

Effect of Fillers on Kinetics of Epoxy Cure

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Synopsis

The effect of fillers on the reaction of liquid epoxy systems cured with *m*-phenylenediamine has been studied within the temperature range 70–170°C using a Perkin–Elmer differential scanning calorimeter. Quantitative studies have been made with regard to the effect of fillers on the kinetics of cure. Mathematical expressions have been devised to describe the curing reaction as a function of time, temperature, and filler content. These kinetic expressions were found to yield results which were in good agreement with the experimental data for the two fillers studied.

INTRODUCTION

The physical, electrical, and ultimate mechanical properties of commercial thermosetting polymers are dependent to a large extent on the filler content and degree of cure. Therefore, a knowledge of the reaction kinetics is essential for relating the physical properties to the extent of reaction of the system. An understanding of the effect of filler content on the curing process itself is of fundamental importance for the optimization of part properties and performance. Thus, the kinetic characterization of filled thermosetting systems is necessary for a better understanding of structure–property relationships and improved product quality.

A variety of experimental techniques have been developed for following the cure reaction of thermosets. These methods and techniques include chromatography,^{1,2} infrared spectroscopy,^{3–5} nuclear magnetic resonance,^{2,6,7} Raman spectroscopy,⁸ chemical analysis,^{9–12} and changes in physical properties such as refractive index,¹³ density,¹⁴ electrical resistivity,^{15,16} and viscosity.^{3,17–21} In addition, the exothermic curing reaction of thermosetting systems in general, and epoxy resins in particular, has been studied by means of dynamic mechanical measurements^{22,23} and calorimetry.^{20,24–32}

Isothermal differential scanning calorimetry has been used for the estimation of kinetic parameters by assuming that the exothermic heat evolved during cure is proportional to the extent of reaction. In most cases, the reaction rate has been described by means of a simple *n*th-order kinetic expression governed by a single Arrhenius rate constant. However, since the epoxy cure reaction has been found to be autocatalytic,²⁷ a simple *n*th-order kinetic expression is unable to provide an accurate quantitative description of the entire curing process. Kinetic expressions describing the autocatalytic behavior of epoxy systems have been discussed in the literature.^{20,24,27,32} Some of the proposed expressions are essentially semiempirical in nature, while others are based upon the detailed chemical mechanisms of epoxy cure. In these kinetic expressions the rate of cure is described by more than a single rate constant.

Although a considerable amount of research has been undertaken with regard

to the cure kinetics of epoxy resin systems, very little information has been reported on epoxy systems containing fillers. In general, the cure kinetics of filled thermosetting polymers has received relatively little attention.

Choi³³ and Willard³⁴ have conducted studies on filled diallyl phthalate molding compounds using differential scanning calorimetry. Choi investigated the dependence of mechanical and flow properties on the extent of polymerization whereas Willard studied the effect of fillers on the heat of polymerization. Pappalardo³⁵ used calorimetry to determine reaction rate constants and activation energies for several epoxy-glass composites. The effects were found to depend on the specific filler and polymer system that was used.

In the present study differential scanning calorimetry has been used to investigate the effect of a carbon black and a silica filler on the cure kinetics of a model epoxy resin cured stoichiometrically with an aromatic diamine.

THEORETICAL ANALYSIS

Previous studies relating to the mechanism of the uncatalyzed reaction of an epoxy resin with a primary amine indicate that a secondary amine is produced which subsequently reacts with another epoxide group to yield a tertiary amine. These reactions are catalyzed by the hydroxyl groups which are produced during cure.^{24,27,36} Earlier investigations have also established that reaction only occurs between the epoxy and the amine and that etherification is practically negligible.³⁶ In addition, the reaction of primary amine with epoxy successively from secondary to tertiary amine was found to proceed without any significant selectivity.^{27,36}

For epoxy-amine systems it has been found that the initial reaction rate has a nonzero value.^{20,24,32} This suggests that in addition to autoacceleration, reaction occurs between the epoxy and other extraneous material present in the system. These agents are possibly hydrogen-bond donor molecules which may be present either as moisture or impurities.³² If it is assumed that the hydrogen atoms in the amine are equally reactive,²⁷ then the curing of the epoxy resin can be presumed to occur by two simultaneous amine-epoxy reactions, the first being initiated and catalyzed by hydrogen-bond donor molecules while the second is catalyzed internally by the hydroxyl groups present in the reaction products. Taking into account that the filler may also play an active role in this reaction scheme, the rate of cure $\dot{\alpha}$ may be expressed as follows:

$$\dot{\alpha} = \frac{d\alpha}{dt} = k'_1 f_1(c) x (1 - \alpha)^n + k_2 f_2(c) \alpha^m (1 - \alpha)^n \quad (1)$$

where α is the degree of cure, x is the concentration of hydrogen-bond donor molecules, c is the filler concentration, $f_1(c)$ and $f_2(c)$ are functions of the filler content, k'_1 and k_2 are rate constants, and m and n are kinetic exponents. If x is assumed to be essentially constant for the systems studied, then

$$k_1 = k'_1 x \quad (2)$$

Allowing the rate constants themselves to be functions of filler content yields

$$k_1^* = k_1 f_1(c) \quad (3)$$

$$k_2^* = k_2 f_2(c) \quad (4)$$

For the case of an unfilled system, the rate constants are represented as follows:

$$k_{10} = k_1 f_1(0) \tag{5}$$

$$k_{20} = k_2 f_2(0) \tag{6}$$

Therefore, for an unfilled system, eq. (1) becomes

$$\dot{\alpha} = \frac{d\alpha}{dt} = (k_{10} + k_{20}\alpha^m)(1 - \alpha)^n \tag{7}$$

The kinetic expression given by eq. (7) is of the same general form as that described by Kamal et al.²⁰ for the curing behavior of unfilled polyester and epoxy systems.

The cure time t that is required to achieve a given degree of cure α_t can be obtained by integration of eq. (1) as follows:

$$t = \int_0^{\alpha_t} \frac{d\alpha}{\dot{\alpha}} = \int_0^{\alpha_t} \frac{d\alpha}{(k_1^* + k_2^*\alpha^m)(1 - \alpha)^n} \tag{8}$$

In order to evaluate the integral given in eq. (8), the term $(1 - \alpha)^{-n}$ is approximated by means of the following infinite series³⁷ for $|\alpha| < 1$ and integer values of n :

$$\frac{1}{(1 - \alpha)^n} = \frac{1}{(n - 1)!} \sum_{i=0}^{i=\infty} (i + 1)(i + 2) \dots (i + n - 1)\alpha^i \tag{9}$$

Since $0 \leq \alpha \leq 1$, eq. (9) may alternatively be expressed as

$$\frac{1}{(1 - \alpha)^n} = \sum_{i=0}^{i=\infty} \frac{\Gamma(n + i)}{i! \Gamma(n)} \alpha^i \tag{10}$$

for any positive value of n . Substitution of eq. (10) into eq. (8) yields

$$t = \sum_{i=0}^{i=\infty} \frac{\Gamma(n + i)}{i! \Gamma(n)} \int_0^{\alpha_t} \frac{\alpha^i d\alpha}{(k_1^* + k_2^*\alpha^m)} \tag{11}$$

The integral appearing in eq. (11) can be expressed by means of the following relationship^{37,38}:

$$\int_0^{\alpha_t} \frac{\alpha^i d\alpha}{(k_1^* + k_2^*\alpha^m)} = \sum_{j=0}^{j=\infty} \frac{(-k_1^*)^j \alpha_t^{[i+1-(j+1)m]}}{k_2^{*j+1} [i + 1 - (j + 1)m]} \tag{12}$$

Substituting eq. (12) into eq. (11) gives rise to the following expression for the cure time:

$$t = \sum_{i=0}^{i=\infty} \sum_{j=0}^{j=\infty} \frac{\Gamma(n + i)}{i! \Gamma(n)} \frac{\alpha_t^{[i+1-(j+1)m]}}{i + 1 - (j + 1)m} \frac{(-k_1^*)^j}{k_2^{*j+1}} \tag{13}$$

Equation (13) satisfies both the ratio test and the root test for convergence and can therefore be used to predict the cure time t for a given degree of cure α_t .

EXPERIMENTAL

Materials and Properties

The epoxy resin that was used in this study was a commercial diglycidyl ether of bisphenol A (Allied Resin Corp., DER-332). The high purity and low viscosity of the resin facilitated the dispersion of the filler in the system. This liquid epoxy resin was cured stoichiometrically with *m*-phenylenediamine (Aldrich Chemical Co., 99+ % purissimum grade).

Two commercial-grade fillers were used in the present study, namely, a Cabot furnace-process carbon black (Sterling V, Cabot N-660, Cabot Corporation of Canada Ltd.) and a surface-treated Novacite (silica) manufactured by Malvern Mineral Co. under the tradename Novakup. The specific grade of silica filler that was used in this work was L-207A Novacite with Z-6020 silane coupling agent (aminofunctional) attached to its surface. The physical properties of both fillers are given in Table I.

All of the above materials were used as supplied without further purification.

Equipment

The thermal and kinetic data were obtained using a Perkin-Elmer differential scanning calorimeter (Model DSC-1b) connected directly to a rotameter (Matheson, Model 620) in order to regulate the nitrogen flow rate through the instrument. A permanent record of the differential power signal was obtained by means of a Leeds and Northrup (Speedomax, Model W) strip-chart recorder.

Procedure

Calibration. The temperature and power calibration of the DSC was optimized for the temperature range of 325–600 K. Melting points of high-purity elements (DSC calibration standards) and organic compounds (Fisher thermetric standards) were used for the temperature calibration. The power calibration was made using the heats of fusion of benzoic acid and naphthalene as standards.

TABLE I
Physical Properties of Commercial Fillers

	Carbon black	Novakup
Average particle size	50 μm	4 μm
Surface area	35 m^2/g	2 m^2/g
Bulk density	27 lb/ft^3	82.75 lb/ft^3 (dense packed)
Specific gravity	1.8	2.65 (70°F)
pH	7.5	6.0–6.3 (in distilled water)
Chemical composition	fixed carbon 99%; volatile content 1%	Silica, SiO_2 99.12% Fe_2O_3 0.04% TiO_2 0.015% Al_2O_3 0.61% loss 0.20%

Thermal and Kinetic Characterization. Isothermal studies were conducted in the temperature range of 343–443 K at various filler concentrations in order to determine the rate of heat generation as a function of time. In addition, dynamic scanning experiments were carried out in order to obtain the maximum possible extent of cure at each filler level.

Initially, the required amount of filler was weighed and dispersed in the epoxy resin. In order to achieve good dispersion the epoxy resin was heated to approximately 80°C and the filler was then added to the low-viscosity resin. The mixture was subsequently stirred for about 10 min. Owing to the good dispersibility of both fillers, a uniform mixture was easily obtained. In order to ensure that no interactions occurred between the filler and the liquid epoxy resin, a small sample of the mixture was scanned at 10°C/min. No deviation from baseline could be detected, indicating that no measureable interaction took place between these constituents.

On the most sensitive range the calorimeter signal was zeroed to the recorder baseline by adjusting the "slope" potentiometer. The appropriate range setting was selected, and the isothermal baseline was established at the preset cure temperature by using a fully cured sample and an empty sample pan. The required amount of amine was added to the epoxy-filler mixture and introduced into the sample holder. The exothermic reaction was considered to be complete when the recorder pen leveled off to the initial isothermal baseline. The observed weight loss of the sample was negligible in all cases. The range and recorder chart speed were selected so as to yield a reasonably large exotherm for accuracy in data analysis.

The complete heat of cure was determined by scanning a sample from an initial temperature of 333 to 600 K at a scan speed of 10°C/min. The reaction was generally found to be complete at a temperature of 570 K. The baseline was approximated by joining the two ends of the cure exotherm by means of a straight line.

The cumulative heat generated during cure was obtained as a function of time by numerically integrating the rate data using Simpson's one-third rule with the aid of a digital computer (Cyber CDC173). The complete or ultimate heat of cure was obtained in a similar fashion from the dynamic DSC trace. The number of ordinates used for the integration varied from 50 to 80.

Further details relating to the calibration and characterization procedures are described elsewhere.³⁹

RESULTS AND DISCUSSION

Isothermal and Ultimate Heats of Cure

Figure 1 shows the rate of heat generation as a function of time at three different temperatures. As expected, an increase in temperature facilitates the curing reaction, thereby reducing the reaction time. At a given isothermal temperature the area under the rate curve corresponds to the total amount of heat generated or isothermal heat of cure, Q_T . Figure 2 shows the variation of Q_T with temperature for the unfilled epoxy system. Similar results were obtained for all of the filled systems. The variation of Q_T with temperature can be accurately described by means of a quadratic equation at all filler concentrations. Therefore,

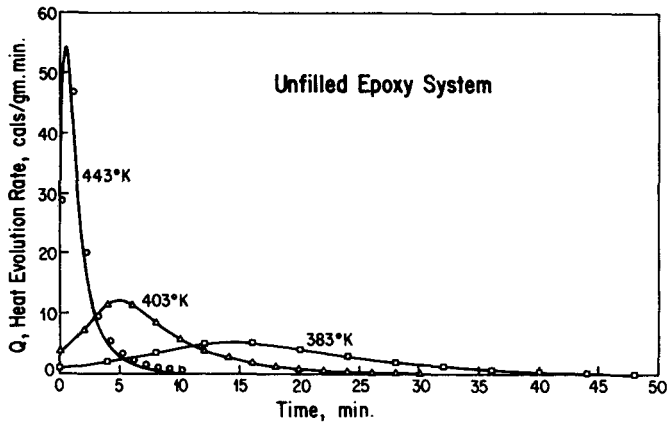


Fig. 1. Rate of heat generation as function of time.

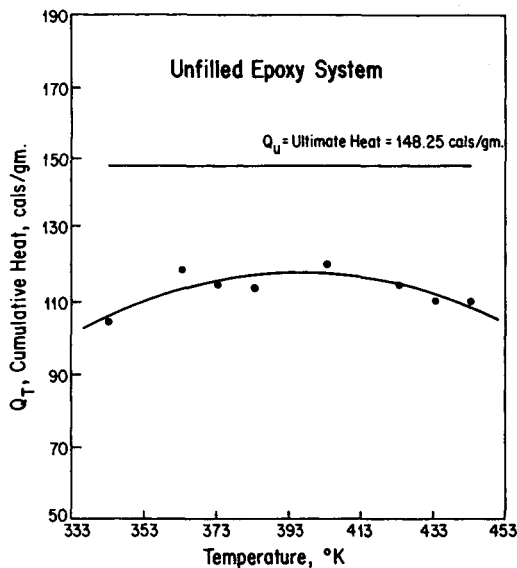


Fig. 2. Cumulative and ultimate heat of cure as function of temperature.

$$Q_T = C_0 + C_1T + C_2T^2 \quad (14)$$

The quadratic coefficients C_0 , C_1 , and C_2 are given in Table II for all of the systems studied.

The complete or ultimate heat of cure Q_U as determined from dynamic scanning experiments was found to be 148 cal/g resin (25.8 kcal/g-mole resin) for the unfilled epoxy system. Similar results for unfilled epoxy-amine systems have been reported by Horie et al.,²⁷ Sourour and Kamal,³² and Klute and Viehmann.⁴⁰ For the filled epoxy systems, the ultimate heat of cure was found to be essentially independent of filler level. In the case of the carbon black filler, Q_U was determined to have an average value of 148 ± 6 cal/g resin (25.8 ± 1 kcal/g-mole resin), similar to that for the unfilled system. However, for the

TABLE II
Temperature Dependence of Q_T for Different Epoxy Systems^a

Filler conc., wt. %	$-C_1$, cal/g	C_2 , cal/g K	$-C_3 \times 10^2$, cal/g K ²	T_{max} , K	Q_{max} , cal/g
Unfilled Epoxy System					
0	560.9	3.43	0.433	396.2	118.8
Carbon Black-Filled Epoxy System					
1	991.3	5.55	0.696	398.9	115.9
2	774.2	4.51	0.571	395.2	117.4
4	537.3	3.22	0.396	406.2	116.1
6	926.9	5.38	0.691	389.0	118.8
Novakup-Filled Epoxy System					
1	712.0	4.23	0.544	389.2	111.9
4	322.2	2.15	0.268	400.9	108.6
6	1597	8.68	1.100	394.3	113.8
10	1432	7.91	1.010	391.7	117.9

^a Q_{max} is the maximum isothermal heat of cure; T_{max} is the temperature at which Q_{max} occurs.

Novakup-filled epoxy systems, Q_U was found to be significantly different, having an average value of 168 ± 3 cal/g resin (29.2 ± 0.6 kcal/g-mole resin).

Isothermal Rate Curves

Based upon the assumption that the exothermic heat evolved is directly proportional to the extent of cure, the cumulative heat generated Q can be normalized in order to define a relative degree of cure α as follows:

$$\alpha = Q/Q_T \quad (15)$$

With the aid of eq. (15), the rate of heat generation Q can be converted to an isothermal reaction rate $\dot{\alpha}$ as depicted in Figure 3. The maximum in the reaction rate curve indicates the presence of an autoaccelerating mechanism during the cure reaction. In addition, a nonzero initial reaction rate is observed. Similar results have been observed for all of the filled systems.

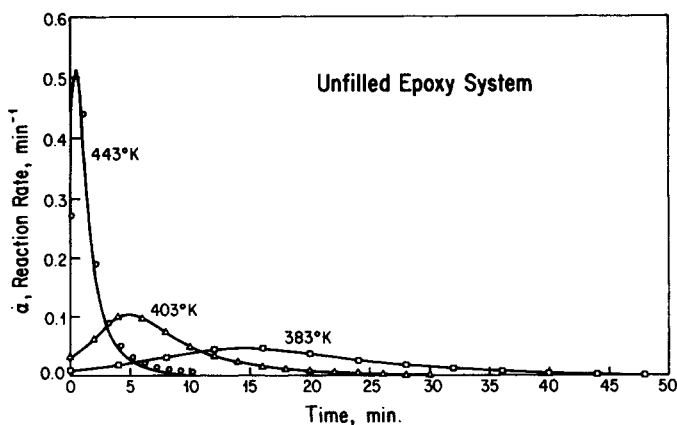


Fig. 3. Isothermal reaction rate as function of time.

The isothermal reaction rate curve can be integrated so as to obtain an integral cure curve depicting the time dependence of the relative degree of cure α . Figure 4 gives a comparison between the integral cure curves for the two filled systems at the same filler concentration. It is evident that the carbon black filler has a more pronounced effect on the curing process.

Kinetic Parameters

At the onset of the cure reaction, $t = 0$ and $\alpha = 0$; and thus eq. (1) simplifies to the following expression:

$$\left(\frac{d\alpha}{dt}\right)_{t=0} = k_1^* \quad (16)$$

Therefore, k_1^* can be directly obtained from the isothermal reaction rate curve. The rate constant k_2^* and the kinetic exponents m and n were obtained by fitting eq. (2) to the experimental rate data using a nonlinear least-squares technique. The kinetic rate constants were found to vary with temperature according to an Arrhenius relationship having correlation coefficients in the range from 0.995 to 0.998. Figure 5 shows the dependence of the logarithms of k_{10} and k_{20} with reciprocal absolute temperature for the unfilled epoxy system. The activation energies associated with the rate constants k_{10} and k_{20} were found to be 15.4 and 10.9 kcal/g-mole, respectively. The rate constant k_1^* was observed to be significantly smaller in magnitude than the rate constant k_2^* , indicating that the internally autocatalyzed epoxy-amine reaction plays a predominant role during the curing process. Similar values for the activation energy have been reported in the literature and are summarized in Table III.

The kinetic exponents m and n were found to be temperature dependent. The exponent factor m varied from 0.6 to 1.2 within the temperature range studied, irrespective of the type and concentration of filler used. Figure 6 shows the

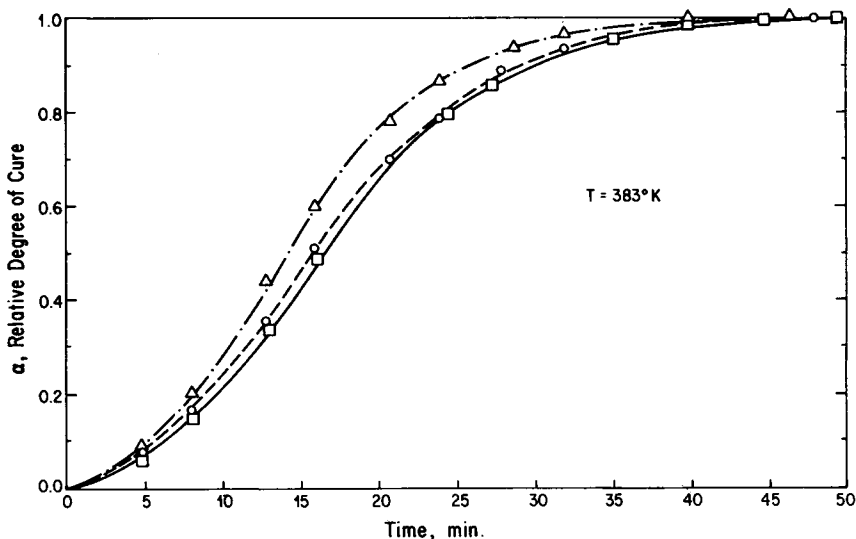


Fig. 4. Integral cure curves for different epoxy systems: (□) unfilled; (○) 6% Novakup filled; (△) 6% carbon black filled.

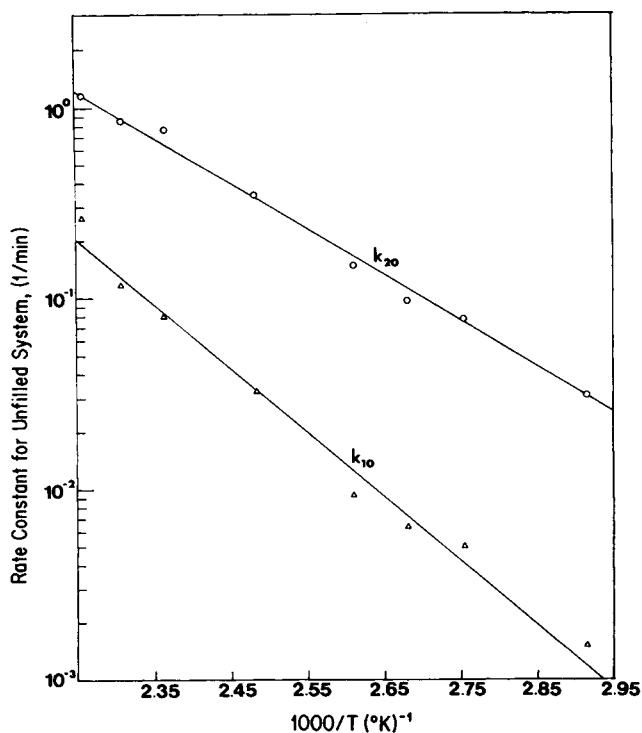


Fig. 5. Logarithm of k_{10} and k_{20} as a function of reciprocal absolute temperature.

TABLE III
Comparison of Kinetic Activation Energies for Epoxy Systems

Investigator	System	Method	Activation energy, kcal/g-mole
Acitelli et al. ²⁹	DER 332-amine	reaction rate	12.3
Kamal et al. ²⁰	DER 332-amine	reaction rate	14.8, 11.5
Kamal et al. ²⁰	DER 332-amine	gel time	13.6
Aukward et al. ¹⁵	glycidyl ether amine	resistivity	14
Gough et al. ⁴¹	glycidyl ether amine	gel time	14-16
Kakurai et al. ¹⁷	glycidyl ether amine	viscosity	12-13
Smith ²⁴	glycidyl ether amine	gel time	14-16
Miller ¹⁶	glycidyl ether amine	resistivity	14
Horie et al. ²⁷	glycidyl ether amine	reaction rate	13.9, 13.4
Kil et al. ³	glycidyl ether amine	reaction rate	14.2, 11.4
Kil et al. ³	glycidyl ether amine	gel time	13.6
Jenkins et al. ⁵	Shell Epon 828 diamine	infrared	11.0
Babayevski et al. ²³	glycidyl ether amine	dynamic mechanical properties	11.8

variation of the kinetic exponent m with temperature. This temperature dependence can be approximated by means of the following relationship:

$$m = 7.032 \exp(-0.0054T) \tag{17}$$

where the temperature T is expressed in K. The experimental results also indicated that the sum of the exponent factors ($m + n$) was essentially constant

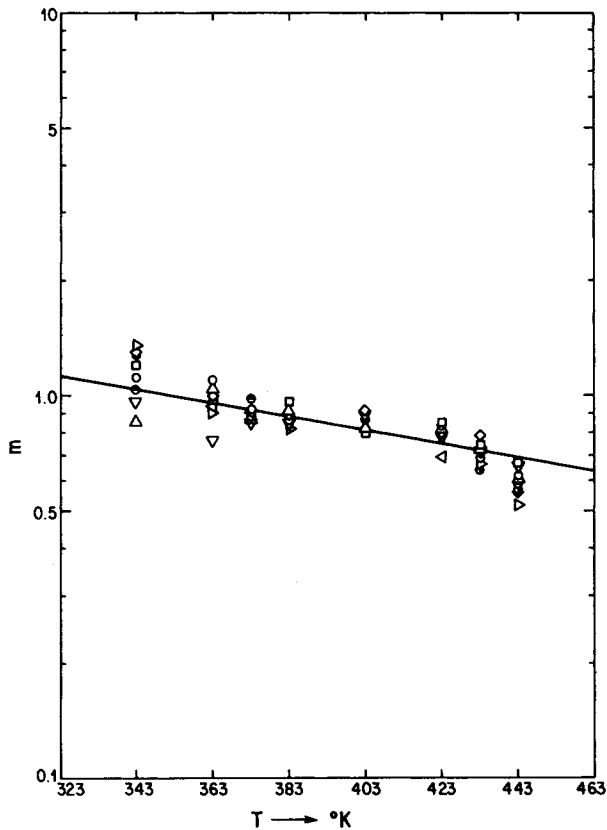


Fig. 6. Temperature dependence of kinetic exponent m : (○) unfilled; (△) 1% (wt. % resin) carbon black filler; (▽) 2% (wt. % resin) carbon black filler; (□) 4% (wt. % resin) carbon black filler; (◇) 6% (wt. % resin) carbon black filler; (●) 1% (wt. % resin) Novakup; (▷) 4% (wt. % resin) Novakup; (◁) 6% (wt. % resin) Novakup; (⊙) 10% (wt. % resin) Novakup.

for all of the systems studied and for all of the temperatures considered. Thus, the experimental results gave the following value:

$$m + n = 1.94 \pm 0.06 \quad (18)$$

For practical purposes, eq. (18) was approximated as

$$m + n = 2 \quad (19)$$

and the value of the exponent factor n was then determined from eq. (19) and the value of the kinetic exponent m .

Kinetic Model

Unlike the simple n th-order kinetic models that have been described in the literature,^{26,28,31} the kinetic expression represented by eq. (1) is capable of describing the peak in the isothermal rate curve as well as the presence of a nonzero initial reaction rate smaller in magnitude than the reaction rate observed at the peak. A typical comparison between the experimental data and the predictive ability of the kinetic model is shown in Figure 7 for the 4% Novakup-filled epoxy

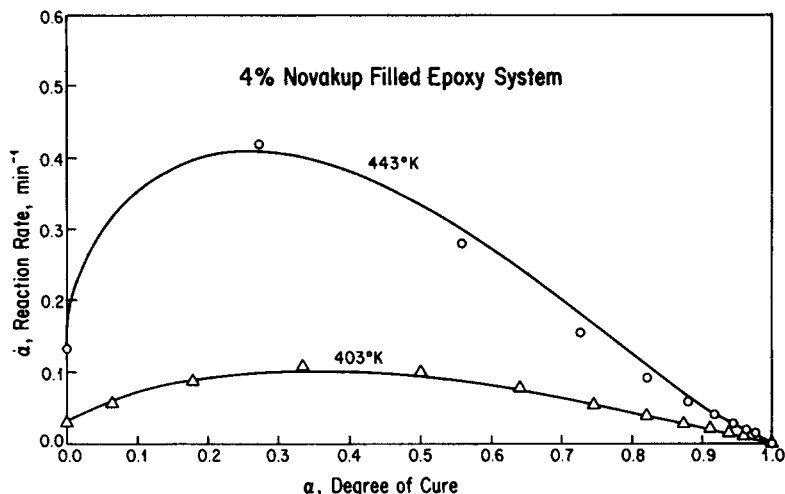


Fig. 7. Comparison of predicted and experimental cure curves: (O, Δ) experimental.

system. Figure 8 shows a comparison between the experimental and predicted results for the integral form of the cure curves given in Figure 7. In all cases the experimental data were found to be in good agreement with the predicted results given by eq. (1).

It should be noted that even though the kinetic expression has been described in terms of a relative degree of cure α , the kinetic expression can equally well be described in terms of an absolute degree of cure α_a , which is defined as follows:

$$\alpha_a = Q/Q_U \tag{20}$$

In eq. (20), the ultimate heat of cure Q_u has been used as the normalizing parameter for determining α_a , whereas Q_T has been used as the normalizing parameter for determining α as is readily apparent from eq. (15). Both definitions for the degree of cure were found to yield accurate and consistent results.

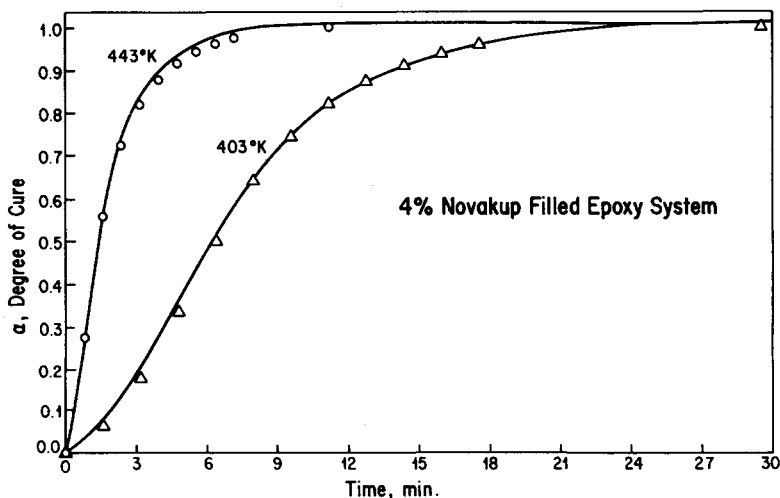


Fig. 8. Comparison of predicted and experimental cure curves: (O, Δ) experimental.

Filler Effects

As mentioned previously, the sum of the kinetic exponents was found to have a constant value of approximately 2, irrespective of the temperature, type, and concentration of filler contained in the system. This second-order behavior of epoxy cure has been discussed in the literature.^{20,24,42} From the results reported here it can be inferred that the filler does not significantly affect the overall reaction order of the system but does influence the reaction rate by altering the rate constants k_1^* and k_2^* .

Figures 9 and 10 show the variation of the rate constants k_1^* and k_2^* with filler concentration for the carbon black-filled systems. At any given temperature the rate constant decreases to a minimum value at approximately 2% filler concentration. Beyond this filler level the rate constant increases and gradually levels off to a constant value. This variation becomes more pronounced with increasing temperature.

Figure 11 depicts similar behavior for the rate constant k_1^* for the Novakup-filled systems. However, the variation of k_2^* with filler concentration exhibits a somewhat different trend, as can be seen in Figure 12. Although there are some fluctuations, the value of k_2^* remains essentially unchanged with filler level at any given temperature.

The activation energy associated with the rate constant k_2^* was observed to be unaffected by the type and amount of filler present in the system, having an average value of 10.9 kcal/g-mole. The activation energy associated with the rate constant k_1^* was found to be essentially the same for both the unfilled and carbon black-filled systems, having an average value of 15.4 kcal/g-mole. However, the activation energy was less for the Novakup-filled systems, having a value of 14.4 kcal/g-mole.

The functions $f_1(c)$ and $f_2(c)$ appearing in eqs. (3) and (4) were described by means of the following third-order polynomials for the carbon black filler:

$$f_1(c) = 1 - 0.22c + 7.82 \times 10^{-2}c^2 - 6.49 \times 10^{-3}c^3 \quad (21)$$

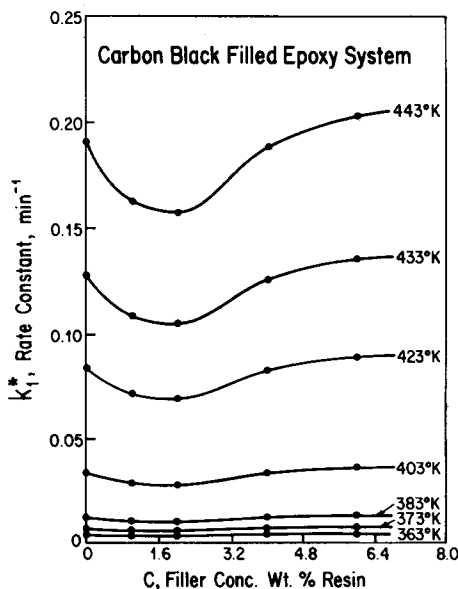


Fig. 9. k_1^* as function of filler concentration.

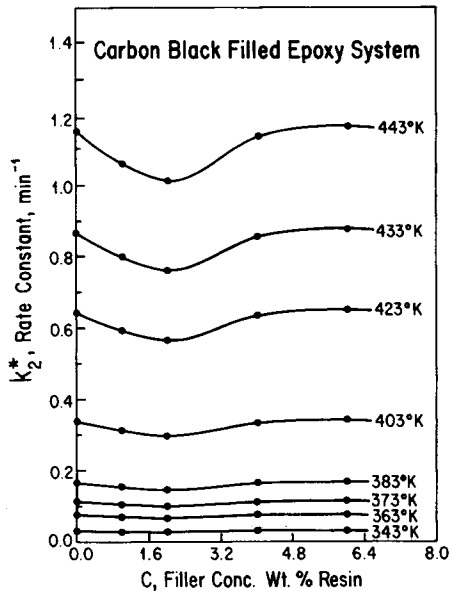


Fig. 10. k_2^* as function of filler concentration.

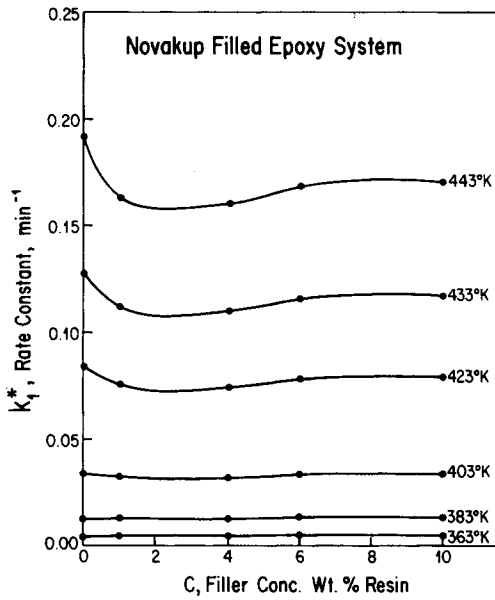


Fig. 11. k_1^* as function of filler concentration.

$$f_2(c) = 1 - 0.14c + 5.10 \times 10^{-2}c^2 - 4.35 \times 10^{-3}c^3 \tag{22}$$

where $0 \leq c \leq 6$. Since the activation energy E_1 associated with the rate constant k_1^* for the Novakup filler differed from the activation energy of the unfilled system, E_{10} , the functions $f_1(c)$ and $f_2(c)$ were expressed as

$$f_1(c) = 0.26 \exp[(E_{10} - E_1)/RT] \tag{23}$$

$$f_2(c) = 1.0 \tag{24}$$

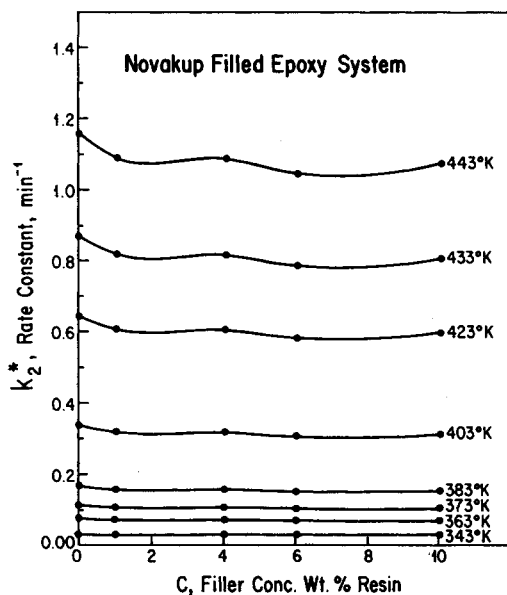


Fig. 12. k_2^* as function of filler concentration.

for $1 \leq c \leq 10$. It therefore appears that the carbon black filler affects kinetic rate constants k_1^* and k_2^* through the Arrhenius frequency factor, whereas the Novakup influences only the kinetic rate constant k_1^* through the activation energy.

It is likely that carbon black influences the curing process due to the presence of chemical complexes on the carbon black surface. The major constituents found on the carbon black surface are phenolics, carboxylics, quinones, hydroquinones, and lactones.⁴³⁻⁴⁵ The enormous catalytic effect of some of these groups on the epoxy cure reaction has been well established in the literature.³⁶ The possibility of surface complexes affecting the cure reaction appears to be a likely one. On the other hand, the Novakup filler appears to have no significant effect on the autocatalyzed reaction. This might be attributed to either the lower specific surface area or to a relatively complex-free surface. Further investigations will be necessary in order to elucidate the detailed mechanisms responsible for these observed experimental effects.

CONCLUSIONS

The kinetic effects caused by the presence of a filler during the cure of an epoxy-amine system have been studied. The experimental cure measurements indicate that the carbon black filler has a more significant effect than the Novakup filler on the reaction rate of the curing process. However, unlike the carbon black, the Novakup filler was found to give rise to an increase in the ultimate heat of cure. The overall reaction order of the system was unaffected by the presence of filler. The curing behavior of these filled epoxy systems could be accurately described by means of a simple kinetic model.

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References

1. P. Banks and R. H. Peters, *J. Polym. Sci. A1*, **8**, 2595 (1970).
2. M. G. Rogers, *J. Appl. Polym. Sci.*, **16**, 1953 (1972).
3. T. A. Kil, A. I. Aksenov, and G. S. Kitukhina, *Sov. Plast.*, **3**, 16 (1972).
4. P. E. Willard, *Polym. Eng. Sci.*, **12**, 120 (1972).
5. R. Jenkins and L. Karre, *J. Appl. Polym. Sci.*, **10**, 303 (1966).
6. T. F. Saunders, M. F. Levy, and J. F. Serino, *J. Polym. Sci. A1*, **5**, 1609 (1967).
7. H. Batzer and S. A. Zahir, *J. Appl. Polym. Sci.*, **19**, 601 (1975).
8. J. L. Koenig and P. T. K. Shih, *J. Polym. Sci. A2*, **10**, 721 (1972).
9. Y. Tanaka and H. Kakiuchi, *J. Appl. Polym. Sci.*, **7**, 1063 (1963).
10. Y. Tanaka and H. Kakiuchi, *J. Appl. Polym. Sci.*, **7**, 1951 (1963).
11. A. Matsumoto and M. Oiwa, *J. Polym. Sci. A1*, **8**, 751 (1970).
12. S. D. Lipshitz, F. G. Mussatti, and C. W. Macosko, *Soc. Plast. Eng. Tech. Papers*, **21**, 239 (1975).
13. H. Dannenburg, *Soc. Plast. Eng. J.*, **15**, 875 (1959).
14. W. Fisch, W. Hoffman, and R. Schmid, *J. Appl. Polym. Sci.*, **13**, 295 (1969).
15. J. A. Aukward, R. W. Warfield, and M. C. Petrie, *J. Polym. Sci.*, **27**, 199 (1958).
16. B. Miller, *J. Appl. Polym. Sci.*, **10**, 217 (1966).
17. T. Kakurai and T. Noguchi, *Kobunshi Kagaku*, **19**, 547 (1962).
18. A. E. Moehlenpah, A. T. Dibenedetto, and O. Ishai, *Polym. Eng. Sci.*, **10**, 170 (1970).
19. D. Craig, *Soc. Plast. Eng. Tech. Papers*, **18**, 533 (1972).
20. M. R. Kamal, S. Sourour, and M. Ryan, *Soc. Plast. Eng. Tech. Papers*, **19**, 187 (1973).
21. P. E. Willard, *Polym. Eng. Sci.*, **14**, 273 (1974).
22. R. P. Krehling and D. E. Kline, *J. Appl. Polym. Sci.*, **13**, 2411 (1969).
23. P. G. Babayevsky and J. K. Gillham, *J. Appl. Polym. Sci.*, **17**, 2067 (1973).
24. I. T. Smith, *Polymer*, **2**, 95 (1961).
25. R. A. Fava, *Polymer*, **9**, 137 (1968).
26. O. R. Abolafia, *Soc. Plast. Eng. Tech. Papers*, **15**, 610 (1969).
27. K. Horie, H. Hiura, M. Sawada, I. Mita, and H. Kambe, *J. Polym. Sci. A1*, **8**, 1357 (1970).
28. R. B. Prime, *Anal. Calorim.*, **2**, 201 (1970).
29. M. A. Acitelli, R. B. Prime, and E. Sacher, *Polymer*, **12**, 335 (1971).
30. R. B. Prime and E. Sacher, *Polymer*, **13**, 455 (1972).
31. R. B. Prime, *Polym. Eng. Sci.*, **13**, 365 (1973).
32. S. Sourour and M. R. Kamal, *Thermochim. Acta*, **14**, 41 (1976).
33. S. Y. Choi, *Soc. Plast. Eng. J.*, **26**, 51 (1970).
34. P. E. Willard, *Am. Chem. Soc. Polym. Prepr.*, **14**, 1, 497 (1973).
35. L. T. Pappalardo, *Soc. Plast. Eng. Tech. Papers*, **20**, 13 (1974).
36. I. Shechter, J. Wynstra, and R. P. Kurkijy, *Ind. Eng. Chem.*, **48**, 94 (1956).
37. V. Mangulis, *Handbook of Series for Scientists and Engineers*, Academic, New York, 1965.
38. R. C. Weast, Ed., *Handbook of Chemistry and Physics*, 54th ed., Chemical Rubber, Cleveland, Ohio, 1974.
39. A. Dutta, M.Sc. Thesis, State University of New York at Buffalo, Buffalo, New York, 1978.
40. C. H. Klute and W. Viehmann, *J. Appl. Polym. Sci.*, **5**, 86 (1961).
41. L. J. Gough and I. T. Smith, *J. Appl. Polym. Sci.*, **3**, 362 (1960).
42. P. Peyer and W. D. Bascom, *Anal. Calorim.*, **4**, 534 (1974).
43. D. S. Villars, *J. Am. Chem. Soc.*, **70**, 3655 (1948).
44. M. L. Studebaker, in *Proc. 5th Conference on Carbon, Penn. State, 1961*, Vol. II, Pergamon, New York, 1963.
45. B. R. Puri, in *Chemistry and Physics of Carbon*, Vol. 6, P. L. Walker, Ed., Marcel Dekker, New York, 1970.

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