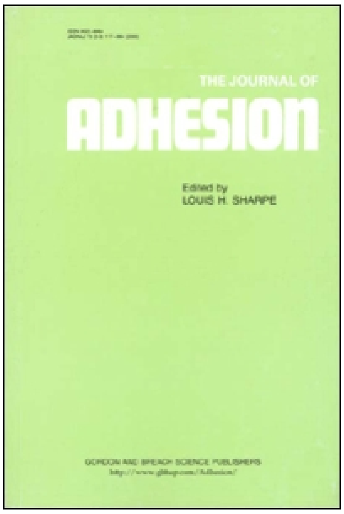

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Comment on "Linking Cure Process to Adhesive Bulk Strength by Differential Thermal Analysis" {*J. Adhesion*, **25**, 185(1988)}

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KEY WORDS Kinetic reaction cure model; pre-reaction; differential thermal analysis; glass transition temperature; adhesive bulk strength; full cure; epoxy adhesive.

INTRODUCTION

Thermal analysis (TA) is practically indispensable to the study and characterisation of modern structural adhesives, particularly those based on epoxies. Because a recent paper in this journal—"Linking Cure Process to Adhesive Bulk Strength by Differential Thermal Analysis" by Jozavi and Sancaktar[1]—advocates TA to those familiar with aspects of adhesion other than analysis and chemistry of adhesives, it is more open to comment than is usual.

In considering the relation between the degree of cure and strength of an epoxy adhesive Jozavi and Sancaktar used TA to develop a kinetic model for the cure of Metlbond 1113, and made allowance for voids present in the tensile specimens. They gave an encompassing kinetic expression for cure which was perhaps too detailed, but were insufficiently critical of an assumed reaction order and extent of pre-reaction reported earlier. Jozavi and Sancaktar concluded that optimum strength resulted "when the cure (of Metlbond 1113) is governed by approximately first order kinetics." While aspects of both mechanical and thermal analysis are open to dispute, it is the possibility that the paper gives a wrong impression of the utility of TA that gives the greatest concern. Comprehension of the chemistry of an adhesive is needed for successful application of TA to quantitative kinetics of curing, but there are many successful applications of descriptive qualitative and semi-quantitative TA techniques.

GENERAL KINETIC EQUATION

Briefly, the reaction was described,[1] during heat-up and isothermal cure, by the standard expressions.

$$\frac{d\alpha}{dt} = kf(\alpha) = Ze^{-E/RT}f(\alpha) \tag{1}$$

and

$$\int_{\alpha_0}^{\alpha} \frac{d\alpha}{f(\alpha)} = \underbrace{\frac{Z}{\phi}\int_{T_0}^{T_c} e^{-E/RT}\,dT}_{\text{Heat up}} + \underbrace{Z\int_0^{t_c} e^{-E/RT_c}\,dt}_{\text{Isothermal}} \tag{2}$$

where α is the fractional extent of reaction,
α_0 is the extent of pre-reaction,
T_0, T_c are the initial and cure temperatures (K),
ϕ is the heating rate,
t_c is the time at the cure temperature, and
k is the reaction rate constant with an assumed Arrhenius temperature dependance so that,
Z is the pre-exponential factor,
E is the activation energy and
R is the gas constant.

If the usual expression[2,3] for the first integral on the RHS of Eq. (2) is now used this becomes:

$$\int_{\alpha_0}^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{Z}{\phi}\left[\frac{E}{R}p(x)\right]_{T_0}^{T_c} + Ze^{-E/RT_c}t_c \tag{3}$$

where

$$x = E/RT$$

and

$$p(x) = e^{-x}(x^{-1}) - \int_x^{\infty} e^{-x}(x^{-1})\,dx$$

While it is simple, with current computational capacity, to use tabulated values of $p(x)$ directly, it is more usual to use standard approximations[3] for the open integral. Eq. (4), used to generate the theoretical curves for the cure of the adhesive[1], was obtained in this way.

$$\int_{\alpha_0}^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{RZ}{\phi E}\left[e^{-E/RT}\left(1 - \frac{2RT}{E}\right)T^2\right]_{T_0}^{T_c} + Ze^{-E/RT_c}t_c \tag{4}$$

Before Eqs. (3) or (4) can be used a kinetic expression and suitable values of E, Z and α_0 are needed. When first order kinetics are applicable

$$\int_{\alpha_0}^{\alpha} \frac{dx}{f(\alpha)} = \ln(1 - \alpha_0)/(1 - \alpha) \tag{5}$$

and E and Z can be determined by the ASTM E698-79 method (multiple heating rates). This is based on the isoconversion method of Ozawa[4] and Flynn and Wall[5] which relates E to the heating rate and the temperature at which the same degree of conversion occurs. When the reaction is first order, the temperature of maximum reaction rate (T_{max}) is an easily obtained isoconversion point, and E and Z can be determined without quantitative measurement of α or $d\alpha/dt$.

Quantitative thermal analysis is required when the reaction is not first order. Modern equipment has software packages which operate variously on single or multiple rate heating rate TA curves to provide best fit values of the kinetic parameters for *n*th order or, in some cases, autocatalytic reactions. In commercial formulations the mixtures of resins, hardeners, and accelerators may not lead to a single chemical reaction, so that the relevance of kinetic parameters derived for an "average" reaction needs to be very carefully evaluated, particularly when results from dynamic heating rates are applied to isothermal cure at significantly lower temperatures.

FIRST ORDER KINETICS

Jozavi and Sancaktar[1] found support for the assumption of first order cure of Metlbond 1113 in an earlier report[6] of its isothermal cure, and in the linearity of the log ϕ *vs* T_{max}^{-1} plot. Schiraldi *et al.*[6] obtained an overall phenomenological first order reaction for cure of this adhesive at 100°C, but they were at pains to eschew the application of results at other temperatures, on the grounds that product structures and reactions were temperature dependent.[7,8] Moreover, even in that report there is a strong suggestion that in the short term the reaction may not be first order (Figure 3e,[6] see also below).

With other adhesives we have obtained apparently linear plots of log ϕ *vs* T_{max}^{-1}, although the isoconversion requirement has not been achieved and the isothermal cure was autocatalytic and involved more than one reaction. The similarity of E for Metlbond (found from this plot) to E for another modified epoxy resin does not confirm reaction order; the reference cited by Jozavi and Sancaktar[1] shows that the kinetic parameters are responsive to changes of formulation. Elsewhere they compare Metlbond to a common laboratory formulation. The diversity of epoxy adhesives cannot be ignored, and comparison of properties in the absence of a knowledge of a composition requires care.

PRE-REACTION

Jozavi and Sancaktar[1] followed Schiraldi *et al.*[6] in considering the extent of pre-reaction or advancement in the adhesive. There are good reasons for doubting both the value and the manner of obtaining it.

The trivial objection concerns the wisdom of assuming the identity of reactive commercial materials seven years and an ocean apart: substantial differences can be attributed to time and distance[9] and in the present case the values of the peak exotherm temperatures (140°C at 2°C/min[6], and 130°C at 5°C/min[1]) for the two materials are inconsistent, faster heating should shift the peak to higher temperatures. The materials appear to be different and this could be due to batch variation or aging, in either case it is unlikely that α_0 will be the same.

A more serious objection is that the methodology[6] for determining the initial extent of reaction is in error. Schiraldi used an iterative numerical method to fit the heat of reaction after various isothermal cure times to an empirical expression. The difference between the extrapolated uncured value and the actual uncured value of heat of reaction was taken to indicate the extent of pre-reaction. In the absence of an independent measurement, it is not possible to determine the initial concentration of the reactant(s) from the shape of the reaction curve. A change in the intensive quantity—molar heat of reaction—will have the same effect on the shape of the curve as the equivalent change in the extensive quantity—concentration of the active principles. For a simple nth order reaction the effect of pre-reaction will be the same as dilution with an inert material. Thus a significant difference between the extrapolated and actual heat of reaction at zero cure time is an indication of the deviation from the chosen empirical equation rather than pre-reaction. In considering cure at the given temperature the distinction is marginal, after a certain lag time the kinetic expression approximates to the one found empirically. Since the lag time will vary with temperature, it cannot be assumed that the apparent pre-reaction will be constant for different cure temperatures.

CONVERSION CURVES

The isochronal conversion curves (Figure 2[1]) given by Jozavi and Sancaktar[1] are calculated using all the terms in Eqs. (4) and (5). The expression can be much simpler; the presumed pre-reaction (α_0) should be ignored; so can the initial state (T_0) terms, since, as expected when there is no significant room temperature

TABLE I
Predicted α for Metlbond 1113 "fully cured at different temperatures"

Cure condition (K, min)	α a	 b	 c
400, 10	0·931	0·918	0·927
389, 20	0·955	0·940	0·945
375, 60	0·989	0·987	0·987

a. From Ref. 1.

b. Using Eqs. (4) and (5), no pre-reaction ($\alpha_0 = 0$) and ignoring the initial (T_0) state.

c. Using a cruder approximation to $p(x)$; such that

$$\alpha = 1 - \exp\left\{-Ze^{-E/RT_c}\left(\frac{RT_c^2}{\phi E} + t_c\right)\right\} \qquad (6)$$

reaction, they make no contribution to the value of Eq. (4) at any practical level of precision. Since the validation of the present model has only been attempted at completion of the reaction, and gave agreement over a very limited range, further simplification, to Eq. (6), would be possible without significantly worsening agreement, as is shown in Table I. However it must be pointed out that many epoxy cure reactions are clearly not first order[6,9] and the determination and validation of a suitable kinetic expression would require a considerable amount of quantitative DSC or other analysis.

GLASS TRANSITION OF UNCURED ADHESIVE

A point of some concern is that identification[1] of the glass transition temperature, T_g, of the adhesive in the uncured state is in doubt. The assignment of an effect at 90°C to T_g of the uncured material is at variance with both expectations for this class of adhesive, and the value (−11°C) reported by Schiraldi[6] (who reports a T_g of around 90° after 87% cure). Jozavi and Sancaktar[1] found that after full cure the T_g was only raised by 22°C. Clearly either the material had advanced to an unacceptable degree, or the experimental conditions were unsuited to unequivocal identification of T_g. The T_g is usually easily accessible by thermal analysis and is a particularly convenient indicator of the state of cure of many of these thermosets, although Schiraldi[7] has claimed marked differences in the T_g *vs* α plots for an epoxy adhesive cured at different temperatures.

TENSILE PROPERTIES

In considering the bulk tensile strength of Metlbond 1113, Jozavi and Sancaktar[1] allowed for the effect on the cross-sectional area of the test piece of voids, which occur when the adhesive is cured without application of the recommended pressure. Inspection of Figure 7[1] shows that the correction increases with cure temperature, and from rough measurement it can be calculated that void area increases from 10 to 20%. This correction substantially diminishes the apparent reduction in strength[10] of Metlbond 1113 cured at less than recommended pressure, and flattens the optimum cure envelope. The correction for voids in the test specimen did not consider stress concentration effects. Given that the sensivity to voids may change as cure proceeds, that the number and/or size of voids varies with cure temperature, and that the bulk properties of the adhesive are affected by annealing (cooling rate),[10] it would be imprudent to assign the residual variation (<10%) in apparent bulk strength to an ill-defined extent of cure.

GENERAL COMMENTS

There is no doubt that many epoxy reactions are autocatalytic and complex, that industrial adhesives are complex mixtures, and that the properties of cured materials can vary markedly with curing temperature. The utility of thermal analysis in studies of adhesives is not at issue, and we have considered these matters in more detail elsewhere.[9] What is relevant is this particular application of thermal analysis, and the impression of complexity that is conveyed.

It is easy to cure an adhesive in a DSC apparatus by ramping to temperature and curing isothermally. This will give indications of the time to cure, and the T_g can be determined from the sample after cure. Shorter isothermal times can be used to determine residual heat of cure after partial reaction. Longer heating periods or higher temperatures (either in the apparatus or in an oven) may give indications, by change of T_g, of completion of cure or degradation. The effects of annealing and quenching (slow and fast cooling) may also be seen in the DSC curves in the T_g region. Most of this work would need to be done to develop and validate an empirical kinetic model which would be of doubtful utility, since the final properties of thermosets are developed in the last stages of cure during a relatively small extent of reaction. The model equations given are relatively insensitive at the completion of the reaction, and accurate independent analysis of the extent of reaction is not easy. In the paper under discussion there was some confusion between "full cure" as defined by absence of any residual exotherm, by achievement of "optimum" tensile strength, and by reaching some percentage of modelled full cure.

As indicated earlier, the kinetic model given by Jozavi and Sancaktar[1] is unnecessarily complex for a first order reaction, and cannot be assumed for other adhesives without validation. The degree of difficulty is greatly increased when the phenomenological order of reaction is not unity. Even when the reaction is first order it is not necessary, or possible, to determine the extent of pre-reaction by thermal analysis in the absence of independent analysis or calibration. While modelling the progressive cure of commercial epoxy adhesives is not be undertaken lightly, thermal analysis can afford penetrating insights into the process.

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