FALSE COMPENSATION EFFECT IN STUDIES OF KINETICS OF CURE BY DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT

The kinetics of cure have been studied by DSC for a series of seven samples of a carbon fiber prepreg (Hercules 3502/AS-4) which had been thermally treated for varying time periods prior to the kinetic study. A single DSC exotherm for each of the samples was analyzed in terms of a three-parameter cure model. A linear relationship was found between kinetic parameters $\ln A/\phi$ and E for the seven samples. Further analysis of the single DSC exotherm for each individual sample of the series showed that a linear relationship between $\ln A/\phi$ and E with the same slope as that for the series of samples could be obtained for each sample by varying the order of the reaction parameter, n, in the cure model. Thus, the linear variation observed for the seven samples is believed to be the result of a "false compensation effect" rather than the result of the thermal treatment. This work suggests that for the study of any chemical or physical modification of a reacting system which utilizes the analysis of single DSC scans for a series of samples, the possibility of false compensation should be considered. A method of testing results for false compensation is discussed.

INTRODUCTION

Dynamic thermal analysis is often used in the study of the kinetics of cure of thermosetting polymers. Prime [1] has reviewed this subject and has divided the means of extracting kinetic parameters from dynamic experiments into three categories, which he calls Methods A, B, and C. This discussion is confined to Method A (analysis of one exotherm) and to the experimental technique (dynamic scanning calorimetry, DSC). The method is based on the early work of Borchardt and Daniels [2].

Prime [1] stated that the analysis of a single exotherm is very attractive because of the abundance of information contained. He also made the observation that for a majority of reactions the method gives high values of the kinetic parameters A and E when compared to those obtained from analysis of multiple isothermal experiments. For example, Barrett [3] found that for the first-order decomposition of azobisisobutyronitrile (AIBM) both A and E increased with temperature scan rate, ϕ, over the range 4 to 32°C min^{-1}. Swarin and Wims [4] also found variations in kinetic parameters with

ϕ for the decomposition of AIBM and benzoyl peroxide (BP). They found good agreement between the parameters obtained by extrapolation to $\phi = 0$ with those obtained from isothermal experiments. Barrett [3], however, reported that parameters obtained at $\phi = 16°C$ min^{-1} agreed best with previously reported literature values. Numerous other examples exist for which there are large discrepancies between kinetic parameters obtained from dynamic DSC and isothermal experiments.

In spite of the criticisms of the analysis of a single exotherm, it continues to have utility as a convenient means of comparing changes in kinetics for reactions of samples which have been modified to varying degrees by chemical or physical treatments. One recent example is the work of Ibrahim and Seferis [5] in which the influence of a catalyst, salicyclic acid (SA), on the kinetics of cure of the resin system, tetraglycidyl-4,4'-diaminodiphenyl methane (TGDDM) and diaminodiphenyl sulfone (DDS), were examined. Four samples, identical in all respects except for variations in SA concentration, were analyzed in the dynamic mode, each at $\phi = 5°C$ min^{-1}. Kinetic parameters E and A varied with SA concentration and achieved maximum values at intermediate SA concentrations. One interesting characteristic of the variation of kinetic parameters is that from sample to sample, E and A both varied in the same direction. A plot of E versus $\ln A$ could be fit by a straight line with excellent accuracy (correlation coefficient $= 0.99995$).

We recently applied this technique in an attempt at determining changes in kinetic parameters for prepreg samples which had been partially cured for various lengths of time at a constant temperature.

EXPERIMENTAL

Seven examples of a commercial carbon fiber prepreg (Hercules 3502/AS-4) containing resin consisting of TGDDM, DDS, and a polyglycidyl ether of bisphenol A novalac were heated at 129°C for time periods ranging from 0 to 405 min. These samples were scanned at $\phi = 20°C$ min^{-1} on a Perkin-Elmer (Model 1B) differential scanning calorimeter. In a separate set of experiments it was determined that the DDS concentration of samples heated at 129°C decreased linearly with time of heating. Samples heated for 130 min or greater were depleted of DDS.

THEORY

All of the experimental data could be well represented by a three-parameter cure model

$$\frac{d\alpha}{dT} = \frac{A}{\phi} \exp(-E/RT)(1 - \alpha)^n \tag{1}$$

where α = fractional conversion based on unreacted materials present in the samples after the isothermal heat treatment at 129°C. There are two convenient transformations which can be used for fitting the model to experimental data. One form is

$$\ln\left[(1 - \alpha)^{-n}\frac{d\alpha}{dT}\right] = \ln\frac{A}{\phi} - \frac{E}{RT} \tag{2}$$

which is a linear equation at a constant value of n. Swarin and Wims [4] used this form of the model and fit DSC data by a trial-and-error procedure. It involves performing linear least-squares analyses of the data in the form of $\ln[(1 - \alpha)^{-n}\,d\alpha/dT]$ versus $1/T$ for various assumed values of n. The n value which yields the best straight line through the data is considered the optimal value. Parameters E and A are determined from the slope and intercept of the best straight line, respectively.

Another transformation of the model is

$$\ln\left[\frac{d\alpha}{dT}\right] = \ln\left[\frac{A}{\phi}\right] - \frac{E}{RT} + n\ln(1 - \alpha) \tag{3}$$

This equation is of the general form

$$y = C_0 + C_1 X_1 + C_2 X_2 \tag{3a}$$

and can be solved with multiple linear regression. Equation (3) is the basic equation used in DuPont's "DSC Borchardt and Daniels Kinetics Analysis Program" [6].

The two methods should yield similar but not identical sets of the parameters E, A and n. Butt [7] has discussed the problems associated with obtaining corresponding values of kinetic parameters from different forms of the same rate equations.

RESULTS AND DISCUSSION

Table 1 lists the optimal values of kinetic parameters which were found by analyzing DSC data by both of the regression analysis methods. Coefficients of correlation for all runs were near unity. As expected, there are some differences between parameters obtained by the two methods, i.e.

$$\left[\,|E_M - E_L|_{max} = 1.5, \left|\ln\frac{A_M}{\phi} - \ln\frac{A_L}{\phi}\right|_{max} = 1.5 \text{ and } |n_M - n_L|_{max} = 0.07\right]$$

where subscript L refers to linear least squares and M refers to multiple regression. However, the aim of this work was to measure changes in kinetic parameters as a function of time of cure; the causes of differences between parameters obtained by the two different regression analyses were not investigated but assumed to have resulted from using two different transformations of the kinetic model.

TABLE 1

Results of linear and multiple regression analyses of DSC data at $\phi = 20°C$ min^{-1} for samples partially cured at 129°C

Sample	Time of heating at 129°C (min)	E_L	E_M	$ln[A_L/\phi]$	$ln[A_M/\phi]$	n_L	n_M	CC_L	CC_M
1	0	24.2	23.7	18.8	18.3	0.40	0.38	0.9997	0.9983
2	30	23.8	23.4	18.2	18.0	0.42	0.38	0.9990	0.9988
3	60	23.8	23.1	18.3	17.8	0.43	0.39	0.9994	0.9986
4	90	25.2	24.3	19.7	19.0	0.60	0.54	0.9980	0.9918
5	140	24.8	23.6	19.4	18.3	0.53	0.47	0.9994	0.9985
6	230	24.4	22.9	18.9	17.4	0.44	0.38	0.9990	0.9981
7	405	23.7	22.6	18.4	17.3	0.38	0.31	0.9989	0.9986

L = linear regression; M = multiple regression; CC = correlation coefficient.

Table 1 shows that there is only a slight variation of parameters with time of cure. There appears to be a slight downward trend in each of the parameters with time of cure for the four samples heated for 90–405 min regardless of method of data analysis used. One might expect changes in kinetics for these samples since it had been determined in separate experiments that the DDS was depleted from samples heated for more than 130 min.

We observed linear relationships between parameters $ln\ A/\phi$ and E for both sets of data listed in Table 1 (see Fig. 1, data points and solid lines). Linear least-squares analyses of these two sets of parameters led to the following two relations

$$ln\frac{A_L}{\phi} = 1.03E_L - 6.07 \tag{4}$$

correlation coefficient = 0.9914

$$ln\frac{A_M}{\phi} = 0.99E_M - 5.19 \tag{5}$$

correlation coefficient = 0.9853

Such linear relationships have often been reported in the kinetics literature, especially in relation to heterogeneous catalysis, and are referred to as a "compensation effect". The effect is sometimes observed when a reaction is carried out over a series of different catalysts, or over a series consisting of the same catalyst modified by different pretreatments, or when a series of reactions are studied with one catalyst. Satterfield [8] has discussed this effect and showed that it may either represent a real phenomenon, or merely a false correlation arising from scatter in the experimental data.

An investigation of "false compensation" was extended to the present dynamic DSC experiments by utilizing the linearized form of the kinetic model (eqn. 2). The trial-and-error procedure described in the previous
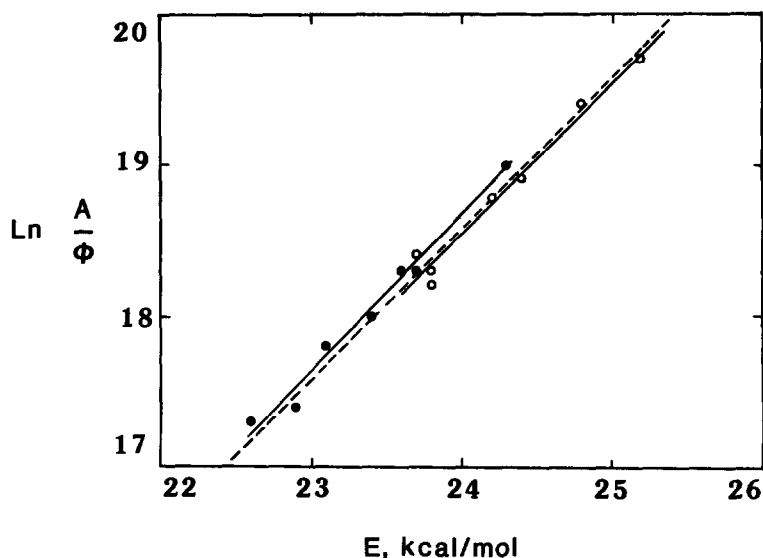
Fig. 1. Relationship between kinetic parameters obtained by analysis of single DSC exotherms. (●) optimal parameter values obtained by multiple linear regression using eqn. (3); (○) optimal parameter values obtained by linear least-squares analysis using eqn. (2); (——) best linear least-squares fit; (- - - - -) parameter values obtained at various assumed values of n, obtained by linear least-squares analysis using eqn. (2).

section yields values of E_s and A_s for various assumed values of n. Table 2 shows the results of such an analysis for one of the samples. (The subscript s indicates that all values were obtained from the same sample.) The optimal value of the n parameter for the sample is 0.4. As n deviates in a positive direction from the optimal value, the values of E_s and A_s both increase. The opposite is also true. Data from ref. 4 also showed such a deviation in E_s and A_s with assumed values of n. A plot of the ln A_s/ϕ versus E_s values from Table 2 could be accurately fit by a straight line (Fig. 1, dashed line) with the equation

$$\ln A_s/\phi = 0.98 E_s - 5.04 \tag{6}$$

correlation coefficient $= 0.99998$

TABLE 2

Kinetic parameters obtained by linear least-squares analysis using eqn. (2) and data for sample No. 1

n (assumed)	E_s	$\ln[A_s/\phi]$	CC_s
0	15.7	10.5	0.9555
0.25	20.9	15.5	0.9963
0.40	24.2	18.8	0.9997
0.50	26.0	20.5	0.9981
0.75	31.2	25.5	0.9891
1.00	36.3	30.7	0.9783

Trends in parameters for the other six samples could also be represented with straight lines that had slopes of approximately 1.0 and intercepts which ranged between 4.5 and 6.

Although it was not discussed in ref. 4, the data from Table 1 of that paper, when plotted as ln A versus E also yielded a straight line with a correlation coefficient of 0.99999. Equation (6) is nearly identical to eqn. (4) and shows that the linear variation in kinetic parameters for the seven samples is most likely the result of "false compensation", perhaps due to a small experimental error, rather than any physical or chemical differences in the sample.

CONCLUSIONS

These results illustrate yet another problem associated with studying kinetics by analysis of a single exotherm. It is well known that a kinetic study of a series of samples which differ in some physical or chemical property can lead to kinetic parameters which vary as a function of that property. We have shown, however, that in the application of regression analysis, using the three-parameter cure model, a variation in one parameter can have a significant influence on the other two. For example, variation in n causes E_s to vary linearly with ln A_s/ϕ. These observations lead to the conclusion that any study of the influence of chemical or physical modification of a reacting system which utilizes the analysis of single DSC scans should be verified in order to rule out the possibility that the variation in kinetic parameters is the result of a false compensation effect. One method of testing the results has been illustrated in this paper. It involves comparing a plot of the optimal values of ln A_L/ϕ versus E_L for the series of samples with a plot of the values of ln A_s/ϕ versus E_s for various assumed values of n for an individual sample of the series. If straight lines through both sets of parameters have approximately the same slope and intercept, it can be concluded that the trend is probably the result of false compensation. If, however, the slope of the line through the optimal parameter values is much steeper than that through the parameter values obtained by varying n, the possibility of false compensation can be ruled out. That the trend is the result of the chemical or physical modification of the samples can only be verified by evidence from other types of experiments.

The previously mentioned work of Ibrahim and Seferis [5] contains, in addition to kinetic parameters from dynamic experiments, results of isothermal experiments which show a trend in degree of cure versus SA concentration similar to the variation of E and ln A with SA concentration. Thus, these authors have presented results of experiments which support their observed variations in reported kinetic parameters.

ACKNOWLEDGMENTS

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