ELSEVIER

Thermochimica Acta 323 (1998) 37–42

thermochimica acta

Curing behavior of an unsaturated polyester system analyzed by Avrami equation

M.G. Lu[a], M.J. Shim[b], S.W. Kim[a,*]

[a] *Department of Chemical Engineering, The University of Seoul, Seoul 130-743, South Korea*
[b] *Department of Life Science, The University of Seoul, Seoul 130-743, South Korea*

Received 10 October 1997; received in revised form 27 February 1998; accepted 5 July 1998

Abstract

The isothermal cure behavior of an unsaturated polyester resin system is studied by differential scanning calorimetry. The reaction heats (at different curing temperatures) are presented and compared to the results of the previous studies. Various kinetic parameters as well as details of the curing process can be obtained and elucidated, based on the Avrami theory. The experimental results reveal that this analytical method is valid for describing the curing behavior of unsaturated polyester resins. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Avrami equation; DSC; Isothermal cure; Reaction kinetics; Unsaturated polyester

1. Introduction

Unsaturated polyesters (UP) have a leading role in the development of fiberglass reinforced products, having tremendous versatility and very low costs. The use of unsaturated polyesters in bulk and sheet-molding compounds results in composite materials that have high strength, dimensional stability, and very good surface quality [1]. The properties of the cured resin depend, as would be expected, on its composition but, in addition, they are markedly dependent on the extent of cure. Therefore, an understanding of the curing reaction is important for process control and optimization.

Curing of unsaturated polyester resin is achieved by using an initiator. Styrene polymerizes and connects the double bonds on the UP prepolymer chains. The copolymerization of styrene with fumarate which was transformed from maleic acid MA in the course of polyesterization reaction forms microgels, even at conversion levels as low as 3–4%. The microgels are locally distributed during the initial periods and are densely distributed at the final stages of copolymerization. Therefore, cross-linking is intramicrogel-dominated during the initial periods and intermicrogel-dominated in the final stages. Hence, a three-dimensional network is formed owing to cross-linking [2,3].

The kinetics of curing polyester resins is normally very complex because many reactive processes occur simultaneously, including the chemical decomposition of an initiator, releasing free radicals that can react with the inhibitor, styrene, or with the polyester. From this moment on, the chains of polymer will grow and cross each other, according to three possible

---

*Corresponding author. Tel.: +82-2-210-2447; fax: +82-2-210-2310; e-mail: swkim@uoscc.uos.ac.kr

PII: S0040-6031(98)00506-1

reactive processes: styrene–polyester copolymerization, styrene homopolymerization, and polyester homopolymerization. In the terminal stage, there are multiple reactive processes, and all the free radicals in the reaction medium can recombine, thus ending the growth of the chains. If the curing temperature is sufficiently high, there may be thermal decomposition of the initiator, can lead to another process of polymerization [4].

In general, kinetic expressions may be phenomenological or mechanistic. The phenomenological models relate to the main features and do not take into account each and every reaction. In our opinion, the phenomenological model is preferred since the cure process is so complex that it is difficult to identify each and every reaction or reaction stage.

The Avrami theory, based on phase changes, was most often used to describe polymer crystallization kinetics. In a broad sense, crystallization can be considered as a physical form of cross-linking. Meanwhile, microgels formed, even at conversion levels as low as 3–4% in the curing process of unsaturated polyester resin, have been observed as mentioned above. We analyzed the curing kinetics of epoxy resins using Avrami theory, and the results obtained were in very good agreement with those from other analytical methods [5]. In this paper, preliminary data obtained on a typical unsaturated polyester–styrene system are reported.

2. Experimental

2.1. Materials

The resin used in this study is a commercial unsaturated polyester based on propylene glycol, phthalic anhydride, and furamic acid (POLYCOAT OS-108 for SMC, Aekyung Chemical). The resin was supplied with an average molecular weight of 2950, calculated from its acid number, and a styrene content of 32.6%. The initiator for the curing reaction is *tert*-butyl peroxybenzoate with a purity of 98% and an active oxygen content of 8%.

2.2. Differential scanning calorimetry

The calorimetry measurements are made on a SEIKO I-5000 series. Isothermal experiments are performed over a range of temperatures of 70–110°C in a nitrogen atmosphere. At higher temperatures, the curing time is of the order of minutes so that the heat absorbed as the sample equilibrated at the curing temperature partially concealed the exotherm. After all the isothermal curings, a dynamic scan is conducted from 20–300°C to determine the residual heat. Dynamic curings of 20–300°C are also conducted at the heating rate of 10°C min^{-1} to determine the total reaction heat.

3. Results and discussion

3.1. Heat of reaction and degree of cure of UP

As we have stated, the curing of unsaturated-polyester resins is complex, and includes several reactive processes. Assuming that the process only has a thermal effect, the reaction advance will be directly proportional to the amount of heat generated and the maximum degree of curing reached when all double bonds that could have reacted have done so.

The fraction of double bonds reacted during the curing reaction, or the relative degree of cure, at time *t* is defined as

$$\alpha = \frac{Q_{\mathrm{t}}}{Q_{\mathrm{T}} + Q_{\mathrm{S}}} \tag{1}$$

where Q_{t} is the heat that is evolved isothermally corresponding to partial cure condition at time *t*, Q_{T} the total heat of reaction that is measured at the end of an isothermal run at temperature *T*, and Q_{S} the heat evolved due to the residual isothermal reactivity of the sample at temperature *T* (Q_{S} is determined by a dynamic post-curing after each isothermal experiment), $Q_{\mathrm{T}}+Q_{\mathrm{S}}$ represents the maximum possible heat of cure at an initial isothermal cure temperature. The experimental heats-of-reaction values under isothermal conditions are listed in Table 1.

In fact, the total heat of cure cannot be easily measured by a single isothermal run because the reaction becomes highly diffusion-controlled during the advanced stages of cure and a very long time is required to reach completion under isothermal conditions. Otherwise, as pointed out by several authors, at low temperatures, at the start and end of the reaction the heat cannot be detected by DSC if the sensitivity of

Table 1
Isothermal heats of reaction

T/°C	Q_T/(J g^{-1})	Q_S/(J g^{-1})	Q_T+Q_S
70	174.4	139.3	313.7
80	214.6	125.8	340.4
90	247.1	113.6	360.7
100	248.6	94.8	343.4
110	275.1	70.5	345.1

the apparatus is not sufficient, and, at high temperatures, parts of the reaction heat may be lost during the heating of the sample and the stabilization of the DSC [6]. Thus, the value of (Q_T+Q_S) is not a real total heat of reaction as can be seen in Tables 1 and 2, but is lower than that obtained by a dynamic run.

The total heat of cure was measured by scanning at a constant heating rate of 10°C min^{-1}, from room temperature (20°C) to 350°C. The reaction was complete at ca. 200°C, and the total measured heat of cure Q_{tot} was 385.8 J g^{-1}. Fig. 1 is a typical dynamic DSC curve. The exotherm reaction shows two peaks, probably related to the cross-link process and to homopolymerization of the polyester double bonds (first and second peaks, respectively) [7]. However, many facts have revealed that it is difficult for maleic autopolymerization to occur in the presence of styrene. The reaction related to the second peak in the curve may be attributed to the thermal polymerization of polyester–styrene, as suggested by several investigators [8,9]. No matter what reaction mechanism takes place in the curing process, the total heat of cure remains practically constant although the area and position of peaks are changeable for different scan rates [9].

The heat of polymerization value for unsaturated polyester resins depends on the chemical composition of polyester, concentration of styrene, and the curing system. The results found by several investigators are listed in Table 2. As can be seen, there is a wide range of reaction heats for different systems. It is reasonable, since the curing of thermosetting resins is complicated by interaction of the chemical kinetics and the changing physical properties, and, likewise, the morphology of samples. Generally, an increase in the amount of MA increases the heat of reaction. This must be due to a change in the conformation of the polymer chain.

Table 2
Heats of reaction for unsaturated polyester resins

Investigators	Q_{tot}/(J g^{-1})
Kamal and Sourour [10]	305.2
Kubota [11]	391.2
Ng and Manas-Zloczower [12]	415.0
Batch and Macosko [13]	426.0
Present study	385.8

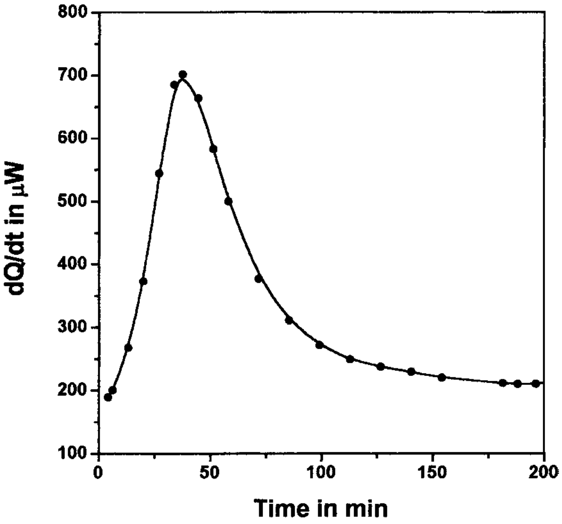

Fig. 1. Isothermal DSC curve at 80°C.

Thus, it is necessary to correct the degree of cure by the total heats of reaction obtained from a dynamic run, and the corrected degree of conversion can be defined as

$$\alpha_t^c = \frac{Q_t}{Q_T + Q_S}\frac{Q_{tot} - Q_S}{Q_{tot}} \equiv \frac{Q_t}{Q_{tot}}\frac{Q_{tot} - Q_S}{Q_T + Q_S} \quad (2)$$

Figs. 2 and 3 shows the degree of conversion according to time, using Eqs. (1) and (2). It is clear that samples do not reach a total conversion at all curing temperatures because of unreacted molecules trapped in the cross-linked network, the latter being caused by the immobility of chain segment (vitrification). It reflects the observation reported in the literature that some styrene remains unreacted [14]. It is also one of reasons why the total heats of reaction under isothermal conditions are lower than those by dynamic run.

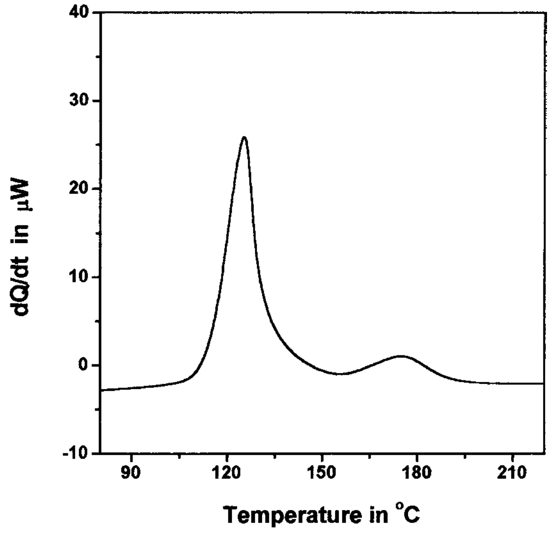

Fig. 2. Dynamic DSC curve conducted at 10°C/min.

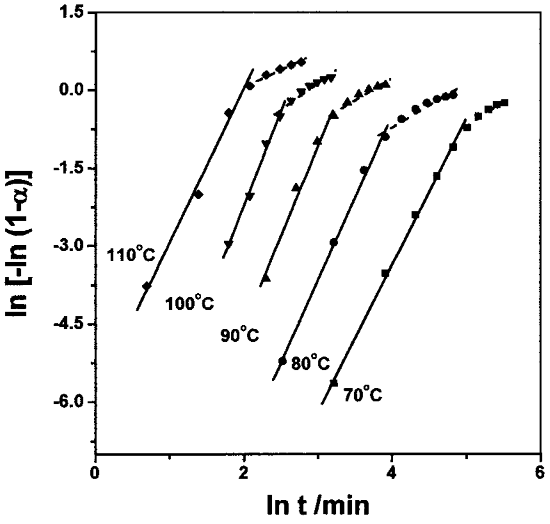

Fig. 4. Avrami plots at various temperatures.

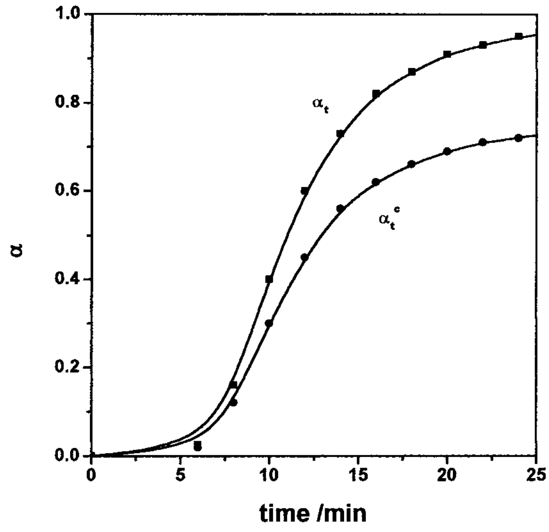

Fig. 3. Degree of cure, and corrected degree of cure, as function of time.

3.2. Kinetic analysis

The isotherms determined by DSC are analyzed by means of the simple Avrami equation

$$1 - \alpha = \exp(-Kt^n) \tag{3}$$

where α is the corrected degree of cure. The rate constant K and the Avrami exponent n can be obtained from a plot according to the following relation:

$$\ln\left[-\ln\left(1-\alpha\right)\right] = \ln K + n \ln t \tag{4}$$

However, as can be seen from Figs. 4 and 5, the Avrami plots are nonlinear and show a remarkable change in slopes; moreover, the degree of conversion is ca. 35% at 70°C when the transformation occurred. As observed, the degree of conversion at transforma-

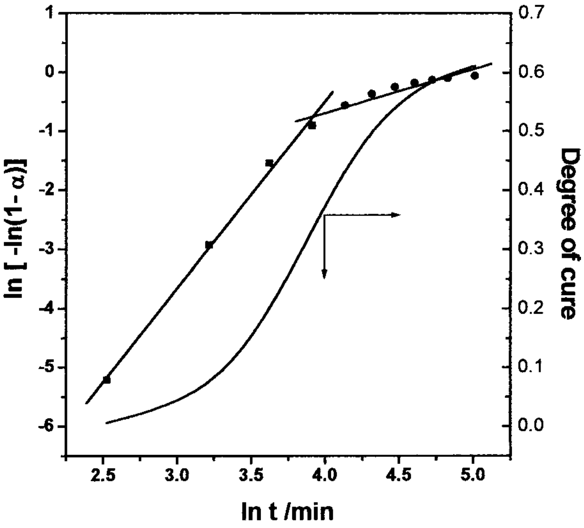

Fig. 5. Avrami plot and the relation between degree of cure and time at 80°C.

Table 3
The kinetic parameters for the curing behavior of polyester resin

Temp/K	n_1	n_2	$K_1/(10^2\ \mathrm{min}^{-3})$	$K_2/(\mathrm{min}^{-1})$	$E_1/(\mathrm{kJ\ mol}^{-1})$	$E_2/(\mathrm{kJ\ mol}^{-1})$
343	2.83	0.95	0.72	0.16		
353	3.17	0.86	1.34	0.25		
363	3.24	0.87	2.22	0.34	198.5	96.8
373	3.52	1.04	4.24	0.37		
383	2.97	0.76	14.0	0.66		

tion increases slightly with increasing temperatures. Since the slope is a measure of the Avrami exponent n, we believe that the results indicated a marked change in polymerization mechanism, although they cannot provide the qualitative information on the nature of nucleation and the growth processes as described in polymer crystallization. A summary of Avrami exponent n and kinetic constant K values for the curing behavior of polyester resin is presented in Table 3.

The change of n value from ca. 3 to 1 implies that the free growth of microgels was replaced by the diffusion-limiting (reaction) in the advance of curing. On the other hand, at the early stage of cure, the copolymerization of styrene with fumarate forms microgels which are dispersed in monomer and oligomer. In view of the low concentration, the microgels are locally distributed and cross-linking is intramicrogel dominated during early periods. In this case, the growth of microgels is practically space-unrestricted. Since the rate of radical polymerization is so rapid, it is reasonable to consider the early curing process as a three-dimensional growth by instantaneous nucleation, and it is consistent with the results expressed by the Avrami exponent (n=3). As the reaction proceeds, the number of microgel particles increases and becomes densely distributed. Eventually, they are forced to impinge on each other and the intermicrogel cross-linking becomes dominated, which results in a marked increase in viscosity. The curing process or the development of microgels is restrained (n value decreased). On the other hand, the curing reaction becomes diffusion-controlled. The results obtained in the Avrami model correspond with the facts found by many researchers [15].

Since the Avrami plots are not straight lines over the whole curing time and show two differentiated sections, the kinetic parameters can be determined from each section by assuming an Arrhenius-type dependence for the reaction constant, i.e.

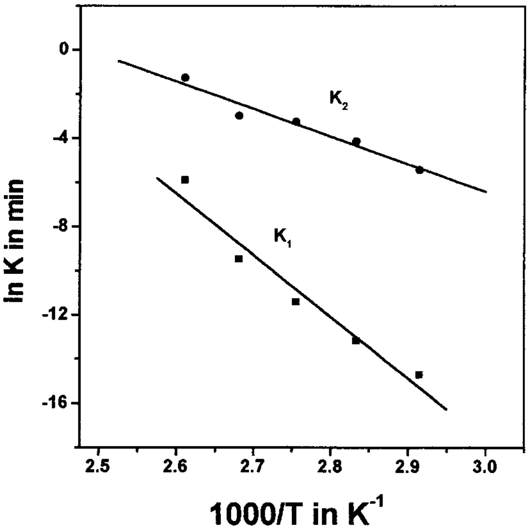

Fig. 6. Arrhenius plots of rate constants.

$$K = A\exp\left(-\frac{E}{RT}\right) \tag{5}$$

The values of rate constant can be obtained from the intercepts in Avrami plots for different sections. It is worthy to note here, that the unit of the reaction rate constant is min^{-n} and is different for both sections since the n value is 3 and 1, respectively. Fig. 6 shows the good linear relationship between the logarithm of K and the inverse of temperature. It gives a slope in which activation energy is evolved. As shown in Table 3, the value of activation energy, 96.8 kJ/mol, becomes approximately one-half its value observed at the early stage of cure. Such a decrease in apparent activation energy is commonly observed in heterogeneous reactions, especially when diffusion limitations set in [16]. The values of the kinetic parameters have been obtained by some investigators. As expected, and previously reported in literature, the kinetic parameters obtained by different DSC methods do not match very well. The difference can be caused by different chemical composition of the polyester resin and different initiator used in the system. For example, the activation energy usually decreases when an accelerator is used [12].

4. Conclusions

The foregoing discussion demonstrates how the Avrami expressions may be employed to characterize thermoset cure. Various kinetic parameters have been obtained. The change of Avrami exponent reveals that there are different reaction mechanisms occurring in the different curing stages. The results are in good agreement with the experimental data. Meanwhile, the heats of reaction (at different temperatures) indicate that the samples do not reach complete conversion in the general measuring times.

References

[1] J.C. Salomone, Polymeric Materials Encyclopedia, Vol. 11, CRC Press, Inc., 1996.
[2] Y.J. Huang, C.J. Chen, J. Appl. Polym. Sci. 47 (1993) 1533.
[3] Y.S. Yang, C.J. Lee, Polymer 29 (1988) 1793.
[4] J.M. Salla, X. Ramis, J.L. Martin, A. Caderato, Thermochim. Acta 134 (1988) 261.
[5] S.W. Kim, M.G. Lu, M.J. Shim, Polym. J. 38 (1998) 80.
[6] R.A. Fava, Polymer 9 (1968) 137.
[7] M. Avella, E. Martuscelli, M. Mazzola, J. Therm. Anal. 30 (1985) 1359.
[8] J. Brandrup, E.H. Immergut, Polymer Handbook, Interscience, NY, 1989.
[9] G. Malescot, B. Jaase, Eur. Polym. J. 11 (1975) 669.
[10] M.R. Kamal, S. Sourour, M. Ryan, SPE Tech. Papers 19 (1973) 187.
[11] H. Kubota, J. Appl. Polym. Sci. 19 (1975) 2279.
[12] H. Ng, I. Manas-Zloczower, Polym. Eng. Sci. 29 (1989) 1097.
[13] G.L. Batch, L.W. Macosko, SPE ANTEC Tech. Papers 33 (1987) 974.
[14] X. Ramis, J.M. Salla, J. Appl. Polym. Sci. 45 (1992) 227.
[15] E.A. Turi, Thermal Characterization of Polymeric Materials, Chap. 5, Academic Press, New York, 1983.
[16] C.G. Hill, An Introduction to Chemical Engineering Kinetics and Reactor Design, Chap. 12, Wiley, New York, 1977.