initiator decomposition, primary radical formation, inhibition, propagation, and termination respectively for the overall reaction; k_{p0} and k_{t0} the rate constants of propagation and termination respectively on the surface of radical centers.

EXPERIMENTAL

Unsaturated Polyester

Unsaturated polyester was polymerized from isophthalic acid (IPA), fumaric acid (FA), and propylene glycol (PG) by the usual condensation method. The mole ratio of the final composition of the polyester resin determined by NMR was IPA/FA/PG = 1/1.64/3.23. Thus, the final unsaturated polyester has the following specifications: acid value about 28 mg KOH/g, $M_n = 1800 \text{ g mol}^{-1}$ and $M_w/M_n = 4.3$. The resin with a styrene/polyester weight ratio of 33/67 was used for DSC and FTIR curing reactions.

Initiator

The peroxide was *tert*-butyl peroxybenzoate from Akzo Chemie Co. with a purity of 98% and an active oxygen content of 8.0%. In this study, 1% by weight of initiator was added into the resin.

Differential Scanning Calorimetry (DSC)

A Du Pont 910 DSC was used to measure the exothermic reaction of curing. Hermetic DSC pans were used to minimize loss of volatile materials (such as styrene monomer) during the heating of the sample in the DSC cell. The weight of the sample used ranges from 4 mg to 6 mg. A small sample size was required in order to achieve isothermal operating during cure.

Fourier Transform Infrared Spectroscopy (FTIR)

A Perkin-Elmer FTIR 1745X was used to measure the concentration of the unreacted C=C bond and styrene C=C bond in the curing system. Absorptions at $\lambda_{\max}^{-1} = 982 \text{ cm}^{-1}$ of ester C=C bond and $\lambda_{\max}^{-1} = 912 \text{ cm}^{-1}$ of styrene C=C bond were used to determine the unreacted ester C=C bond and residual styrene monomer content respectively. The absorption peak at $\lambda_{\max}^{-1} = 1750 \text{ cm}^{-1}$ of C=O was taken as an internal standard.

TMA Glass Transition Temperature Measurements

The glass transition temperature was measured by Thermal Mechanical Analysis (TMA Du Pont 945) with a heating rate of $10^\circ\text{C min}^{-1}$. The sample size for TMA measurement is $4 \text{ mm} \times 4 \text{ mm} \times 3 \text{ mm}$.

RESULTS AND DISCUSSION

Glass Transition Temperature and Free Volume Fraction

To determine parameters T_{gPE}^∞ and K_2 of eq 3, unsaturated polyester resins with initial styrene monomer content from 12.0% to 50.0% were prepared and cured isothermally

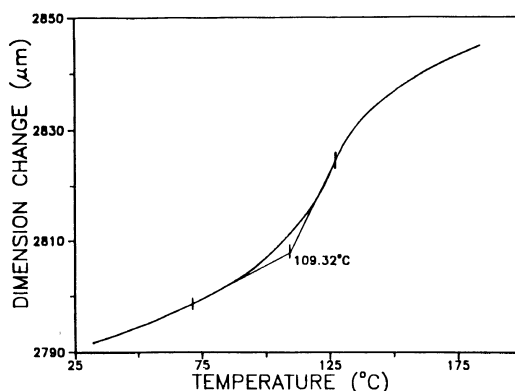


Figure 1. TMA curve of the unsaturated polyester with 30% styrene monomer cured under 100°C for 2 hours.

at 100°C for 2 hours. The glass transition temperature of the partially cured unsaturated polyester could not be measured by DSC because of additional cure reactions that are the immediate results of reacting at the glass transition. Thermal mechanical analysis (TMA) was used to determine the glass transition in this work. Figure 1 is the TMA curve of unsaturated polyester with 30% styrene monomer cured at 100°C for two hours. The crosslinked density, X_C , residual unreacted styrene monomer content, W_S , were determined by Fourier Transform Infra Red Spectroscopy (FTIR).

In eq 3, we have two variables W_{PS} and X_C and two unknown parameters K_2 and T_{gPE}^∞ to be estimated. The parameters T_{gPE}^∞ and K_2 obtained from a least squares fit of our experimental data to eq 3 are 313 K 1.21 respectively. The value of $T_{\text{gPE}}^\infty = 313 \text{ K}$ is consistent with that predicted from the chemical structure of unsaturated polyester using the van Krevelen and Hoftyzer theory.^{6,20} The value of $K_2 = 1.21$ is consistent with that of the styrene/divinylbenzene system which was estimated by DiBenedetto.^{5,6}

By rearranging eq 3, we obtain eq 12:

$$\left(\frac{T_g - T_{g,S} W_S}{W_P} \right) \left(\frac{T_{\text{gPS}}^\infty (1 - W_{\text{PS}}) + T_{\text{gPE}}^\infty W_{\text{PS}}}{T_{\text{gPS}}^\infty T_{\text{gPE}}^\infty} \right)$$

$$= 1 + K_2 \frac{X_C}{1 - X_C} \quad (12)$$

By substituting $T_{gPE}^\infty = 313\text{ K}$ into eq 12, and plotting the left hand side of eq 12 vs. $X_C/(1 - X_C)$ the slope is K_2 . The plot of eq 12 is shown in Figure 2.

By rearranging eq 3, we obtain eq 13:

$$\left(\frac{W_p}{T_g - T_{g,S} W_s} \right) \left(1 + K_2 \frac{X_C}{1 - X_C} \right) = \frac{1}{T_{gPE}^\infty} + \left(\frac{1}{T_{gPS}^\infty} - \frac{1}{T_{gPE}^\infty} \right) W_{PS} \quad (13)$$

By substituting $K_2 = 1.21$ into eq 13, and

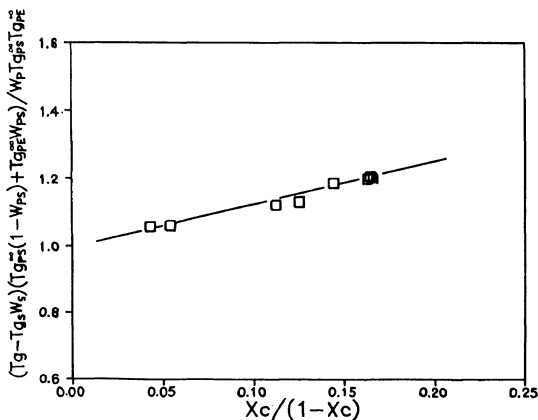


Figure 2. Plot of eq 12. (□), experimental data; (—), theoretical curve.

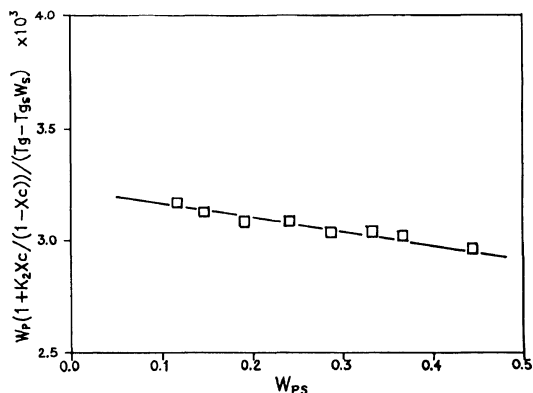


Figure 3. Plot of eq 13. (□), experimental data; (—), theoretical curve.

plotting the left hand side of eq 13 vs. W_{PS} the intercept is $1/T_{gPE}^\infty$. The plot of eq 13 is shown in Figure 3.

Table I shows experimental data of T_g , X_C , and W_s of the cured resin and corresponding T_g predicted from eq 3. The first column in Table I is the initial total styrene content of the uncured resin.

Figures 4 and 5 show FTIR absorption spectra of styrene vinyl at 912 cm^{-1} and ester vinyl at 982 cm^{-1} respectively of the unsaturated polyester resin with a styrene content of 33.0% with various curing time with the curing temperature being 110°C . The conversion, α , residual styrene monomer, W_s , and crosslinked density, X_C , at each curing time are listed in Table II. The corresponding T_g were calculated from eq 3 using $K_2 = 1.21$ and $T_{gPE}^\infty = 313\text{ K}$. The variation of free volume V_f vs. reaction time was calculated from glass transition temperature using eq 4 and 5. The glass transition temperature and the free volume fraction V_f at each curing time stage are also listed in Table II.

The relation between the T_g and conversion α can be described by the following equation:

$$T_g = K_1 \exp(K_3 \alpha) \quad (14)$$

T_g data listed in Table II vs. conversion α together with the curve fitted to eq 14 are plotted in Figure 6. K_1 and K_3 of eq 14 obtained from least squares fit of these data to eq 14 are 252.0 and 0.54, respectively.

Table I. Properties of unsaturated polyester isothermal cured at 100°C for 2 hours

| Sample (Styrene %) | X_C | W_s | T_g/K (Expt.) | T_g/K (Theory) |
|--------------------|--------|---------|------------------------|-------------------------|
| 12.0 | 0.0514 | 0.00368 | 335.2 | 336.2 |
| 15.0 | 0.0409 | 0.00424 | 335.3 | 333.5 |
| 20.0 | 0.1008 | 0.00992 | 355.9 | 361.6 |
| 25.0 | 0.1114 | 0.0125 | 360.0 | 369.2 |
| 30.0 | 0.1260 | 0.0184 | 382.3 | 378.1 |
| 35.0 | 0.1422 | 0.0265 | 388.3 | 387.5 |
| 40.0 | 0.1403 | 0.0545 | 382.4 | 381.5 |
| 50.0 | 0.1413 | 0.1018 | 377.3 | 374.7 |

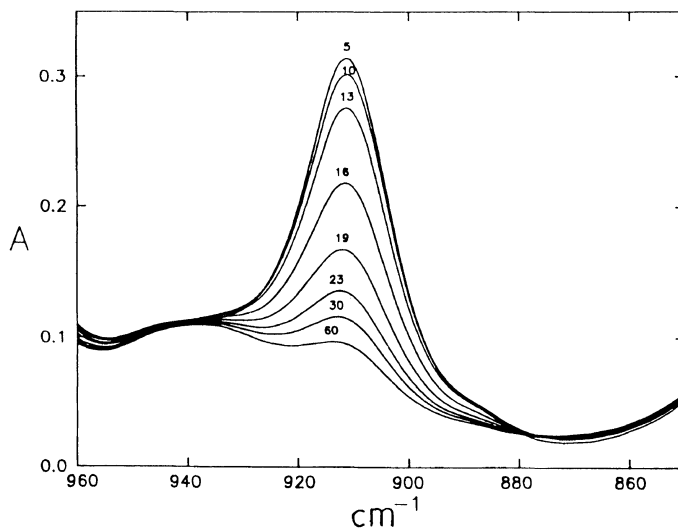


Figure 4. FTIR absorption spectra at 912 cm^{-1} of the unsaturated polyester with a styrene content of 33% cured at a temperature of 110°C . The numeric values in the graph is the curing time.

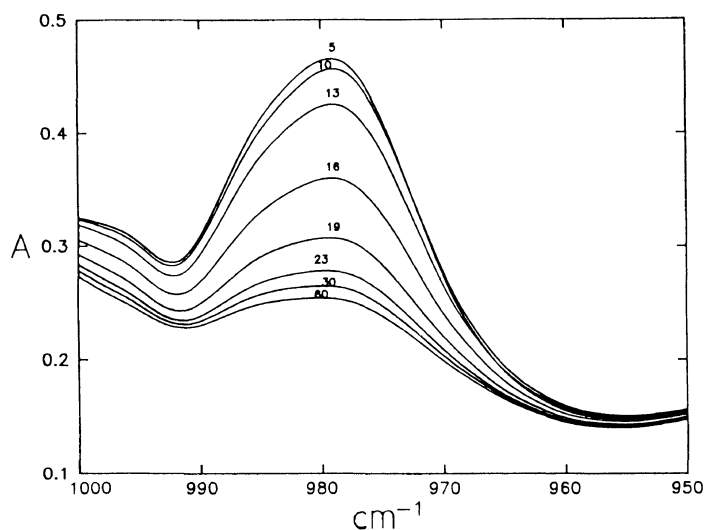


Figure 5. FTIR absorption spectra at 982 cm^{-1} of the unsaturated polyester with a styrene content of 33% cured at a temperature of 110°C . The numeric values in the graph is the curing time.

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 cure (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:

$$\frac{d\alpha}{dt} = \frac{1}{Q_{\text{tot}}} \left(\frac{dQ}{dt} \right)_T \quad (15)$$

The subscript "T" refers to isothermal curing reaction. Integrating eq 15 with respect to time, one obtains the degree of conversion, α ,

Table II. FTIR curing data of unsaturated polyester at 110°C (initial styrene content of the uncured resin is 33%)

| Curing time min | Conversion/ % | Residual styrene/% | Crosslink density/ % | T_g /K | V_f |
|--------------------|------------------|-----------------------|-------------------------|----------|--------|
| 0 | 0.0 | 32.9 | 0.0 | 252.4 | 0.0835 |
| 5 | 0.0 | 32.9 | 0.0 | 252.4 | 0.0828 |
| 8 | 2.15 | 32.0 | 0.24 | 255.2 | 0.0816 |
| 10 | 5.24 | 30.9 | 0.84 | 259.3 | 0.0789 |
| 13 | 15.2 | 27.7 | 3.17 | 273.2 | 0.0704 |
| 16 | 37.6 | 20.5 | 8.29 | 308.2 | 0.0524 |
| 17 | 45.3 | 18.0 | 9.95 | 321.5 | 0.0466 |
| 19 | 56.2 | 14.3 | 12.25 | 341.4 | 0.0382 |
| 21 | 63.5 | 11.6 | 13.63 | 355.5 | 0.0337 |
| 23 | 67.8 | 10.2 | 14.57 | 364.2 | 0.0308 |
| 25 | 70.5 | 9.2 | 15.02 | 369.2 | 0.0292 |
| 30 | 74.2 | 7.7 | 15.52 | 376.8 | 0.0269 |
| 35 | 76.1 | 6.9 | 15.82 | 380.7 | 0.0257 |
| 41 | 77.6 | 6.3 | 16.02 | 383.8 | 0.0250 |
| 45 | 78.3 | 5.9 | 16.1 | 385.2 | 0.0250 |
| 50 | 79.2 | 5.6 | 16.3 | 387.1 | 0.0250 |

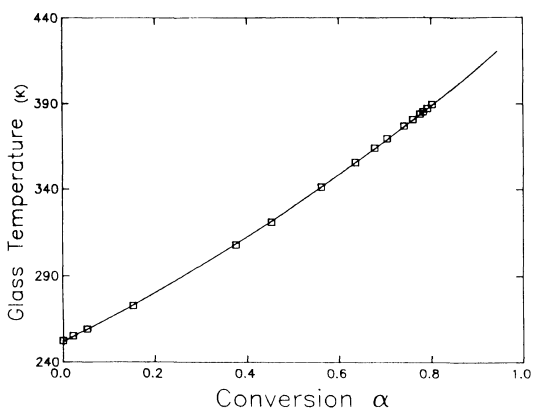


Figure 6. Glass transition temperature (T_g) vs. conversion (α) together with the curve fitted to eq 14.

$$\alpha = \frac{1}{Q_{tot}} \int_{t_1}^t \left(\frac{dQ}{dt} \right)_T dt \quad (16)$$

where $Q_{tot} = Q_T + Q_R$, Q_T is the heat generated during isothermal DSC runs and Q_R is the residual heat released when the sample was heated to 200°C on completion of an isothermal curing reaction, at the rate of 5°C min⁻¹. The isothermal DSC curing curves $d\alpha/dt$ vs. curing time at temperatures 100°C,

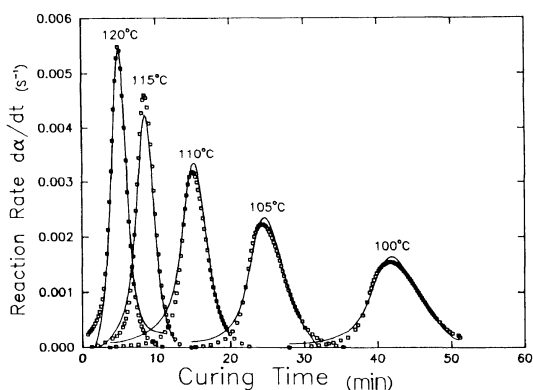


Figure 7. DSC isothermal curing data together with simulation curves. The curing temperatures are 100°C, 105°C, 110°C, 115°C, and 120°C. (\square), experimental data; (—), simulation curve with π_2 calculated from eq 22.

105°C, 115°C, and 120°C are plotted in Figure 7 with square symbols. Plots of α , vs. curing time are shown in Figure 8. Since we are not able to obtain the crosslinked density, and residual styrene monomer content etc. from DSC curing curves, the variation of T_g during the curing reaction can not be calculated from eq 3. We used eq 14 to calculate the variation of T_g for the isothermal DSC curing reaction.

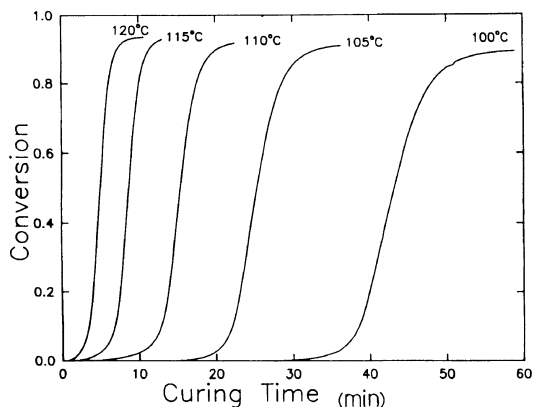


Figure 8. Conversion α calculated from DSC curing rate data vs. curing time. The curing temperatures are 100°C, 105°C, 110°C, 115°C, and 120°C.

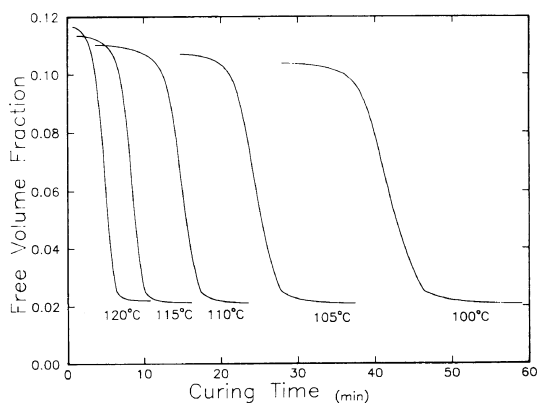


Figure 10. Free volume fraction V_f calculated from T_g vs. curing time. The curing temperatures are 100°C, 105°C, 110°C, 115°C, and 120°C.

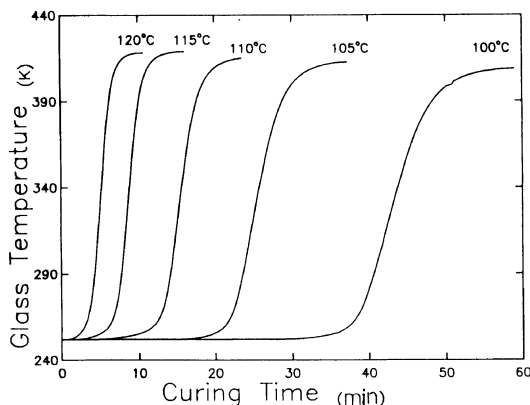


Figure 9. Variation of T_g vs. curing time. The curing temperatures are 100°C, 105°C, 110°C, 115°C, and 120°C.

Equation 14 was derived from FTIR conversion data. The variation of T_g vs. DSC curing time at 100°C, 105°C, 115°C, and 120°C is plotted in Figure 9. The corresponding free volume fraction vs. curing time calculated from T_g by using eq 4 and 5 are also plotted in Figure 10.

Curing Kinetics

The dissociation constant of *tert*-butyl peroxybenzoate initiator can be obtained from the following equation:

$$k_d = A_1 \exp(-E/RT) \quad (17)$$

where $A_1 = 5.55 \times 10^{15} \text{ min}^{-1}$, $E = 1.34 \times 10^5 \text{ J mol}^{-1}$, and $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$. The data of the constants A_1 and E were obtained from the Akzo Chemie Co.²¹

From eq 8, 9, and 11, we obtain:

$$\pi_2 \pi_3 = FfI_0k_{p0}[1 - \exp\{-[k_d(t-t_z)]\}] \quad (18)$$

By substituting eq 10 and 18 into eq 7, we obtain:

$$\begin{aligned} & \frac{1-\alpha}{d\alpha/dt} [1 - \exp\{-[k_d(t-t_z)]\}] \\ &= \frac{1}{2FfI_0k_{p0}} + A_M \left[\exp\left(\frac{B_M}{V_f}\right) \right. \\ & \quad \left. \times (1 - \exp\{-k_d(t-t_z)\}) \right] \quad (19) \end{aligned}$$

F is usually found to be constant at the later stage of reaction ($F=1$). From the later stage of reaction (the totally diffusion-controlled region for both free radical chains and monomers), π_3 and π_4 can be evaluated. Taking the later stage of DSC data, by varying the constant B_M and plotting the left hand side of eq 19 vs. $1 - \exp\{-k_d(t-t_z)\} \exp(B_M/V_f)$, the slope equals A_M and the intercept equals $1/2FfI_0k_{p0}$. In this work, we obtained the best fit of 19, by assuming $B_M=0.09$. In eq 19, the value of V_f was calculated from eq 14, 4,

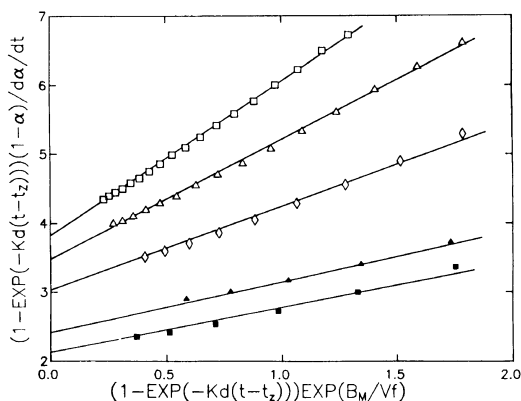


Figure 11. Plot of the left hand side of eq 19 vs. $\{1 - \exp[-k_d(t - t_z)]\} \exp(B_M/V_f)$. (□), 100°C; (△), 105°C; (◇), 110°C; (▲), 115°C; (■) 120°C.

and 5. Figure 11 is the plot of eq 19 for unsaturated polyester resin cured at temperatures 100°C, 105°C, 110°C, 115°C, and 120°C. Using the data extracted from Figure 11, eq 20 and 21 for the variations of A_M and FfI_0k_{p0} with temperature were obtained as,

$$A_M(s) = 7.308 \times 10^{-14} \exp(11606/T) \quad (20)$$

$$FfI_0k_{p0} (s^{-1}) = 1.234 \times 10^4 \exp(-4.285.7/T) \quad (21)$$

Substituting eq 20 for A_M and eq 14, 4, and 5 for V_f into eq 10, π_4 can be obtained. Substituting eq 17 and 21 into eq 9, π_3 can be obtained.

In their work, Huang *et al.*^{17,22} estimated π_2 by fitting whole the reaction curve to the following empirical equation: $\ln(A_p/F) = a + b \ln(1/V_f) + c [\ln(1/V_f)]^2$, where a , b , and c are three polynomial coefficients to be estimated. In the present work, π_2 was evaluated by fitting the whole reaction curve to eq 22 which is similar to the equation used by Huang *et al.*

$$\pi_2 = \frac{A_p}{F} \exp\left(\frac{B_p}{V_f}\right) = A + \frac{B}{V_f} + \frac{C}{V_f^2} + \frac{D}{V_f^3} \quad (22)$$

where A , B , C , and D are parameters to be estimated. Figure 12 is the plot of the left hand

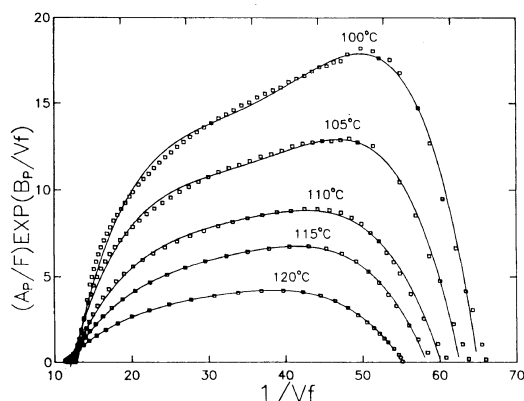


Figure 12. Plot of the left hand side of eq 22 vs. $1/V_f$.

side of eq 22 vs. V_f for unsaturated polymer, the constants A , B , C , and D with temperature are obtained:

$$A = 5.370 \times 10^{-16} \exp(14681/T) \quad (23)$$

$$B = 4.155 \times 10^{-17} \exp(14901/T) \quad (24)$$

$$C = 1.725 \times 10^{-19} \exp(15781/T) \quad (25)$$

$$D = 3.100 \times 10^{-21} \exp(15815/T) \quad (26)$$

Substituting π_2 , π_3 , and π_4 into eq 7, the values of $d\alpha/dt$ vs. curing time can be obtained. The simulation curves for unsaturated polyester cured at 100°C, 105°C, 110°C, 115°C, and 120°C are shown in Figure 7 together with DSC experimental data. Good agreement between the experimental results and the simulation curves was found.

However, π_2 can also be estimated from eq 28 which is obtained by substituting eq 11 into eq 8.

$$\pi_2 = \frac{1}{k_d} \{ \exp[k_d(t - t_z)] - 1 \} \quad (28)$$

Substituting the π_2 values estimated from eq 28 together with π_3 , and π_4 into eq 7, the values of $d\alpha/dt$ vs. curing time are shown in Figure 13 with dashed curves. From Figure 13, we found that the reaction rate of the simulation data is much fast than the DSC experimental data. Huang *et al.* assume that the termination

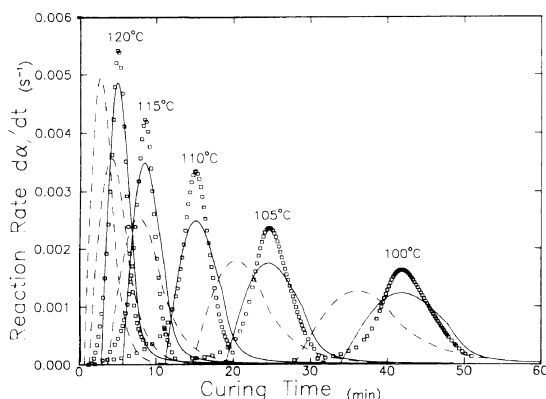


Figure 13. DSC isothermal curing data together with simulation curves. The curing temperatures are 100°C, 105°C, 110°C, 115°C, and 120°C. (□), experimental data; (-----), simulation curves with π_2 calculated from eq 28; (—), simulation curves with π_2 calculated from eq 29.

of the curing reaction of unsaturated polyester is totally diffusion controlled in the whole period of the reaction. The reason for deviation between the simulation and the experimental data may be due to negligence of the kinetic effect on termination in the initial period of the curing reaction of the model eq 7. Thus, if π_2 is calculated from eq 29 in which the induction time t_z of eq 28 is substituted by gel time t_{gel} , better agreement between the simulation and experimental results is found. The simulation curves obtained by using π_2 calculated from eq 29 are also shown with full lines in Figure 13.

$$\pi_2 = \frac{1}{k_d} \{ \exp[k_d(t - t_{gel})] - 1 \} \quad (29)$$

CONCLUSIONS

In most cases, one may obtain residual styrene monomer and unreacted residual ester double bonds in the cured polyester network. Because of the additional cure reactions immediate after the glass transition, the glass transition temperature of the partially cured unsaturated polyester cannot be obtained by DSC. In this work, we demonstrated that TMA is a good means to determine the glass transition temperature of thermosetting poly-

mers. A theoretical equation of T_g for crosslinked unsaturated polyester based on DiBenedetto's theory and the experimental results of TMA and FTIR was developed. The free volume during the period of the curing reaction calculated from T_g by using Simha-Boyer's free volume equation was applied to Huang's curing kinetic model. In our present work, we show that the simulation curves with π_2 calculated from eq 29 rather than eq 28 have better agreement with the experimental results. The reason for this may be that the termination of the curing reaction is not totally diffusion controlled and the kinetic effect on the termination in the initial period of the curing reaction is neglected in the model eq 7.

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REFERENCES

1. K. W. Lem and C. D. Han, *Polym. Eng. Sci.*, **24**, 175 (1984).
2. S. W. Shalaby and H. E. Bair, *Thermal Characterization of Polymeric Materials*, E. A. Turi, Ed., Academic Press, New York, 1981.
3. J. D. Ferry, "Viscoelastic Properties of Polymers," John Wiley & Sons, New York, 1980, Chapter 1.
4. L. E. Nielson, *J. Macromol. Sci. Rev. Macromol. Chem.*, **C3(1)**, 69 (1969).
5. H. Stutz, K.-H. Illers, and J. Mertes, *J. Polym. Sci., Polym. Phys. Ed.*, **28**, 1483 (1990).
6. S. C. Ma and T. L. Yu, *J. Polym. Eng.*, to appear.
7. (a) R. Simha and R. F. Boyer, *J. Chem. Phys.*, **37**, 1003 (1962).
(b) R. F. Boyer and R. Simha, *J. Polym. Sci., Polym. Lett. Ed.*, **11**, 33 (1973).
8. M. R. Kamal, S. Slurour, and M. Ryan, *SPE ANTEC Tech. Papers*, **19**, 187 (1973).
9. S. Y. Pusatcioglu, A. L. Fricke, and J. C. Hassler, *J. Appl. Polym. Sci.*, **24**, 937 (1979).
10. L. J. Lee and C. W. Macosko, *Int. J. Heat Mass Transfer*, **23(1)**, 479 (1980).
11. M. R. Barone and D. A. Caulk, *Int. J. Heat Mass Transfer*, **22**, 1021 (1979).
12. J. N. Cardenas and K. F. O'Driscoll, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 883 (1976).
13. J. N. Cardenas and K. F. O'Driscoll, *J. Polym. Sci.*,

The Curing Behavior of Unsaturated Polyester Resin

- Polym. Chem. Ed.*, **15**, 883 (1977).
14. J. N. Cardenas and K. F. O'Driscoll, *J. Polym. Sci., Polym. Chem. Ed.*, **15**, 2097 (1977).
 15. F. L. Marten and A. E. Hamielec, *ACS Symp. Ser.* No. 104, 43 (1979).
 16. W. Y. Chiu, G. M. Carratt, and D. S. Soong, *Macromolecules*, **16**, 348 (1983).
 17. Y. J. Huang and L. J. Lee, *AIChE J.*, **31**(10), 1585 (1985).
 18. J. F. Stevenson, paper presented at the 1st International Conference on Reactive Processing of Polymer, Pittsburgh. Oct., 1980.
 19. L. J. Lee, *Polym. Eng. Sci.*, **21**, 483 (1981).
 20. D. W. Van Krevelen and P. J. Hoftyzer, "Properties of Polymers," 2nd ed, Elsevier Science, Publishers, Co., 1976.
 21. Akzo Chemie Co., Technical Data Sheet, Product Catalog, Deventer, the Netherlands (1986).
 22. Y. J. Huang, J. D. Fan, and L. J. Lee, *Polym. Eng. Sci.*, **30**, 684 (1990).