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PILOT PREPREG LINE: A COMPREHENSIVE ANALYSIS OF PREPREG QUALITY

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ABSTRACT

A pilot prepreg line was used to produce an S2 glass epoxy/anhydride prepreg. It was found that the pilot line produced high quality unidirectional glass epoxy tape. The prepreg was evaluated from three standpoints; processing, chemistry, and material properties. Both fiber- and matrix-dominated material properties compared favorably with structural S2 glass epoxy laminate data found in published literature. The prepreg line metering and mixing system yielded a consistently well mixed and metered resin. Close attention to collimation of the fiber tows was found to be essential to maintaining tape quality. The prepreg was B-staged at room temperature and this reaction was found to be governed by first order kinetics. The service temperature of the cured laminate was typically found to be about 100°C, but was highly sensitive to the presence of moisture in the B-staging environment.

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INTRODUCTION

Background

Ongoing polymer composite research and development (R&D) programs at the U.S. Army Materials Technology Laboratory (MTL) require the use of prepregs with custom fiber and matrix combinations. Developmental work to improve a pilot prepreg line was carried out at MTL and has been completed.* Fundamentals of the art and science of prepregging were established as a result of this work.

MTL has begun operating the pilot prepreg line for use in supporting R&D programs where custom prepregs are needed. The addition of this equipment has expedited the R&D process for engineers and scientists while giving them a wide degree of flexibility and control over the final product. In addition, the cost of in-house prepreg is substantially lower in most cases.

Objective

The purpose of this study was to thoroughly evaluate S2 glass epoxy prepreg made on the pilot line from chemical, mechanical, and processing standpoints. A comprehensive judgement of the pilot line performance as reliable support equipment for ongoing and future MTL programs is made.

EXPERIMENTAL

Prepregging Equipment

The prepreg tape evaluated in this study was fabricated in-house on the MTL pilot prepreg line. Properties were compared to those of similar composites found in published literature. This was done as a means of quantitatively judging the quality of the in-house product. Figures 1a and 1b show a schematic of the prepreg line and a photo of the actual equipment.

Prepreg fabrication is a new technology area at MTL. A simple resin and fiber system was initially selected to avoid processing problems. The raw starting materials were S2 glass 1510 m/kg (750 yd/lb) roving treated with an epoxy compatible sizing agent (Owens Corning Fiberglass Company); diglycidyl ether of bisphenol A (DGEBA) type epoxy resin, Epon 828 (Shell Chemical Company); and anhydride curing agent, methyl tetrahydrophthalic anhydride (MTHPA, Anhydrides and Chemicals, Inc.); and an accelerator, benzyldimethyl amine (BDMA, Allied Resin). All materials were used as received. The three resin components were mixed in a ratio of 100:80:1 by weight, respectively.

Prior to a production run, the MTHPA and BDMA were premixed by hand. During the run the prepreg line computer-controlled metering system mixed the epoxy with the MTHPA/BDMA premix in the ratio of 100:81 by weight. High metering accuracy of the two liquid streams was achieved by a programmable microprocessor that controlled two digital stepping motors which each drive a high quality gear metering pump. The two streams combine in a heated static mixer at a point where a 20-inch long series of static mixing elements begins. The resin components were mixed under a head pressure which varied between 69 KPa and 140 KPa (10 psi and 20 psi) during the production run.

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*S. R. Ghiorse, MTL Technical Note (in publication).

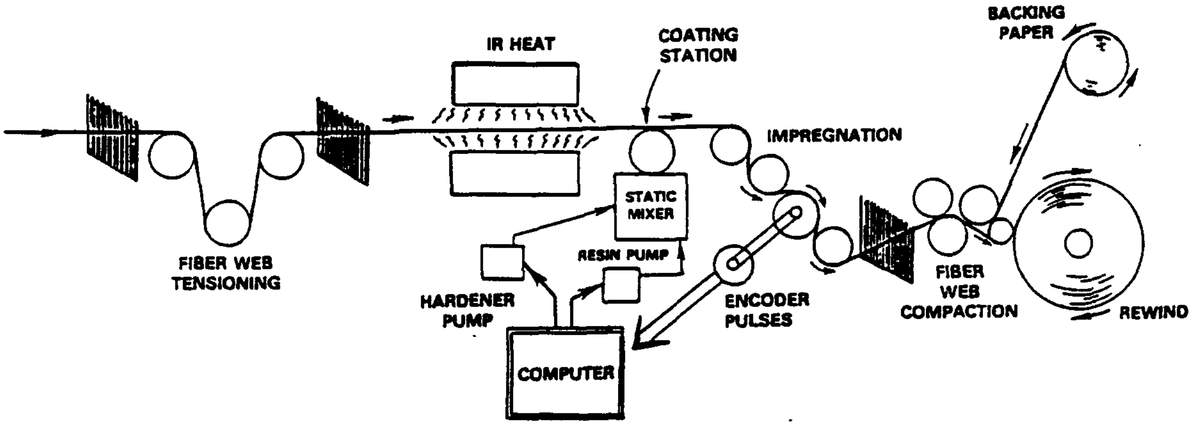

Figure 1a. Schematic diagram of the MTL pilot prepreg line.

Figure 1b. Photograph depicting actual MTL pilot prepreg line equipment.

The mixed and warmed resin system next entered a coating station and was coated onto 72 S2 glass rovings in a ratio of 1:1 by volume. This ratio of fiber to resin was also controlled by the prepreg line computer.

The fiber web was then preheated by an infrared element located immediately prior to the coating station. Preheating both fiber and resin is important as this keeps the resin viscosity down. This results in superior wet-out and thorough impregnation of the fiber tows, with the additional function of removal of surface moisture present within the roving bundle. The tows were drawn over fluted drillings located at the top of the coating station; three tows were passed over each dispensing port. The resin was then impregnated throughout the fiber by heated impregnating rollers which work the resin into the fiber tows by passing the wetted tows through a series of four rollers with tight clearance nipping gaps. The impregnating rollers also serve to begin spreading the fiber tows into their final flat ribbon geometry.

Next, the impregnated tows pass through a final collimation and compaction stage. The collimating comb was set at a spacing of 5.5 ends/cm for this study. When 1510 m/kg yield S2 glass is spaced at 5.5 ends/cm, the resulting areal fiber weight is 372 g/m^2. Immediately following alignment, the coated fibers pass through three compacting rollers. The product emerges as a 13 cm wide flat, impregnated tape and is rewound onto the take-up reel with siliconized backing paper.

The final step is to advance the A-stage resin to B-stage. This was done by simply sealing the spool in an airtight bag and letting it sit at room temperature for six to seven days.[1] The prepreg was then stored in a freezer at -20°C for subsequent hand layup of test laminates.

Laminate Fabrication

The procedure for laying up the in-house prepreg was similar to that for any common commercial epoxy prepreg. Two preforms were vacuum-bagged and cured together in an autoclave under 620 KPa (90 psig) according to the cure cycle shown in Figure 2. However, an in-house study of the epoxy/anhydride resin system showed that special care is needed because of the resin sensitivity to moisture.[1,2] In addition, since the pilot line was not equipped with an edge trimming system, individual pieces of prepreg were slit by hand with a straight edge and razor blade prior to layup to get clean butting edges.

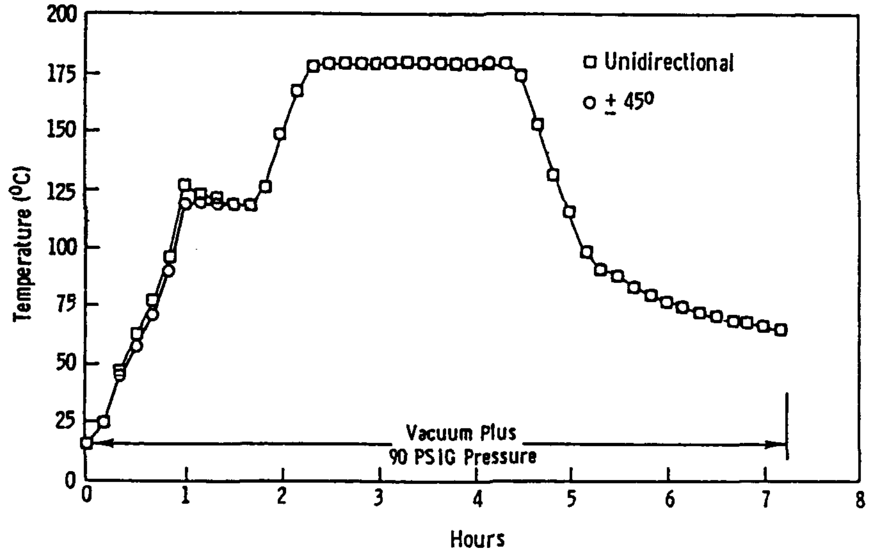

Figure 2. Epoxy/anhydride cure cycle used to process the prepreg into composite laminates.

Two laminated plates were made from the B-staged prepreg; a six-ply unidirectional laminate (0_6), and an eight-ply laminate with ±45° orientation $(\pm 45_{2s})$. The prepreg was laid up on 46 cm x 46 cm aluminum caul plates covered with a high temperature halogen release film. Interior butting edges of the prepreg were staggered apart to minimize weakness associated with their stacking. At the outset of this work, the extent of the viscosity drop of the B-staged resin during the autoclave cycle was unknown. It was empirically determined that

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[1] ZUKAS, W. X., and GHIORSE, S. R. *Room Temperature Staging of Epoxy/Anhydride Resin Formulations*. Proc. of SPE 47th ANTEC, May 1989, p. 1083.

[2] ZUKAS, W. X., and GHIORSE, S. R. *Staging of Epoxy/Anhydride Formulations*. ACS Polymer Reprints, v. 31, no. 1, 1990, p. 265.

the viscosity remained high enough for processing at 620 KPa. Excessive bleeding did not occur.

Resin and Laminate Testing

Table 1 lists the tests which were run on the prepreg and fabricated laminates.

Table 1. TEST MATRIX USED TO STUDY THE PREPREG AND LAMINATES

	Chemical/Material Test	Test Objective	Mechanical Test	Test Objective
Uncured Epoxy/Anhydride ResinSystem	Differential scanning calorimetry	Determine extent of cure and glass transition temperatures		
	Torsional braid analysis	Determine galation and vitrification times		
	High performance liquid chromatography	Quantify individual chemical species in reacting mixture		
	Fourier transform infrared spectroscopy	Quantify chemical functional groups		
Cured Laminate	Fiber burnout (ASTM D 2584)	Determine fiber volume fraction and variation	0° Tension (30 cm streamline)	Check fiber collimation (E_{11}) and strength (S_{11})
	Differential scanning calorimetry	Check on proper cure and service temperature	±45° Tension (30 cm streamline)	Check for proper impregnation (fiber/matrix interfacial bond); measure shear modulus G_{12}
	Optical microscopy	Determine void volume fraction	90° Tension (ASTM D 3039)	Check for proper impregnation (fiber/matrix interfacial bond); measure transverse strength and modulus (S_{22} and E_{22})
			Short beam shear (ASTM D 695)	Check for proper impregnation (interlaminar shear strength)
			Torsional pendulum (ASTM D 2236)	Check on proper cure and service temperature

Chemical/Material Testing

Since the treatment of the resin system in this work during B-staging varied from standard practice, chemical tests were run to analyze and monitor the resin formulations. The formulations used in chemical analysis consisted of Epon 826* and Epon 828 with MTHPA and BDMA. All materials were used as received. The formulations were mixed in the same weight ratio as the processed resin; i.e., 100:80:1.

*Epon 826 is quite similar to Epon 828. For reasons of availability, it was used in parts of the chemical analysis.

Differential scanning calorimetry (DSC) was used to assess the extent of cure, thermal behavior, and the effect of moisture on the uncured and cured resin systems. DSC was carried out under nitrogen on a Perkin-Elmer DSC-2 equipped with an intercooler. DSC specimens were prepared while the resin was liquid. Room temperature (20°C) B-staging of these samples was carried out under four conditions:

- Sealed DSC pans
- DSC pans open to air dry (0% R.H.)
- DSC pans open to controlled laboratory air (50% R.H.)
- DSC pans open to wet air (100% R.H.)

Open pans were sealed just prior to scanning. All samples were scanned first at either 10°C/min or 1.25°C/min from 300°K to 500°K, cooled to 300°K at 80°C/min, then heated to 500°K at 10°C/min. The initial heating ramp was used to determine the residual heat of reaction after a specific room temperature B-staging time. The second heating ramp was used to determine the T_g of the cured material.

Torsional braid analysis (TBA) was carried out on an automated TBA system (Plastics Analysis Instruments, Inc.). A glass braid would be wetted with the resin formulation and introduced into the sample chamber where the relative rigidity and log decrement were monitored as a function of B-staging time at 26°C under helium. The sample was then cooled to 0°C and scanned at 3°C/min to 200°C and back to 0°C. The heating scan was utilized to measure the T_g of the B-staged material and the cooling scan was used to measure the T_g of the cured material.

Reverse-phase high performance liquid chromatography (HPLC) was run using a Waters Associates Model ALC/GPC 244 chromatograph with autoinjector and a Perkin-Elmer LC75 UV detector at 214 nm. Samples of the 828 formulation were B-staged in sealed DSC pans then opened and immediately dissolved in acetonitrile for analysis using an acetonitrile/water mobile phase. Peaks associated with the epoxy and anhydride moieties were monitored as a function of B-staging time.

Fourier transform infrared (FTIR) spectra were obtained on a Perkin-Elmer 1550 FTIR spectrometer equipped with a 7500 series data station. Sixty-four scans at a resolution of 4 cm^{-1} were made on cryogenically milled samples in KBr pellets.

Fiber volume fraction was determined in accordance with ASTM D 2584 (fiber burnout). Optical microscopy was used for void volume fraction determination.

Quasi-Static Mechanical Testing

ASTM test methods were used as a reference for all mechanical testing. Quasi-static mechanical tests were run on an Instron Model 1331 servohydraulic test system. The load was transmitted to the specimens by means of constant pressure hydraulic grips which were adjusted according to the layup of the specimen under investigation. The testing speed used on all specimens was 0.13 cm/min.

For testing 0^{o} and $\pm 45^{o}$ stacking sequences a 30 cm "streamline" specimen was used.[3] A 30 cm x 2.5 cm wide strip was used for testing 90^{o} specimens in accordance with ASTM D 3039. Short beam shear tests were performed in accordance with ASTM D 695. A minimum of five specimens were used for each of these tests. The tests were run under the ASTM standard conditions for temperature (22^{o}C), relative humidity (50%), and preconditioning time under these environmental conditions. Specimen strain values were measured by either strain gauge or extensometer. Modulus values were calculated by linear regression to 0.1% strain.

Shear properties were obtained using the $\pm 45^{o}$ coupon under tension. For this test, the shear stress is half the normal stress and shear strain is obtained by addition of the normal and transverse strains.[4]

Dynamic Mechanical Testing

Dynamic mechanical testing (ASTM D 2236) of the laminates was carried out using an automated version of a Vermont Instruments Company torsional pendulum. Design retrofits for automation, as well as the software, were constructed and written at MTL.* Glass transition temperatures and shear storage moduli of cured laminate specimens were obtained. The specimens were 0.89 cm x 6.3 cm with a 3.8 cm gauge length. The pendulum oven chamber was ramped at 1.0^{o}C/min. Automated excitation and data acquisition of the pendulum were simultaneously controlled by an IBM PC/AT via a Keithly Series 500 I/O system. This system drove a digitally compatible clamping and twisting device, while simultaneously logging the temperature and the damped sine wave signal from the pendulum transducer. The software was written to take data points at 60 second intervals in the plateau regions of the curves and at 30 second intervals in the T_g region. The data sets were stored to disk and reduced by the computer after the run was completed.

RESULTS AND DISCUSSION

Prepreg Processing

Fiber wandering was found to be a problem. A tow aligned by a guide comb would wander out of place unless it was soon attended to by another comb. Fiber wandering caused problems at the two locations along the prepreg line shown in Figure 3. Upon leaving the creel and passing through the tensioning rollers (Region A) cumulative slacking occurred in several tows. It was observed that slightly misaligned tows would accumulate slack. To correct this problem, combs were placed immediately before and after the tensioning rollers. This arrangement ensured all tows were parallel and passed through the tensioning rollers with the same path length, eliminating the slacking problem.

Fiber wandering was also a problem during the final rewind (Region B). Without an alignment comb near the take-up reel, the final tape would be of poor quality with many fiber crossovers and gaps. By placing a comb immediately before the compaction rollers the wet fibers were

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*L. L. Ghiorse, MTL Technical Note (in publication).

[3] OPLINGER, D. W., PARKER, B. S., GHANDI, K. R., LAMOTHE, R., and FOLEY, G. *On the Streamline Specimen for Tension Testing of Composite Materials.* Advances in Composites in the United States and Japan, ASTM STP 864, J. R. Vinson and M. Taya, Eds., American Society for Testing and Materials, Philadelphia, 1985, p. 532.

[4] HAHN, H. T. *A Note on Determination of the Shear Stress-Strain Response of Unidirectional Composites.* J. Comp. Mats., v. 7, July 1973, p. 383.

laid accurately into position onto the rollers and the frictional viscous forces of the resin held the fibers in place. The fibers were kept in constant contact with roller surfaces all the way onto the take-up real. This resulted in uniform lay-down of the A-staged web onto the backing paper. The comb placements described resulted in consistent and problem free fiber paythrough and a well collimated final tape.

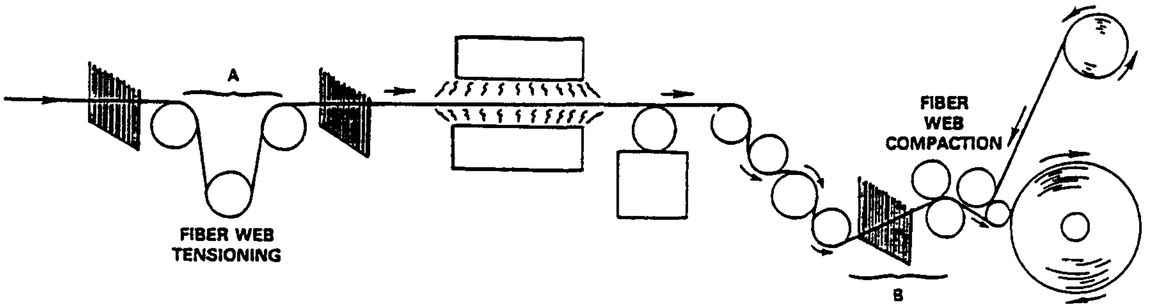

Figure 3. Problem areas where fiber wandering occurred during prepreg processing.

The coating station (see Figure 1) coated the resin system across the 13 cm width of the fiber web. The one-sided entry of the resin, however, did visibly show a larger percentage of resin being dispensed on the inlet side of the coater. A bead of excess resin tapered down across the inlet side between the first and second roller nip gap and, to a lesser extent, between the third and fourth roller nip gap. The same distribution pattern of excess resin appeared again at the first compaction roller nip gap, verifying that the fibers were exiting the impregnation zone with the resin nonuniformly dispensed across the fiber web. At the compacting rollers an adjustment is available which allows the operator to nip down more closely on the excess side forcing the resin bead to spread uniformly across the nip gap. It is assumed that some residual excess resin remained along the inlet side of the final prepreg tape. Randomization of ply layup, resin flow on heating, and application of pressure in the autoclave all acted to further reduce this resin nonuniformity. The fiber-to-resin ratio was sampled in the cured laminate at various locations (away from bled edges) to check for variation in the fiber volume fraction. The results shown in Table 2 indicate no abnormal variation.

Table 2. VARIATION OF FIBER VOLUME FRACTION IN THE CURED LAMINATES

Specimen Count	Fiber Volume Fraction* (% ± σ)
11	54.0 ± 2.8

*Zero void volume fraction determined by optical microscopy.

Impregnation of the fiber tows was found to be complete. Representative micrographs of polished cross sections (see Figure 4) of the cured laminates show the porosity level to be nearly zero. This finding is supported by the resin-dominated mechanical test data shown in Tables 4 and 5 (transverse tension, 45° tension, and interlaminar shear) in which the presence of voids is known to dramatically reduce ultimate strengths, as documented by Judd and

Wright and Yakota.[5,6] Although the coating station design could be improved, the process in place yielded a consistent fiber content in the final product.

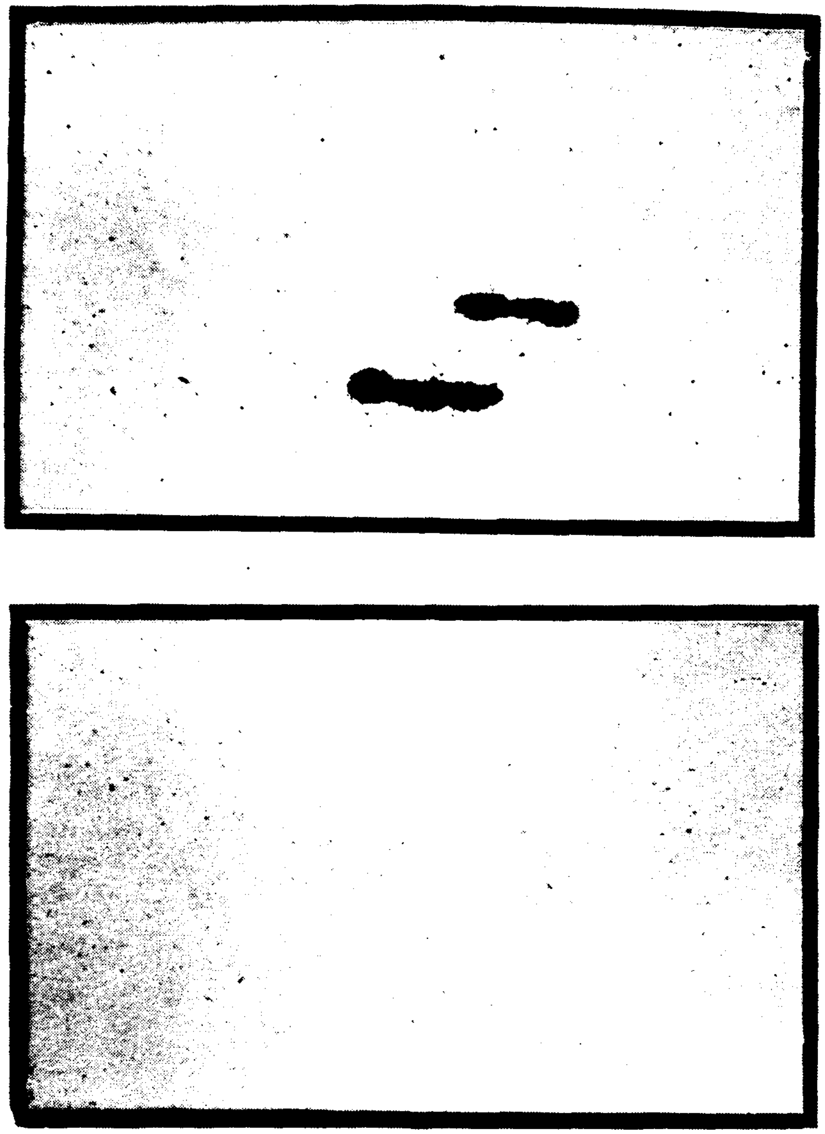

Figure 4. Representative micrographs of the cured laminate cross section, Mag. 50X. Porosity was nearly zero.

The computer-controlled mixing system was tested for consistency using HPLC. Samples of resin were taken during the beginning, middle, and end of each run and HPLC used to determine the ratio of Epon 828 to the remainder of the resin system. The 100:81 ratio is 55.2% when expressed in terms of volume fraction percent of 828. The measuring and mixing system produced resin mixtures which varied within ±2.5% of the programmed 55.2% mixing ratio. It was observed that the hardener pump consistently delivered slightly less

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5. JUDD, N. C. W., and WRIGHT, W. W. *Voids and Their Effects on the Mechanical Properties of Composites - An Appraisal.* SAMPE Journal, January 1978.
6. YOKOTA, M. J. *In Process Controlled Curing of Resin Matrix Composites.* SAMPE Journal, v. 14, no. 11, July/August 1978.

volume than it was programmed to pump. This is attributed to the low 30 cps viscosity of the MTHPA/BDMA premix. At this viscosity the mixer head pressure creates a back pressure across the pump of 69 KPa to 137 KPa (the pump inlet pressure was zero as the hardener was siphoned from a container) and subsequent slight leakage of the hardener backward through the hardener pump.

B-Stage Processing

As a first approach to obtaining proper tack for hand layup, the resin was advanced to B-stage by simply sealing the A-staged spool in an airtight bag and letting it advance for six to seven days at room temperature (approximately 20°C).[1] Tack was periodically checked by opening the bag and qualitatively judging when the prepreg was suitable for hand layup. Unlike most commercial prepregs, this resin system was not formulated for long out times (see Figure 5). Once the B-stage roll was brought to room temperature, only four to five additional days were available to process the prepreg. Beyond this time the prepreg became too advanced, was too boardy to handle, and its flow in the autoclave restricted. This method of B-staging was easily implemented and was used throughout this study. Extrapolation of the data obtained by TBA and DSC indicates an approximate shelf life of about one year for the A-staged formulation at -20°C.

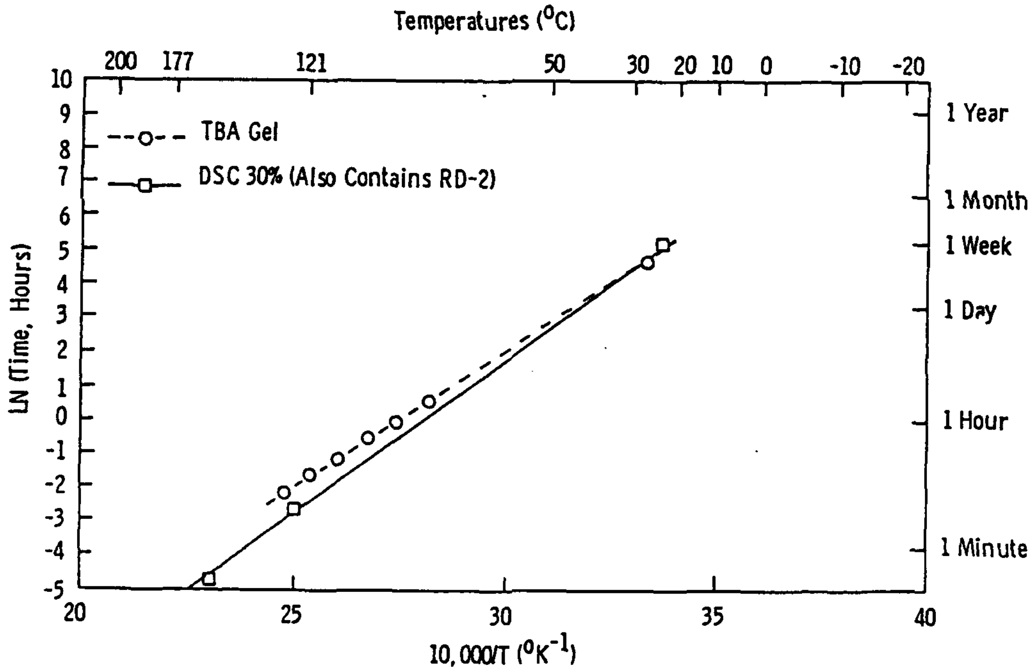

Figure 5. TBA and DSC gel curves indicating out-time and shelf life of the epoxy/anhydride formulation. The shelf life is extrapolated from the data.

B-Stage Chemistry

The extent of reaction by DSC is assumed to be proportional to the fraction of the total heat of reaction evolved. Previous work on similar formulations had shown the total heat of reaction to be a function of heating rate.[7] Fava also observed a decrease in heat of reaction for another anhydride-cured resin with increasing heating rate.[8] Although obtaining an accurate value for the total heat of reaction was questionable, the values obtained from a selected heating rate reflect the relative amount of reaction remaining. B-staging of the DSC samples in this study was initially carried out using samples sealed immediately after preparation followed by the residual heat of reaction determination at 10°C/min.

First order kinetics have shown to describe the reaction mechanism for tertiary amine catalyzed epoxy/anhydride cure at elevated temperatures.[7,9] This implies that the logarithm of the residual heat of reaction versus time should yield a linear plot if both first order kinetics apply and the residual heat is proportional to the extent of reaction. This type of plot is shown in Figure 6 for the 828 formulation B-staged at 20°C. Linear regression was carried out for this plot of the natural logarithm of the residual heat of reaction versus time. Linear relationships for the first week of room temperature B-staging were thus established for the variations in residual heat of reaction with time.

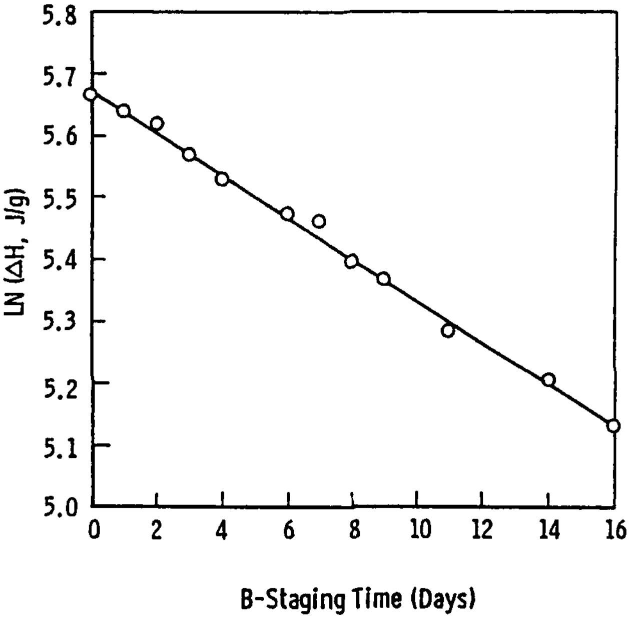

Figure 6. Natural logarithm of the heat of reaction versus B-staging time for the epoxy/anhydride formulation at 20°C.

A second DSC heating scan of the same sample, after the initial 10°C/min scan, showed an increasing T_g with the B-staging time (see Figure 7). The initial T_g of 75°C to 80°C for both resin formulations with no B-staging time increased to 100°C to 105°C after two weeks of room temperature B-staging with slightly higher values obtained for the 828 formulation. A series of samples of the 826 formulation were scanned at 1.25°C/min after various B-staging times, and only slightly higher values for residual heat of reaction were obtained when compared to identical B-staging conditions followed by scanning at 10°C. However, the T_g values obtained on the second scan, after

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[7] ZUKAS, W. X., and TESSIER, N. *Thermal Analysis for Pultrusion Process Modelling.* Proc. 32nd SAMPE Symposium and Exhibition, v. 32, 1987, p. 1288.

[8] FAVA, R. A. *Differential Scanning Calorimetry of Epoxy Resins.* Polymer, v. 9, 1968, p. 137.

[9] PEYSER, P., and BASCOM, W. D. *Kinetics of Epoxy Resin Polymerization Using Differential Scanning Calorimetry.* J. Appl. Polym. Science, v. 21, 1977, p. 2359.

the 1.25°C/min scans, revealed a T_g of approximately 125°C, independent of B-staging time. The slower scan, or longer B-staging time, apparently allows a different reaction route to occur which leads to more cross-linking. The 1.25°C/min heating rate is approximately that seen during the autoclave cycle. HPLC revealed that the higher oligomers of the DGEBA resins would react faster with respect to the monomer under the room temperature B-staging conditions. The reactions involving the higher oligomers may account for the differences observed in the T_g's by DSC.

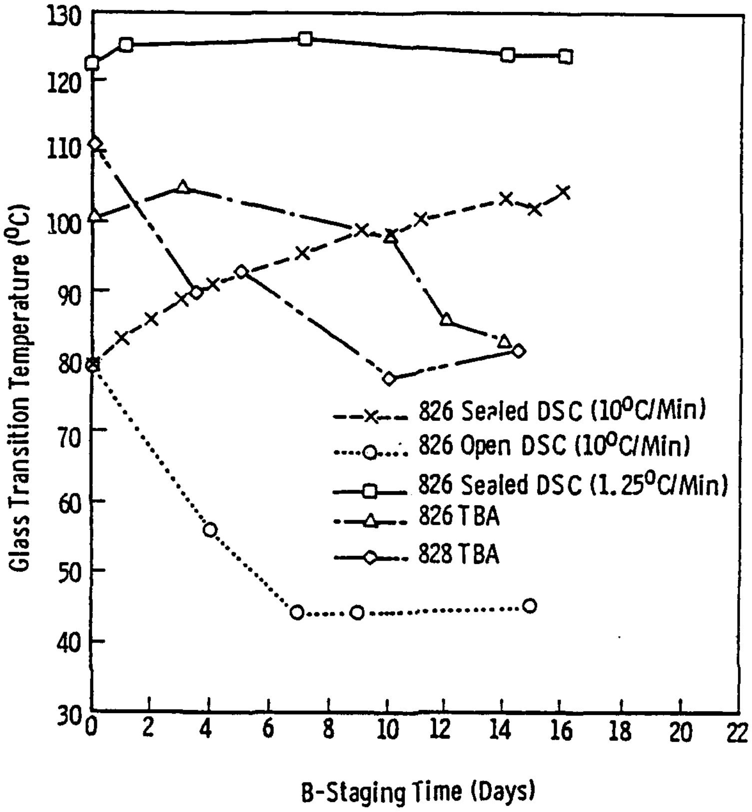


Figure 7. TBA and DSC glass transition temperatures versus B-staging time at 20°C.

Previous work on a similar resin formulation showed gelation by TBA for elevated temperature isothermal cures to occur very close to the conversion of the theoretical gel point of 58%.[7] A comparison of the DSC and TBA data in this study indicates that gelation is occurring at approximately 20% conversion. TBA was run at somewhat higher temperatures, but this would appear to account for no more than an additional 5% conversion at gelation. Also, TBA revealed a decreasing T_g with longer B-staging times, contrary to the DSC results. Unstaged resin led to T_g values of approximately 111°C and 101°C for the 828 and 826 formulations, respectively. These values decreased to approximately 80°C to 85°C for both resin formulations after two weeks of B-staging. The relative rigidity of the rubbery plateau also decreased as a function of the B-staging time. The difference between the two techniques is exposure to an open atmosphere. The DSC results were obtained to this point with hermetically sealed pans while the TBA samples were exposed to a flowing inert atmosphere.

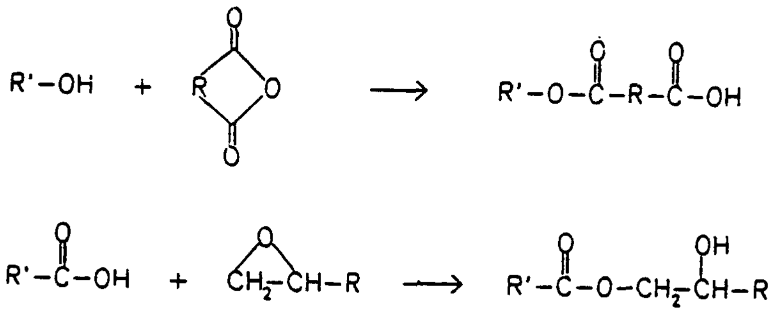
A series of DSC samples of the 826 formulation were then B-staged in DSC pans open to laboratory conditions and sealed immediately prior to scanning at 10°C/min. These samples showed a faster decrease in the residual heat of reaction values and a decrease in T_g to a value of approximately 45°C after just one week of B-staging. Neither a weight loss or gain was observed within the accuracy of the balance (0.5%) on the DSC open B-staged samples. Loss of BDMA or sorption of water was suspected as possible causes of the apparent change in mechanism for the open versus closed system experiments. The open system experiments led to a faster reaction, as evidenced by the lower residual heat of reaction and the sooner-than-expected gelation times. The same reactions also led to lower cured T_g's, as shown by both DSC and TBA.

Another series of DSC samples of the 826 formulation were B-staged for each of the conditions described earlier (sealed, air, dry, and wet B-staged). Values for residual heat of reaction, T_g, and % weight gain are listed in Table 3. The open and dry B-staged sample set showed only a slight decrease in weight and essentially the same decrease in residual heat of reaction and increase in T_g as the sealed set. The open air B-staged samples showed a slight increase in weight and slightly faster decrease in residual heat of reaction than the sealed set with a decrease in T_g with B-staging time as observed for the previously B-staged open to laboratory condition series. The greatest differences from the sealed set were observed for the open and wet B-staged samples. After only two days a lower residual heat of reaction was observed which did not decrease much further with additional B-staging time. A significant increase in weight and no measurable T_g of the fully cured samples were also observed. A sample B-staged wet for 14 days, then scanned, was found to be completely soluble in tetrahydrofuran, indicating no cross-linking had taken place. This series of DSC samples clearly shows that the presence of moisture, and not the loss of BDMA, would account for the decreasing T_g observed for the materials B-staged open to the atmosphere.

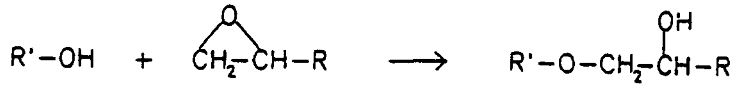
Table 3. BEHAVIOR OF THE ROOM TEMPERATURE B-STAGED EPOXY/ANHYDRIDE RESIN FORMULATION VERSUS TIME UNDER SEALED, OPEN LABORATORY AIR, OPEN DRY AIR, AND OPEN 100% HUMIDITY AIR ENVIRONMENTS

		B-Staging Time (days)						
Conditions	Values	0	1	2	4	7	10	14
Sealed	Residual Heat of Reaction (cal/g)	69	70	68	59	53	48	40
	Glass Transition (°K)	353	356	360	362	374	374	377
	Weight Gain (100%)	0	0	0	0	0	0	0
Open Lab. Air	Residual Heat of Reaction (cal/g)	-	-	74	64	52	46	37
	Glass Transition (°K)	-	-	365	349	343	339	338
	Weight Gain (100%)	-	-	0.8	2.0	2.3	2.6	2.7
Open Dry Air	Residual Heat of Reaction (cal/g)	-	-	70	67	57	49	40
	Glass Transition (°K)	-	-	364	368	372	375	376
	Weight Gain (100%)	-	-	-0.2	-0.4	-0.6	-0.6	-0.7
Open 100% R.H. Air	Residual Heat of Reaction (cal/g)	-	-	58	57	48	46	47
	Glass Transition (°K)	-	-	-	-	-	-	-
	Weight Gain (100%)	-	-	20	23	24	26	28

Epoxy/anhydride cure is generally accepted to proceed through two reactions:



with a third reaction:



In the presence of water, the diepoxy DGEBA behaves as a difunctional instead of a tetraunctional molecule in reacting with the difunctional cyclic anhydride and, at best, forms a linear polymer.

FTIR spectra on specimens cured open and closed confirmed that more hydroxyl groups were present in the open B-staged specimens. FTIR results on cured hand mixed, A-staged resin were also compared with cured hand mixed, B-staged resin and cured machine mixed, B-staged resin. The results indicated no significant differences between the three samples sets.

Quasi-Static Mechanical Testing

The mechanical test results for the in-house prepreg are shown in Table 4. Typical tensile stress/strain behavior is shown in Figure 8. The extent of nonlinearity in the shear and transverse tensile test is evident; therefore, there is a modulus variation with increasing strain. Selection of the appropriate portion of the curve for comparison purposes is critical as the data can be misleading. Data obtained from the literature for various structural S2 epoxy composites (see Table 5) represents an average of 21 specimens for 0^{o} tension, and 11 specimens for 90^{o} tension. Comparison of the epoxy/anhydride data with data from the literature indicates that the prepreg line collimates (E_{11}) and impregnates (S_{22}; i.e., fiber/matrix adhesion) well.

Table 4. TENSILE DATA OF THE COMPOSITE LAMINATES (0°, 90°, ±45°)

Test	Specimen Count	Average Modulus (MPa ± σ)	Average Strength (MPa ± σ)
0° Tension	6	46100 ± 680	1490 ± 90
90° Tension	6	13800 ± 2400	66.7 ± 0.48
±45° Tension	6	5730 ± 690	Yielding

Table 5. COMPARISON OF MATERIAL PROPERTIES OF IN-HOUSE FABRICATED PREPREG COMPOSITE VERSUS TYPICAL VALUES FOUND IN THE LITERATURE

Material Property	In-House (MPa)	Published Literature (MPa)
E_{11}	46100	43500*
E_{22}	13800	10300
G_{12}	5730	—
S_{11}	1490	1610*
S_{22}	67.7	48

*Normalized to 60% fiber volume.

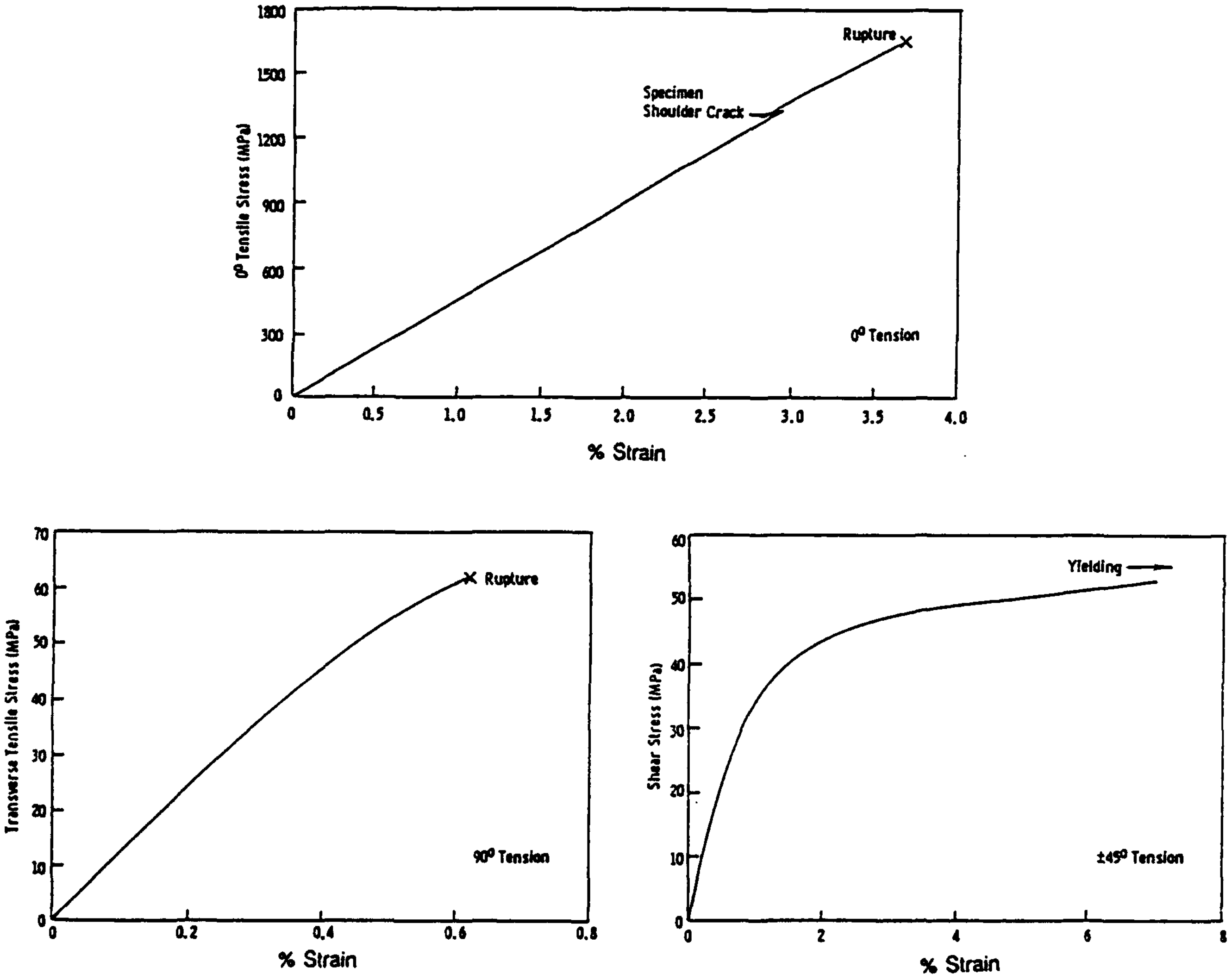


Figure 8. Representative tensile stress/strain behavior of the composite.

Short beam shear specimens did not fail exclusively in shear, but rather under combined modes (shear, bending, and bearing). This is thought to have been caused by the specimen thinness (in spite of an aspect ratio within the range recommended by ASTM D 2344). Nevertheless, the minimum average shear value obtained was 54.9 MPa which compares favorably with typical S2 glass epoxy short beam shear values found in published literature.

Dynamic Mechanical Testing

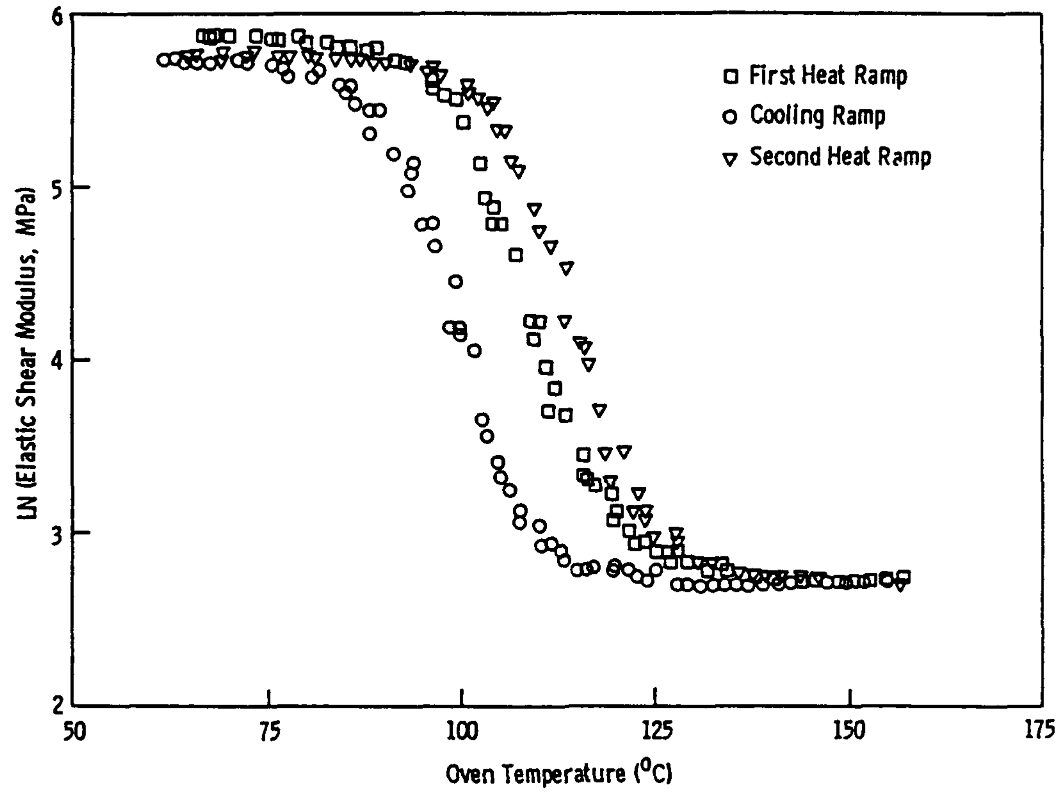
During torsional pendulum analysis (TPA) testing it was suspected that a temperature lag effect associated with the 1°C/min ramping of the torsional pendulum oven chamber was causing an artificial shift in the apparent T_g. The T_g ranges of the two processed laminates should be in close proximity to one another since the T_g should depend solely on the matrix and not the laminate configuration. This shift occurred despite the fact that both laminates were made from the same lot of prepreg, laid up on the same day, and cured together in the same autoclave run. Aside from ply orientation, the only remaining significant difference between the two laminates was their thickness. It was suspected that the added thickness of the eight-ply laminate (0.22 cm as opposed to 0.16 cm of the six-ply) and poor heat transfer (the oven was nonconvecting) were causing an artificially high T_g to be recorded.

A separate set of TPA tests were run to quantify the temperature lag created by specimen thickness at the ramp rate of 1°C/min. This was done by cycling the oven temperature at 1°C/min. If there was no lag effect, the heating and cooling curves would have approximately retraced each other. This was not found to be the case (see Figure 9). Since the apparent specimen temperature trails the oven temperature by the same amount whether heating or cooling, the average of these two curves is a good representation of the relative T_g of these specimens as measured by TPA (see Figure 10).

Table 6 shows the corrected TPA results. Good agreement is observed for the corrected data. Composite chips taken from the TPA specimens were run on DSC. The DSC results, included in Table 6, support the fact that the T_g shift was caused simply by poor heat transfer and that the other, more complex loss mechanisms were not involved. The second heating curve of both laminates indicates a small but distinct 5°C increase in T_g (see Figure 9) due to the high temperature exposure during the TPA temperature cycling.

Table 6. CORRECTED TPA GLASS TRANSITION TEMPERATURE DATA

	Onset (°C ± σ)	Midpoint (°C ± σ)	DSC Midpoint (°C)
Six-ply	96 ± 0.5	106 ± 2	96
Eight-ply	96 ± 0.5	108 ± 0.3	97



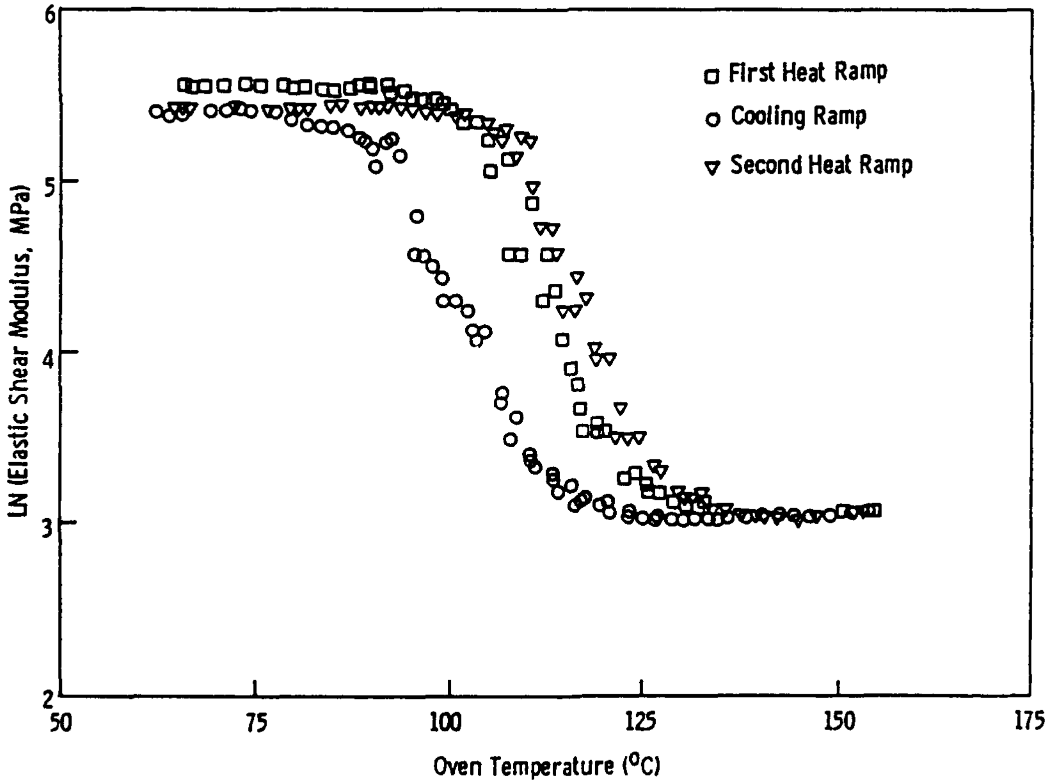


Figure 9. TPA heat cycling data: above, six-ply undirectional laminate; and below, eight-ply $\pm 45_{2s}$ laminate.

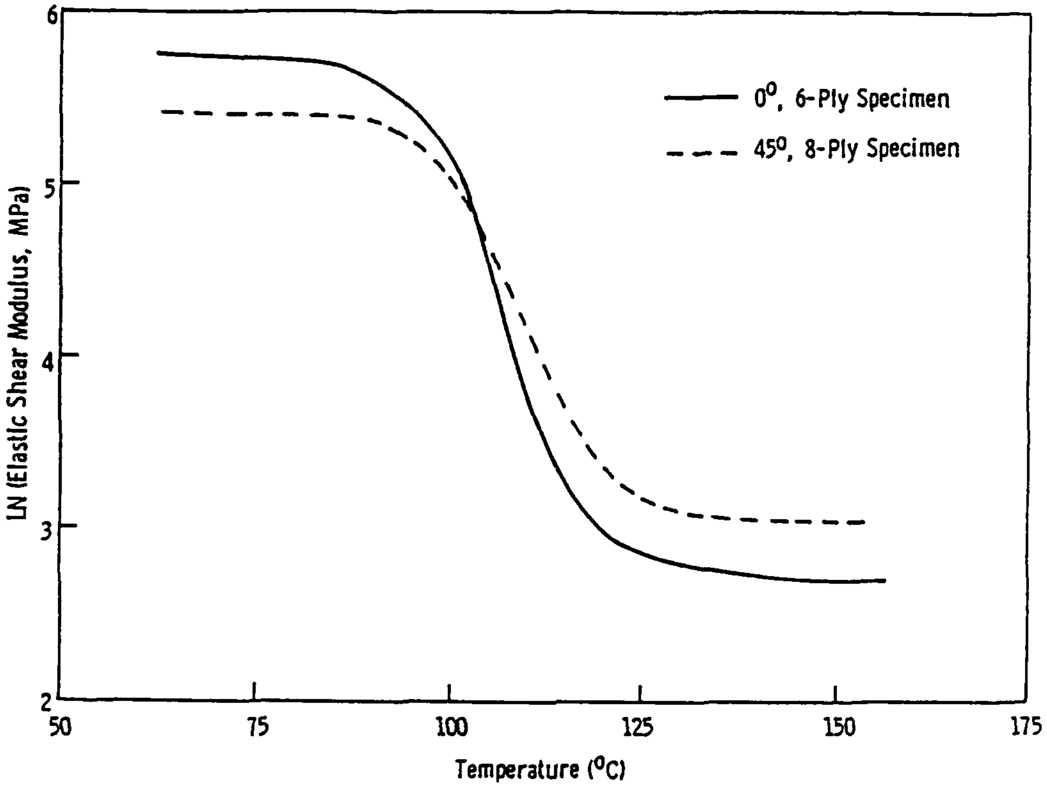


Figure 10. Corrected TPA curves.

SUMMARY

Successful collimation of the fiber tows was achieved on the pilot prepreg line. The final tape was of high quality and consistency. Guiding the fiber tows with combs was found to be essential to stop fiber wandering and to maintaining a highly collimated fiber web. E_{11} was found to compare about evenly or perhaps slightly higher than structural S2 glass epoxy data found in published literature, bearing out the fact that successful collimation was achieved.

Successful fiber impregnation of the fiber web was also achieved on the pilot prepreg line. S_{22} and optical micrographs of the composite indicate a high degree of quality in the final product. The line also successfully attained consistent fiber volume fraction in the final laminate, in spite of obvious uneven dispensing of the resin across the fiber web during processing. Simple adjustment of the final nip gap corrected problems with the materials and processes used.

The service temperature of the particular epoxy/anhydride system investigated was determined to be about 100°C and highly sensitive to the B-staging environment. The decrease in T_g associated with the open systems can be attributed to the presence of moisture. Care should be exercised to exclude moisture during processing, B-staging, and layup of this resin system. A shelf life of approximately one year at -20°C was estimated from thermal analysis results.

The prepreg line metering and mixing system worked reliably. HPLC results on the liquid resin and mechanical tests on the cured laminates showed the resin system was consistently well mixed.

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