Hydrolysis and Blistering of Cyanate Ester Networks

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ABSTRACT: The hydrolysis of a cyanate ester network made from the monomer 2,2′-bis(4-cyanatophenyl)isopropylidene (bisphenol A dicyanate homopolymer) was studied. Hydrolysis reactions were performed isothermally at temperatures from 150 to 180°C under conditions of excess water. The kinetics of the reaction were characterized by the decrease in T_g as measured by differential scanning calorimetry. The rate of change of T_g was found to be adequately described as first order in T_g, which is an indirect measure of the concentration of crosslink junctions. The activation energy of the reaction was found to be 115 kJ/mol. In addition, moisture-conditioned, glass-reinforced laminate samples were heated and the time to delamination or blistering was recorded as a function of temperature. The blister time at solder temperatures ($T = 220-260°C$) was modeled using the above kinetic results. Heat transfer to the laminate was considered and the criteria used for blister time was the time at $T = T_g$ of the sample. At lower temperatures ($T < 220°C$), loss of water from the laminate is sufficiently fast to prevent blistering. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64**: 107–113, 1997

INTRODUCTION

Networks made from cyanate esters are known to exhibit advantageous properties such as a high T_g, good fracture toughness, and the ability to be toughened using thermoplastics.[1,2] While these properties have made cyanate esters attractive for structural composites, their principal use continues to be laminate substrates for multilayer printed circuit boards. Because cyanate esters have the properties listed above, coupled with a low dielectric constant, low dissipation factor, and good metal adhesion, they have been a promising substitute for or modifier of epoxies in the microelectronics industry. In the 1970s, however, initial attempts at using cyanate esters as laminates were halted after it was found that boards stored in humid conditions, when heated rapidly to solder temperatures ($T \sim 250°C$), would delaminate or form blisters (Fig. 1).[3] More recent applications of unmodified cyanate ester networks have also encountered the same hydrolysis and blistering phenomenon which requires that boards be dried before being heated to solder temperatures.[1,4]

Although cyanate ester networks absorb less water than do epoxies, the solder float time for moisture-conditioned cyanate ester boards to blister is less than that of epoxy boards.[5] This has suggested that blistering is caused by hydrolysis of the network which produces gaseous products and lowers the T_g and strength of the matrix. Studies of cyanate ester network hydrolysis have shown the presence of phenols, CO_2, and cyanuric acid as reaction products.[4,6,7] By incorporating these ideas, the reaction sequence can be written down as shown in Figure 2.
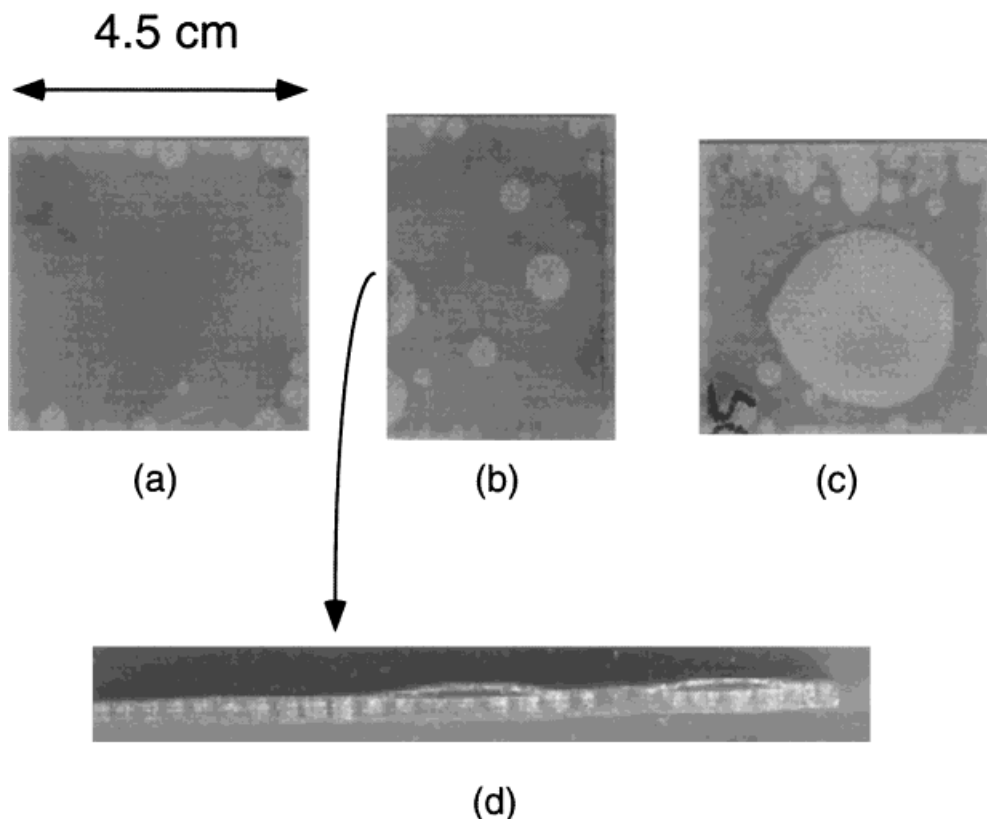
Figure 1 Photographs of blistered laminates: (a) blisters appear first at edges; (b) appearance of blisters in middle used as blister time; (c) blisters can grow as large as 2.5 cm in diameter; (d) view of edge of sample (c); blisters appear on heated side of sample.

In the present study, we investigate the kinetics of the hydrolysis reaction by monitoring the decrease in T_g of the network by differential scanning calorimetry. We also measure the blister times of moisture-conditioned laminates and attempt to model their behavior using the kinetics measured by DSC and assumptions regarding the failure criteria of the board. Two simple procedures for avoiding blisters are suggested.

EXPERIMENTAL

Hydrolysis experiments were performed on a cured sample of 2,2′-bis(4-cyanatophenyl)isopropylidene (DCBA). The monomer was supplied by CIBA-GEIGY and was found to be > 99.0% pure by HPLC. The sample was cured using 100 ppm of Mn^{2+} (Mn^{2+} octoate from Pfaltz & Bauer) at 120°C for 2 h followed by a ramp to 210°C over 2 h and then held at 210°C for 12 h. The initial reaction at 120°C was done under air in a three-neck flask in an oil bath. Further curing at 210°C was done in an oven under vacuum. The cured sample was found to have a T_g of 266°C and a residual heat of reaction (ΔH_{res}) of 43.6 J/g. Using published data of T_g as a function of conversion[8] and published values of the heat of reaction,[9] the conversion of cyanate groups in the final sample is approximately 95%. All subsequent hydrolysis experiments were done using parts of this sample.

Samples were hydrolyzed isothermally at temperatures of 150, 160, 170, and 180°C for four lengths of time each. High-pressure, stainless-steel DSC pans (Perkin-Elmer) were used as reaction bombs ($P < 25$ atm). The pans were charged with 30–35 mg of resin and 10–30 mg of H_2O and then placed in a thermostated oil bath. The bombs were removed from the oil bath, quenched in air, opened, and the sample recovered. Samples were then immediately dried under vacuum at 100°C for 1 h. Samples were stored in sealed DSC pans after drying for less than 1 week before thermal analysis.
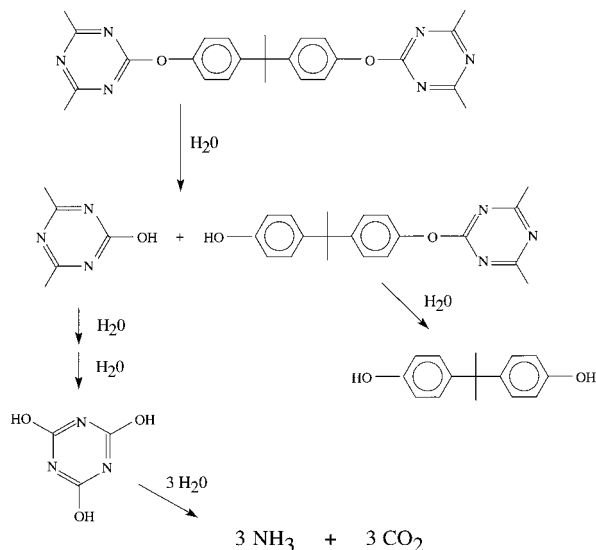
Figure 2 Proposed degradation of the network by hydrolysis of the ester bond followed by hydrolysis of cyanuric acid to ammonia and carbon dioxide.[4,6,7] Additional reactions, e.g., aminolysis of the cyanaurate linkage with ammonia to form melamine structures, have not been precluded.

The T_g of the samples was measured using a Perkin-Elmer System 7 DSC. The sample, 5–10 mg, was sealed in aluminum volatile sample pans and scans were done at 10°C/min from 10°C to either 200 or 350°C. The samples were then quenched and rescanned for reproducibility. The T_g of two samples from each hydrolyzed sample were measured. The T_g of the hydrolyzed samples was taken as the onset of the endothermic shift and the T_g of the unhydrolyzed sample was taken as the onset of the reaction exotherm.

Experiments on the blistering of laminates were done using $\frac{1}{16}$ in.-thick board supplied by Roger Tietze at CIBA-GEIGY (7-ply, biaxial, E-glass, $\sim$ 40 wt % resin, $T_g = 250$°C). The board was cut into 1.75 × 1.75 in. squares and moisture conditioned for 2 h in saturated steam at 15 psi ($T = 120$°C). Following moisture conditioning, the samples were weighed for water absorption and placed on a hot plate to simulate the standard solder bath test used for epoxy resins (IPC-TM-650). Blister times were recorded at temperatures of 220, 230, 250, and 280°C.

RESULTS AND DISCUSSION

Hydrolysis Kinetics

Figure 3 shows DSC scans of an unhydrolyzed sample and a sample hydrolyzed at 180°C for 1 h.

The first scan on the hydrolyzed sample shows T_g = 120°C. At temperatures greater than 290°C, the DSC curve shows an endothermic shift which may indicate further hydrolysis of the network by H_2O unremoved in the brief drying process prior to DSC or may be the known thermal decomposition of cyanuric acid to cyanic acid.[10] A second scan after the sample is quenched shows a decrease in T_g of approximately 10°C. For these reasons, only the T_g of the first scan was used for data analysis and the maximum temperature for most runs was set to 200°C to avoid bursting the pan.

Figure 3 also shows that the ΔH_{res} peak of the unhydrolyzed sample does not appear in the hydrolyzed samples because of the hydrolysis of residual cyanate groups. The hydrolysis of cyanate groups to carbamates is known[11] with the possibility of the carbamate reacting further to produce phenol, CO_2, and ammonia.[8,12] It is not believed, however, that this route causes blistering because laminates with lower conversions of cyanate groups show improved resistance to blistering.[5] This may be because of the smaller equilibrium water content of undercured networks or the consumption of H_2O by residual cyanate groups which does not significantly affect the strength or the T_g of the matrix.

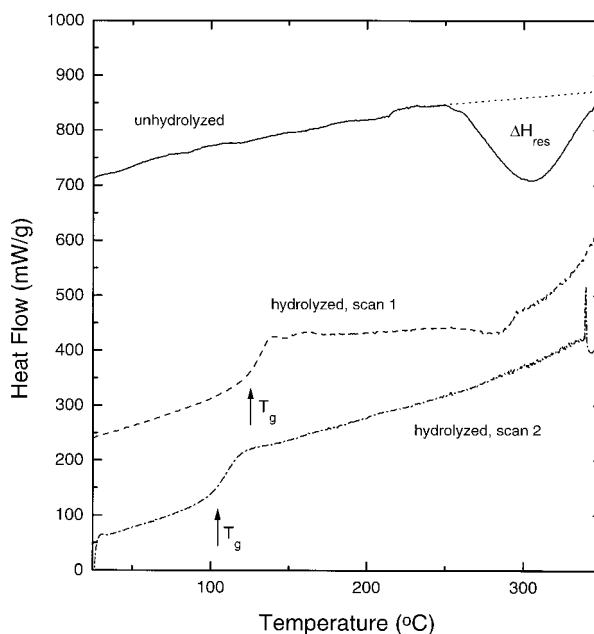Figure 4 shows a series of DSC scans for samples hydrolyzed at 150°C for 12, 18, 24, and 30 h.

Figure 3 DSC scans of hydrolyzed ($T = 180$°C, $t = 1$ h) and unhydrolyzed sample: (– – –) first scan of hydrolyzed sample; (– · – ·) second scan.
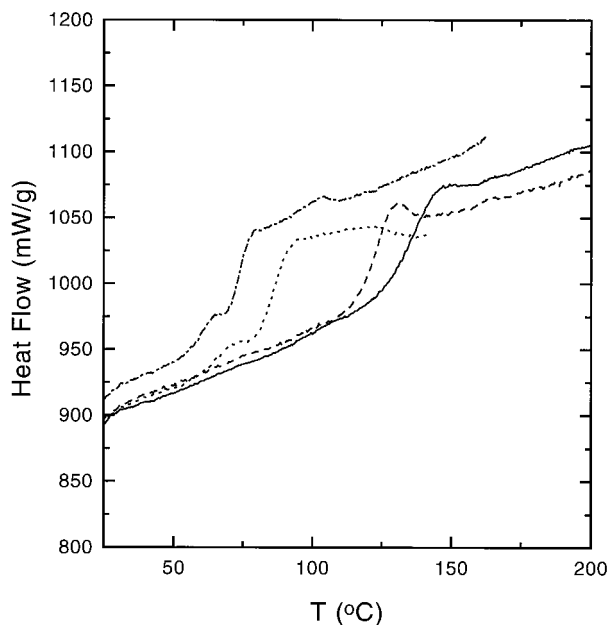
Figure 4 DSC scans of samples hydrolyzed at T = 150°C: (———) 12 h; (— — —) 18 h; (· · ·) 24 h; (— · — ·) 30 h.

The 12 and 18 h samples show typical DSC traces with a small endothermic overshoot. The 24 and 30 h samples, however, show a small bump immediately before the dominant T_g shift which may reflect either nonhomogeneous reaction in the pressure cell reactor or an additional physical aging peak. Annealing the samples prior to measuring the T_g would have removed the aging peaks and given both a more accurate T_g measurement as well as possibly confirming the origin of the pre-T_g peaks. However, we were initially concerned about causing further reaction of the samples in the DSC pans and so did not anneal the samples.

T_g as a function of time for all four temperatures tested is shown in Figure 5. The rate of change of T_g is related to the rate equation for the hydrolysis reaction which is expected to have the form

$$\frac{d[x]}{dt} = -k[H_2O][x] \qquad (1)$$

where $[x]$ is the concentration of imidocarbonic ester bonds. Since T_g is expected to be proportional to $[x]$ or the concentration of crosslinks, and water is in excess, eq. (1) can be rewritten as

$$\frac{dT_g}{dt} = -k_h(T_g - T_{g,f}) \qquad (2)$$

where $T_{g,f}$ is the T_g of the sample after complete hydrolysis and k_h is a pseudo-first-order rate constant equal to $k[H_2O]$.

The data were first fit to eq. (2) by allowing both $T_{g,f}$ and k_h to vary. The average value of $T_{g,f}$ found from the four different hydrolysis temperatures was 70 ± 15°C (± 1σ). Because of the uncertainty in the value of $T_{g,f}$ and since the region of interest for blistering behavior is the initial drop in T_g, the data was fit fixing the value of $T_{g,f}$ at 70°C. The fits shown in Figure 5 with $T_{g,f}$ fixed were used to determine k_h and the temperature dependence of the hydrolysis reaction.

Figure 6 plots $\ln(k_h)$ against $1/RT$ with its fit to an Arrhenius expression. The fit gives an activation energy (E_a) of 115 kJ/mol and preexponential factor (A) of 2.12×10^{13} h^{-1}. Allowing $T_{g,f}$ to vary in the fitting process gives an E_a of 114 kJ/mol. Shimp constructed a plot of time to 50% flexural strength vs. temperature from 100 to 150°C that yields an activation energy of 126 kJ/mol, which agrees favorably with the activation energy determined in this study.[12]

Blister Behavior and Modeling

Figure 1 shows pictures of three samples after being moisture-conditioned and placed on a hot plate. Moisture conditioning caused the laminates
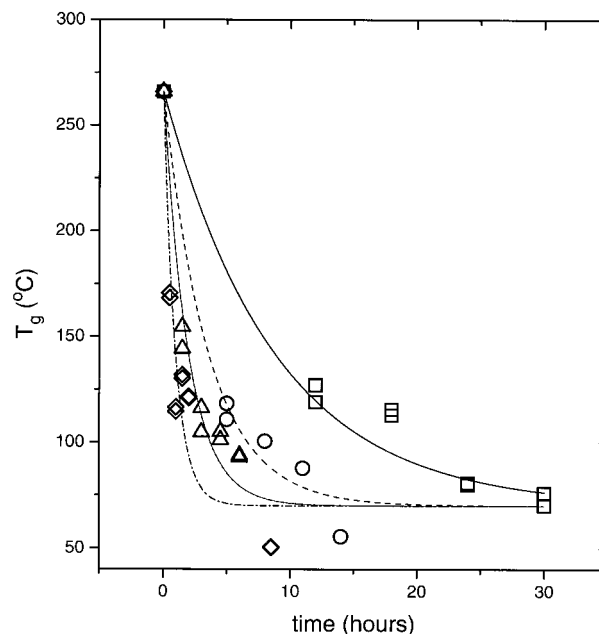

Figure 5 Onset of T_g peak as a function of hydrolysis time: (□) 150°C; (○) 160°C; (△) 170°C; (◇) 180°C. Lines are the fit to eq. (1) with $T_{g,f}$ = 70°C.
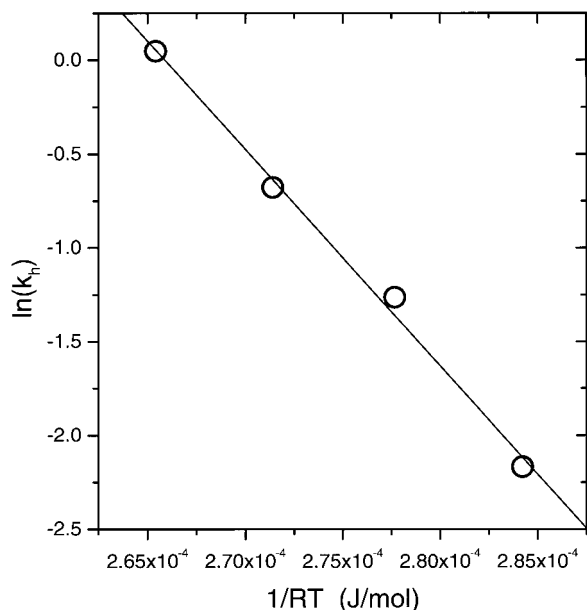
Figure 6 Arrhenius plot of rate constants determined by drop in T_g.

to absorb ~ 0.3 wt % of H_2O. The samples were first observed to discolor slightly, probably from oxidation. The blisters on the edges of the sample appear first and with greater frequency because of the increased size and concentration of flaws caused by cutting the samples. Only flaws $\frac{1}{8}$ in. in from the edge were counted in determining the blister time. Blisters in the center of the sample were observed to appear after approximately 30 s. The first blisters occurred on the heated side of the sample between the first and second glass ply, suggesting the importance of heat transfer in determining the blister time. Because of the translucent nature of the samples, the appearance of blisters on the heated side could be observed from above as small white dots. The growth of the blisters was slow, with blisters growing to diameters of 2–10 mm on the order of seconds. Blister sizes as large as 25 mm were observed.

To predict blister time, we considered two scenarios: The first is that gasses produced by the hydrolysis of the network gather in inherent flaws and build pressure. When sufficient pressure is built up, the crack grows and the first blisters appear. Using these considerations, the blister time as a function of solder temperature should correlate directly with the temperature dependence of the hydrolysis reaction. However, if the reaction scheme proposed in Figure 2 is correct, there is no net production of gas with which to build pressure. For the six molecules of H_2O con-

sumed in the complete hydrolysis of a network junction, three CO_2 and three NH_3 molecules are produced. The lack of gas production and the slow growth of the blisters suggests that blister growth does not occur by the brittle failure of cracks because of a buildup of pressure.

The second scenario that we considered is that hydrolysis of the network lowers the T_g and strength of the sample in some local region. When the T_g of the sample at that point becomes less than the temperature of the resin, pressure from either vaporized water or products of the hydrolysis reaction can expand to form a blister. By assuming the laminate to be a semiinfinite solid, the temperature of the sample as a function of time and distance from the heated surface can readily be written down as

$$\frac{T - T_s}{T_0 - T_s} = \mathrm{erf}\left(\frac{x}{\sqrt{4\alpha t}}\right) \tag{3}$$

where all parameters and the values used are defined in Table I. Substituting the above equation into eq. (2), the T_g of the resin at some time (t) and distance (x) from the heated surface is given as

$$\ln\left(\frac{T_g - T_{g,f}}{T_{g,i} - T_{g,f}}\right) = \int_0^t - A$$

$$\times \exp\left(\frac{-E_A}{R\left(\mathrm{erf}\left(\frac{x}{\sqrt{4\alpha s}}\right)(T_0 - T_s) + T_s\right)}\right) s\, ds \tag{4}$$

where all parameters and the values used are defined in Table I. As shown in Figure 7, the above equation can be solved for the drop in T_g between the first and second ply of the laminate and the blister time is taken as the intersection of the T vs. t and T_g vs. t curves.

Figure 8 shows blister times taken at four temperatures in addition to the prediction of the above model. The small difference of 7 s between the blister times at 250 and 280°C reflects the importance of heat transfer. The limiting process is raising the laminate's temperature from 25°C rather than the rate of decrease in T_g, which has a stronger temperature dependence. At lower temperatures, the process is complicated by the competing mechanism of mass transfer of H_2O out of the laminate. At 220°C, blisters sometimes did

Table I   Blister Time Model Parameters and Values

Parameter	Value	Description	Source
x	0.5 mm	Distance of middle of first and second ply to heated surface	
T_o	25°C	Initial temperature of laminate	
$T_{g,f}$	70°C	T_g of completely hydrolyzed resin	
$T_{g,i}$	250°C	Initial T_g of laminate matrix	
A	2.12×10^{13} h^{-1}	Preexponential	Observed
E_a	115 kJ/mol	Hydrolysis activation energy	Observed
α	2.1×10^{-7} m^2/s	Thermal diffusivity $(= k/(\rho C_p))$	Estimated
C_p	1×10^3 J/kgK	Heat capacity of resin	Estimated
k	0.25 J/(s m K)	Thermal conductivity of resin	Estimated
ρ	1200 kg/m^3	Density of resin	Observed

not form at all or, if they did, only at the edges of the sample. The data point at 220°C in Figure 8 is the time for blisters to form at the edge of the sample. In addition, ramping the temperature to solder temperatures after exposing the laminate to temperatures below 220°C for a few minutes did not cause blisters to form. The inclusion of mass transfer into the model would require considerably more information on the system. Such things as the dependence of the rate of change of T_g on water concentration, the diffusion coef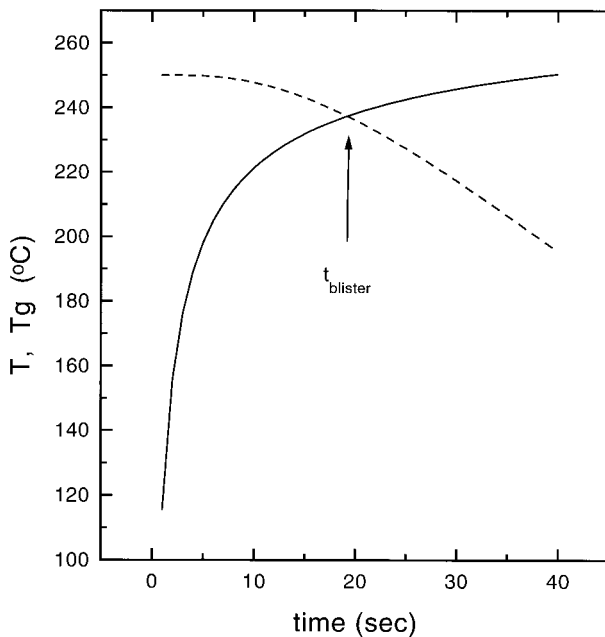ficient of steam in the resin, the initial size of flaws, and the critical pressure needed to expand a blister would all be needed.

The apparent importance of mass transfer at lower temperatures does, however, suggest that blistering can be prevented in resoldering operations by preheating the area of the board affected to temperatures as high as 200°C for 1–2 min before increasing to solder temperatures. The advantage would be in avoiding lengthier drying operations at lower temperatures. The predrying operation can also be eliminated by employing low melting solders which apply at temperatures below 210°C, such as the tin–bismuth eutectic (185°C) reported by Gudul and Carlson.[14]
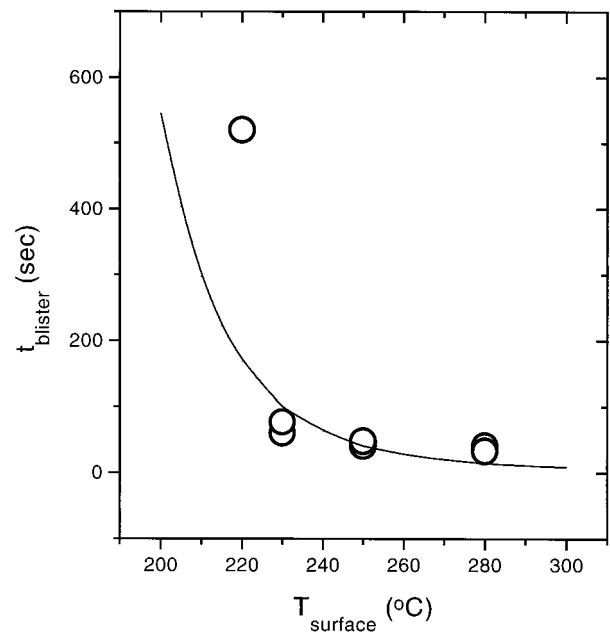

Figure 7   Model predictions of (——) T and (– – –) T_g as a function of time between the first and second ply of the laminate closest to the heated surface (x = 0.5 mm). The blister time is given as the time at T = T_g.

Figure 8   Blister time as a function of temperature of moisture-conditioned laminates: (○) observed values; (——) model prediction.

While blistering can be avoided through drying the boards prior to heating, improvement in the hydrolytic stability of the network is preferred. This may especially be the case when the material is exposed to temperatures above 250°C on multiple occasions rather than a one-time resoldering operation in printed circuit board manufacturing. Incorporation of bulky side groups has been suggested to significantly decrease the rate of hydrolysis by steric hindrance.[6] In particular, methyl groups ortho to the cyanate group of the monomer have been shown to be effective in increasing hydrolytic stability.[15,16]

CONCLUSIONS

The kinetics of the hydrolysis reaction have been characterized through the decrease in T_g as measured by DSC. The rate of change in T_g was described as first order in T_g, which is an indirect measure of the concentration of crosslink junctions. The temperature dependence of the rate constant gave an activation energy of 115 kJ/mol. The kinetics of the hydrolysis of the pure resin was related to the blister time of laminates at solder temperatures ($T \approx 250$°C) when heat transfer to the laminate was also considered. The criteria used for the growth of blisters was the time at $T = T_g$ between the first and second ply closest to the heated surface. At lower temperatures ($T < 220$°C), loss of water from the laminate is sufficiently fast to either delay or prevent blister formation.

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