

Prepreg Aging in Relation to Tack

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SYNOPSIS

Thermoanalytical measurements and tack tests were both performed using a commercially available carbon fiber/epoxy prepreg system (Hercules 3501-6) to examine changes caused by aging as they affect handling and processability of thermosetting matrix-based composites. Combining these techniques, a relationship between prepreg bulk and surface characteristics in relation to aging was investigated. Isothermal kinetic studies at low temperatures showed maximum conversions (α_m) that increased with increasing cure temperatures. In addition, a linear relationship between glass transition temperatures (T_g) and conversions (α) was observed regardless of aging (or cure) temperatures. Energy of separation of prepreg stacks, which may be viewed as a measure of prepreg tack, showed a maximum value at a specific temperature. The maximum energy of separation was observed in the temperature range of 20–25°C above the glass transition temperature for a given sample. However, the maximum energy of separation values decreased with increasing aging times (or conversions), implying that prepreg tack was a viscoelastic property rather than a viscous property of the resin matrix in the prepreg.

INTRODUCTION

Carbon-fiber-reinforced, high-performance composites are widely used in load-bearing structural applications because of their excellent mechanical properties, weight savings advantage, and ease of processing. The starting composite material form most often used is the prepreg, which is manufactured by impregnating the reinforcing fibers with a partially cured (B-staged) thermosetting resin matrix.^{1,2} The B-staged form provides a desirable tack and drape with which the thermosetting matrix based prepreps are easily laid-up on various shaped tools and cured at elevated temperature and pressure using either an autoclave or a press.³⁻⁶ The curing process, which may be viewed as a time/temperature-dependent crosslinking reaction process, has been widely investigated, especially for epoxy resins.⁷⁻¹¹ Even at or below ambient temperature, crosslinking may still take place in the resin matrix,

giving rise to an aging phenomenon, since not all reactive sites are available during subsequent elevated temperature processing. However, the aging process may be somewhat different from the curing process taking place at elevated temperatures since aging may be retarded by vitrification before gelation.¹²

From a practical viewpoint of composite processing, several problems can be encountered in relation to prepreg aging, such as moisture absorption and chemical reaction of the resin matrix in the prepreg, that all may affect the tack. Moisture absorption by the epoxy resin matrix usually accelerates the cure reaction, but may also result in void formation in a cured laminate.^{13,14} Both moisture absorption and cure reaction are time/temperature-dependent processes. The prepreps are usually stored in a freezer kept at 0°F (–18°C) and then exposed to an ambient environment for a short period of time during cutting and lay-up. Thus, both phenomena of cure and moisture absorption continuously take place as the material is handled. The traditional thermoanalytical methods (differential scanning calorimetry and dynamic mechanical analysis) used to characterize prepreps focus on bulk property behavior and may

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not be sensitive to aging effects, especially at or below ambient conditions.

On the other hand, prepreg tack has been found to be sensitive to the aging process even at an ambient temperature.^{4,5} Tack is an important characteristic of the thermosetting matrix-based prepreps that relates their ability to assume and hold a shape during lay-up as well as in consolidation processing. However, tack has different meanings in different applications; hence, the definition, as well as the testing methods of tack, must be adopted according to the way the materials system is utilized for a specific application.^{5,6} In the composite field, prepreg tack is required for individual plies to adhere to each other so that multiple plies can be stacked and maintained at a desired orientation. The reinforcing fibers in a prepreg prevent intimate contact of resin matrix across the composite thickness, and thus provide rough surfaces between adjacent prepreg plies during lay-up operation.^{5,6} The elastic behavior of the fiber reinforcement is strong enough to substantially influence the apparent viscosity of the prepreg, which in turn produces pronounced viscoelastic behavior.^{5,6} Accordingly, Seferis et al. proposed that prepreg tack is considered to be a bulk property rather than a surface property, depending on viscoelastic and surface characteristics of the individual prepreg plies.³⁻⁶ Furthermore, a testing method to measure prepreg tack has been developed and analysis of the data has identified both intrinsic and extrinsic parameters affecting tack using a viscoelastic modeling approach.³⁻⁶ In contrast to the traditional thermoanalytical measurements, the tack test developed is capable of measuring bulk, but surface-sensitive, prepreg properties.

Accordingly, in this study the tack of a commercially available carbon fiber/epoxy prepreg system was examined as a function of temperature with samples naturally aged at ambient conditions, as well as at elevated temperatures and moisture levels. In addition, by characterizing the prepreg with

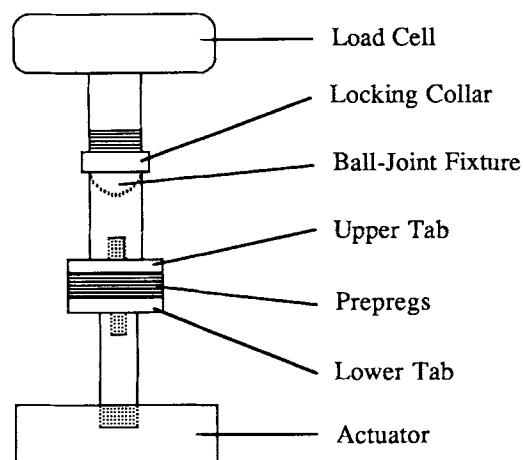


Figure 1 Schematic diagram of the experimental prepreg tack test setup.⁵

standard thermoanalytical techniques a relation between prepreg tack and aging characteristics as viewed from the exhibited glass transition was investigated.

EXPERIMENTAL

A commercially available prepreg system, Hercules 3501-6, was used in this study. This is a carbon-fiber-reinforced epoxy system of tetraglycidyl 4,4'-diaminodiphenylmethane (TGDDM) and 4,4'-diaminodiphenylsulfone (DDS) nominally with a 1.1% boron trifluoride (BF₃) catalyst.¹⁵ The resin content is approximately 42% by weight, while the heat of reaction is 474 J/g for the neat resin, or 197 J/g for the prepreg.⁹ The prepreg samples were prepared to simulate conditions usually met during the prepreg storage. Sample A was a fresh prepreg, sample B was kept at 0°F (-18°C) for 46 months, and sample C was kept at 0°F (-18°C) for 46 months and followed by curing at 75°C for 3 h. More details of aging conditions and glass transition temperatures are summarized in Table I.

Tack tests were performed using an Instron 1350 servo hydraulic mechanical testing machine interfaced to an Instron 2150 controller and an IBM computer. The experimental set-up used to measure prepreg tack is similar to a flat-wise tension/compression fixture, as shown in Figure 1. Five prepreg plies were stacked and compressed together at a specific load and time and then pulled out at a specific loading rate. Prepreg tack, calculated as an energy of separation, was measured in a wide range of temperature, $0 < T < 70^{\circ}\text{C}$, using an environmental chamber interfaced to a liquid nitrogen tank.

Table I Aging Conditions and Glass Transition Temperatures of the Prepreg Samples Examined in This Study

Sample	Aging Condition	T_g (°C) ^a
A	6 months at 0°F (-18°C)	5
B	46 months at 0°F (-18°C)	13
C	46 months at 0°F (-18°C) followed by 3 h at 75°C	24

^a Measured by a DSC at a heating rate of 5°C/min.

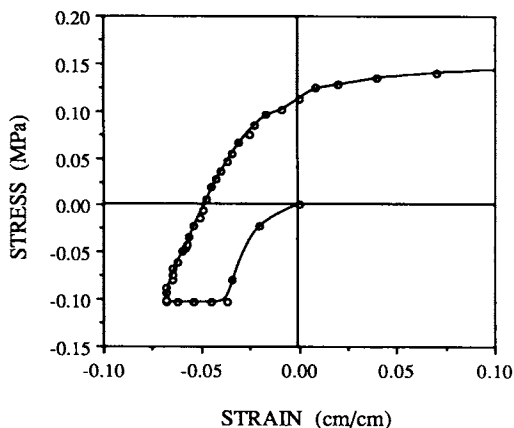


Figure 2 Typical stress-strain curve of the tack test.

A typical stress-strain curve of the tack test is shown in Figure 2. Details of the test procedure can be found in several references.³⁻⁶

Thermal analysis of unaged and aged prepreg samples were performed using both T. A. Instruments 912 differential scanning calorimetry (DSC) and a T. A. Instruments 982 dynamic mechanical analyzer (DMA) with a liquid nitrogen cooling accessory (LNCA), all interfaced to a T. A. Instruments 2000 Controller. Both glass transition tem-

perature (T_g) and degree of cure (α) were measured using DSC at a heating rate of $5^\circ\text{C}/\text{min}$. The glass transition temperature was measured as an onset point in the dynamic DSC scan (Fig. 3). For comparison, a DMA was also used to measure the glass transition temperature calculated from the exhibited maximum of loss modulus (E'') as a function of temperature plot (Fig. 4). DMA measurements were performed at a heating rate of $2^\circ\text{C}/\text{min}$ in resonance frequency with an amplitude of 0.4 mm using horizontal clamps.¹⁶

RESULTS AND DISCUSSION

Typical DSC and DMA results for sample B aged at 75°C for 2 d are shown in Figures 3 and 4, respectively. The glass transition temperature calculated from the maximum loss modulus (E'') as a function of temperature in the DMA plot was higher than that calculated from the onset point in DSC measurements. However, the glass transition temperature calculated from the onset point of storage modulus (E') in DMA measurements was comparable to that measured by DSC as expected for these systems.¹⁷ Accordingly, for all subsequent calcula-

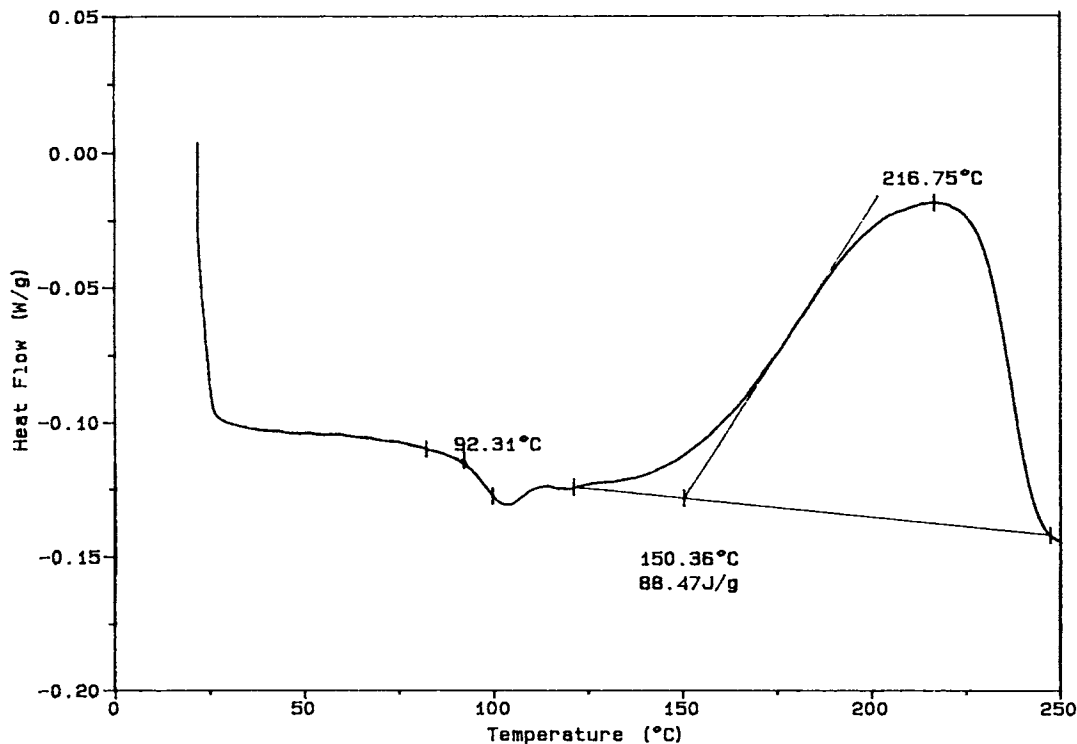


Figure 3 Dynamic DSC scan exhibiting the glass transition temperature (T_g) as well as the degree of cure (α) of sample B aged at 75°C for 2 d (heating rate = $5^\circ\text{C}/\text{min}$).

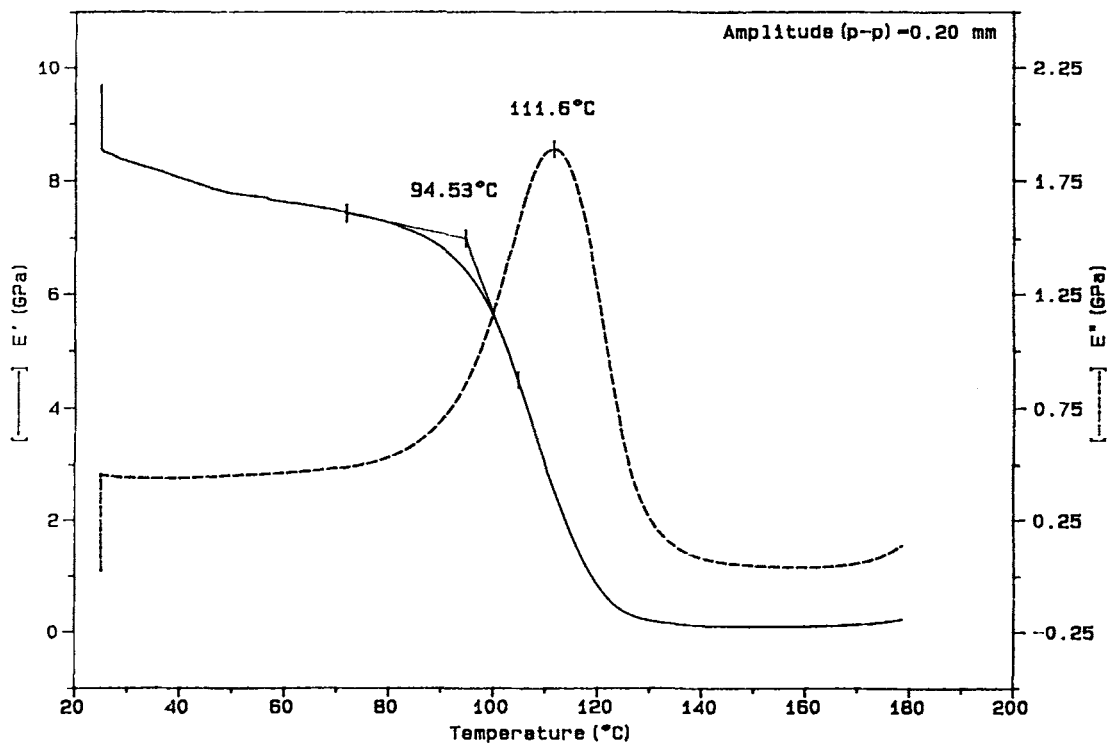


Figure 4 Dynamic DMA scan exhibiting the glass transition temperature (T_g) of sample B aged at 75°C for 2 d. (heating rate = 2°C/min).

tions, T_g was measured from the maximum loss modulus as a function of temperature in the DMA plot since it provided the most convenient experimental method.

The degree of cure (α) of the prepreg was calculated by measuring the residual heat of reaction as follows:

$$\alpha = \frac{\Delta H_{\text{fresh}} - \Delta H_{\text{aged}}}{\Delta H_{\text{fresh}}}, \quad (1)$$

where ΔH_{fresh} and ΔH_{aged} are the heat of reactions of fresh and aged samples, respectively. For fresh Hercules 3501-6 prepreg, the heat of reaction has been determined at 470 J/g based on neat resin and/or 197 J/g based on prepreg.⁹ As shown in Figure 5(a), prepreg sample B, which had been kept at 0°F (-18°C) for 46 months, was already "aged" with a heat of reaction of 175 J/g, which corresponds to $\alpha = 0.11$. The DSC thermograms depicted in Figure 5 show the effect of aging at 75°C for sample B. As aging time increased, the glass transition temperature increased and the heat of reaction decreased. In addition, the reaction peak temperature also increased with increasing aging times.

The changes of conversion (α) as a function of

aging (or curing) time at ambient ($T = 25^\circ\text{C}$) and elevated ($T = 75^\circ\text{C}$) temperatures are shown in Figure 6 for sample B. For a reasonably long period of time (800 h), an isothermal kinetic study at low temperatures showed maximum conversions of the resin matrix (α_m), which increased with increasing cure temperatures. However, the maximum conversion values for both 25 and 75°C did not approach completion. Similar observations have been reported for the DGEBA epoxy^{10,11} and unsaturated polyester resins.^{18,19} This may be attributed to the fact that vitrification takes place before gelation when the cure or aging temperature is lower than the material's glass transition temperature at the gel point, which usually occurs at a constant level of conversion.¹² Accordingly, the traditional autocatalytic reaction equation may not be applicable at low temperatures. Nicolais et al. proposed a modified semi-empirical kinetic equation accounting for diffusion-controlled effects as follows¹⁹:

$$d\alpha/dt = k(\alpha_m - \alpha)^a \alpha^b, \quad (2)$$

where k is the rate constant of reaction depending on temperature, while a and b are exponents relating to reaction orders. Theoretically, this equation can

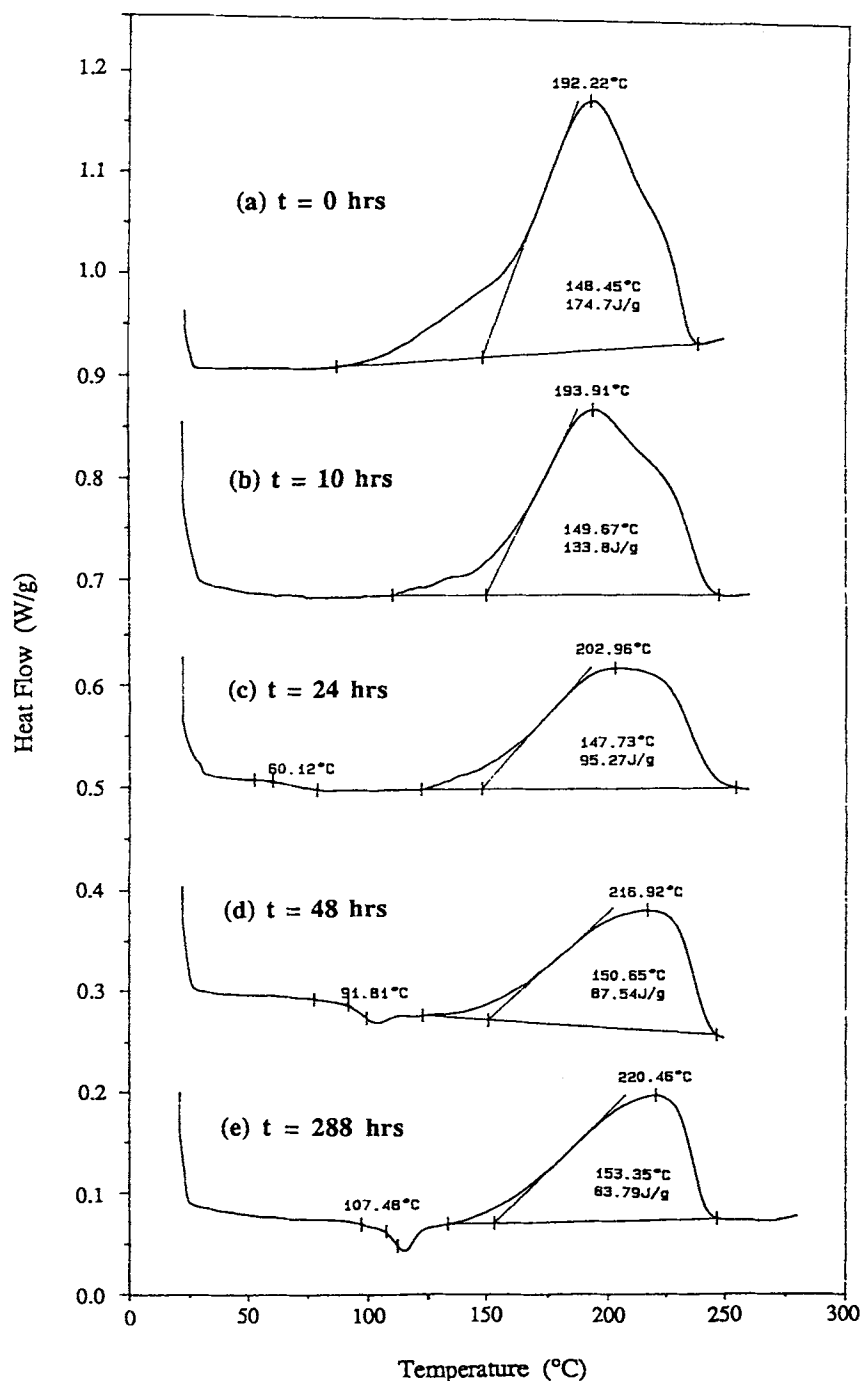


Figure 5 Dynamic DSC scans showing the effects of aging time at 75°C on the glass transition temperature (T_g) as well as the heat of reaction of sample B (heating rate = 5°C/min).

describe the experimental observation that the reaction rate becomes zero when the degree of cure approaches an equilibrium value (α_m).

Glass transition temperatures (T_g) measured by the maximum loss modulus as a function of temperature in the DMA plot are plotted as a function

of conversion (α) in Figure 7. Regardless of aging temperatures, a linear relationship between glass transition temperature and conversion was observed. The glass transition temperatures at the equilibrium state were higher than the isothermal aging (or cure) temperatures by 20–25°C. This may be partially at-

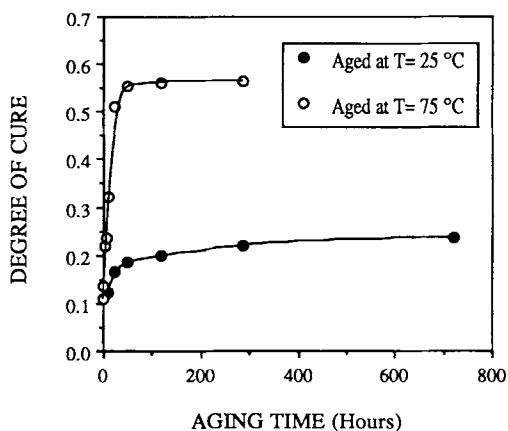


Figure 6 Degree of cure (α) as a function of aging time for sample B aged at different temperatures.

tributed to dynamic measurements of glass transition temperatures in a DSC and/or evaporation of the absorbed water in an epoxy resin during the measurements.

Energy of separation, which may be viewed as a measure of prepreg tack, was measured from the stress-strain curve of the tack test as shown in Figure 2.³⁻⁶ The 90% of maximum stress ($\sigma_{90\%}$) was used instead of maximum stress (σ_{max}) to calculate energy of separation due to data scatter attributed to instrument control. Thus, the following expression was utilized^{5,6}:

$$\text{energy of separation} = \int_{\epsilon_{0\%}}^{\epsilon_{90\%}} \sigma d\epsilon, \quad (3)$$

where $\epsilon_{0\%}$ and $\epsilon_{90\%}$ are strain values corresponding to zero stress and $\sigma_{90\%}$, respectively. In Figure 8, the

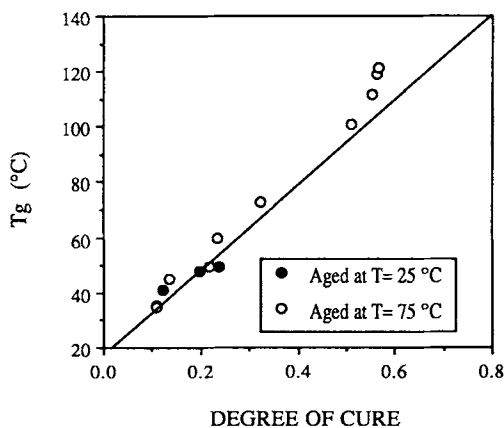


Figure 7 Glass transition temperatures (T_g) as a function of degree of cure (α) for sample B aged at different temperatures.

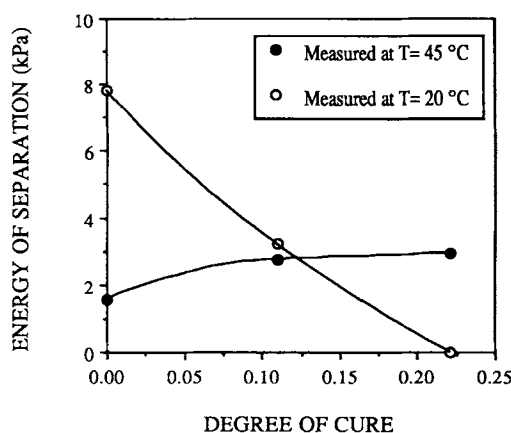


Figure 8 Energy of separation as a function of degree of cure (α) for sample A measured at different temperatures.

energy of separation is plotted as a function of conversion (α) for sample A. As seen in the figure, the prepreg tack was dramatically changed with conversion depending on the temperature at which tack measurements were made. At a low temperature ($T = 20^\circ\text{C}$), the prepreg tack decreased with increasing conversions of resin matrix, while the opposite results were observed at a high temperature ($T = 45^\circ\text{C}$). These observations imply that the prepreg tack does not only correspond to the chemorheological behavior of the resin matrix, but is also influenced by all components of the system including the fiber. Therefore, it should be viewed as a truly viscoelastic phenomenon.^{5,6}

Energy of separation measured through a wide temperature spectrum is shown in Figure 9. The energy of separation dramatically decreased for the

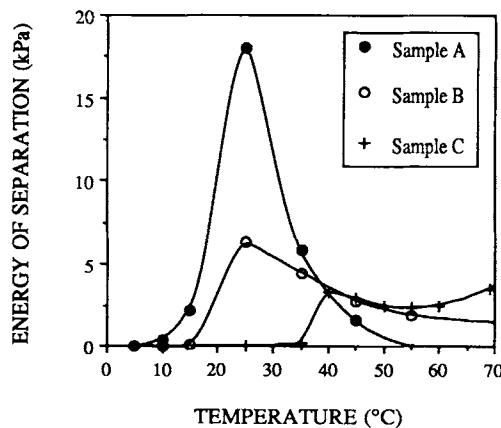


Figure 9 Energy of separation measured at different temperatures for the prepreg samples aged at different conditions.

aged prepregs such as samples B and C. However, all the prepreg samples showed a maximum energy of separation at specific temperatures. Below these temperatures, energy of separation increased with increasing temperatures, which was attributed to an increase in contact (or wetting) area. In this temperature range, energy of separation may be controlled by transient prepreg behavior attributed to wetting and/or resin matrix flow.^{5,6} At high temperatures, wetting takes place instantaneously because of low resin matrix viscosity, while the mechanical properties of the resin matrix, such as modulus, decreases with increasing temperatures. Accordingly, tack is mainly controlled by resin mechanical properties at high temperatures.^{5,6} In Figure 8, the decrease of energy of separation with aging times (or conversions) measured at low temperature (20°C) was therefore attributed to a decrease in contact (or wetting) area due to aging. On the other hand, a small increase of energy of separation with aging times measured at high temperature (45°C) was attributed to an increase in the mechanical properties of the resin matrix resulting from advancement of cure.

The temperature, at which maximum energy of separation was observed, was influenced by the conditions at which samples were exposed to. In general, the temperature corresponding to maximum energy of separation increased with aging time (or conversion). Plotting the energy of separation as a function of $(T - T_g)$, the maximum energy of separation was observed in the temperature range between 10–20°C above glass transition temperatures, i.e., $10^\circ\text{C} < (T - T_g) < 20^\circ\text{C}$, as shown in Figure 10. However, the maximum energy of separation values decreased with aging, e.g., 16 kPa for sample A, 7 kPa for sample B, and 3 kPa for sample C. These observations imply that prepreg tack is a viscoelastic property rather than a viscous property of the resin matrix in a prepreg, as has been previously assumed. The prepreg tack can only be explained by phenomena attributed to chemorheological, mechanical, and surface characteristics of the prepreg.^{5,6}

Conclusively, aging may reduce or enhance prepreg tack depending on both material conditions before aging and operating conditions at which the prepreg lay-up is made. Commercially available thermosetting prepregs generally show maximum tack values around room temperature before aging so that aging reduces the prepreg tack due to the increase of resin viscosity, as well as the changes of prepreg surface characteristics caused by resin migration.⁵ However, the effect of prepreg aging on composite manufacturing is still not clearly under-

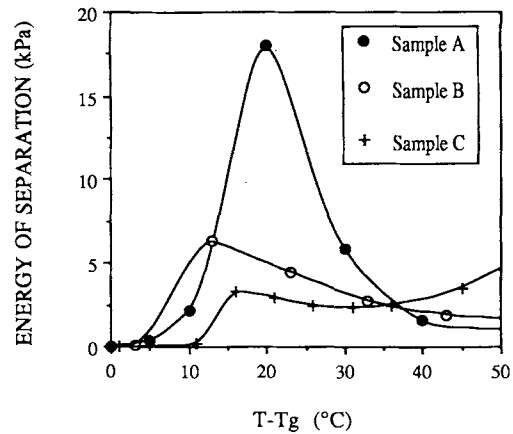


Figure 10 Energy of separation plotted as a function of $(T - T_g)$ for the prepreg samples aged at different conditions.

stood. In addition to deteriorating the prepreg tack, aging may also produce undesirable resin-rich areas in a cured laminate due to reduced resin flow. On the other hand, Campbell et al. reported that aged Hercules 3501-6 prepregs slightly increased the glass transition temperature of a cured laminate, which could be due to reactions that may have occurred during the aging period.¹⁵ Furthermore, the aged prepreg may result in production of void-free laminates by reducing the interlaminar closed pores, which are one of the sources of producing voids in a cured laminate.^{15,20} Accordingly, these conflicting observations that have been encountered in composite manufacturing can now begin to be evaluated in view of the findings in this work.

CONCLUSION

Thermoanalytical measurements and tack tests were performed using a commercially available carbon fiber/epoxy prepreg system (Hercules 3501-6) to examine changes caused by aging as they affect handling and processability of thermosetting matrix-based composites.

Isothermal aging studies at low temperatures showed maximum conversions (α_m) that increased with increasing cure temperatures. However, the maximum conversion values for both 25 and 75°C did not approach completion. This may be attributed to the fact that vitrification takes place before gelation when the cure or aging temperature is lower than the material's glass transition temperature at the gel point, which usually occurs at a constant level of conversion. A linear relationship between

glass transition temperatures (T_g) and conversions (α) was observed regardless of aging (or cure) temperatures.

Energy of separation of a prepreg stack, which may be viewed as a measure of prepreg tack, showed a maximum value at a specific temperature. At low temperatures, energy of separation increased with increasing temperatures, which was attributed to an increase in contact (or wetting) area. On the other hand, at high temperatures energy of separation decreased with increasing temperatures, which was attributed to a decrease in the mechanical properties of the resin matrix with increasing temperature. The maximum energy of separation was observed in the temperature range between 20–25°C above glass transition temperatures. However, the maximum energy of separation values decreased with increasing aging times (or conversion). These observations implied that the prepreg tack was a viscoelastic property rather than a viscous property of the resin matrix in a prepreg.

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