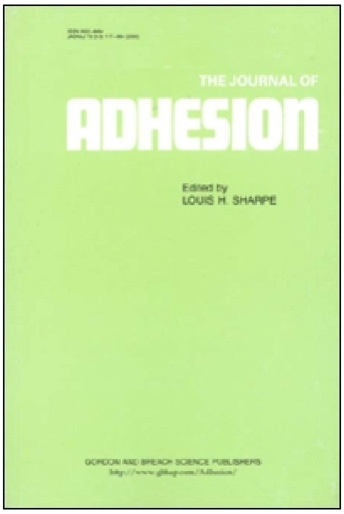

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The Effect of Adherends on the Curing of an Epoxy Adhesive*

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The effect of E-glass, cured vinyl ester resin, and silica gel on the curing of an epoxy-anhydride adhesive was examined. The techniques used were calorimetry in both isothermal and scanning modes and Fourier transform infrared spectroscopy in the attenuated total reflectance (ATR-FTIR) mode. Isothermal calorimetry was used to obtain the exotherm, conversion rate, and curing kinetic parameters, and scanning calorimetry was used to obtain the glass transition temperature. ATR-FTIR was used to study the curing kinetics and chemistry of the adhesive. The results suggest either the immobilization of a layer of the epoxy adhesive adjacent to inert solid surfaces or selective adsorption of the accelerator or both, each of which suppresses the cure reaction. This was reversed by the presence of adsorbed water. At least for this epoxy-anhydride system, adsorbed water seems to have had the beneficial effect of increasing the crosslink density in the interfacial region between the adhesive and adherend. Water seems also to change the overall cure reaction, causing more ether formation and less ester formation than without water. An additional finding was that the cured vinyl ester surface appeared to have a catalytic effect on the reaction, perhaps in conjunction with the accelerator, benzyldimethylamine.

KEY WORDS effect of adherend on adhesive curing; epoxy-nadic methyl anhydride; moisture; heat of reaction; attenuated total reflection-FTIR; epoxy cure reaction kinetics.

INTRODUCTION

When an adhesive joint fails, it often fails at the interface or in the interfacial region between the adhesive and adherend.[1–4] This indicates either a special sensitivity to the interfacial region or that there is often weakness in this region. In either case, this region can have a profound effect on the mechanical, chemical, and thermal durability of the bond.[5–9] The adherend may play an important role in determining the structure of the interfacial region. The adherend is potentially capable of influencing the ingress and egress of heat in thermal cures of the adhesive, of presenting adsorbed chemical species or its own functionality to the adhesive[6,8,10] or adsorbing chemical species from the adhesive[8] and, being usually a rigid surface, of lowering the reactant mobility in its vicinity.[11]

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* One of A Collection of papers honoring Lawrence T. Drzal, the recipient in February 1994 of *The Adhesion Society Award for Excellence in Adhesion Science, Sponsored by 3M.*

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In the present study, the effect of E-glass and cured vinyl ester resin on the curing of an epoxy-anhydride adhesive was examined. E-glass and vinyl ester resin are the constituents of E-glass/vinyl ester fiber composite materials that are of interest to the durable-goods industry, epoxy resins are widely used in adhesives because of their excellent bondability to organic and inorganic adherends and their toughness, and anhydrides are common curing agents. This work was motivated by repair considerations of E-glass/vinyl ester fiber composite structures.

The structure and properties of epoxy adhesives have been found to depend on the extent to which they are fully cured,[12,13] with the bond strength increasing with increasing degree of cure.[14] Hence, the bond strength can be affected by how the adherend affects the curing of the adhesive at the interface,[4,10,15] with the possible occurrence of an under-cured interface, even though the bulk adhesive has achieved a sufficient degree of cure.

Because the interfacial region between the adhesive and adherend usually has a thickness of several hundred nanometers or less, it is difficult to study and requires that model systems be used. Such systems can involve the use of different materials to represent the adherends or an increase in the adherend surface area by dispersing it in the adhesive as a fine powder. These approaches have been applied, for example, to the study of the interfacial regions of carbon and aramid fiber reinforcements[10,11,15-20] and to the effect of mineral surfaces on resin curing.[16,21]

In this study, the effect on the curing of an epoxy-anhydride adhesive of wet and dry powdered E-glass, fully-cured vinyl ester resin, and a high-surface area silica gel, to represent an "inert" solid surface, were examined with several techniques. The techniques were calorimetry in two different modes and Fourier transform infrared spectroscopy (FTIR). Calorimetry in an isothermal mode was used to obtain the exotherm, conversion rate, and curing kinetic parameters and in a scanning mode to obtain the glass transition temperature. For both, a differential scanning calorimeter (DSC) was used. The maximum exotherm was previously used to examine the effect of mineral surfaces on resin curing[16,21] and the curing kinetics also has proved useful.[16,22-26] The glass transition temperature is a further useful measure of a crosslinked polymer because it generally increases with increasing degree of crosslinking, thus providing an index of the degree of cure.[11,12,24,26-31] FTIR in an attenuated total reflectance (ATR) mode was used to study the curing kinetics and chemistry of the particulate-filler epoxy adhesive. FTIR in this mode has been used to study the curing kinetics and chemistry of the adhesive in the interfacial region.[25,32-37]

EXPERIMENTAL

Materials

The epoxy resin used was DER 332 (Dow Chemical Company), which consisted largely of the diglycidyl ether of bisphenol A. Volatile contaminants were removed by degassing at 70°C. The curing agent used was nadic methyl anhydride (NMA), obtained from Aldrich Chemical Company. Benzyldimethylamine (BDMA), also obtained from Aldrich, was used as a catalyst. The curing composition was 100 parts epoxy resin, 93 parts NMA and 1 part BDMA. The samples were prepared by mixing epoxy and anhydride and stirring at 30°C for 10 min. The BDMA was added from a microsyringe and stirring was continued for another 15 min.

The adherends studied, which were ground into powders and added to the adhesive as fillers, were (cured) vinyl ester resin and E-glass. The vinyl ester resin was Derakane 411-C50 (Dow Chemical Company), which was cured with 2 wt% methyl ethyl ketone peroxide (9% active) initiator and 0.5 wt% cobalt naphthanate (Conap, 6% active) as a promoter. The curing conditions were 3 h at 121°C. The E-glass fibers were obtained from Owens-Corning Fiberglass Company without sizing on the fiber surface. Silica gel (Cabosil, Cabot Corporation) having a very high surface area was also used to simulate an adherend surface.

The cured vinyl ester resin and E-glass fibers were ground into fine powders by milling for 20 min at −196°C with a freezer mill. To ensure that they were of uniform fineness after grinding, the powders were passed through a 400 mesh screen with 38 μm openings. Table I shows the surface areas of the adherend powders measured by the BET method using nitrogen gas.

The adherend powders were conditioned to various states of wetness and dryness before being mixed with the epoxy/NMABDMA mixture. "Wet" adherend materials were obtained by exposing powders at 25°C to nearly 100% relative (but not condensing) humidity for 24 hr. "Dry" vinyl ester material was obtained by drying the powder in an air circulating oven at 100°C for 2 hours before mixing with the adhesive. "Dry" E-glass and silica gel materials were obtained by heating the powders in a furnace at 600°C overnight to remove physically-adsorbed water and probably some chemically-adsorbed water as well.

After the adherend powders had been conditioned, they were incorporated into the adhesive at 5–49 wt% loading by mixing with a spatula.

Testing Procedures

The curing process of the adhesive, filled (or not) with the various adherends, was followed by differential scanning calorimetry (DSC) (Perkin-Elmer DSC-7) and by Fourier-Transform Infrared spectroscopy (FTIR) (Nicolet 7199, 400 scans at 4 cm^{-1} resolution) with an ATR fixture.

DSC tests The DSC data were obtained in both isothermal and scanning experiments. In the isothermal experiments, the exotherm, conversion rate, and curing

TABLE I
Surface area of various adherends measured by BET method

Adherend	Surface area (m^2/g)
Curved vinyl ester powder	0.2
E-glass powder	0.8
Silica gel	231.8

* The specimens were conditioned at 120°C for 2 hours before surface area measurement.

kinetics of the adhesive were obtained by measuring the change in the curing heat. In the scanning experiments, the glass transition temperature, T_g, was obtained.

For isothermal testing, the DSC instrument was preset to the curing temperature and stabilized at that temperature, which could take several days. Then, specimens weighing 8–10 mg were transferred to sealed aluminum micropans and placed in the instrument. After the reaction started, it usually took 5 to 6 h until the reaction was complete. The exothermic heat of reaction is given by the difference between the DSC curve and the baseline obtained in the absence of reaction. Hence, an accurate baseline was necessary for quantitative work.[25,26] The baseline for the isothermal data was established by back extrapolating the final data points, as shown in Figure 1, which, after the reaction was completed, were essentially constant with time.[25,26] The reported heat of reaction was the average of at least four experiments. Three curing temperatures were used: 110, 130, and 150°C.

The same specimens that were cured in the isothermal tests were equilibrated at 30°C and then scanned at 10°C/min from 30°C to 300°C. The glass transition temperatures were obtained from the step in the thermogram.

FTIR-ATR tests With the FTIR-ATR technique, the chemistry and kinetics occurring in an interfacial region can be studied by measuring changes in the absorption of particular functionalities. To use this method, the uncured adhesive/adherend mixture was spread onto two opposite surfaces of a 45°-incidence germanium attenuated total reflection (ATR) element (Fig. 2(a)). The adhesive/adherend layers were covered with clean, dry Pyrex microscope slides. Because the refractive index of the element was much higher than that of the adhesive, the IR beam within the element was totally reflected from the surfaces on which the specimen had been placed. A schematic representation of the ATR interface characterization technique is shown in Figure 2(a). The penetration of the ATR beam into the specimen allows it to sample IR absorption in the surface layers of the adjacent polymer matrix, as shown in Figure 2(b). The sampling depth is wavelength-dependent, but at mid-IR

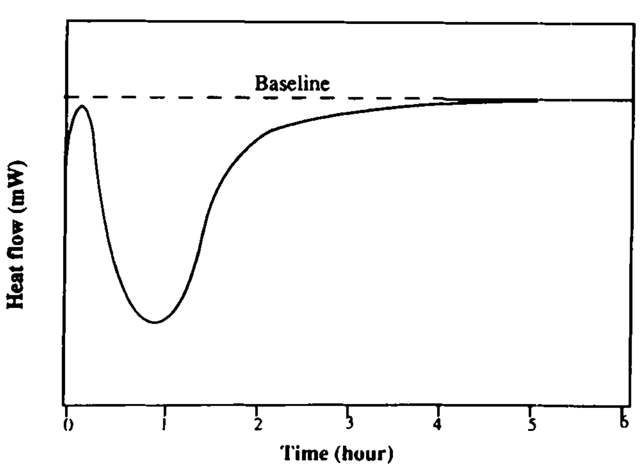

FIGURE 1 Typical plot of heat flow *versus* reaction time in the isothermal DSC test.

frequencies, it can be reduced to less than 1 µm, thus allowing the curing of the adhesive adjacent to the surface of the element to be studied.

Curing was induced by placing the ATR element and holder in an oven. The cure cycle used for this study was 3 h at 100°C and 3 h at 150°C. Spectra were obtained of the starting material and of the same sample after various periods in the cure oven. The most noticeable difference between the uncured and cured samples was the decrease in absorption at 1780 cm^{-1} (anhydride) and the increase in absorption at 1740 cm^{-1} (ester) that occurred as the curing progressed. Although the resulting IR spectrum was obviously the sum of the IR absorptions from the adhesive and adherend filler, the spectrum of the uncured specimen showed little absorption from ester groups in the vinyl ester filler. Therefore, the progress of the curing reaction could be followed through the characteristic absorption of the ester (1740 cm^{-1}) as well as of the anhydride (1780 cm^{-1}) groups.

On completion of the ATR experiment, the polymer was removed by placing the element in boiling phenol.

RESULTS

DSC Tests

Total reaction heat The curing of an epoxy resin is exothermic, and the magnitude of the heat evolved can be used to follow the progress of cure. Figures 3 to 5 show the reaction heats associated with the cure of the epoxy adhesive with and without

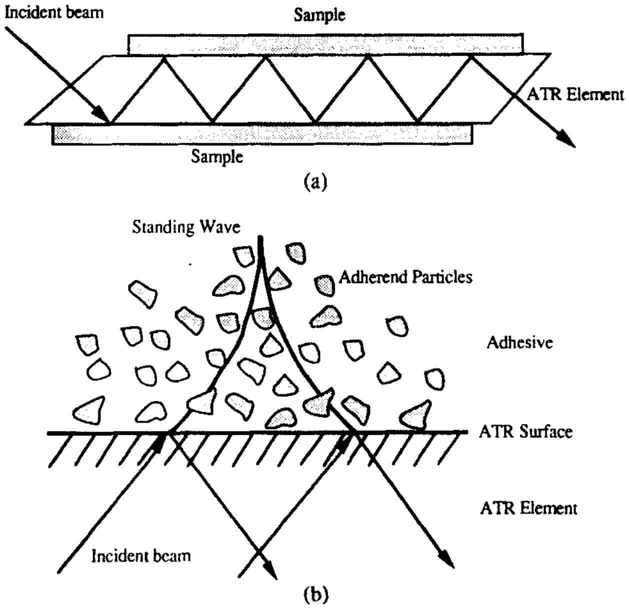

FIGURE 2 (a) ATR element sandwiched between two layers of the adhesive. (b) Standing wave that can penetrate at most 1 µm into the adhesive.

various adherend fillers at 110, 130, and 150°C, respectively. The reaction heats have been normalized with respect to the mass of epoxy adhesive in each specimen. The results from Figures 3–5 can be summarized as follows.

(1) The reaction heat was greater for the wet than for the dry versions of each adherend. This behavior was found at all three curing temperatures, 110, 130, and 150°C.

(2) Except for dry E-glass/adhesive and dry silica gel/adhesive, the reaction heat increased when the adhesive was cured with adherend fillers.

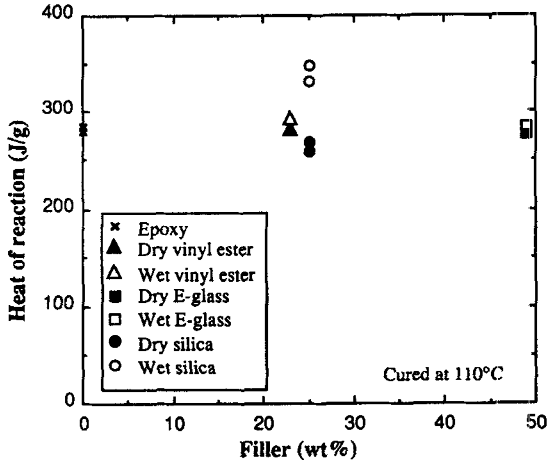

FIGURE 3 Heats of reaction of the epoxy-anhydride filled with various adherends at 110°C.

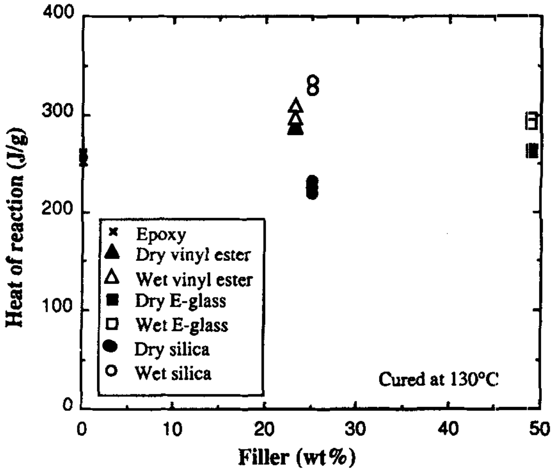

FIGURE 4 Heats of reaction of the epoxy-anhydride filled with various adherends at 130°C.

(3) The reaction heats appeared to decrease as the curing temperature increased, irrespective of filler content. This was probably due to the inability to measure the reaction heat in the initial 3 min of the test, while the specimens were being heated to the test temperature. Because the results from the three curing temperatures showed the same trend, the recorded reaction heats appear to be consistent otherwise.

Conversion and conversion rates Under the assumption that the extent of the curing reaction at any given time is proportional to the cumulative heat evolved, the fractional reaction or conversion is given by

$$\text{Conversion} = \frac{H_r(t, T)}{H_0(T)} \tag{1}$$

where $H_r(t, T)$ is the cumulative heat evolved up to time, t, at temperature, T, for either the adhesive or any of the adhesive-filler systems, normalized for the amount of adhesive, and $H_0(T)$ is the total heat of reaction at the same temperature for the adhesive without filler. Plots of conversion of the epoxy adhesive at 130°C *versus* time are shown for the adhesive and the various adhesive-filler mixtures in Figures 6 to 8. There was little or no effect of the 23% cured vinyl ester or 49% E-glass fillers, whether wet or dry, on the rate of conversion in the early stages of the reaction (Figs. 6 and 7). But the final apparent conversion of the adhesive was affected by the filler. The apparent conversion exceeded 100% with both wet and dry vinyl ester and with wet E-glass fillers and possibly, though only slightly, with dry E-glass filler. (An apparent conversion of greater than 100% simply means that the heat liberated has exceeded the total heat liberated by the adhesive without filler.) For the silica gel-adhesive mixtures, the apparent conversion rate of the adhesive with wet silica gel, and possibly also with dry silica gel, exceeded that of the adhesive without filler in the early stages of the reaction. The final conversion also exceeded 100% with wet

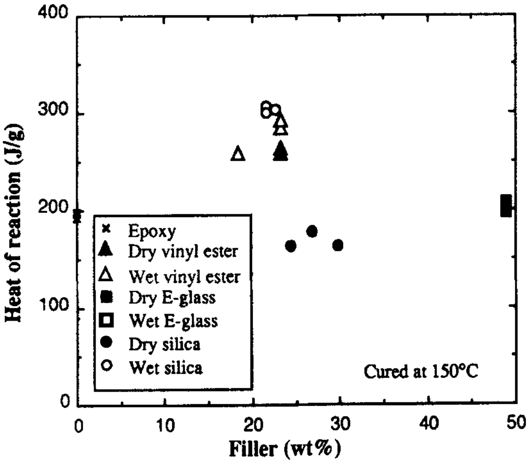

FIGURE 5 Heats of reaction of the epoxy-anhydride filled with various adherends at 150°C.

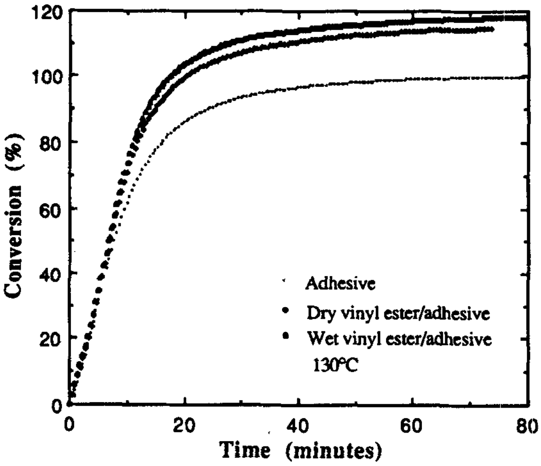

FIGURE 6 Curing conversion of the epoxy-anhydride containing 23 wt% vinyl ester filler at 130°C.

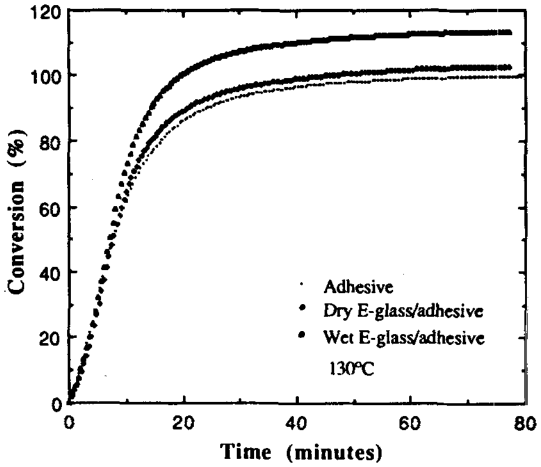

FIGURE 7 Curing conversion of the epoxy-anhydride containing 49 wt% E-glass filler at 130°C.

silica gel, but was less than 100% for dry silica gel (Fig. 8). Similar results were found at the other two curing temperatures.

The kinetic parameters for the adhesive cure reactions can be estimated from the rate of heat evolution in the above isothermal DSC experiments. As with many reactions, the curing reactions shown in Figures 6 to 8 can be described approximately by a simple n-th order equation

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \tag{2}$$

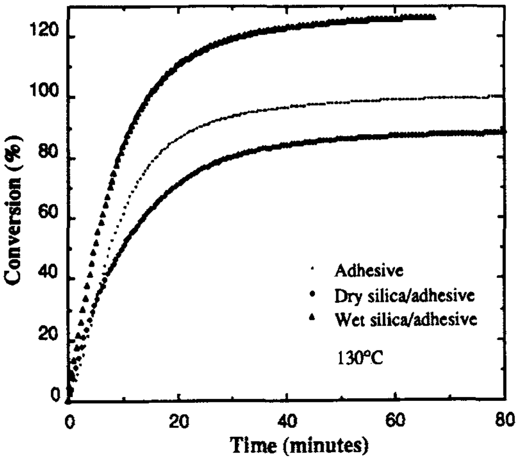

FIGURE 8 Curing conversion of the epoxy-anhydride containing 25 wt% silica gel at 130°C.

where α is the extent of reaction, k is the apparent rate constant, and n is the order of the reaction. Assuming that the extent of reaction is proportional to the evolution of heat,

$$\alpha(t)=\frac{H_r(t,T)}{H_r(\infty,T)} \tag{3}$$

where $H_r(\infty, T)$ is the total heat of the reaction. Equation (2) can be written in linear logarithmic form as

$$\ln r=\ln k+n\ln(1-\alpha) \tag{4}$$

where $r=d\alpha/dt$ is the reaction rate. The apparent rate constant, k, is usually related to the temperature through an Arrhenius-type equation,

$$k=A\exp(-E/RT) \tag{5}$$

where A is the "front factor," E is the Arrhenius activation energy (kJ/mole), R is the gas constant, and T is temperature (in degrees K). Equation (5) can be written in linear logarithmic form as

$$\ln k=\ln A-E/RT \tag{6}$$

Hence, a plot of $\ln k$ against $1/T$ for reactions at different isothermal temperatures should give a straight line of slope E/R and an intercept of $\ln A$ if the above assumptions are correct.

A least-squares fitting to equation (4) of the time-derivatives of the experimental data in Figures 6–8 and similar data obtained at 110° and 150°C gave the reaction orders, n, and the apparent rate constants, k, listed in Table II. Except for wet silica gel, the effect of the filler on the reaction rate constant, k, was modest and became more modest as the temperature increased to 150°C. Wet silica gel also had the

TABLE II
Rate constants, activation energies, and reaction orders for adhesives curved with and without adherends as fillers

Materials	Rate Constant (1/min) × 10^2 Curing temperature 110°C	130°C	150°C	Activation Energy (kcal/mole)	Reaction Order Curing temperature 110°C	130°C	150°C
Epoxy	1.7	6.4	13.5	16.7	2.0	1.8	1.8
w/23% dry vinyl ester	2.0	6.5	13.7	15.2	1.8	1.5	1.6
w/23% wet vinyl ester	2.2	6.6	14.4	14.9	1.7	1.5	1.7
w/50% dry E-glass	1.7	6.4	13.6	16.7	1.9	1.7	1.7
w/50% wet E-glass	1.8	6.7	13.9	16.3	1.7	1.7	1.6
w/5% dry silica	1.6	6.1	13.2	17.5	1.7	1.6	1.7
w/5% wet silica	5.5	9.1	20.9	10.6	1.5	1.4	1.4

largest effect on the reaction order, n, causing n to be 1.4 to 1.5. Without filler, the reaction order, n, was equal to two or slightly less for the epoxy adhesive. The addition of filler caused n to fall below two, with wet filler having a generally larger effect than dry filler. The least effect arose from dry E-glass.

The activation energies were obtained from least-squares plots of the reaction rate constants fitted to equation (6), and these also are given in Table II. The activation energy for the epoxy-anhydride system, 16.7 kcal/mole, is similar to that reported for this same system by Peyser and Bascom,[23] 14.7 kcal/mole, which they obtained from the early part of the reaction only by assuming the reaction order $n = 2$. The variation in the activation energy is similar to that in the reaction order. All filler, except dry E-glass and dry silica gel, caused the activation energy to fall below that of the adhesive without filler, with the wet form of the filler having the generally larger effect. Dry E-glass caused no change to the activation energy, dry silica gel caused a slight increase in the activation energy, from 16.7 to 17.5 kcal/mole. Wet silica gel caused the activation energy to fall by about one-third, from 16.7 to 10.6 kcal/mole.

Glass transition temperature Glass transition temperatures (T_g) were measured on the same adherend/adhesive specimens that were used in the isothermal tests. The results are listed in Table III. The T_g's generally increased with curing temperature. In addition, the T_g's were affected by the adherend fillers. The dry fillers tended to decrease the T_g's, the dry silica gel substantially, and the wet fillers tended to increase the T_g's.

FTIR-ATR Tests

The curing chemistry of the adhesive was examined with FTIR-ATR. Figure 9 shows example spectra of the vinyl ester resin-filled epoxy/NMA/BDMA mixture on a germanium ATR element after subtracting the ATR element spectrum. Absorption of the ATR element itself limits the quality of the spectroscopic information below 800 cm^{-1}. Curve (a) in Figure 9 shows the FTIR-ATR spectrum of the uncured

TABLE III
Glass transition temperatures *vs* curing temperature for adhe-sives curved with and without adherends as fillers

Materials	T_g(°C) Curing temperature 110°C	130°C	150°C
Epoxy	132.4	141.6	148.6
w/23% dry vinyl ester	131.5	140.3	146.5
w/23% wet vinyl ester	134.3	143.9	149.1
w/50% dry E-glass	132.7	141.0	147.3
w/50% wet E-glass	133.1	143.2	150.3
w/5% dry silica	122.2	132.3	142.1
w/5% wet silica	135.3	147.1	151.2

epoxy containing cured vinyl ester. Curve (b) is the spectrum after curing at 100°C for 3 h. The absorption due to the anhydride (1780 cm^{-1}) is seen to have decreased, and absorption due to ester groups (1740 cm^{-1}) has increased. Curve (c) is the spectrum after curing at 100°C for 3 h and at 150°C for 1 h. Curve (d) is after a further 2 h at 150°C. Absorption due to the anhydride has continued to decrease, and absorption due to ester groups has continued to increase with reaction time.

The spectroscopic information can be made quantitative by calculating anhydride and ester indices. The "Anhydride Index" is given by

$$\text{Anhydride Index} = A_t/A_0 \tag{7}$$

where A_t is the absorption of anhydride group at time t, and A_0 is the anhydride

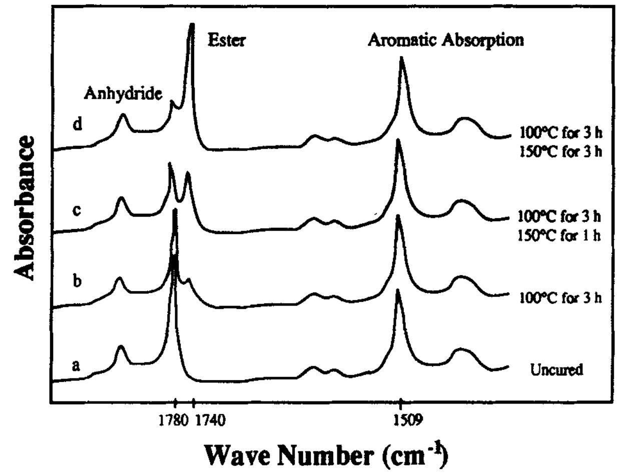

FIGURE 9 Typical spectra of the vinyl ester-filled epoxy/NMA/BDMA mixture after subtraction of the ATR element spectrum.

absorption of the uncured specimen. The "Ester Index" is given by

$$\text{Ester Index} = E_t/A_0 \tag{8}$$

where E_t is the ester absorption at time t. Since small changes in contact area between the specimen and the ATR element from shrinkage during the curing process can result in changes in anhydride and ester absorptions, the latter were normalized to constant phenyl absorption at 1509 cm^{-1}.

The anhydride and ester indices for the vinyl ester resin-filled adhesives are given in Figures 10 and 11, and those for E-glass-filled adhesives are given in Figures 12 and 13. The information from these results can be summarized as follows.

(1) By comparison with the unfilled adhesive, the presence of 23 wt% dry vinyl ester resin tended to increase the consumption rate of anhydride functionality and to reduce the yield of ester groups (Figs. 10 and 11). But there was also a tendency for saturation to occur with the dry vinyl ester filler at 100°C. Though the anhydride consumption rate was higher initially with both wet and dry filler than without, the rate slowed enough later with dry filler so that after 3 h, the anhydride index was the same as that without filler (Fig. 10). Similarly, the rate of increase of the ester index with dry vinyl ester filler, which was initially faster than that with wet filler, though less than that without filler, later slowed at 100°C, so that the ester index after 3 h was about the same as that with wet filler (Fig. 11). But after a subsequent 3 h at 150°C, the anhydride index was about the same for the two vinyl ester-filled adhe-sives, wet and dry, slightly below that without filler, and the same was found for the ester index.

(2) The wet E-glass filler caused the anhydride and ester indices to behave like those for dry vinyl ester filler, but the dry E-glass finer had little effect on the curing of the adhesive (Figs. 12 and 13).

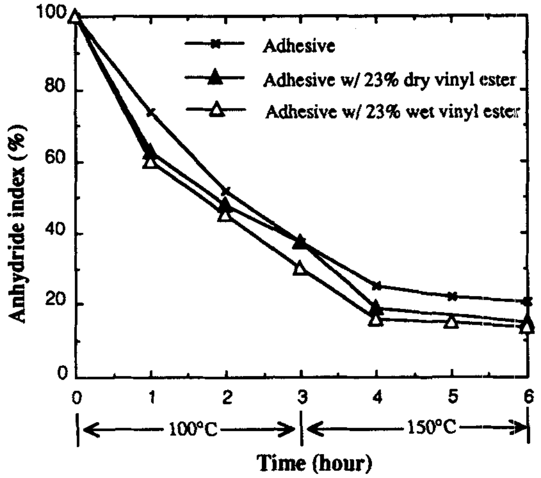

FIGURE 10 Anhydride index obtained from the epoxy-anhydride with and without vinyl ester filler.

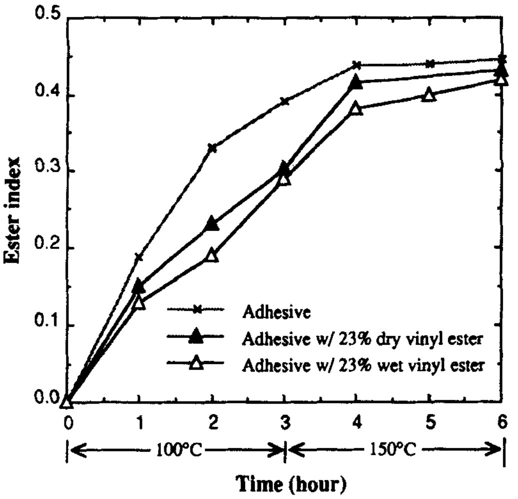

FIGURE 11 Ester index obtained from the epoxy-anhydride with and without vinyl ester filler.

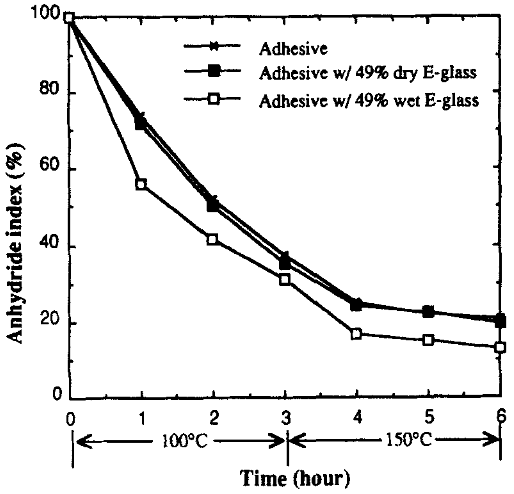

FIGURE 12 Anhydride index obtained from the epoxy-anhydride with and without E-glass filler.

DISCUSSION

For each filler studied, cured vinyl ester resin, E-glass, and silica gel, both dry and wet, changes were found in one or more of the experimental observations of the curing of the adhesive system, epoxy/nadic methyl anhydride/benzyldimethylamine.

The influence of the filler is generally expected to be confined to a region near the filler surface. The fraction of the adhesive affected by the surface can be estimated in the following way. Assuming the bulk densities of 1.2, 1.2, 2.56, and 2.5 g/cm^3 for the

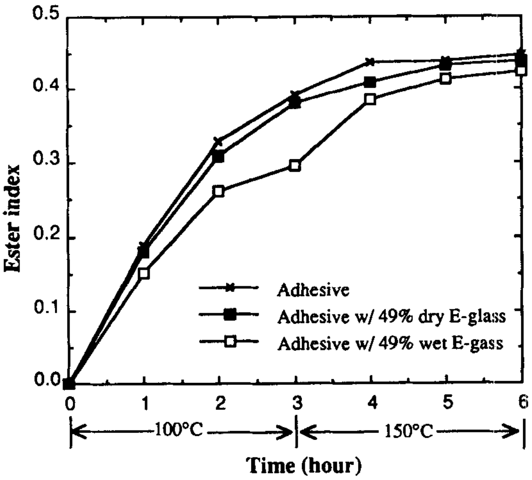

FIGURE 13 Ester index obtained from the epoxy-anhydride with and without E-glass filler.

epoxy resin, the cured vinyl ester resin, the E-glass, and the silica gel, respectively, the volume fractions of filler in the adhesive mixtures studied are calculated to be 23 vol% cured vinyl ester resin, 31 vol% E-glass, and 14 vol% silica gel. Assuming that the influence of the filler extends into the adhesive resin bulk by 10 nm, then the fractions of the adhesive so affected are 7.2×10^{-4} by the cured vinyl ester resin, 9.2×10^{-3} by the E-glass, and 0.93 by the silica gel, in these respective specimens.

Considering the small fractions of the adhesive expected to be affected by the presence of the filler surface, especially for the cured vinyl ester resin and the E-glass, a surprisingly large effect of these fillers on the curing behavior of the adhesive was found. The adhesive filled with dry silica gel probably shows most clearly the effect of an "inert" solid surface. Both the reduced total reaction heat and the reduced T_g indicate a suppression of the curing reactions.

The least apparent effect of the filler on the cure reaction was found with the dry E-glass. But the results with dry silica gel likely apply to E-glass as well, and it is only the small fraction affected ($\approx 1\%$ according to the above estimate) that prevented the appearance of much effect.

Extent of Adhesive Cure and Kinetics

The effects of the fillers on the heat evolution during the isothermal cure of the adhesive indicate surface specificity. The least effect was caused by dry E-glass, yet, on the basis of surface area, its effect was not expected to be least. Rather, dry vinyl ester, if not also wet vinyl ester, would be expected to have had the least effect. The generally higher heat of reaction with the vinyl ester, especially at higher curing temperatures, might suggest an evolution of heat from a further curing of this material, though pains had been taken to reach a state of complete cure before it was ground to a powder. In addition, there is no indication in Figure 6 of a superposition of a further vinyl ester cure on that of the epoxy cure. The somewhat reduced activation energy for the vinyl ester-adhesive mixtures, to 15.2 and 14.9 kca/mole with dry and wet vinyl ester, respectively, from 16.7 kcal/mole without, suggests instead that vinyl ester may have had a catalytic effect on the reaction, or at least part of it. That the vinyl ester resin filler, with such a low surface area, had the relatively large effect that it did further suggests a catalytic effect, and additional evidence for this was found with FTIR-ATR results discussed below.

The large suppression of the reaction heat and reduction in rate constant by the inert dry silica suggests the possible occurrence of an immobilized layer of adhesive at the solid surface. The slightly increased activation energy caused by the dry silica gel filler may indicate the additional temperature-dependence that this layer contributes to the overall reaction. But the immobilization seems to be reversed by the presence of water, perhaps by a plasticization. Wet silica gel considerably enhanced the reaction heat and rate constant over that of the adhesive without filler, and an increased reaction heat and rate constant was noted for each of the fillers when wet compared with when dry. A similar suppression of the cure reaction of this epoxy-anhydride system against variously treated and dried carbon black was found by Garton and Stevenson.[15] They suggested an alternative explanation, *viz.*, the selective adsorption of the accelerator, benzyldimethylamine. According to this mechanism, the effect of adsorbed water would be to prevent the adsorption of benzyldimethylamine. Whether the suppression of the cure reaction by dry silica arose from immobilization or from selective adsorption or from both or neither cannot be decided without further study.

Water may have had the additional effect of changing the overall cure of the reaction. This is certainly consistent with the larger total reaction heat found with each of the wet fillers. But the degree to which water affected the cure reaction is uncertain. Water is more likely to affect the reaction rate than the total reaction heat but, except for the silica gel-filled adhesive, little effect on the rate was seen.

The mechanisms of epoxy-anhydride polymerization in the presence of a tertiary amine catalyst, like benzyldimethylamine, are complex and not fully understood. But water is believed to be involved as a cocatalyst.[38] The reaction between the anhydride and epoxy is governed by the method of ring opening, whether by Lewis base or by active hydrogen. When the ring is opened by benzyldimethylamine acting as a Lewis base, the reaction rate depends on the catalyst and cocatalyst concentrations together. Hence, the concentration of water is expected to have a decisive affect on the reaction kinetics.[38] Such is not seen, however, except with the silica gel. The initial rates for the cure reactions at 130°C seen in Figures 6 and 7 seem to be unchanged from those of the adhesive without fillers, and the reaction rate constants in Table II, again with the exception of that with silica gel, are about the same as, or only modestly different from, that without filler. At somewhat higher moisture levels, the water alone can open the epoxy ring, and the rate of reaction is again expected to depend on the moisture concentration.

Although the reaction heat has been presented as if the cure reaction had been brought to a state of completion in each case, this may not have occurred. The reactions were terminated when the evolution of heat was no greater than the noise level of the detection system, including the uncertainty of the baseline. Also, all of the cure reactions were carried out below, or in the vicinity of, the glass transition temperature. Hence, it is likely that complete cure was not always achieved, and an additional effect of water on the total reaction heat may have arisen from its plasticization effect on the state of cure. That the effect of filler on the reaction rate constant, k (Table II), was minimal at 150°C, except for silica gel, and became significant only as the cure temperature was lowered is further evidence of this.

Glass Transition Temperatures of the Cured Adhesive

The glass transition temperatures (T_g) in Table III are seen to have been affected by the curing temperature as well as by the adherend fillers. The wet fillers tended to increase the glass transition temperatures, and the dry fillers tended to decrease the T_g's, the dry silica gel substantially.

The glass transition temperature has proven to be a useful index of the degree of cure.[26] Generally, the higher T_g, the higher the degree of cure and crosslink density.[29] The increase in T_g's by the wet adherend powders, therefore, suggests an increase in crosslink density in the interfacial region between the adhesive and adherend.

On the other hand, the decreased T_g's of the adhesive filled with dry vinyl ester, dry E-glass, or dry silica gel, especially, indicates a decreased crosslink density in the adhesive adjacent to the solid surface. This suggests a stagnation of the reaction, presumably leaving unreacted epoxy at the end of the cure. The unreacted functionalities could be prone to attack by humidity, thus reducing the durability of the bond.

Adhesive Curing Chemistry from FTIR-ATR Results

By comparison with the unfilled adhesive, the presence of wet or dry vinyl ester (Figs. 10 and 11) or wet E-glass fillers (Figs. 12 and 13) tended to increase the consumption rate of anhydride functionality and to reduce the yield of ester groups, but the dry E-glass filler had little effect on the curing of the adhesive. There was also a tendency for saturation to occur with the dry vinyl ester at 100°C, relative to both the adhesive without filler and the adhesive with wet vinyl ester. Though the anhydride consumption rate was higher initially, like that with wet vinyl ester, it slowed enough later so that after 3 h the anhydride index with dry vinyl ester was the same as that without filler (Fig. 10). Similarly, the rate of increase of the ester index with dry vinyl ester, which at 100°C was initially faster than that with wet vinyl ester, though less than that without filler, later slowed, so that the ester index after 3 h was about the same as with wet vinyl ester (Fig. 11). But after a subsequent 3 h at 150°C, the anhydride index was about the same for the two vinyl ester-filled adhesives, wet or dry, slightly below that without filler, the same as was found for the ester index.

The increase in the rate of loss of anhydride in the presence of the wet vinyl ester and wet E-glass is not especially surprising. The adsorbed water seems able to enhance the rate of hydrolysis of anhydride to a diacid. The little or no effect of dry E-glass on the loss of anhydride is also unsurprising. What is surprising is the early rapid rate of anhydride loss with dry vinyl ester. This suggests that the vinyl ester surface, though it is not especially great in extent, has a special effect on the loss of the anhydride, as if there were catalytic activity, perhaps in conjunction with the benzyldimethylamine. The details of this activity are not known, though the apparent saturation of the enhancement with time suggests the formation of a complex of some sort whose crystal melting or glass transition temperature is above 100°C.

Because wet vinyl ester and wet E-glass fillers enhanced the rate of anhydride loss and increased the T_g of these systems, indicating greater crosslinking, the concomitant decrease in the formation rate of ester is perhaps surprising. It is likely, however, that crosslinking has occurred by a different path, such as by ether formation. The reaction of the epoxy ring with the hydroxyls resulting from previous ring-openings to form ether linkages is catalyzed by acids.[38] Hence, the enhanced anhydride loss, presumably to a diacid, is expected to make ether formation more likely than it would be in the absence of wet fillers.

The decreased formation of ester linkages with dry vinyl ester is consistent with the slightly reduced T_g's of these compositions.

CONCLUSIONS

(1) The significantly reduced total reaction heat and glass transition temperatures with dry silica gel suggests either an immobilization of a layer of the epoxy adhesive adjacent to inert solid surfaces or selective adsorption of the accelerator.

(2) The considerable enhancement of the reaction heats, rate constants, and glass transition temperatures by wet fillers, suggests that the immobilization or selective adsorption is reversed by the presence of adsorbed water, perhaps by a plasticization of the layer or prevention of the adsorption or both.

(3) Water seems also to have the additional effect of changing the overall cure reaction. The combination of enhanced rate of anhydride loss and decreased rate of ester fomation suggests that network development at adherend interfaces having adsorbed water occurs with more ether formation and less ester formation than without water.

(4) The tendency for wet fillers to increase the glass transition temperatures of the cured epoxy adhesive suggests a beneficial effect of water in causing an increase in crosslink density in the interfacial region between the adhesive and adherend.

(5) The generally higher heat of reaction, the somewhat reduced activation energy, and the early rapid rate of anhydride loss with dry vinyl ester, though it had a low surface area, suggests that vinyl ester may have had a catalytic effect on the reaction. The catalytic activity may occur in conjunction with the benzyldimethylamine in a complex whose crystal melting or glass transition temperature is above 100°C.

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