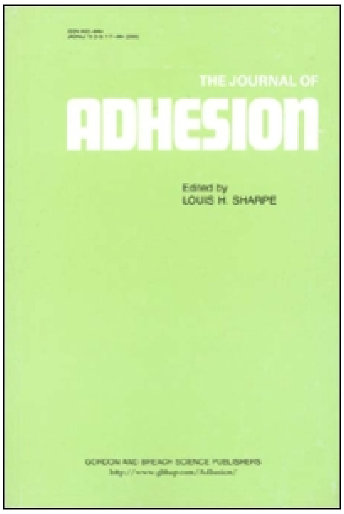

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Viscoelastic and Processing Effects on the Fiber-Matrix Interphase Strength. Part II. The Effects of Cure Temperature Time and Curing Agent Content

Aydin Turgut[a]; Erol Sancaktar[b]
[a] Mechanical Engineering Department, Firat University, Elazig, TURKEY [b] Mechanical and Aeronautical Engineering Department, Clarkson University, Potsdam, NY, U.S.A.

To cite this Article Turgut, Aydin and Sancaktar, Erol(1992) 'Viscoelastic and Processing Effects on the Fiber-Matrix Interphase Strength. Part II. The Effects of Cure Temperature Time and Curing Agent Content', The Journal of Adhesion, 38: 1, 111 — 129

To link to this Article: DOI: 10.1080/00218469208031270

URL: http://dx.doi.org/10.1080/00218469208031270

J. Adhesion, 1992, Vol. 38, pp. 111–129
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United Kingdom

Viscoelastic and Processing Effects on the Fiber-Matrix Interphase Strength. Part II. The Effects of Cure Temperature-Time and Curing Agent Content*

AYDIN TURGUT

Mechanical Engineering Department, Firat University, Elazig, TURKEY

EROL SANCAKTAR

Mechanical and Aeronautical Engineering Department, Clarkson University, Potsdam, NY 13699-5725, U.S.A.

(Received April 25, 1991; in final form January 13, 1992)

The effects of curing agent content, cure temperature and time on the adhesion strength between carbon fibers (treated with epoxy sizing) and a thermosetting epoxy (Epon 815) are studied using the single fiber fragmentation test procedure. Theoretical equations describing a majority of the phenomena affecting the adhesion process are also reviewed. The possibility of superposition between percent curing agent content, cure temperature and time is illustrated based on the analytical models presented. Experimental data are presented in the form of percent relative frequency histograms for the fiber fragments in a collective fashion. Such presentation of the data allows for interpretation of the skewness in the data population. Optimum curing agent, cure temperature and time values resulting in highest interfacial strength are also determined.

KEY WORDS Fiber-matrix interphase; cure temperature–cure time–curing agent content superposition; cure optimization; adhesive viscosity; adhesive molecular weight; kinetics of wetting.

INTRODUCTION

Users of thermoset adhesives are well aware that the cure conditions, namely cure temperature and time, and curing agent content should affect the quality of the resulting bond, since manufacturers state what those conditions should be with their product. A number of studies have been reported in the literature investigating the effects of cure conditions on the bulk,[1–8] tapered double-cantilever cleavage[9] and bonded single lap[10] behavior of thermosetting adhesives. In 1966 Chmura and McAbee[1] showed that bulk tensile strength of cured Epon 826 behaved as a bell-

---

*Presented in part at the 14th Annual Meeting of The Adhesion Society, Inc., Clearwater, Florida, U.S.A., February 17–20, 1991.

shaped curve with cure temperature. With constant cure time, the tensile strength increased with cure temperature up to a limit (approximately 69 MPa) and then dropped off for further increases of cure temperature. Later, this bell-shaped behavior was observed for other adhesive mechanical properties by various researchers. Sancaktar *et al.*[3–8] investigated the behavior of uniaxial tensile strength, rigidity, opening-mode fracture toughness, relaxation time and bulk viscosity for model (rubber-toughened) epoxy adhesives (with and without carrier cloth) in bulk form over a wide range of cure temperatures and times with fast and slow cool-down conditions. A first order kinetic reaction model was utilized to model the cure process.[5] 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 in close proximity to T_g are used. These cure schedules also result in the highest adhesive bulk tensile strength. The cure temperature-time conditions producing the maximum viscosity values did not coincide with those producing maximum tensile strengths and were at higher temperatures.[6] The effects of cure conditions on the stress-whitening behavior of the model adhesives were also investigated.[7,8] Scanning electron photomicrographs were utilized to investigate the effects of cure temperature and time on the crack tip stress-whitening behavior. The formation of inherent voids during the cure process was also investigated since they were observed to enhance the crack tip whitening zones. Experimental results revealed that both the extent of voids produced during the cure process and the size of the crack tip whitening zones on the fracture surfaces increased with increasing cure temperatures. The presence of the carrier cloth produced a similar effect with increases in inherent voiding and stress whitening sizes.

Koutsky *et al.*[9] used bonded hard maple tapered double-cantilever beam cleavage specimens to study the effects of cure time and paraformaldehyde concentration on the (bonded) fracture toughness of phenol resorcinol-formaldehyde resins. The fracture energy of the resin in the bonded form exhibited a bell-shaped, increasing-decreasing behavior as functions of increasing cure time and also increasing paraformaldehyde concentration. Koutsky *et al.* attribute the cure time behavior to "the formation and decomposition of ether linkages with increasing cure time." The paraformaldehyde behavior, on the other hand, is attributed to "the reactivity of the parent resin and generally excessive amounts of paraformaldehyde increases resin solubility and decreases fracture toughness." Koutsky *et al.* also state that[9] "unreacted excess paraformaldehyde might act as a plasticizer or viscosity modifier."

Biswas *et al.*[10] studied the effects of cure temperature on the bonded single lap shear behavior of FM73 and FM73M adhesives (American Cyanamid). The cure temperature range studied varied between 65.6°C and 176.7°C, and the bond shear strength reached its maximum value of approximately 34.5 MPa at 121°C with further increases in cure temperature resulting in strength reductions down to 13.1 MPa at 176.7°C. They observed evolution of bubbles when the adhesive was heated above 121°C and the joint failures became cohesive with adhesive layers containing "blow holes," while joints cured below 121°C failed in the adhesive mode.

Sancaktar *et al.* studied the effects of molecular weight on the single lap shear creep and constant strain rate behavior of a thermoplastic polyimidesulfone adhesive.[11] Their results showed that the viscosity coefficient values calculated on the basis of a viscoelastic model increased with increasing molecular weight at room temperature test conditions. The strain-hardening capacity was also shown to increase with increasing molecular weight. Furthermore, at all temperature levels of experimentation, ultimate shear stress levels and maximum creep stress levels increased with increasing molecular weight corresponding to the levels of zero, one, and three percent end capping. Reductions in molecular weight revealed increased adhesion (less interfacial failure) indicating increased wetting and diffusion during the bonding process, but coupled with reduced cohesive strength of the model adhesive.

In fiber-matrix bonding, which is the topic of this paper, a common method of measuring the quality of adhesion is the single-fiber-fragmentation test procedure. This procedure involves a simple composite sample coupon with a single fiber embedded in a (preferably transparent) matrix. The coupon is loaded in the tension mode globally and the load is transferred to the embedded fiber *via* the interphase which is often assumed to be under a dominant state of shear. The shear stress transferred in this fashion is equilibrated by a tensile stress on the fiber itself. This tensile stress, when larger than the ultimate strength of the fiber, causes the fiber to fragment. Fiber fragmentation continues until the length of the fragment (*i.e.* fragment circumferential surface area) is not enough to transmit the interfacial shear stress as a tensile load high enough to break the fiber. The fiber length at this threshold is called the critical fiber length, l_c, and is assumed to be (linearly) proportional to the interfacial shear stress based on elastic equilibrium conditions and the state of "pure" shear which is assumed to exist at the interphase.

THEORETICAL CONSIDERATIONS

Epoxy resins are rigid, amorphous, glasslike solids. Theories, and evidence based on electron microscopy, suggest that cured epoxy resins have many relatively small three-dimensional branches forming a network of moderate molecular weight material. Due to steric hindrance that minimizes intermolecular reactions, the final size of network during cure is limited. When the molecules polymerize, their rotational and translational freedom is reduced, which reduces the chances for primary bonds to be set up with adjacent molecules.

When the epoxy resin is subjected to cure at elevated temperatures, the increased thermal agitation permits an additional number of sterically-hindered epoxy groups to react. Thus, the size of the crosslink network is increased at the expense of the surrounding lower molecular weight material, which has lower strength, lower hardness and lower solvent resistance than the highly cross-linked network. As mentioned earlier, however, mechanical properties of thermosetting polymers can only be improved up to a limit with increasing cure temperature and time values. Above the glass temperature oxidation and degradation increase quickly, thus dete-

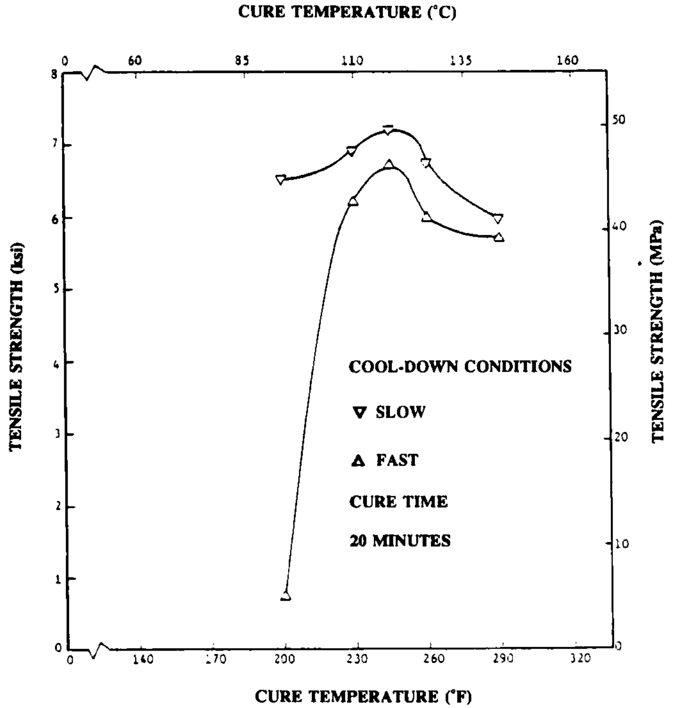

FIGURE 1 The Effect of Cool-Down Condition on the Tensile Strength of Metlbond 1113.

riorating the matrix material properties.[12] For example, the tensile strength when plotted against the cure temperature behaves as a bell-shaped function: first it increases up to a limit and then decreases at elevated temperature cure. Figure 1[3] illustrates this behavior for bulk Metlbond 1113 (Narmco) rubber-modified epoxy with carrier cloth.

Experimental results[3] reveal that increases in cure temperature result in reductions in cure time requirements along with increases in the bulk strength until the maximum strength is obtained. Further increases in the cure temperature may increase the kinetic process but do not result in an increase of the bulk strength but, in fact, may induce molecular changes which would trigger different failure mechanisms and result in strength reduction. Figure 2[7] illustrates this behavior for the cure of bulk Metlbond 1113 adhesive. It should be noted that the diffusion process, which may govern the adhesion mechanism, is also controlled by similar constraints.[13]

Fiber-Matrix Interfacial Shear Stress

Pritykin *et al.*[14] offer a general theory for the strength of the adhesive-adherend interaction, F_{ad}, on the basis of "strength of interaction between the repeating unit

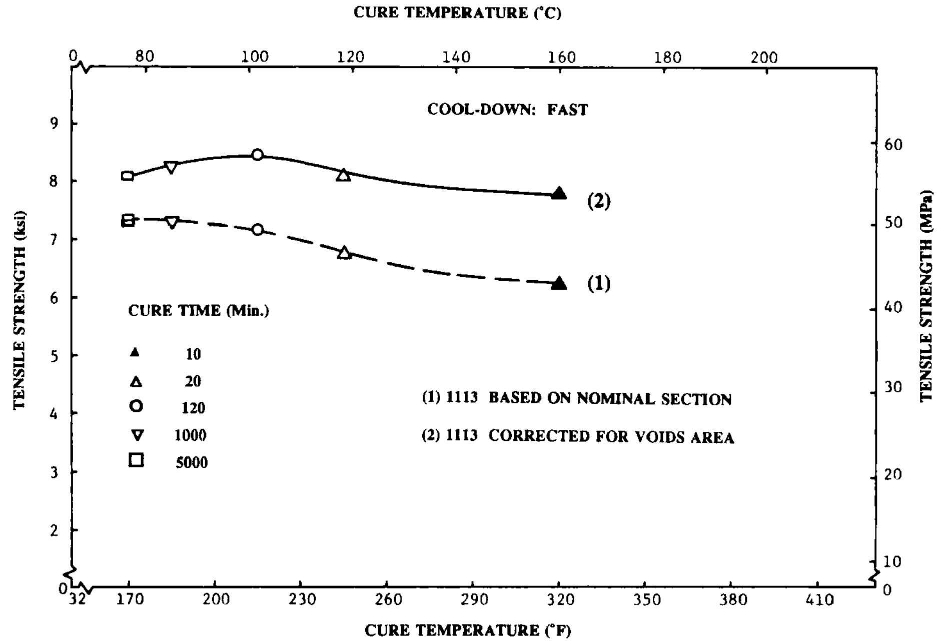

FIGURE 2 Metlbond 1113 Optimum Strength-Cure Behavior with and without Void Area Correction.

of the adhesive and adherend, F_{if}," and "the ratio of the real interfacial contact area to its maximum value" *i.e.* extent of molecular contact. The process of molecular contact formation is presented as adsorption of consecutive repeating units on the adherend. It is argued to depend not only on the temperature, internal stresses and molecular mass, but also on the energy and length of the interfacial bond at the molecular level.[14] Accordingly, they express the F_{ad} function in the form

$$F_{ad}(t)=\int_{0}^{t} A(\tau)[\partial N(t-\tau, x)/\partial\tau]\, F_{if}(x)dx\, d\tau \qquad (1)$$

where:

$A(\tau)$ = the time dependence of the interfacial contact area,
$N(t-\tau, x)$ = the number of repeating units of the adhesive at the distance x from the adherend surface at the moment $(t-\tau)$.

Polymer diffusion across the interface between the adhesive and adherend which, in our case, is carbon fibers coated with epoxy material, is governed by time and temperature. Based on this theory, Dara and Loos[15,16] used the following relation for the adhesion strength σ_{ad} of thermoplastic/carbon composites:

$$\sigma_{ad}=m(a_t t_{c,ref})^n \qquad (2)$$

where:
m and n = constants,
a_t = the WLF shift factor,
$t_{c,ref}$ = the contact time.

The shift factor a_t is defined by the relation

$$\log a_t = -a_1(T - T_{ref})/\{a_2 + (T - T_{ref})\} \tag{3}$$

where:
a_1 and a_2 = constants,
T = the temperature,
T_{ref} = the reference temperature.

Consequently, equation (2) dictates that the equivalent contact time at temperatures other than a reference temperature (such as the glass transition temperature T_g) is defined by the equation

$$t_c = a_t t_{c,ref} \tag{4}$$

Note that equation (2) constitutes a specific form of equation (1).

Elevated cure temperature increases the mobility of polymer molecules, therefore promoting diffusion and, hence, adhesion but only up to a level related to the cure temperature. We note that the two important aspects of the diffusion mechanism are the following:

i) The interdiffusion coefficient is inversely proportional to the polymer viscosity.
ii) The activation energies of diffusion and viscous flow are equal.

Based on these premises we can conclude that the intensity of the molecular motion in a polymer can be estimated by its viscosity under given thermal conditions. Increases in the contact temperature, plasticization, and dissolution of the polymer are known to increase the rate of diffusion. Increases in the molecular chain stiffness, the presence of strong polar groups and crosslinking, however, are known to

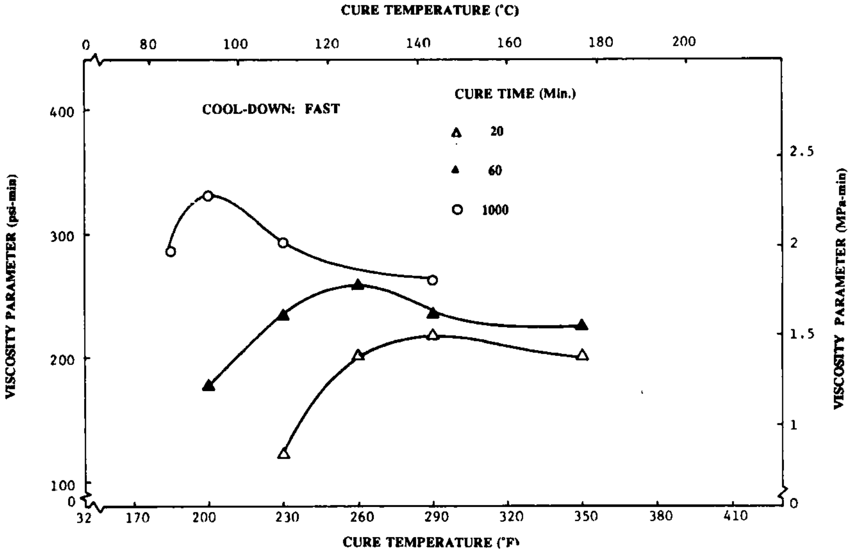

FIGURE 3 The Effects of Cure Conditions on the Short Term (Room Temperature) Relaxation Viscosity Parameter of Metlbond 1113 Based on the Modified Bingham Model.

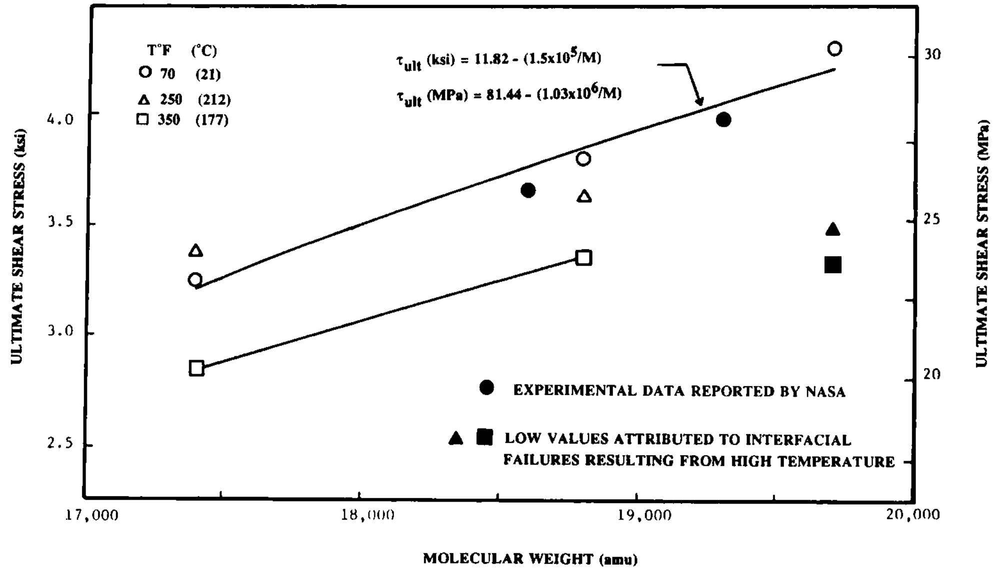

FIGURE 4 Variation of Ultimate Shear Stress with Molecular Weight for Thermoplastic Polyimidesulfone Adhesive.

reduce the rate of diffusion while increasing viscosity. Viscosity values can be affected by the cure temperature and time values as illustrated in Figure 3.[6] Increases in molecular weight and, consequently, the bulk solid viscosity of structural adhesives have been shown to increase ultimate shear stress (Figure 4) and maximum creep (rupture) stress levels in bonded single lap joints.[11] There is evidence, however, that such increases in strength values level off and may even drop beyond a certain molecular weight value.[11].

Diffusion in polymers is governed by an activation-kinetic process which can be described by an Arrhenius type equation:

$$t = A_o e^{Q/RT} \tag{5}$$

where:

t = the time required for completion of a given stage of the diffusion process,

A_o = a constant which depends on the thickness of the material and has the dimensions of time,

Q = the activation energy of diffusion,

T = the cure temperature in degrees Kelvin.

Note that equation (5) provides a general form for equations (3) and (4) combined for the cases when the cure temperature is substantially different from the reference temperature T_{ref}, which is usually assumed to be the glass transition temperature. This constraint arises from the fact that mathematically, for the form of equations (4) and (5) to be similar, the term $\exp(a_2^2 a_1^{-4} \Delta T^{-2})$, where $\Delta T = T - T_{ref}$ and similar terms with higher orders of $1/\Delta T$ in the series expansion of equation (3) need to be approximately equal to one.

An equation similar in form to equation (5) has been used in the literature to represent the polymer viscosity, η, as a function of temperature and the degree of cure, α.[16]

$$\eta = \eta_o \exp[(U/RT) + K\alpha] \tag{6}$$

where:
η_o = a constant,
U = the activation energy for viscosity,
K = a constant independent of temperature.

The molecular weight of a polymer, which is expected to increase with increasing crosslinking for thermosetting materials, has been related to its viscosity with the equation:

$$\eta = A(M)^B \tag{7}$$

where:
A, B = constants which depend on the temperature and the nature of the polymer,
M = polymer's molecular weight.

For polymers having molecular weights above the critical level, M_c, which corresponds to the level at which polymer chains become long enough for chain entanglements to occur, Nielsen[17] reports the values $A = 4.5 \times 10^{-14}$ Mpa-sec and $B = 3.4$. Bulk solid viscosity values calculated by Sancaktar *et al.*[11] for a thermoplastic polyimidesulfone on the basis of a viscoelastic model resulted in the values $A = 2.0 \times 10^{-55}$ and, $B = 13.1$. In either event, it is clear that increasing crosslinking, which results in increased molecular weight, also results in increased polymer viscosity as solidification proceeds in the polymer.

Viscosity values of polymers measured by rheometers have been used to assess their wetting and adhesion properties. When applied to the kinetics of wetting, Eyring rate theory gives:[18]

$$d(\cos\theta_t)/dt = \gamma_{LV}(\cos\theta_\infty - \cos\theta_t)/\eta L \tag{8}$$

where:
γ_{LV} = the surface energy of the polymer melt in equilibrium with its vapor,
η = the viscosity of the polymer,
L = a "jump" distance, and
θ_t and θ_∞ are contact angles related by:

$$\cos\theta_t = \cos\theta_\infty[1 - a\ \exp(-ct)] \tag{9}$$

with a and c being constants.

Consideration of Equations (8) and (9) along with Poiseuille's law results in:[18]

$$x_t^2 = r\gamma_{LV}\cos\theta_\infty[t - (a/c) + (ae^{-ct}/c)]/2\eta \qquad 10$$

where:
x and r = depth and radius of substrate pores.

Obviously, the viscosity of the adhesive plays an important role in its ability to adhere to a substrate.

Measurement of Fiber-Matrix Interfacial Shear Stress

Many researchers use single fiber-resin tensile tests to determine the adhesion between fiber and resin. Assuming uniform fiber strength and diameter, Kelly[19] derived an expression for this adhesion strength (τ_c) in the form

$$\tau_c = (\sigma_f \, d)/(2 \, l_c) \tag{11}$$

where:

τ_c = the shear strength at the fiber resin interface,
d = the fiber diameter,
l_c = the critical fiber fragment size,
σ_f = the fiber tensile strength.

As described by Kelly, when a tensile load is applied to the fiber-matrix composite, the fiber should break into fragments until an l_c is reached which is too short to transfer a stress equal or greater than σ_f. The l_c is believed to indicate the adhesion condition. In other words, shorter l_c means larger shear stress τ_c which shows better adhesion.

Recent research[20] has shown that in the vicinity of a reinforcing fiber there is an "interphase" region having properties different from that of the bulk matrix. A main reason for the presence of such a region is attributed to the sizing applied to assist processing during prepreg or filament winding operations and also to improve adhesion. Obviously, diffusion of this sizing into the matrix can create a concentration gradient. There is a variety of other possible mechanisms which could lead to an interphase region. For example, possible polymeric reptation into the fiber substrate during the adhesion process, selective adsorption of one or more of the components in the matrix before curing, and free volume differences between the bulk polymer and the polymer near the fiber-matrix boundary, possibly created by thermal stresses.

Various elastic and elastic-plastic approaches have been used in the literature to study the micro-mechanics of stress transfer between fiber and matrix. Recent work by Sancaktar *et al.*,[21] however, showed that nonlinear viscoelastic behavior of the matrix and the interphase may have a profound effect on the mechanism of stress transfer especially if high temperature, loading rate, or transient effects are to be accurately accounted for.[22]

Sancaktar's analytical model involves a cylindrical interphase surrounding an elastic fiber of finite length. The interphase region has nonlinear viscoelastic material properties. The region surrounding the interphase (which can be assumed to be the bulk of the adhesive matrix) is also assigned nonlinear viscoelastic properties which are different than those of the interphase. The nonlinear viscoelastic material behavior of the interphase zone and the matrix is represented using a stress enhanced creep. Different interphase diameter values and different material properties for the interphase and the matrix are used to determine their effects on the interfacial shear stress. Results of this analysis reveal that, depending on the relative magnitudes of interphase and matrix viscoelastic material properties, it is possible to have stress reductions or increases along the fiber[21] as shown in Figure 5. Hence, the critical fiber length obtained will also vary accordingly. This result reveals that

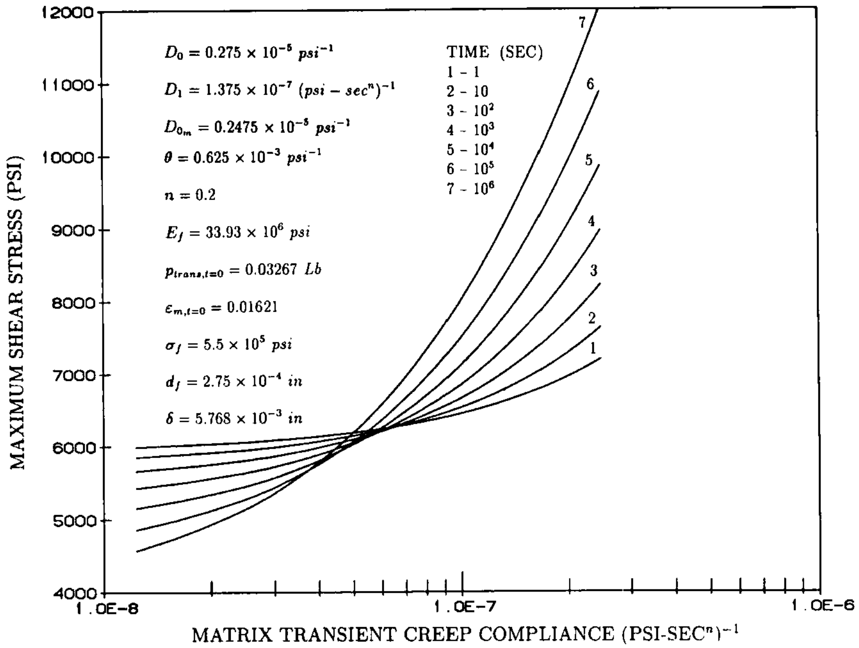

FIGURE 5 The Variation of Maximum Shear Stress with Time and Matrix Transient Creep Compliance Based on Nonlinear Viscoelastic Analysis of a Cylindrical Interphase Zone for Maximum Transferred Load.

not only the quality of adhesion but also the material properties of the bulk matrix and the interphase, all of which can be affected by cure conditions, can affect the critical fiber length which is widely used as the gauge by which fiber-matrix interfacial strength is perceived. For example, Figure 6[21] reveals that the viscoelastic properties of the interphase and the matrix affect the magnitude of the average shear stress along an embedded fiber, and different average shear stress levels result in different fiber fragment lengths as shown in Figure 7.[21]

EXPERIMENTAL PROCEDURES

Single carbon fiber/epoxy resin dogbone-shaped specimens were made from epoxy resin. The epoxy resin used was Shell Epon 815® (Shell Chemical), an epichlorohydrin/bisphenol A-type epoxy resin containing a reactive diluent. Epoxide equivalent weight of Epon 815 is reported by the manufacturer to vary between 175–195 grams (of resin containing one gram equivalent of epoxide, Shell analytical method HC-427D-89). The curing agents were DETA (Diethylenetriamine) and Armocure 100 (Akzo Chemicals). DETA is a liquid polyamine widely used with epoxy resins for fast cures and room temperature cures, providing good resin properties at room temperature (or below 82°C, the minimum heat distortion temperature reported by the manufacturer). The molecular weight of DETA is reported to be 103 by the manufacturer. Since DETA is reported to have five active hydrogen atoms, its

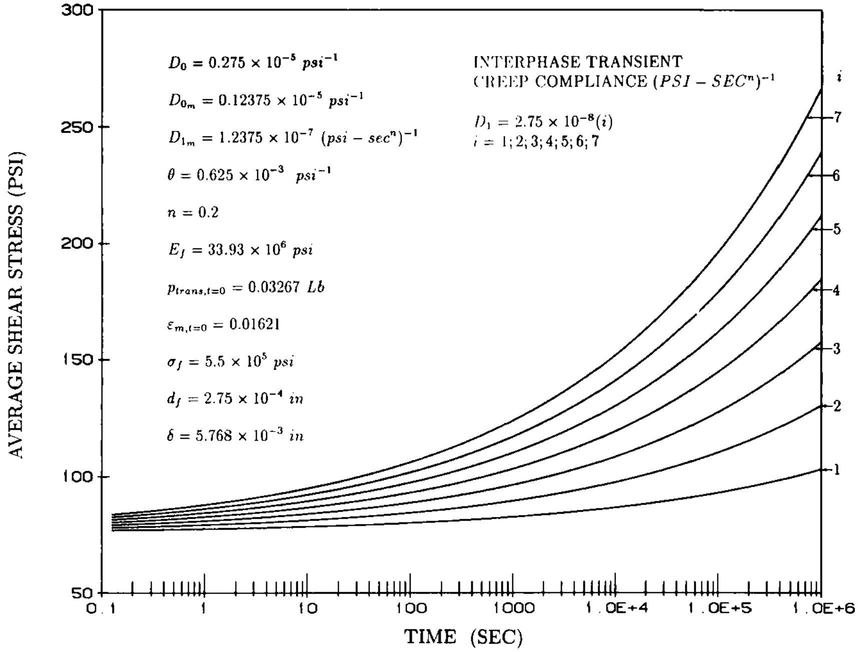

FIGURE 6 The Effect of Interphase Transient Creep Compliance on the Time Dependent Variation of the Average Shear Stresses at the Fiber-Matrix Interphase Based on Nonlinear Viscoelastic Analysis of a Cylindrical Interphase Zone. The Matrix is Assumed to be Nonlinear Viscoelastic.

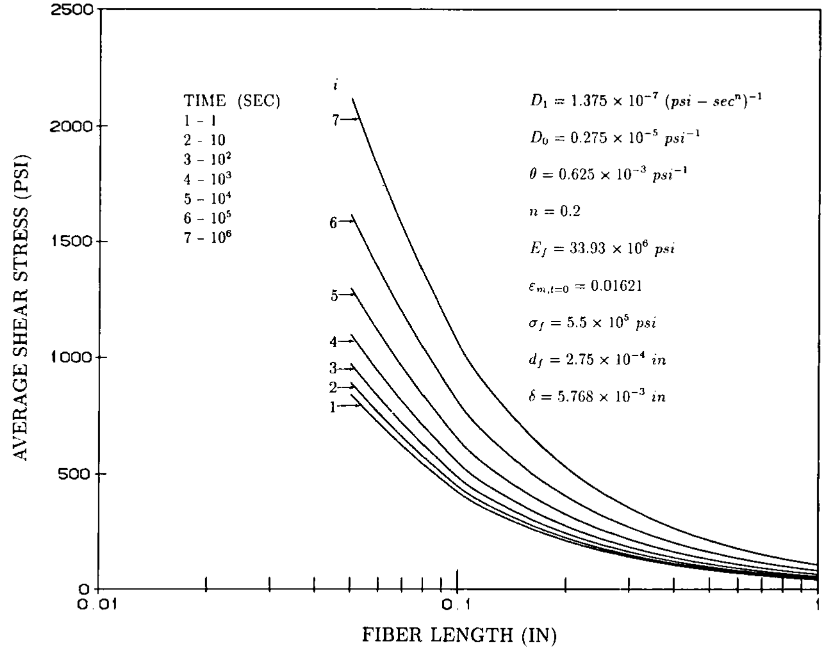

FIGURE 7 The Variation of Average Shear Stress at the Fiber-Matrix Interphase with Time and Fiber Length Based on Nonlinear Viscoelastic Analysis of a Cylindrical Interphase Zone. The Matrix is Assumed to be Nonlinear Viscoelastic with the Material Properties D_{0m} and D_{1m} Shown in Figure 6.

equivalent weight can be calculated as 20.6. Consequently, the DETA curing agent requirements for the Epon 815 resin can be calculated to vary between $(20.6/175)\times 100 = 11.8\%$ and $(20.6/195)\times 100 = 10.6\%$.

Armocure 100 is an aliphatic polyamine providing a tough, flexible, water-resistant and solvent-resistant cured epoxy resin. 12 phr of Armocure 100 was added to the matrix composition to increase its flexibility. The DETA content of the curing agent and the cure temperature and time were test parameters and will be indicated in each figure depicting the results. For experimentation, the weight percentage of DETA was varied between 9.0% and 12.5%. The cure temperature was varied between 37.8°C and 93.3°C and the cure time was varied between 2 hours and 12 hours. Curing was done in a convection oven.

The carbon fiber chosen was 7μm diameter Celion G30 500 (BASF) finished with EP03 which is an epoxy sizing agent deposited by use of an emulsion. The fiber was fixed in an aluminum mold machined specifically to form single fiber tensile specimens. Care was exercised to prevent contamination of the fibers during this process. After the resin was poured into the molds, vacuum devices were used for approximately 20 minutes to remove air bubbles from the molded resin. The molds were then put in a convection oven for curing. After curing, the specimens were removed from the molds and machined to the required shape.

The tensile test machine for the fragmentation tests was a Model 1000 Instron Universal Testing Instrument. Strains were measured using a 4300 Plastics Testing Extensometer with an LVDT Controller. A 7000A/7001A X-Y Recorder was used to plot the stress-strain curves.

A test temperature of 54°C was used to ensure sufficient material deformability to reach 12% strain. The use of this elevated temperature prevented brittle failures and resulted in consistent critical fiber length l_c values. All single fiber specimens for fragmentation test were tested to 12% strain to ensure fragmentation of the fiber to the critical length. The extension rate was a fairly slow rate of 3.2 mm/min to (again) avoid premature brittle failures.

The total number of specimens used was 36 resulting in a total of (approximately) 3144 fiber fragments providing information on the three test parameters: cure temperature, time, and curing agent content. The large number of fragments is obtained due to the use of 140 mm long specimens with 50 mm gage lengths (see Figure 3 in Part III of this series of paper). We think that a gage length fifty to one hundred times larger than the length of fiber fragments obtained is more representative of real-life, long fiber composites.

RESULTS AND DISCUSSION

As described in Part I of this series of papers, statistical analyses were performed with the data obtained using a commercially-available SAS computer program. The data were fitted to a Weibull distribution, assuming a constant origin of 0, and comparing the shape (β) and location (η) parameters. One of the advantages of this method over comparing the simple descriptive statistics is the availability of the shape parameter which gives an indication of the shape of the data. The shape parameter can range from exponential (β = 1.0) to peaked normal (β = 5.0) (Figure 12, Part I of this series). This parameter can, therefore, be used to assess the influence of contributors to fiber fragmentation other than the test parameters applied. These parameters were discussed at the beginning of the Results and Discussion section for Part I as well as in the Theoretical Considerations section of the present paper. Note that when such influence is strong, the parameter β approaches the value one and the standard deviation value for the corresponding data is expected to be high. Consequently, variations in the standard deviation provide additional insight into the data obtained and such data need not be dismissed as uninformative. Especially with the single fragmentation test, use of longer gage lengths, as in this work, increases the likelihood of obtaining high and varying standard deviations. We note, however, that, in this case, longer gage length specimens are better representative of real-life, long fiber composites.

Information on the variations in Weibull shape parameter for fragment length as obtained using different cure conditions was provided in Part I of this series of papers (Figure 13, Part I). The results indicated that the cure conditions of 38°C for 12 hours with 12wt% DETA provide closest to peaked normal data distribution. Other cure conditions result in data distribution varying between exponential to log normal (β = 2.5) and need to be analyzed using the biased histogram method introduced in this paper. These histograms represent the percent relative frequency of occurrence for each 20×10^{-2} mm fragment length by a rectangular bar, the area of which is proportional to the frequency. Such graphs are shown in Figures 8 through 15. The reader should note that in all of the histograms the test conditions

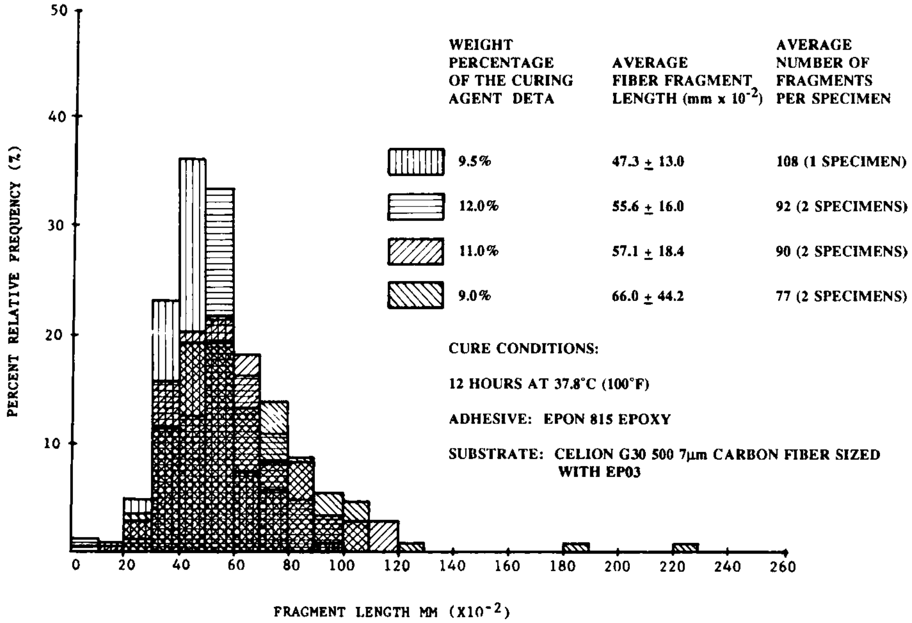

FIGURE 8 The Effect of DETA Content on Fiber-Matrix Adhesion as Indicated by Fragment Size Distribution in Single Fiber Tension Test Specimens Cured for 12 Hours at 37.8°C.

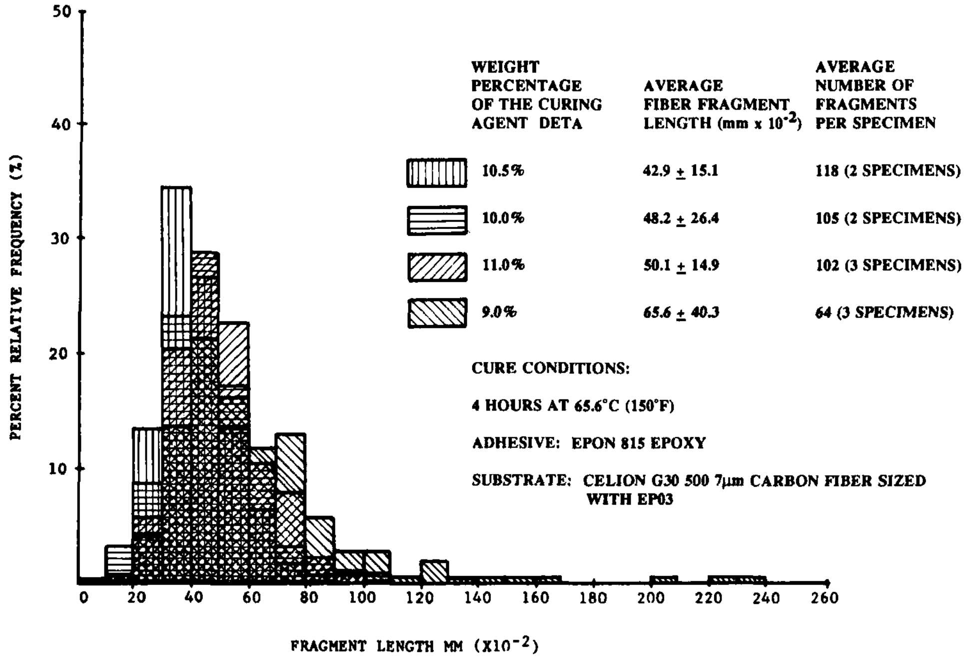

FIGURE 9 The Effect of DETA Content on Fiber-Matrix Adhesion as Indicated by Fragment Size Distribution in Single Fiber Tension Test Specimens Cured for 4 Hours at 65.6°C.

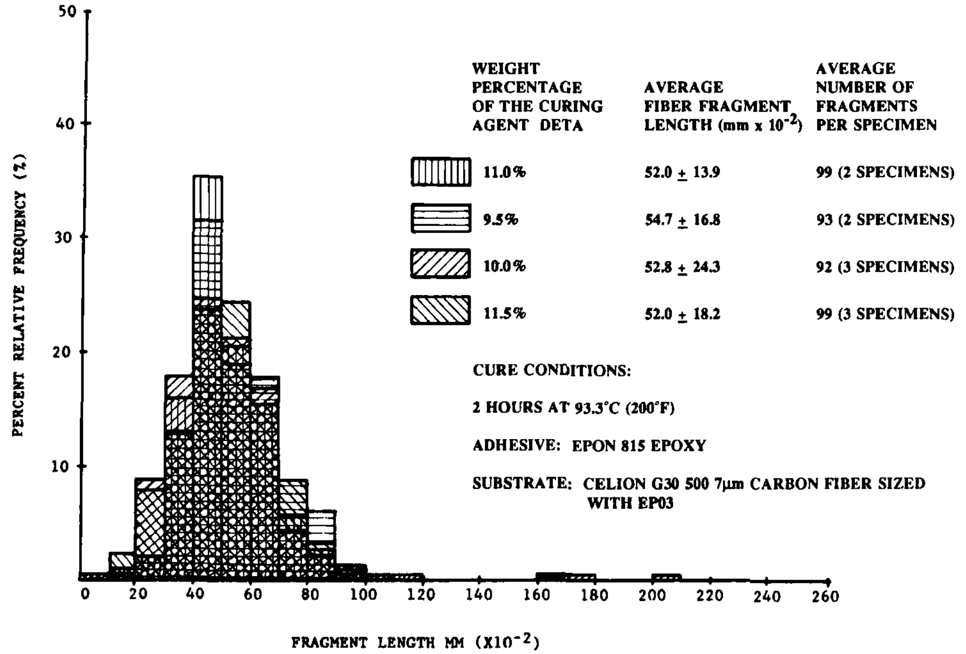

FIGURE 10 The Effect of DETA Content on Fiber-Matrix Adhesion as Indicated by Fragment Size Distribution in Single Fiber Tension Test Specimens Cured for 2 Hours at 93.3°C.

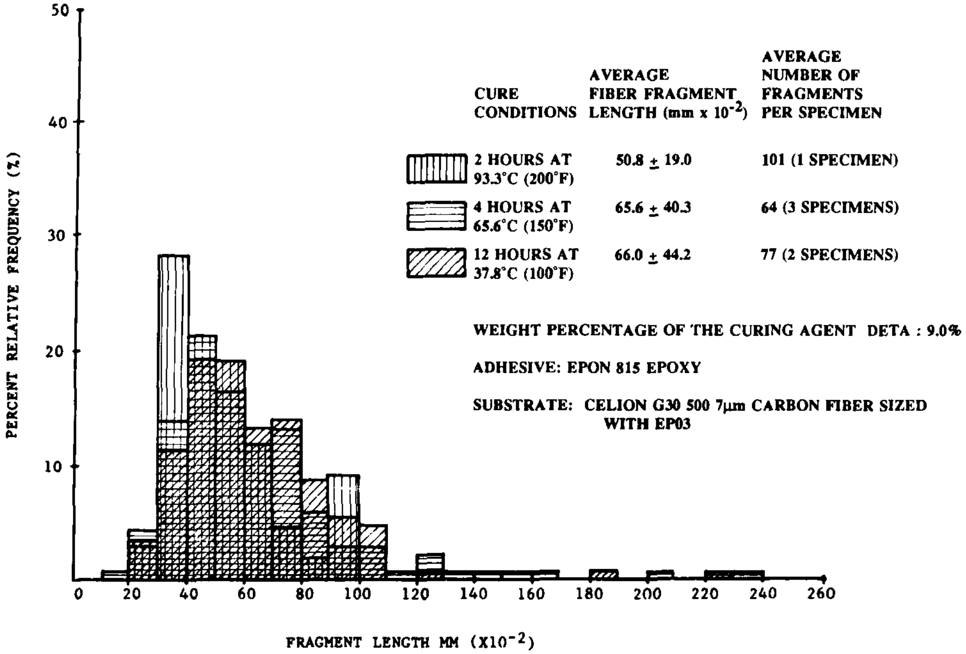

FIGURE 11 The Effect of Cure Conditions on Fiber-Matrix Adhesion as Indicated by Fragment Size Distribution in Single Fiber Tension Test Specimens Containing 9.0 (Weight) Percent DETA.

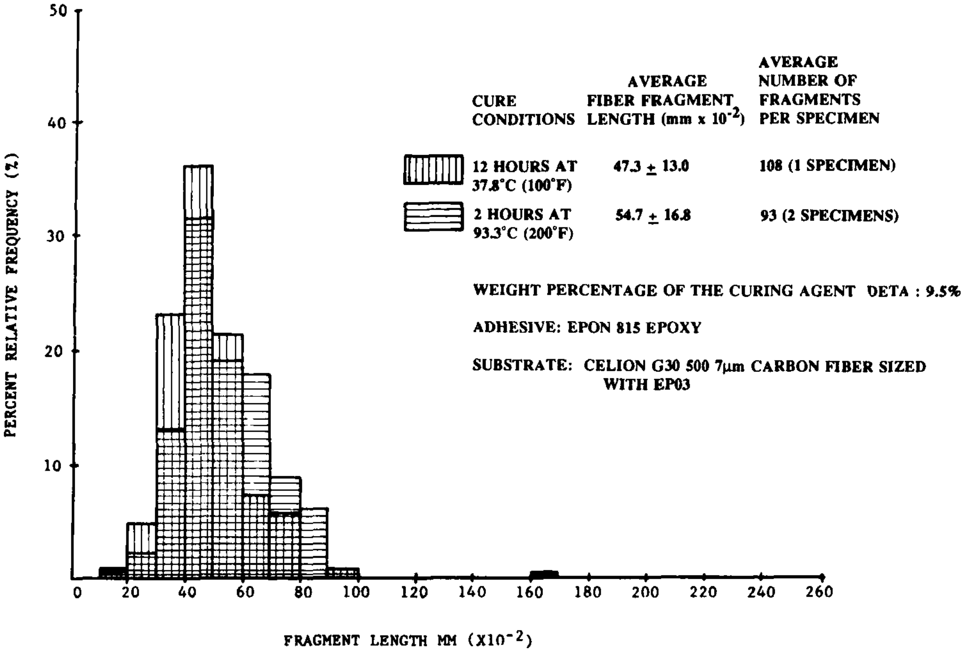

FIGURE 12 The Effect of Cure Conditions on Fiber-Matrix Adhesion as Indicated by Fragment Size Distribution in Single Fiber Tension Test Specimens Containing 9.5 (Weight) Percent DETA.

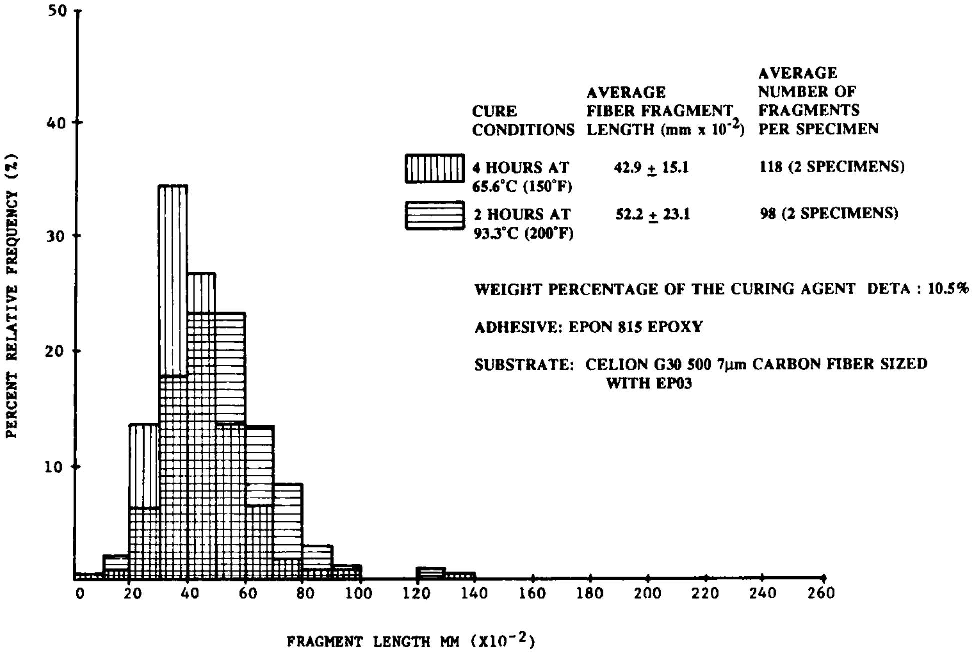

FIGURE 13 The Effect of Cure Conditions on Fiber-Matrix Adhesion as Indicated by Fragment Size Distribution in Single Fiber Tension Test Specimens Containing 10.5 (Weight) Percent DETA.

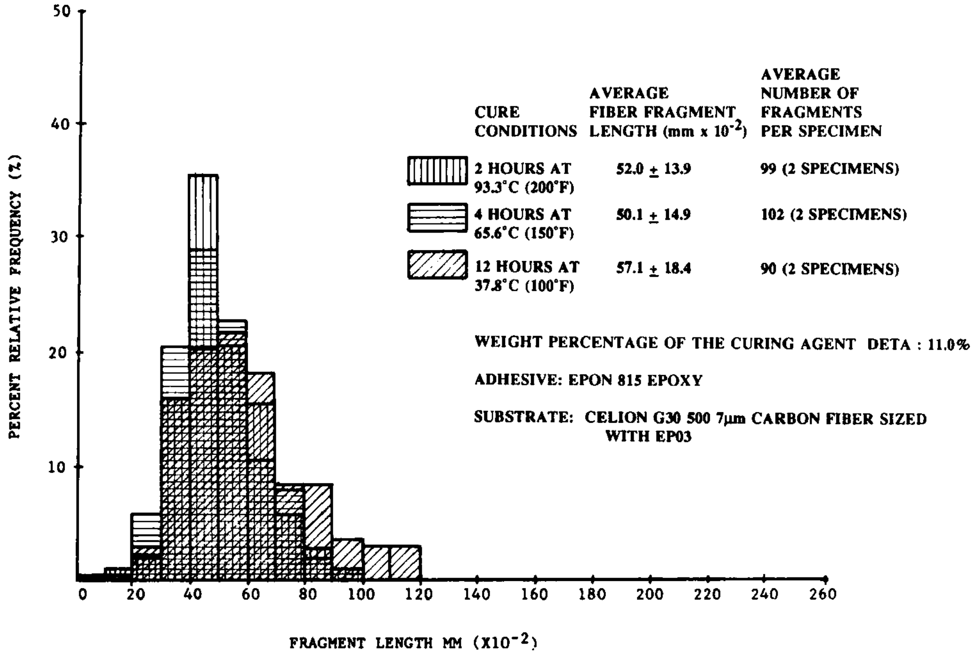

FIGURE 14 The Effect of Cure Conditions on Fiber-Matrix Adhesion as Indicated by Fragment Size Distribution in Single Fiber Tension Test Specimens Containing 11.0 (Weight) Percent DETA.

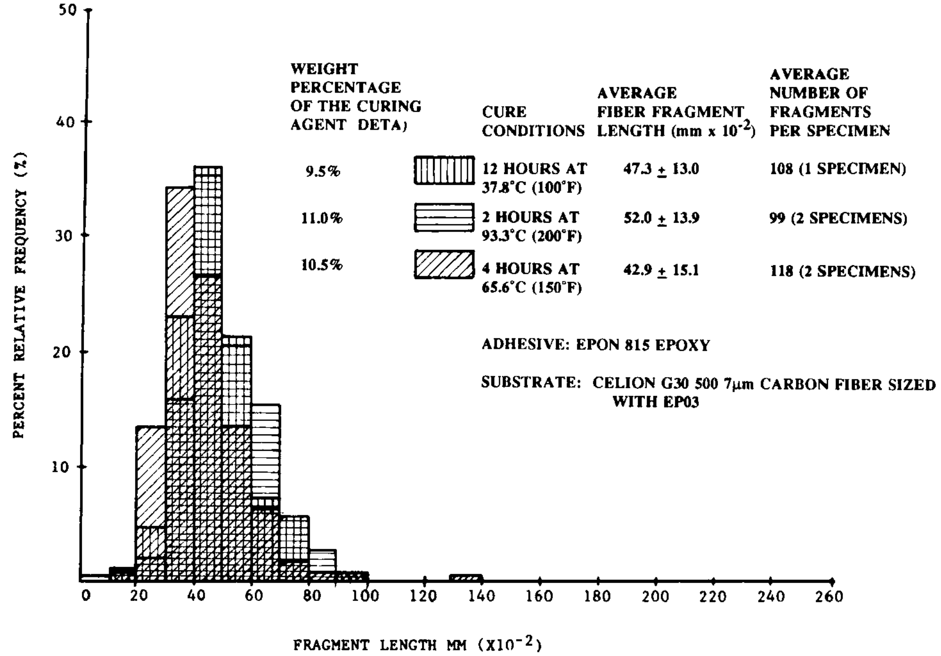

FIGURE 15 Determination of Optimum DETA Content and Cure Conditions for Fiber-Matrix Adhesion as Indicated by Fragment Size Distribution in Single Fiber Tension Specimens.

which result in the lowest average (mean) fragment length values generally result in highest frequency bars, corresponding to shorter fragments on the lefthand side of the diagrams, irrespective of their standard deviation values.

Figure 8 shows the effect of curing agent content for the cure condition of 12 hours at 37.8°C. Highest interfacial strength (*i.e.* shortest fragment length) is obtained with 9.5wt% DETA content. 11.0% and 12.0% levels seem to result in fairly similar, even though lower, interfacial strength.

When cured for 4 hours at 65.6°C it is necessary to use the curing agent at a 10.5wt% level as shown in Figure 9. Any deviation from this percent level seems to result in (progressive) lowering of the interfacial strength with the lowest strength obtained at 9.0% level.

For the fast cure schedule of 2 hours at 93.3°C, the necessary percentage of DETA shifts to even higher levels. Figure 10 reveals that, for the above mentioned cure conditions, percent DETA levels of 10.0%, 11.0% and 11.5% result in practically the same interfacial strength level, as indicated by fragment length of 52×10^{-2} mm. This fragment length, however, is longer than either one of the other two cure conditions which involved longer cure times but lower cure temperatures as reported above. For two hours of cure at 93.3°C, reduction in interfacial strength seems to start with DETA contents of 9.5wt% and lower.

Results shown in Figures 8 through 10 reveal the possibility for superposition between cure time, temperature and curing agent content on the increasing portion of an interfacial strength function. In other words, one can write:

$$\tau_c = \tau_c(T_o,\ a_T t,\ a_V \%CA) \qquad (12)$$

where,

a_V = a shift factor relating the effects of the DETA content and cure temperature and time,

%CA = weight percent DETA.

The a_V can be obtained by using equations (6) through (10) or any other similar phenomenological criteria. Such treatment is in agreement with the general theory given by equation (1). Also note that, in the light of this consideration, equation (2) does not provide a complete description for cure effects on the adhesion strength as it lacks the effect of %CA. The authors think that equation (12) should also include interphase thickness and (ratio of) matrix and interphase material property parameters and the related shift factors. This assessment is made on the basis of the numerical work done by Sancaktar *et al.* earlier.[21]

Figures 11 through 14 provide supporting evidence for applicability of equation (12) using %CA as the fixed parameter and varying the cure temperature and time. These figures reveal that the increasing portion of the interfacial strength function resides between the %CA values of 9.5 and 11.0wt%. As we go to higher levels of %CA above 9.0%, optimum τ_c is obtained at shorter time-higher temperature levels. At 11.0wt% DETA, τ_c becomes insensitive to cure temperature and time conditions due to the high level of the curing agent present. At the 9.0wt% level, again the τ_c is considerably below the optimum value. Furthermore, the competing effects of adhesion and degradation are clearly evident at this %CA level. Figure 11 shows that use of cure times longer than two hours results in deterioration of the τ_c as indicated by the presence of many long fragments. Also, note that the standard deviation values for fragment lengths obtained with the use of such cure times are high (Figure 11).

The optimum curing agent content, cure temperature and time values resulting in highest interfacial strength are shown collectively in Figure 15. This figure reveals that the single optimum combination of %CA, t and T resulting in the highest interfacial strength is 10.5wt%, 4 hours, 65.6°C, respectively.

CONCLUSIONS

The single-fiber fragmentation test procedure was used to study the effects of curing agent content, cure temperature and time on the interfacial strength between epoxy treated carbon fibers and cured Epon 815 epoxy. The optimum curing agent content, cure temperature and time values were determined for the highest interfacial strength. The results revealed the possibility of superposition for cure temperature, time and percent curing agent content for the increasing portion of the interfacial strength function. The competing effects of adhesion *versus* degradation were also demonstrated using a low level of curing agent content (9.0wt%).

Acknowledgements

This work was performed during Dr. Aydin Turgut's sabbatical visit at Clarkson University during April 1989 to mid February 1990. We express our thanks to Firat University, Elazig, Turkey for providing the permission and financial support for Dr. Turgut's sabbatical leave at Clarkson University.

References

1. M. Chmura and E. McAbee, "Correlation of Mechanical Properties of Resins Obtained in an Adhesive Joint and in Bulk Form," Technical Report 3330 (Picatinny Arsenal, Dover, NJ, 1966).
2. J. K. Gillham, *J.A.I.Ch.E.* **30,** 1066 (1974).
3. E. Sancaktar, H. Jozavi and R. M. Klein, *J. Adhesion* **15,** 241 (1983).
4. H. Jozavi and E. Sancaktar, *J. Adhesion* **18,** 25 (1985).
5. H. Jozavi and E. Sancaktar, *J. Adhesion* **25,** 185 (1988).
6. H. Jozavi and E. Sancaktar, *J. Adhesion* **29,** 233 (1989).
7. H. Jozavi and E. Sancaktar, *J. Adhesion* **27,** 143 (1989).
8. H. Jozavi and E. Sancaktar, *J. Adhesion* **27,** 159 (1989).
9. R. O. Ebewele, B. H. River and J. A. Koutsky, *J. Adhesion* **14,** 189 (1982).
10. S. Biswas, A. G. Ludwick and S. Jeelani, private communication.
11. E. Sancaktar and S. K. Dembosky, *J. Adhesion* **19,** 287 (1986).
12. J. B. Enns and J. K. Gillham, *J. App. Poly. Sci.* **28,** 2587 (1983).
13. M. G. Dodin, *J. Adhesion* **12,** 99 (1981).
14. L. M. Pritykin, A. B. Zilberman, I. I. Zilberman and V. L. Vakula, private communication.
15. J. Muzzy, L. Norpoth and B. Varughese, *SAMPE J.* **25,** 23 (1989).
16. W. I. Lee, A. C. Loos and G. S. Springer, *J. Comp. Matl.* **16,** 510 (1982).
17. L. E. Nielsen, *Mechanical Properties of Polymers* (Reinhold Publishing Corp., New York, 1962), pp. 56–57.
18. A. Pocius and C. Dahlquist, *Adhesion and Adhesives* (American Chemical Society, Washington, D.C., 1986), p. 59.
19. A. Kelly and W. R. Tyson, *Mech. Phys. Solids* **13,** 329 (1965).
20. G. C. Knollman and J. J. Hartog, *J. Adhesion* **17,** 251 (1985).
21. E. Sancaktar and P. Zhang. *J. Mech. Design* **112,** 605 (1990).
22. E. Sancaktar, A. Turgut and G. Fei, "Viscoelastic and Processing Effects on the Fiber-Matrix Interphase Strength. Part I. The Effects of Test Temperature, Loading Rate, Fiber Sizing, and Global Strain Level," *J. Adhesion,* this issue.