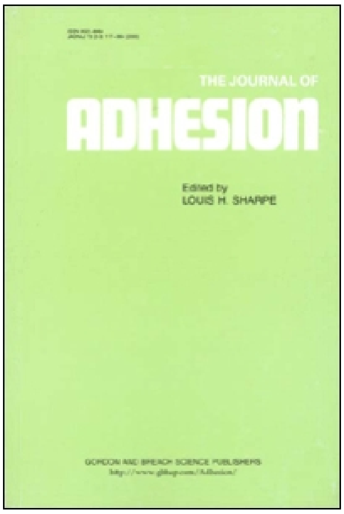

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Linking Cure Process to Adhesive Bulk Strength by Differential Thermal Analysis

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A first order kinetic reaction model is utilized to model the cure process of epoxy adhesive Metlbond 1113. Actual states of full cure corresponding to a spectrum of cure temperature-time schedules are identified using the DTA method. Comparison of these experimental results with the corresponding theoretical predictions reveals that the first order kinetic reaction model provides accurate prediction of full cure when low temperature-long time schedules in close proximity to T_g are used. These cure schedules also result in the highest adhesive bulk tensile strength.

KEY WORDS First order kinetic reaction cure model; differential thermal analysis; adhesive bulk tensile strength; optimization of cure temperature and time; adhesive glass transition temperature; full cure.

INTRODUCTION

Thermal analysis techniques are being widely used for characterization and performance prediction of polymeric materials[1] both in research and quality control. On the study of thermal cure behavior, thermal analysis methods have recently been applied to a large number of structural as well as encapsulant adhesive systems typical of those used in aerospace and electronic industries, to evaluate performance characteristics of those materials. The basic concept used in thermal analysis may be defined as the measurements of a property or a differential change of a physical parameter as a function of temperature. There are a number of thermal analysis methods available to study the polymeric materials.[2] These methods include: i) Static methods associated with weight loss; ii) Dynamic methods associated with weight change, energy and evolved volatiles, e.g. thermogravimetry analysis, differential thermal analysis (DTA), differential scanning calorimetry (DSC) and evolved gas analysis (EGA). In thermogravimetry analysis, the weight change of a substance is recorded *versus* temperature in an environment heated or cooled at a given rate. In DTA, the temperature difference between the substance and a reference material is recorded when both are heated or cooled at the same rate. In DSC, the energy required to establish zero temperature difference between a substance and a reference material is recorded when both are heated or cooled at the same rate.

DSC and DTA plots are usually similar with the difference that in DSC differential heat flux $d\,\Delta Q/dt$ (cal/sec) is measured while in DTA differential temperature (ΔT) is recorded *versus* temperature or time. The two parameters are related through the heat capacity (Cp) and mass (m) of the material. In DSC-DTA methods, a baseline is established first and events taking place during thermal scanning are observed with respect to the baseline. For example oxidation, curing and crosslinking reactions are observed as exothermic peaks (release of energy) while vaporization, charring, decomposition, and melting are observed as endothermic (absorption of energy) ones. Second order reactions such as glass transition (Tg) relaxations are observed as endothermic shifts in the baseline.[2] Accurately monitoring the mass of the sample under study yields similar results from both DTA and DSC measurements.

In this paper the results of thermal analysis using DTA are utilized to model the cure process for the Metlbond 1113 adhesive. Metlbond 1113 is a 100% solids, modified-nitrile epoxy film with a synthetic carrier cloth, and it is commercially available from Narmco Materials Inc. (Costa Mesa, California, U.S.A.) in 0.25 mm-thick, solid film rolls.

The theoretical modelling of the cure process is done on the basis of a first-order kinetic reaction assumption. The actual states of full cure corresponding to a spectrum of cure temperature-time schedules are identified using the DTA method. These experimental results are compared with the theoretical predictions corresponding to the same cure schedules to assess whether the actual cure process is indeed governed by a first-order kinetic reaction.

The cure schedules resulting in reasonable agreement or variation between the theory and experiment (in definition of full cure) are also linked to varying degrees of adhesive bulk tensile strength. Consequently, a link is established between the type of cure reaction and the resulting adhesive bulk strength. Specifically, it is shown that higher adhesive bulk strength is obtained at full cure when the cure reaction is governed by an approximately first-order kinetic reaction.

ANALYTICAL CONSIDERATIONS

Juve[3] introduced the application of general rate law to classical thermal curing of thermosets. Based on general kinetic-controlled reactions for the degree of cure we have:

$$d\alpha/dt = k(1-\alpha)^n \tag{1}$$

where

$$k = Z\exp(-E/RT) \tag{2}$$

α = degree of cure {extent of reaction up to time t(min) at the temperature T (°K)}:

k = specific reaction rate (min^{-1}):

n = reaction order:

Z = pre-exponential factor (frequency factor) (min^{-1}):

E = activation energy for the cure process (J/mole):

R = universal gas constant (=8.32 J/mole °K).

Equation (2) shows that the specific reaction rate (k) obeys the Arrhenius relation for kinetic-controlled reactions. It should be noted, however, that this is not the case for other types of reaction mechanisms, e.g. diffusion-controlled type of mechanisms which may govern the vitrification process. During the vitrification process local viscosity plays an important role.

Schiraldi *et al.*[4] performed quantitative DTA on a number of epoxy adhesives. One of the adhesives they investigated was

Metlbond 1113. They determined that the degree of cure for Metlbond 1113 in the uncured state is $\alpha_0 = 0.14$ and the overall reaction order is $n = 1$.

Using the first order reaction assumption, Eqs (1) and (2) may be combined as:

$$d\alpha/(1-\alpha) = Z\exp(-E/RT)\,dt. \tag{3}$$

Now it should be mentioned that in the actual curing method applied during our investigation (to be described in more detail later) the samples were initially heated up in an environmental oven from room temperature (T_0) up to the isothermal cure temperature T_{cure} at a heating rate of $\phi = 5.6$°C/min (10°F/min). Note also that the cure time t_{cure}(min) is defined as the time interval that the sample is kept at T_{cure}. Therefore, integration of Eq. (3) should be carried out in two steps, *i.e.* one during the heat-up period and the other during isothermal conditions. Therefore, the left-hand-side of Eq. (3) is integrated from the initial to final degree of cure, i.e. α_0 to α_{final} respectively. The right-hand-side of Eq. (3) is integrated from $t = 0$ to t_{final} where t_{final} is the sum of the time during the heat-up period ($t_{\text{heat-up}}$) and the cure time (t_{cure}). Consequently , it follows from Eq. (3) that

$$\begin{aligned}\int_{\alpha_0}^{\alpha_{\text{final}}} d\alpha/(1-\alpha) &= \int_0^{t_{\text{final}}} Z\exp(-E/RT)\,dt\\ &= \int_0^{t_{\text{heat-up}}} Z\exp(-E/R(\phi t + T_0))\,dt\\ &\quad+ \int_{t_{\text{heat-up}}}^{t_{\text{final}}} Z\exp(-E/RT_{\text{cure}})\,dt.\end{aligned} \tag{4}$$

It should be recalled that the temperature T during the heat-up period is increasing linearly with time at a rate ϕ from room temperature (T_0) and that all temperatures are absolute, *i.e.* in degrees Kelvin. Evaluation of the first integral (I) on the right hand side is carried out with a change of variables as follows,

$$I = \int_0^{t_{\text{heat-up}}} Z\exp(-E/R(\phi t + T_0))\,dt \tag{5}$$

Defining $y = E/R(\phi t + T_0)$, it follows $dt = -E\,dy/R\phi y^2$. Integrating by parts results in

$$
\begin{aligned}
I &= \int_{E/RT_0}^{E/RT_{\text{cure}}} - ZE/R\phi y^{-2} e^{-y}\, dy \\
&= ZE/R\phi\{e^{-y}/y^2[1 - 2!/y + 3!/y^2 \cdots]\}\Big|_{E/RT_0}^{E/Rt_{\text{cure}}} \qquad (6)
\end{aligned}
$$

The use of only the first two terms in the above series has been shown to represent a good approximation.[5] After this approximation is made, further simplification of Eq. (6) and substitution into Eq. (4) yields a first-order reaction expression. This expression represents the final degree of cure, α_{final}, for the thermal cure of Metlbond 1113 as

$$\alpha_{\text{final}} = 1 - (1 - \alpha_0) \exp\{-F(T_{\text{cure}}, t_{\text{cure}})\} \qquad (7)$$

where F is described by

$$
\begin{aligned}
F(T_{\text{cure}}, t_{\text{cure}}) = Z \exp(-E/RT_{\text{cure}})\{R/E\phi[&T_{\text{cure}}^2(1 - 2RT_{\text{cure}}/E) \\
&- T_0^2(1 - 2RT_0/E) \exp[-(E/R)(1/T_0 - 1/T_{\text{cure}})]] \\
&+ t_{\text{cure}}\}. \qquad (8)
\end{aligned}
$$

In Eqs (7) and (8) the known parameters are:

$\alpha_0 = 0.14$, initial degree of cure;[4]
$R = 8.32$ J/mole°K, universal gas constant;
$\phi = 5.6$°K/min, heat-up rate used in this work;
$T_0 = 296$°K, room temperature.

The kinetic reaction constants, *i.e.* preexponential factor, Z, and the activation energy, E, for the cure process (crosslinking reaction), however, need to be determined experimentally.

EXPERIMENTAL PROCEDURES

Leckenby[1] applied DSC (Differential Scanning Calorimetry) technique to a series of epoxy resins and determined activation energies of the crosslinking (cure) reaction using the procedure described in ASTM standard method E698-79. He performed DSC at different heating rates and recorded the exotherm peak temperatures. The Arrhenius type of reaction was confirmed due to the fact that the logarithmic heating rates *versus* reciprocal absolute peak temperatures could be fitted to a straight line. The activation energy can then be determined through the slope of this line. The method described in ASTM standard E698-79 is applicable to both DSC and DTA data as long as there is only one exothermic process observed in the thermal analysis.

For the Metlbond 1113 adhesive used in this work, the same ASTM procedure was applied to determine the activation energy, *E*, and the preexponential factor, *Z*. The DTA's on Metlbond 1113 were done using a Perkin-Elmer DTA 1700 system equipped with model 714 thermal analysis controller. Samples from the uncured resin were cut in approximately 5 mm × 10 mm(~25 mg) sizes and wrapped around with aluminium foil, to facilitate removal from the DTA 100 mm^3 sample cup after the analysis. The reference material in DTA used was alumina powder. Purging was done using helium gas at a rate of 40 cc/min starting 15–20 minutes before and continuing during the entire heating process. Three heating rates of 5, 10 and 20°C/min were used for the determination of kinetic constants *E* and *Z*. Figure 1 shows the DTA traces at three heating rates for Metlbond 1113 from the uncured film form. It should be

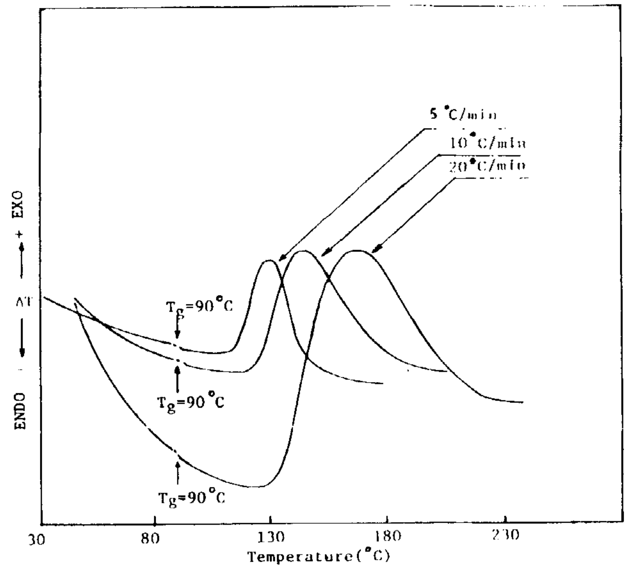

FIGURE 1 DTA traces of Metlbond 1113 adhesive in uncured form with different heating rates.

noted that a different base line was established for each DTA run. Consequently, positive ΔT (upward) corresponds to exothermic process ($T_{\text{sample}} > T_{\text{reference}}$) and negative ΔT (downward) indicates an endothermic process ($T_{\text{sample}} < T_{\text{reference}}$). The DTA thermal curve traces in Figure 1 reveal a glass transition type of relaxation (endothermic shift in the base line) at ~90°C. Exothermic reactions due to the cure (crosslinking) process are also observed along with exotherm peak temperatures. It should be noted that these definitions are consistent with the ASTM standard E698-79. The effect of heating rate on the nonisothermal cure of Metlbond 1113 adhesive is also clear from Figure 1. The exotherm peak temperature as well as the amount of the exothermic heat release increase with increasing heating rates. Similar effects on several other epoxy resins were observed by Olcese *et al.*[6] and Leckenby[1] through the use of DSC method. The glass transition around 90°C for Metlbond 1113 (Figure 1) prior to the exotherm seems to be unaffected by the heating rate. It should be noted that the endothermic shifts in the base lines (Figure 1) were detected after careful examination of the thermal curves since they were not readily observable due to low sensitivity of the high temperature DTA system used. A lower temperature unit may yield much clearer indication of such transitions. The presence of such transitions prior to the main exotherm is believed to be due to a volume relaxation caused by short range ordering of the amorphous molecules.[1]

As mentioned earlier, the information obtained from Figure 1, i.e. the exotherm peak temperatures for different heating rates, was used in order to determine the kinetic constants for Metlbond 1113. The peak temperatures for the 5, 10, 20°C/min heating rates were measured to be 130, 145 and 152°C respectively. It should be mentioned that additional heating rates of 15°C and 25°C were also applied even though they are not shown in Figure 1. When all five heating rate parameters were plotted *versus* inverse peak exothermic temperatures, linear Arrhenius plot could still be obtained. With this information available, the ASTM standard procedure E698-79 was followed and the activation energy (E) and preexponential factor (Z) to be used in Eqs (7) and (8) were found to be 47261 J/mole and $2.6 \times 10^5 \text{ min}^{-1}$ respectively. The (E) value determined compares well with the ~50,000 J/mole value found by Olcese *et al.*[6] for a modified epoxy resin using the DSC method.

During tensile testing of the bulk adhesive the presence of void areas was observed on failure surfaces. Obviously, the presence of void areas reduce the effective cross-sectional area and, therefore, should be accounted for in calculation of stress values.

To obtain a quantitative measure of the percentage area occupied by voids and its variation with cure conditions, photographs were taken from the failure sections of a number of bulk tensile samples using a Stereostar Zoom-T microscope (manufactured by American Optical) and a 35-mm camera attached to it. Void area measurements were manually performed by measuring the diameters of the voids, as they are normally of circular shape. These measurements were done on photographs magnified twenty times. The ratios of the void area (A_v) to the nominal area (A_T) were recorded as a measure of the percentage void area with respect to different cure conditions. Based on the assumptions that the failure sections of the bulk tensile samples contained the largest void area and neglecting the stress concentration effects, it was attempted to incorporate the void area into the engineering stress calculations by using the active load bearing area instead of the nominal section area (A_T). If the void ratio is denoted as A_v/A_T the engineering stress may be *modified by using the active area* $(1-A_v/A_T)$ *ratio.*

Therefore, the corrected stress ($\sigma_{\text{corr.}}$) is calculated as:

$$\sigma_{\text{corr.}} = \sigma/(1 - A_v/A_T) \tag{9}$$

where σ is the engineering stress based on the initial section area (A_T). Formation of voids during the thermosetting cure process of structural adhesives has been discussed in some detail by Bikerman.[7]

RESULTS AND DISCUSSION

In order to obtain a graphical demonstration of the theoretical degree of cure (α_{final}) based on Eqs (7) and (8), cure times (t_{cure}) of 5, 10, 20, 60 and 120 minutes were used for isothermal cure temperatures (T_{cure}) ranging from 27°C (300°K) to 177°C (450°K). Figure 2 shows the variation of the theoretical degree of cure (α_{final}) *versus* cure temperature at different cure times. It can be seen from Figure 2 that for the same T_{cure}, higher degrees of cure may be

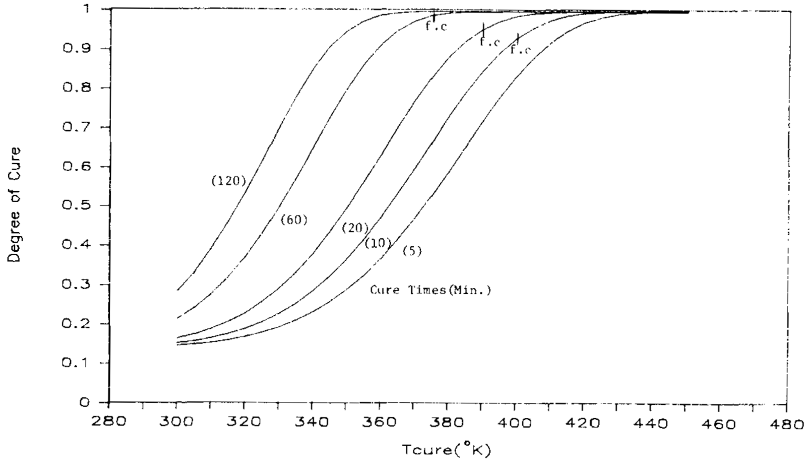

FIGURE 2 Theoretical cure behavior of Metlbond 1113 adhesive based on first-order kinetic reaction assumption.

obtained with increasing cure times (t_{cure}). The increase in the degree of cure with cure temperature up to the full cure condition, i.e. $\alpha_{\text{final}} \sim 1$, seems to be similar to that of half of a bell-shaped curve. Figure 2 also shows that, based on the simple kinetic-controlled reaction assumption, full cures occur at 440, 430, 415, 385 and 370°K for the 5, 10, 20, 60 and 120 minute cure times respectively.

In the DTA traces shown in Figure 1, the exothermic heat release is actually representative of the amount of energy required to cure the samples completely. A second DTA run on the samples (corresponding to Figure 1) indicated no exothermic reaction, thus revealing the fact that the samples were completely cured. Obviously, it is possible to check the state of cure of a partially-cured sample using the DTA method. In doing so, one would compare the residual heat release for a partially-cured sample with that of an uncured sample and use this ratio as the degree of cure of the former. This method was used earlier by Loos *et al.*[8,9] to determine quantitatively the variation of degree of cure for a structural epoxy adhesive.

For the Metlbond 1113 adhesive a semi-quantitative approach was made using DTA on samples cured with different cure histories.

Samples were cured in an ATS environmental oven (series 2911) equipped with a Dual Setpoint Temperature Controller (series 2931). For curing, the samples were heated from room temperature ($T_0 = 23°C$) at 5.6°C/min up to isothermal cure temperature T_{cure} and held in the oven for different cure times (t_{cure}). The cure times used were 10, 20 and 60 minutes and cure temperatures of 93, 110, 127 and 143°C were applied. At the end of each cure time interval samples were removed from the oven and allowed to cool down in the ambient air (room temperature environment, i.e. 23°C). DTA's were performed on each sample at a heating rate of 10°C/min.

Figures 3 through 5 show the DTA traces of the Metlbond 1113 cured samples with different cure histories. Figure 3 shows the effect of cure temperature for 10 minute cure time schedules. The residual heat release for samples cured at 93 and 110°C indicate that these were not completely cured. The lack of any exothermic peak for samples cured at 127 and 143°C, in the same figure, indicate the state of full cure for these cure conditions. Therefore, one may conclude that, for 10-minute cure time, the minimum cure temperature would be approximately 127°C (nominal oven temperature). The glass transition temperatures, corresponding to thermal curves (1) and (2) in Figure 3, were about 92°C which is approximately the same as for the uncured material (Figure 1). However, for the fully-cured samples represented by thermal curves (3) and (4) in Figure 3, no such transition temperature could be detected. The authors attribute lack of evidence for T_g in these thermal curves to the smaller size of samples used as well as the low sensitivity of the high temperature DTA system utilized.

Figure 4 shows the DTA traces corresponding to 20 minute cure. Comparisons of thermal curves (1) and (2) clearly indicate the decreased size of the exothermic peak for the 110°C as compared with that for the 93°C cure temperature and, therefore, the higher degree of cure for the former. The transition temperatures were detected around 92°C as shown in Figure 4. Thermal curves (3) and (4), in Figure 4, indicate a state of full cure and, furthermore, an increase in glass transition temperature up to about 112°C. It should be noted that these T_g values agree well with the values reported by Kinloch[13] and Pearson *et al.*,[14] who determined T_g's in the range of 90°C to 106°C during their studies on a series of rubber-modified epoxies using DTA and DSC methods.

Figure 5 shows the DTA traces for the 60 minute cure time. It

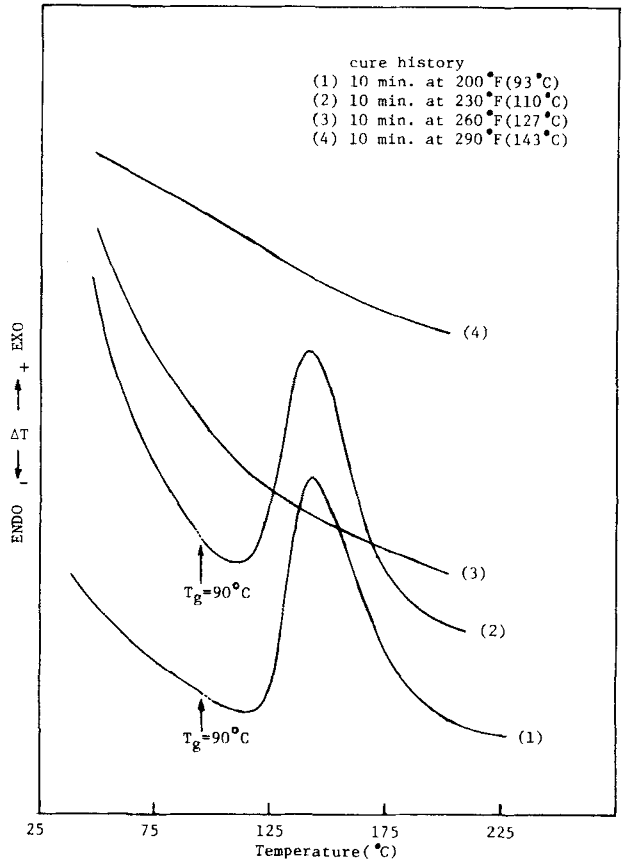

FIGURE 3 DTA traces of cured Metlbond 1113 adhesive (fast-cooled) with different cure conditions (DTA heating rate 10°C/min).

can be seen that full cure is achieved at cure temperatures of 110, 127 and 143°C.

Comparisons of DTA traces in Figures 3, 4, and 5 approximately indicate that the onsets of full cure states occur at lower cure temperatures as the cure time is increased. The onset of full cure (f.c.) states, i.e. absence of an exothermic peak in the DTA thermal curve, may be approximately determined based on these figures to occur at cure temperatures of 127°C (400°K), 116°C (389°K) and 102°C (375°K) for the 10, 20 and 60 minute cure times respectively. These cure temperatures are indicated by "f.c." on the theoretical

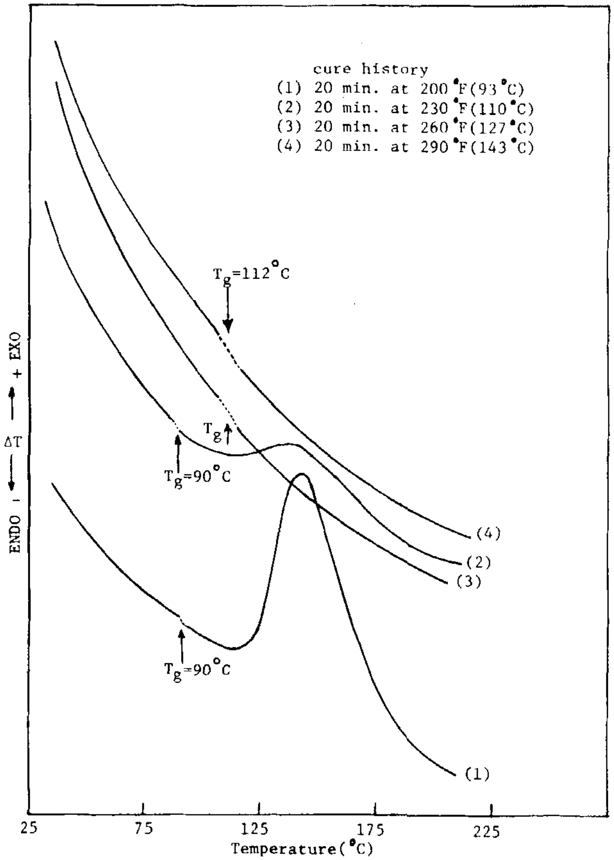

FIGURE 4 DTA traces of cured Metlbond 1113 adhesive (fast-cooled) with different cure conditions (DTA heating rate 10°C/min).

cure behavior curves of Metlbond 1113 (Figure 2). The extrapolation procedure defining the onset of f.c. states in Figures 3, 4, and 5 was done as follows; For 10 minutes cure time, full cure was assumed to occur very close to the 127°C cure condition due to the large size of the exotherm for the 110°C cure temperature. For 20 minutes cure time, f.c. was assumed to occur at the 116°C cure temperature which is at one-third of the scale between 110°C with small exotherm and 127°C which had no exotherm. For 60 minute cure time, f.c. was assumed to occur at 102°C cure temperature

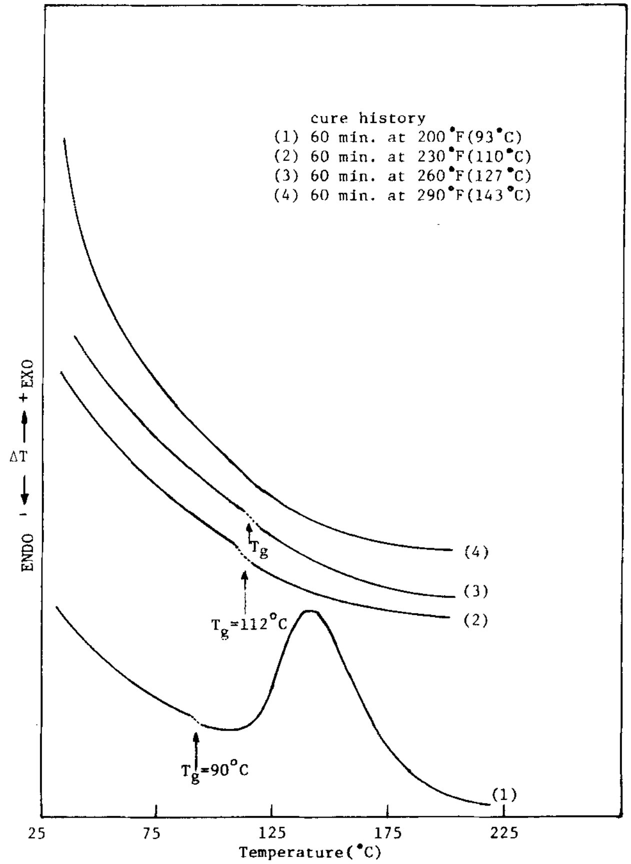

FIGURE 5 DTA traces of cured Metlbond 1113 adhesive (fast-cooled) with different cure conditions (DTA heating rate 10°C/min).

which is the average of 93°C with a medium-sized exotherm and 110°C which had no exotherm. It should be noted that the locations of f.c.'s could be determined more accurately if smaller increments of cure temperatures were used. The corresponding theoretically {Eqs (7) and (8)} predicted degrees of cure for 127°C (440°K), 116°C (389°K) and 102°C (375°K) cure temperatures are 0.931, 0.955 and 0.989 respectively as shown in Figure 2. Obviously, theory and experiment concur better at longer cure times or lower cure temperatures. This may be attributed to several possibilities:

i) The cure process may initially proceed with a simple kinetic-controlled reaction mechanism but, at high degree of cure, the reaction becomes diffusion-controlled. Higher cure temperatures (near vitrification) cause the material to vitrify faster and result in lower degrees of cure than the theoretically-predicted full-cure states.[10] ii) Another possibility may be due to the presence of higher degrees of disorder of the polymer main chain molecules and more random (nonuniform) crosslinking. These conditions may result in lower degrees of cure physically for schedules theoretically corresponding to the full cure (f.c.'s) at higher cure temperatures. It should be noted that a full-cure state may not be achieved when the cure temperature is reduced indefinitely.[10]

The authors believe that the variations in degree of cure and glass transition temperature observed through experimental DTA analysis result in varying polymeric structure and, consequently, may have a direct influence on the resulting mechanical properties of Metlbond 1113 adhesive subjected to different cure histories. One would expect that for a fixed cure time, such bulk mechanical properties as tensile strength would increase with increasing cure temperature in a fashion similar to that of degree of cure. In fact, our experimental results reported earlier[11,12] on the variation of the bulk tensile strength of Metlbond 1113 as a function of cure temperature and time reveal just that. Figure 6 shows that[11] for a given cure time the bulk tensile strength of the model adhesive increases as a function of cure temperature in a fashion similar to that observed in Figure 2 until a peak (full cure) is reached. The decreasing behavior beyond this peak is not governed by the kinetic reaction model {Eqs (7) and (8)} described in this paper and is attributed by the authors to the degradation mechanism prevailing over the thermosetting mechanisms especially at higher cure temperatures. The nature of this degradation mechanism has been discussed in detail by Gillham *et al.*[10] and, consequently, will not be presented here. The important observation to be made, however, is the upward shift in the peak strength values at low-temperature/long-time cure schedules.

When the strength values shown in Figure 6 are corrected for the presence of void areas on the failure section of the specimens, the resulting cure temperature-time optimization curve (Figure 7) shows a peak with cure temperature range of 93°–110°C. Note also that,

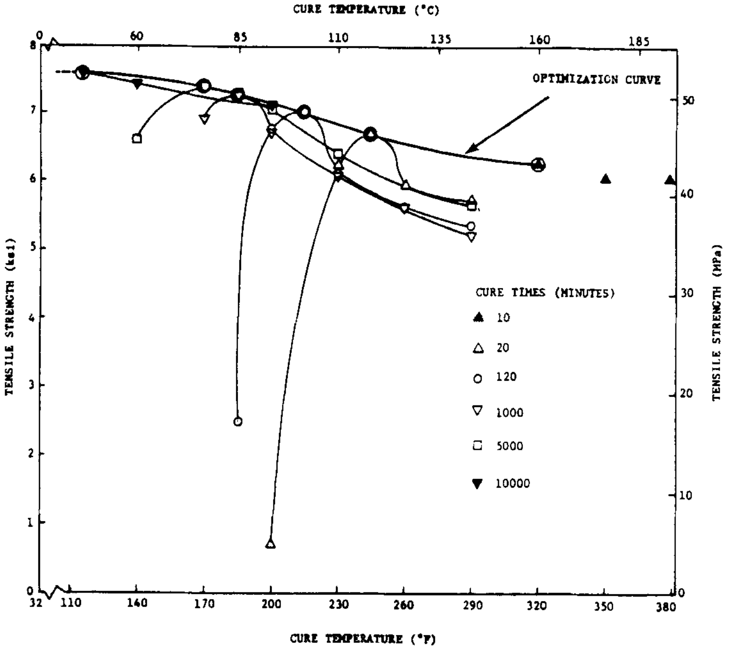

FIGURE 6 Metlbond 1113 strength-cure optimization curve for the fast-cool-down condition.

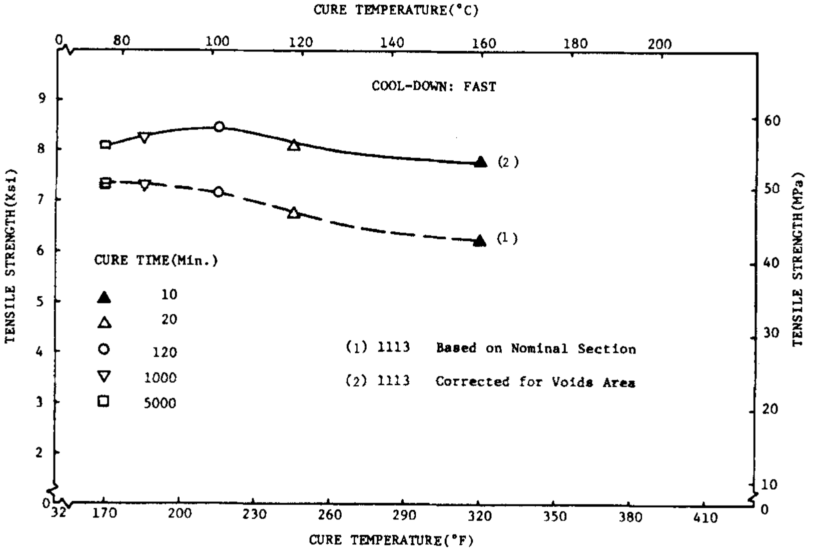

FIGURE 7 Metlbond 1113 optimum strength-cure behavior with and without voids area correction.

based on the DTA results, the maximum glass transition that could be detected for Metlbond 1113 was ~112°C. This temperature range also includes the 102°C-60 minutes cure schedule which had the best agreement between experiment and theoretical prediction as far as the definition of full cure is concerned (i.e. 98.9% full cure, theoretically). It is conceivable that even better agreement (i.e. ~100% full cure, theoretically) may be obtained for another low-temperature/long-time cure condition that was not tested, as long as such condition does not include temperatures far less than 93°C (i.e. it does not fall on the far left decreasing portion of the optimization curve shown in Figure 7). The important conclusion to be drawn from this observation is the ability of our kinetic model {Eqs (7) and (8)} to predict accurately the actual full cure resulting from low-temperature/long-time cure conditions that coincide approximately with the T_g of the model adhesive. This cure schedule also results in the highest mechanical strength for the adhesive. The ability of the theoretical model to predict full cure accurately decreases at high-temperature/short-time cure schedules due to the reasons cited earlier. Such cure schedules also result in lower mechanical strength for the adhesive.

It should be noted that residual (shrinkage) stresses built up in the adhesive material during the cure process may also affect the resulting mechanical properties of the cured product. This is expected to be especially severe at high-temperature/short-time cure schedules.

CONCLUSIONS

A first-order kinetic reaction model was utilized to model the cure process of structural epoxy adhesive Metlbond 1113. Actual states of full cure corresponding to a spectrum of cure temperature-time schedules were identified using the DTA method. Comparison of these experimental results with the corresponding theoretical predictions revealed that the first-order kinetic reaction model provides accurate prediction of full cure when low-temperature/long-time schedules are used. Such schedules fell in close proximity to the T_g for the adhesive and the full-cure state is not expected to be obtained when the cure temperature is reduced much below that value.

The theoretical degree of cure as predicted by the first-order kinetic reaction model was progressively lower for higher-temperature/shorter-time cure conditions which were judged to result in full cure on the basis of the DTA method. Obviously, the first-order kinetic reaction model is not adequate (at least not for the full course of the cure processes) for high-temperature/short-time cure reactions. The adhesive bulk tensile strength resulting from such cure conditions was also found to be lower than that obtained at low-temperature/long-time conditions that fell close to the T_g for the adhesive.

Consequently, it is concluded that higher adhesive bulk tensile strength is obtained at full cure when the cure reaction is governed by an approximately first-order kinetic reaction. Otherwise, the bulk adhesive strength is expected to be lower.

The restrictions of the method presented are: i) The reduction in strength of the model adhesive after the peak value is reached can not be predicted for exposure to temperatures beyond the full-cure state; ii) The lower limit of applicable cure temperatures can not be established.

Acknowledgement

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