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ACETYLENE TERMINATED SULFONE RESIN DEVELOPMENT

Richard P. Chartoff, D. Robert Askins,
John M. Butler, et al.

UNIVERSITY OF DAYTON RESEARCH INSTITUTE
300 COLLEGE PARK AVENUE
DAYTON, OHIO 45469

APRIL 1982

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Charles E. Browning

CHARLES E. BROWNING, Project Engineer
Composites, Adhesives & Fibrous Matls Br
Nonmetallic Materials Division

THEODORE J. REINHART, JR., Chief
Composites, Adhesives & Fibrous Matls Br
Nonmetallic Materials Division

FOR THE COMMANDER:

FRANKLIN D. CHERRY, Chief
Nonmetallic Materials Division

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20. ABSTRACT (*Continue on reverse side if necessary and identify by block number*)

The object of this program was to determine the potential for forming highly reproducible acetylene terminated sulfone (ATS) resin matrix composites. A 45-lb. batch of ATS was synthesized by Gulf R&D Corp. using a newly developed scale-up procedure. A complete characterization of the physical, mechanical, and thermal properties of the cured resin were carried out. Cure optimization

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Dynamic Mechanical Analysis
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20. Abstract (Concluded)

and processing parameter determinations were completed and preferred processing cycles were defined for ATS prepreg and laminates. Finally, mechanical property evaluations were carried out on test laminates produced by the preferred processing methods.

PREFACE

This report was prepared by Dr. Richard P. Chartoff and Mr. D. Robert Askins with the assistance of Dr. John Mann Butler. Work was performed under Contract Number F33615-80-C-5029 by the University of Dayton Research Institute, Center for Basic and Applied Polymer Research, 300 College Park Avenue, Dayton, Ohio 45469. The work was administered under the direction of the Air Force Wright Aeronautical Laboratories/Materials Laboratory (AFWAL/ML), Wright-Patterson Air Force Base, Ohio 45433. The contract was initiated under Project Number 2419-03-18. Dr. Charles E. Browning, AFWAL/MLBC, was the Air Force Project Engineer. The program was conducted during the time period May 1980 through January 1982.

Important contributions to the work effort were made by Messrs. Daniel E. Miller, Ronald J. Kuhbander, William A. Price, Charles W. Griffen, Jerald L. Burkett, and Thomas L. Grossman, who are coauthors of this report. In addition, contributions to the effort by Roger A. Rondeau, Donald R. Byrge, L. Dee Pike, and J. T. Hartness are acknowledged. Typing and compilation were ably performed by Mrs. Jeanne Drake.

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SECTION I

INTRODUCTION, SUMMARY, AND CONCLUSIONS

1. RATIONALE FOR THE PROGRAM

This program was directed toward determining the potential for forming highly reproducible acetylene terminated sulfone (ATS) resin matrix composites with increased temperature capability and durability over currently used epoxy matrix composites. The need for such a program arose because the application of epoxy matrix resin systems is restricted by their limited environmental stability. It is well known that epoxies absorb atmospheric moisture which causes a reduction in the glass transition temperature (T_g) of the resin as well as the rigidity and fatigue resistance of composites. This restricts the maximum use temperature of epoxy resin matrix composites to approximately 250°F, a level insufficient for many applications in supersonic aircraft systems.

In order to take greater advantage of the high strength to weight ratio of composite matrix resins in supersonic aircraft structures, it is necessary to develop matrix resins that are less moisture sensitive and have increased use temperatures. The ATS resin system is a candidate which may be expected to provide such matrix capabilities.

2. ATS AND ITS PROPERTIES; PROGRAM SCOPE

During the past few years acetylene terminated monomers (ATX), whose cure involves the reaction of the terminal ethynyl groups, have been of great interest to the Air Force because of their potential for use as adhesives and matrix resins in composites. Since the ATS monomer has a structure similar to that of commercial polysulfone resins, it is not surprising that ATS has good moisture resistance. For this reason as well as its excellent thermal stability and low viscosity at temperatures below the cure temperature range, ATS has been considered an excellent candidate to replace epoxies in future applications.

Since the original synthesis of ATS, a lower cost synthesis route was developed by Gulf Research and Development Company. The Gulf approach is illustrated in Figure 1.[1] The product obtained from this process contains a percentage of $[\mathrm{ATS}]_n$ oligomers including n=2 (dimer) and greater. For this program a 45-lb. lot of ATS was purchased from Gulf, designated subsequently in this report as ATS_{G-2}. The scope of this program included the complete characterization of the physical, mechanical, and thermal properties of cured ATS_{G-2} as well as the optimization of its cure. Also of interest were processing parameters such as flow viscosity, gel time, and rate of volatile release. Processing parameters were defined for forming quality graphite fiber/ATS_{G-2} prepreg, and optimum processing cycles for ATS_{G-2} laminates. Finally, mechanical property evaluations were carried out on test laminates produced by the preferred processing methods.

3. SUMMARY AND CONCLUSIONS

a. ATS_{G-2} Resin Quality

A 45-lb. lot of ATS was purchased from Gulf R&D Co. for this project. The material was darker in color than previous ATS batches characterized by UDRI, it had a higher melt viscosity, and lower heat of reaction (99.7 cal/g). High Performance Liquid Chromatography (HPLC) analysis disclosed that the sample was quite heterogeneous, containing about 60 percent monomer. The monomer/dimer ratio was 79/21 with the remainder of the sample consisting of higher oligomers.

Particulate impurities of two types also were noted. Small black particles of 50-75μ in size were present as well as fibers similar to those making up a standard filter paper. The particles in particular presented a problem during prepreg processing by plugging the prepreg machine orifices used for fiber impregnating. This limited the uniformity that could be achieved in prepreg resin distribution.

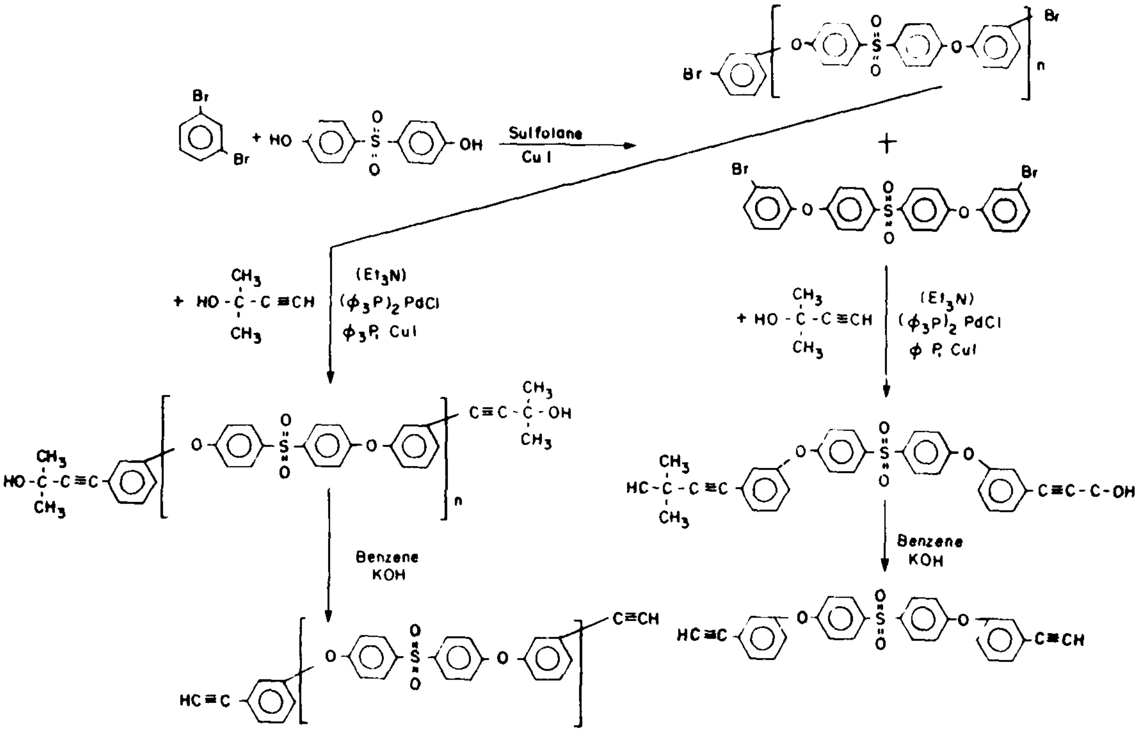


Figure 1. Synthesis of Acetylene-Terminated Sulfone Monomers and Oligomers.

b. Cure Characterization of Neat ATS_{G-2}

Several types of analyses were used to characterize the cure of ATS_{G-2} including Differential Scanning Calorimetry (DSC), Dynamic Mechanical Analysis (DMA), HPLC, and Infrared Spectroscopy (IR) and melt viscosity determination. Each method provided certain information that complemented the others.

Dynamic DSC data provided a reaction window plot and confirmation of its accuracy in identifying ATS cure times was made by isothermal DSC measurements. DSC, DMA, HPLC, and viscosity analyses indicate that gelation occurs at about 20 percent conversion and vitrification occurs simultaneously. Chemical reaction continues in the glassy state beyond the vitrification time as noted by heat evolution and a continuous decrease in acetylene group concentration as measured by IR.

Samples cured isothermally long enough to reach the end of the DSC exotherm were found to exhibit a residual exotherm in subsequent dynamic DSC scans. This indicated that beyond a certain point (approx. 70 percent cure) DSC is not sensitive enough to detect additional reaction in the isothermal mode. IR spectra confirm this and show in addition that considerable unreacted acetylene groups remain even when dynamic DSC measurements of ΔH_P suggest that cure is complete.

The cure characterization data confirm that a reasonable precure beyond vitrification can be achieved at relatively low temperatures in the range 158-186°C for short times of 30 minutes to two hours. DMA and tensile tests confirmed that a postcure is necessary to reach best properties. Samples precured only are too brittle to handle effectively without cracking.

HPLC analysis of partially cured ATS_{G-2} confirms that the initial stage of the cure reaction of ATS is predominately a chain extension. The same distribution of oligomers appears at comparable conversions prior to gelation regardless of temperature. Beyond the gel point the reaction is diffusion controlled, DSC kinetics are nonlinear, and different mechanical properties result from cures taken to the same apparent degree of conversion.

c. Mechanical Characterization of Neat ATS_{G-2}

A series of tensile tests on ATS_{G-2} (micro)dogbone specimens were carried out using cure cycles suggested by our cure characterization studies. Variations in precure and postcure times and temperatures and postcure atmosphere (air and N_2) were considered. The best properties were obtained with precure at 168°C for 1 hr. 37 min. (includes one hour heatup) followed by three hours at 250°C. Maximum values for elongation of 1.5 percent, modulus 500,000 psi, and ultimate strength 6,000 psi were obtained.

DMA tests on portions of the tensile samples indicate that those samples with the best mechanical properties also had larger dynamic loss tangent values at $T<T_g$. T_g values for cured ATS_{G-2} were in the range of 290-310°C.

d. Prepreg and Laminate Processing

Prepreg processing was carried out by U.S. Polymeric Division of HITCO (USP). Six prepreg tape runs were made using a direct application hot melt impregnation method on USP's industrial scale equipment. Three-inch tapes were produced (using a melt temperature of 200°F) which had poor tack and drape properties. Efforts to improve tack and drape by adding 1 percent ethanol to the prepreg resin were only partially successful. Ethanol tended to diffuse out of the prepreg with time. The correct melt temperature for prepregging was predicted by viscosity characterization work done at UDRI.

By successive trials it was found that void-free test laminates could be fabricated by autoclave molding but the prepreg must be vacuum dried beforehand. Prepreg characterization indicated that up to 4 percent volatiles must be drawn off prior to laminate cure. Two percent of this consists of moisture, residual solvent, and diethynylbenzene impurity. The additional 2 percent is of unknown origin.

Optimal prepreg resin content was found to be 42 percent by weight. The final choice of graphite fiber for test laminates was made by matching resin and fiber surface free energies. Using this method Hercules AS-4 fiber was expected to be most compatible with ATS_{G-2}.

The best laminates produced had short beam shear strength values of 11,500 psi, 0° flexure strength (three point) values of 226,000 psi, 90° flexure strength (four point) values of 6,000 psi, and 90° strain to failure values of 0.33 percent. Laminate specific gravities ranged from 1.55 to 1.60. Details on laminate mechanical properties and other characteristics are found in Section IV of the full report. The property levels achieved were considerably lower than those of typical epoxy-graphite laminates.

SECTION II

CURE CHARACTERIZATION OF NEAT ATS RESIN

Although the cure of ATS to form a crosslinked thermoset has been studied[2-6] there yet remains much to be learned about the crosslinking reaction and reaction rates at various temperatures. Dynamic differential scanning calorimetry (DSC) data on a pure ATS sample such as that shown in Figure 2 (scanned at 10°C/min) indicate that ATS begins to cure at 155°C, the maximum exotherm occurs at 236°C, and reaction continues to 290°C.

The curing reaction does not appear to involve simply crosslinking through terminal acetylene groups as originally thought. The initial stages of reaction before gelation involve considerable chain extension[2,3] and proceed by a conventional free radical mechanism with molecular weight governed by a first-order termination reaction. As reaction proceeds, the reaction product is soluble in THF and the molecular weight distribution measured by gel permeation chromatography (GPC) broadens.

The evidence available[2,4,5,6] indicates that prior to gelation the ATS terminal acetylene groups disappear and considerable olefinic unsaturation develops. At this point, however, the actual ATS crosslink routes are open to speculation. It does appear that some cyclic trimerization occurs.[6]

1. DYNAMIC DSC DATA; CURE KINETICS

Reaction window plots for ATS may be developed[2] from dynamic DSC data that specify a series of parametric reaction lines. Each line represents the time and temperature to reach a specified degree of conversion. This type of plot is obtained from a rate equation of the form[7]

$$\log \frac{d\alpha}{dt} = \frac{-E}{2.303} \; \frac{1}{T} + \log A \; (1-\alpha)^n \qquad (1)$$

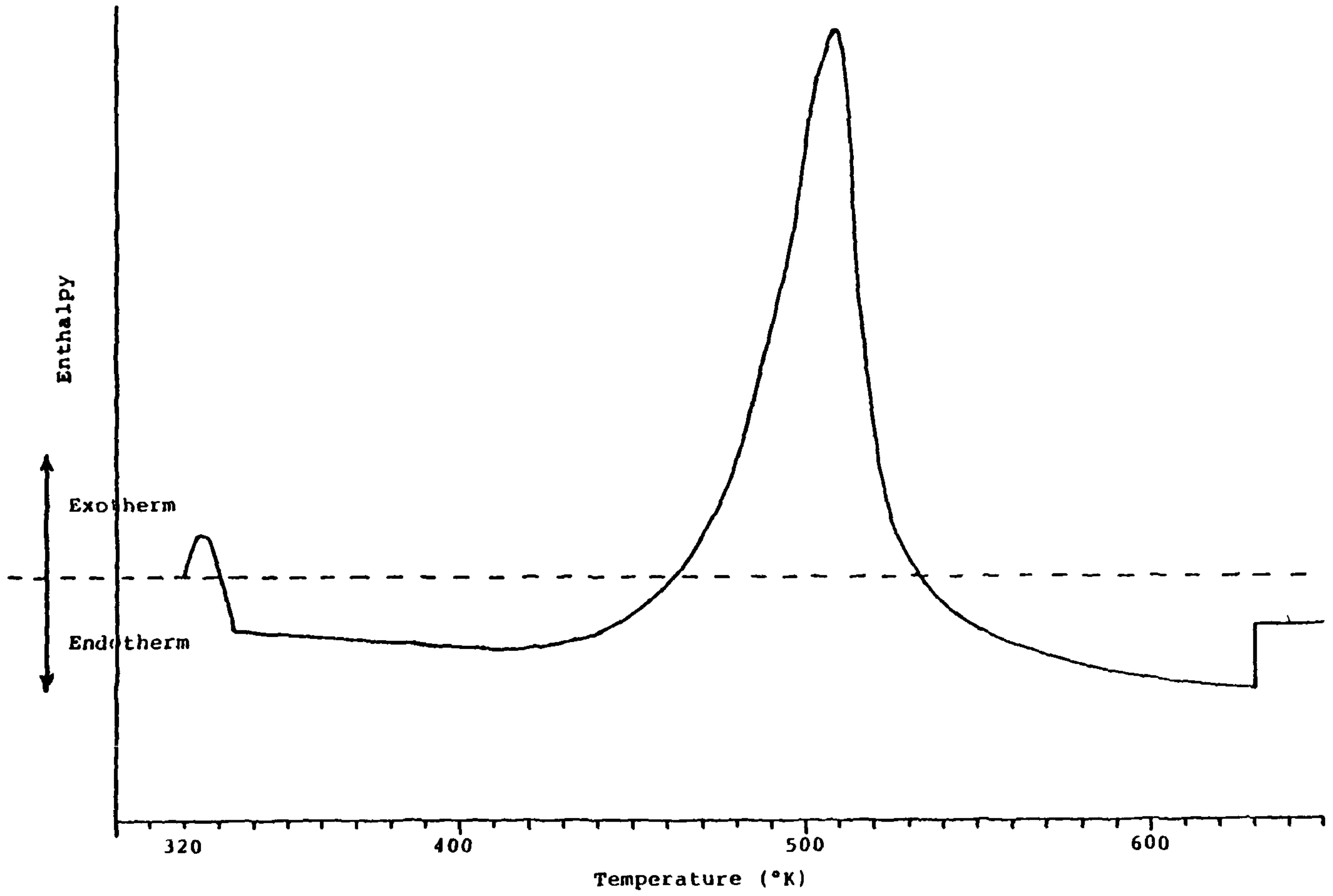


Figure 2. DSC Thermogram for Cure of ATS Monomer.

where α is degree of conversion, t is time, E is the activation energy for reaction, A is an empirical rate constant, and n is the constant reaction order.

A number of assumptions are made in deriving Equation 1 including the notion that a single reaction mechanism applies throughout the temperature-time plane at all degrees of conversion. This, of course, implies that at high conversions near gelation the same events occur as at low conversion independent of system rheology.

The reaction window data for an ATS sample designated ATS_{G-1} are shown in Figure 3. ATS_{G-1} was synthesized by Gulf on a 1-lb. scale prior to ATS_{G-2}. Cure times for a given degree of conversion appear to be longer than those for other ATS samples previously reported.

Figure 4 is an isothermal cure time plot for the same sample. It is likely, in accord with the nonlinear curves, that the reaction does not follow a simple mechanism. The reactions which do occur are probably diffusion controlled at high conversions. The kinetic parameters for the ATS_{G-1} sample are listed in Table 1. These are calculated from the DSC exotherms of Figure 5 by use of equation 1.

Similar DSC exotherms are shown for ATS_{G-2} in Figure 6 with the reaction window plot given in Figure 7. The values of the reaction parameters for this sample are also presented in Table 1. The average value of ΔH_P from the five scans is 99.7 cal/g. This is lower than the ΔH_P values for pure ATS monomer[2,3] and the previous 1-lb. batch of ATS from Gulf, ATS_{G-1}. The peak exotherm (10°C/min. heating rate) is 220°C.

The data indicate that ATS_{G-2} cures more quickly at a given temperature than does ATS_{G-1}. This is illustrated in Figure 8 where reaction isotherms for the two ATS samples are compared.

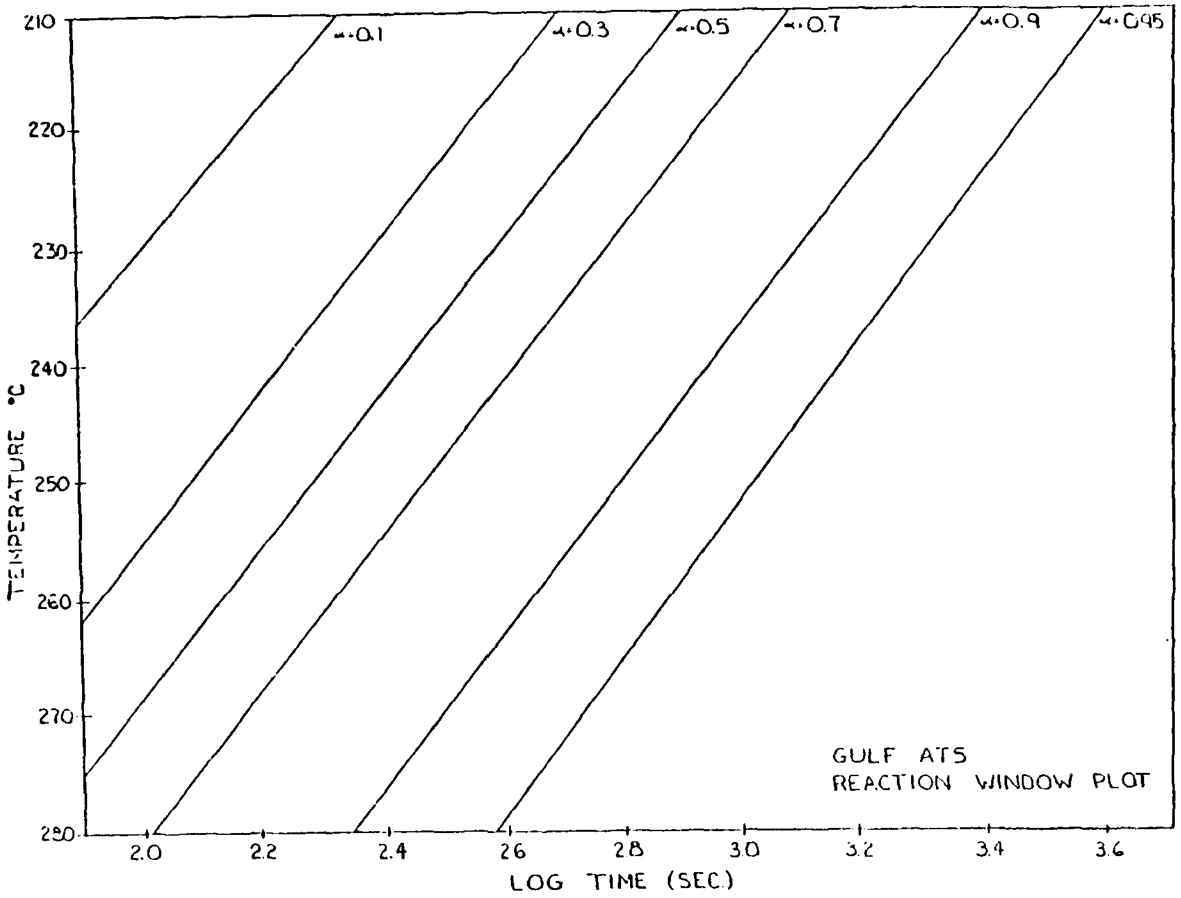


Figure 3. Reaction Window Plot for Gulf ATS_{G-1}; Parameter is Degree of Conversion.

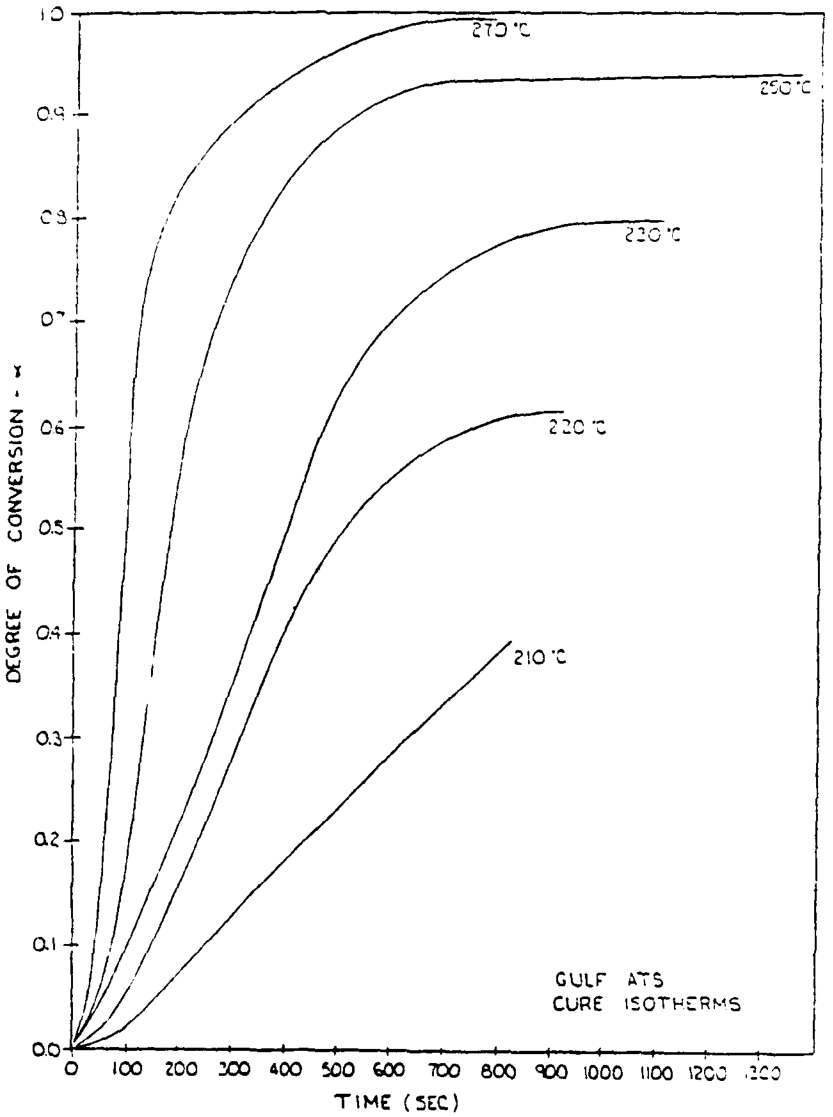


Figure 4. Cure Isotherm Plot for Gulf ATS_{G-1}.

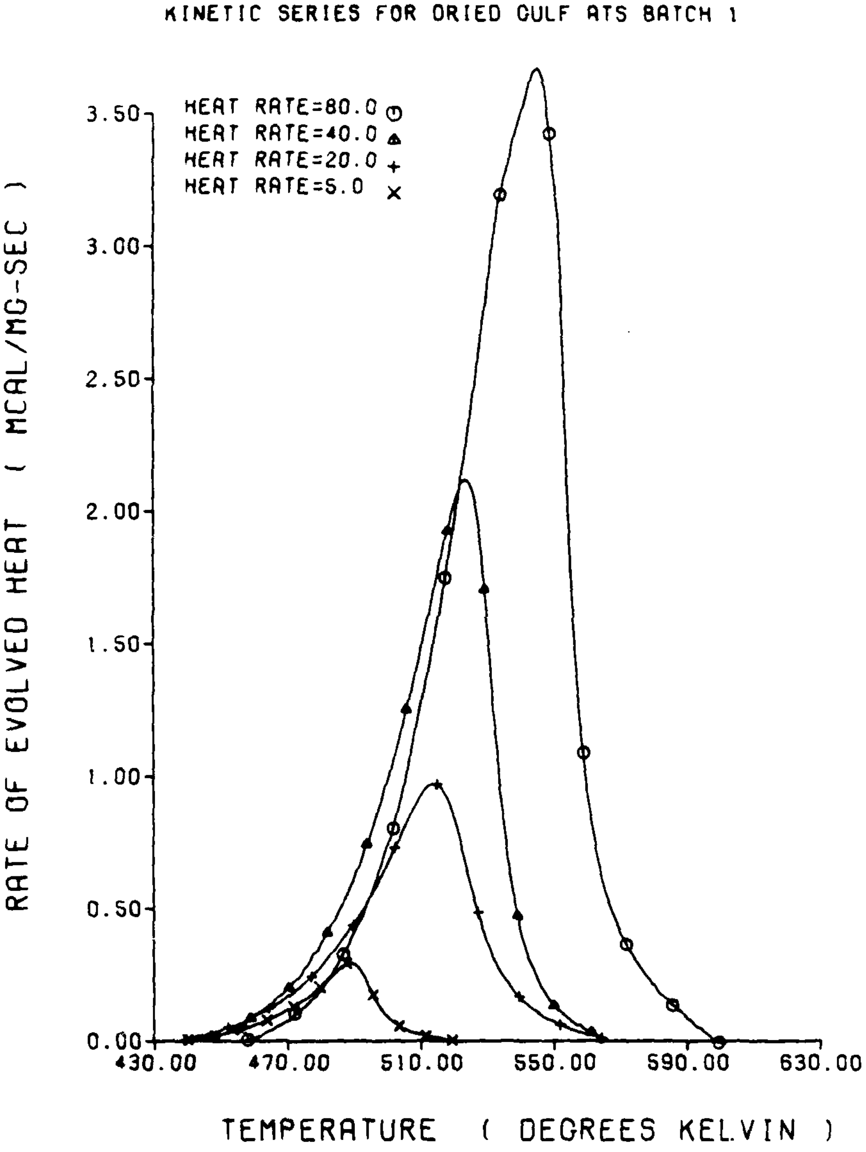


Figure 5. DSC Exotherms for ATS_{G-1} Taken at Various Heating Rates.

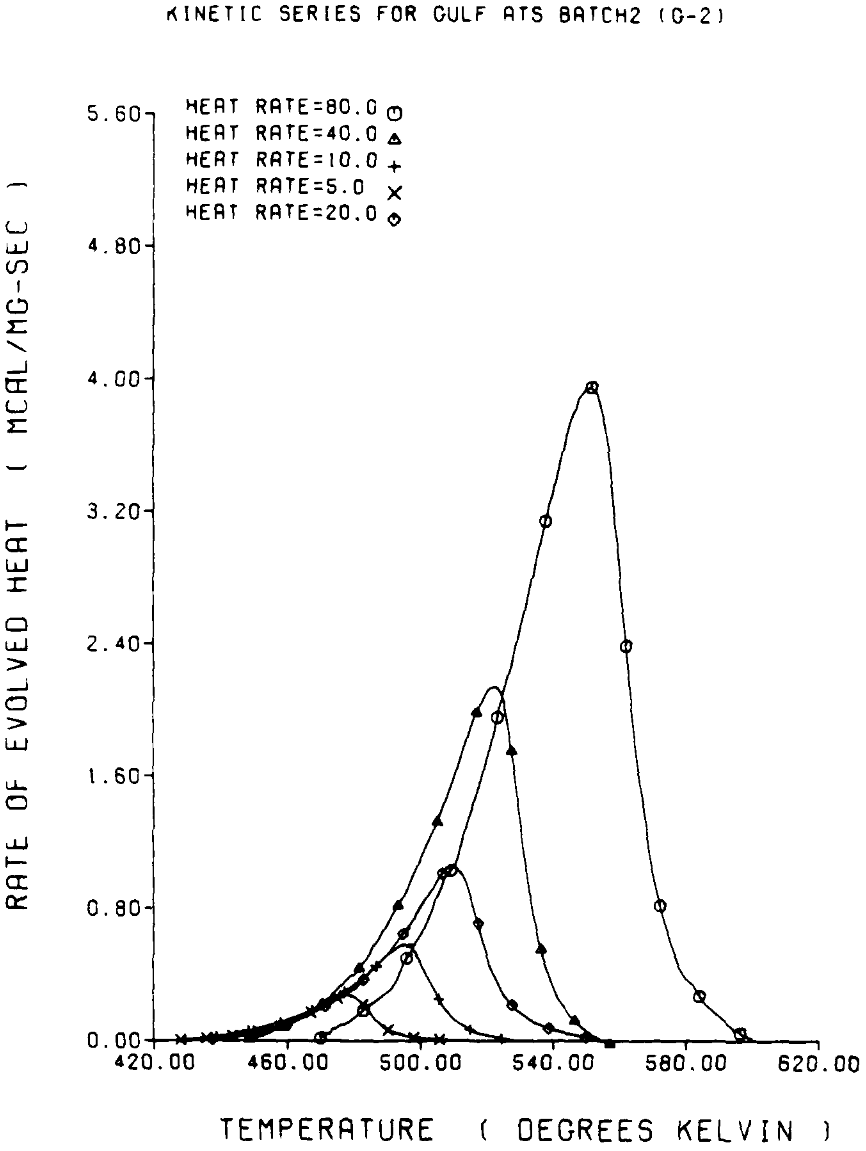


Figure 6. Dynamic DSC Exotherms for ATS_{G-2} Taken at Five Different Scan Rates.

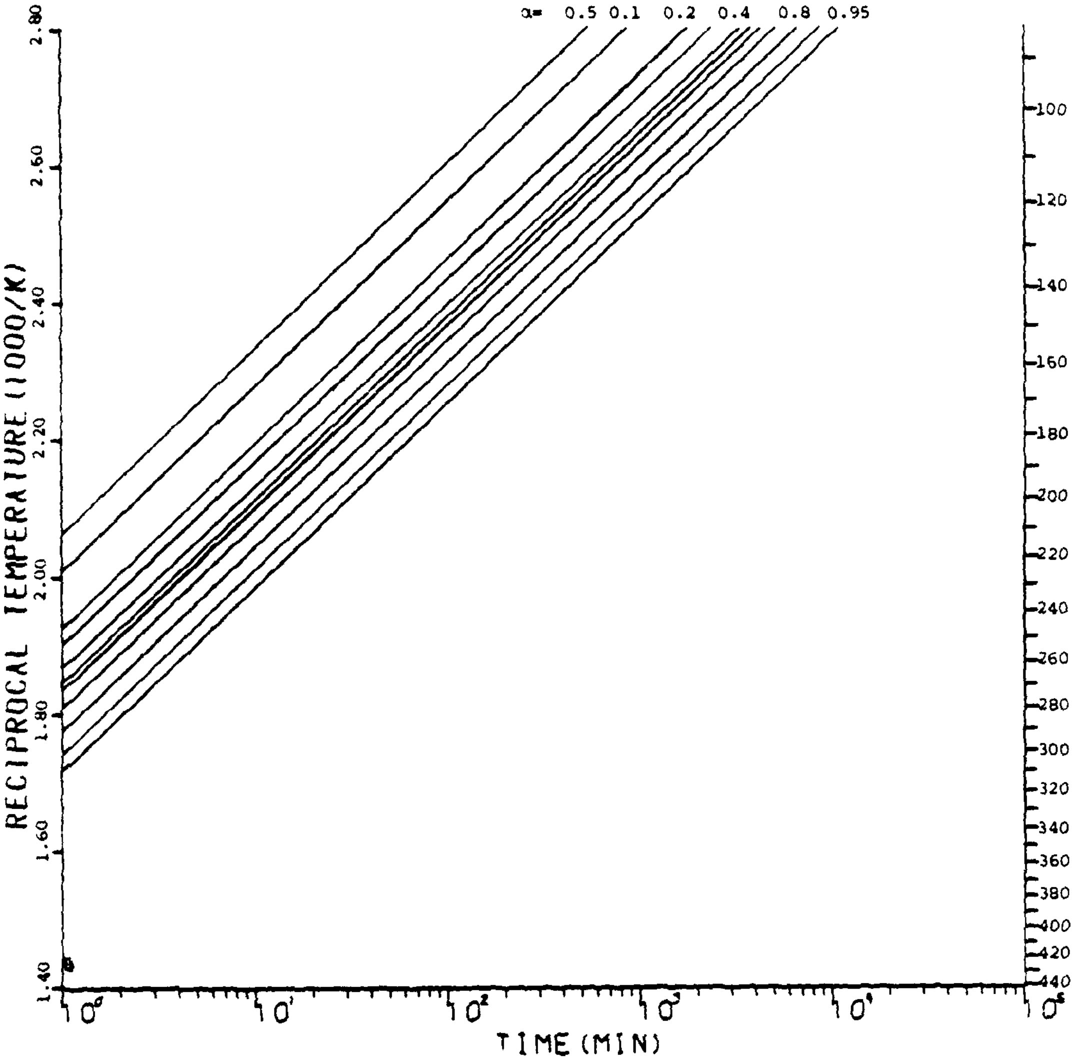


Figure 7. ATS_{G-2} Reaction Window Plot.

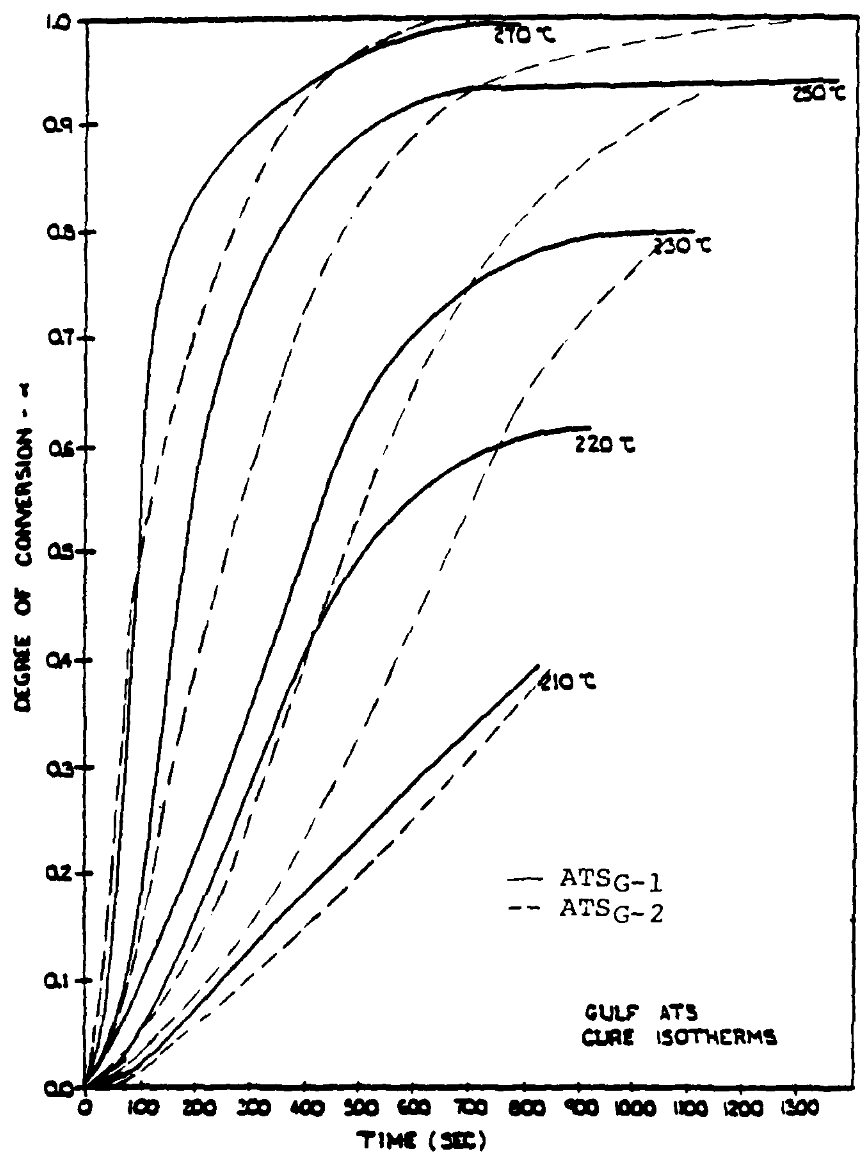


Figure 8. Cure Isotherm Plot for Gulf ATS_{G-2} Showing Comparison with ATS_{G-1}.

These differences in the two samples may arise because of residual catalyst in ATS_{G-2} either in the final lot or at some time prior to final purification. The presence of residual palladium catalyst will reduce both reaction exotherm and exotherm peak temperature. Also it will tend to increase reaction rate.

Palladium doping experiments were carried out by adding various amounts of the catalyst dichlorobis(triphenylphosphine)-palladium (II) to ATS_{G-1} samples and measuring the DSC exotherm for each sample at a heating rate of 10°C/min. The most significant results for this study are presented in Figures 9 and 10, where both the heat of reaction and exotherm peak temperature are shown to depend strongly on the amount of Pd added. As the Pd concentration increases both T_{max} and ΔH_P decrease.

The differences in reaction rates for the two Gulf ATS samples is probably not significant in terms of processing ATS. We merely note at this point that each lot of ATS should be expected to have such differences.

TABLE 1

KINETIC PARAMETERS FOR CURE OF ATS

Sample	log A (sec^{-1})	E_a Kcal/mole	ΔH_P	n
ATS_{G-1}	7.15	21.2	116.3 (cal/g)	0.32
ATS_{G-2}	7.19	21.0	99.7	0.32

2. ISOTHERMAL DSC DATA

Isothermal DSC data were taken for ATS_{G-2} at eight different temperatures in the range 150 to 205°C. Samples were scanned on a time base to complete exotherm as indicated in Figure 11. In addition, each of the isothermal samples was checked for residual heat of reaction subsequently by scanning dynamically at a rate of 10°C/min. The isothermal

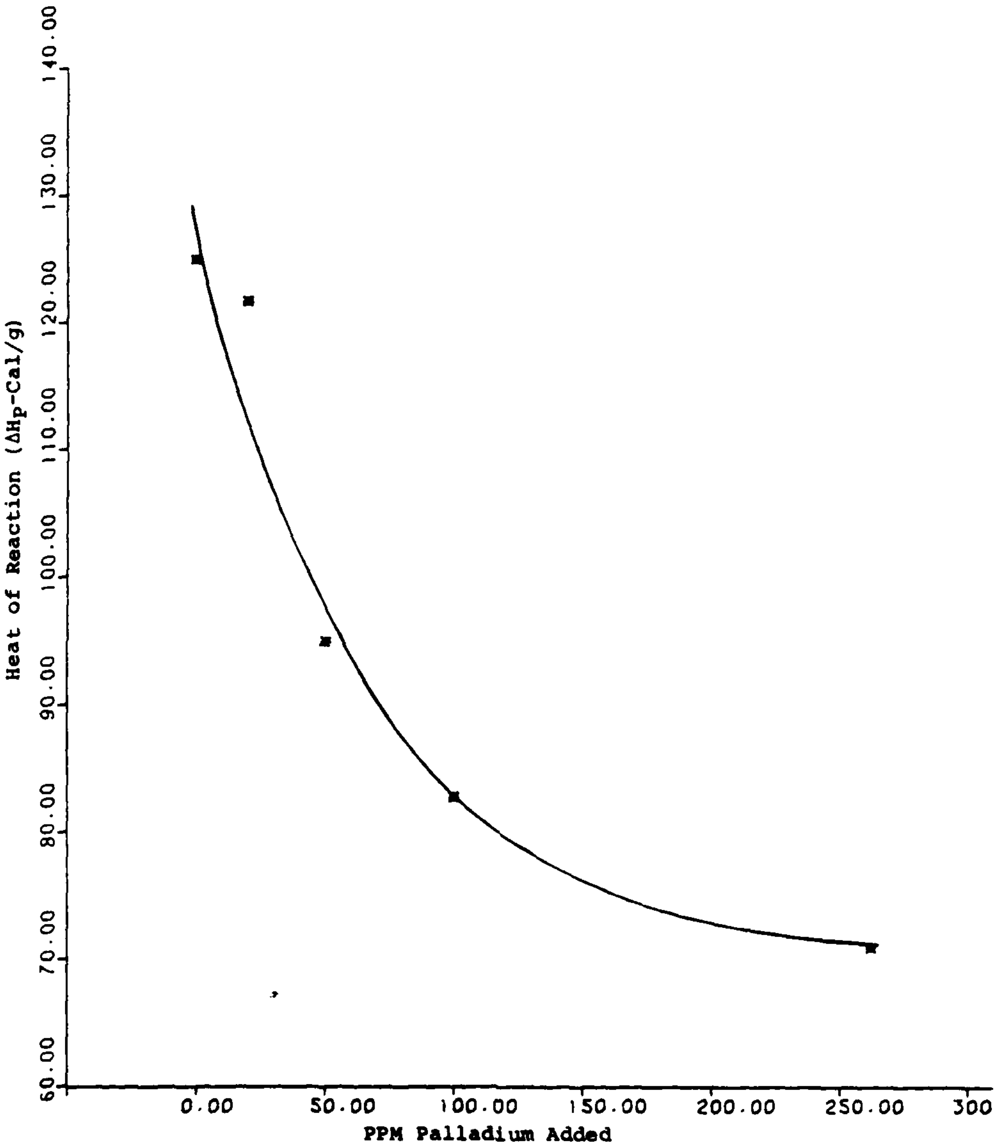


Figure 9. Relationship Between Heat of Reaction for ATS$_G$ Cure and Concentration of Palladium Catalyst.

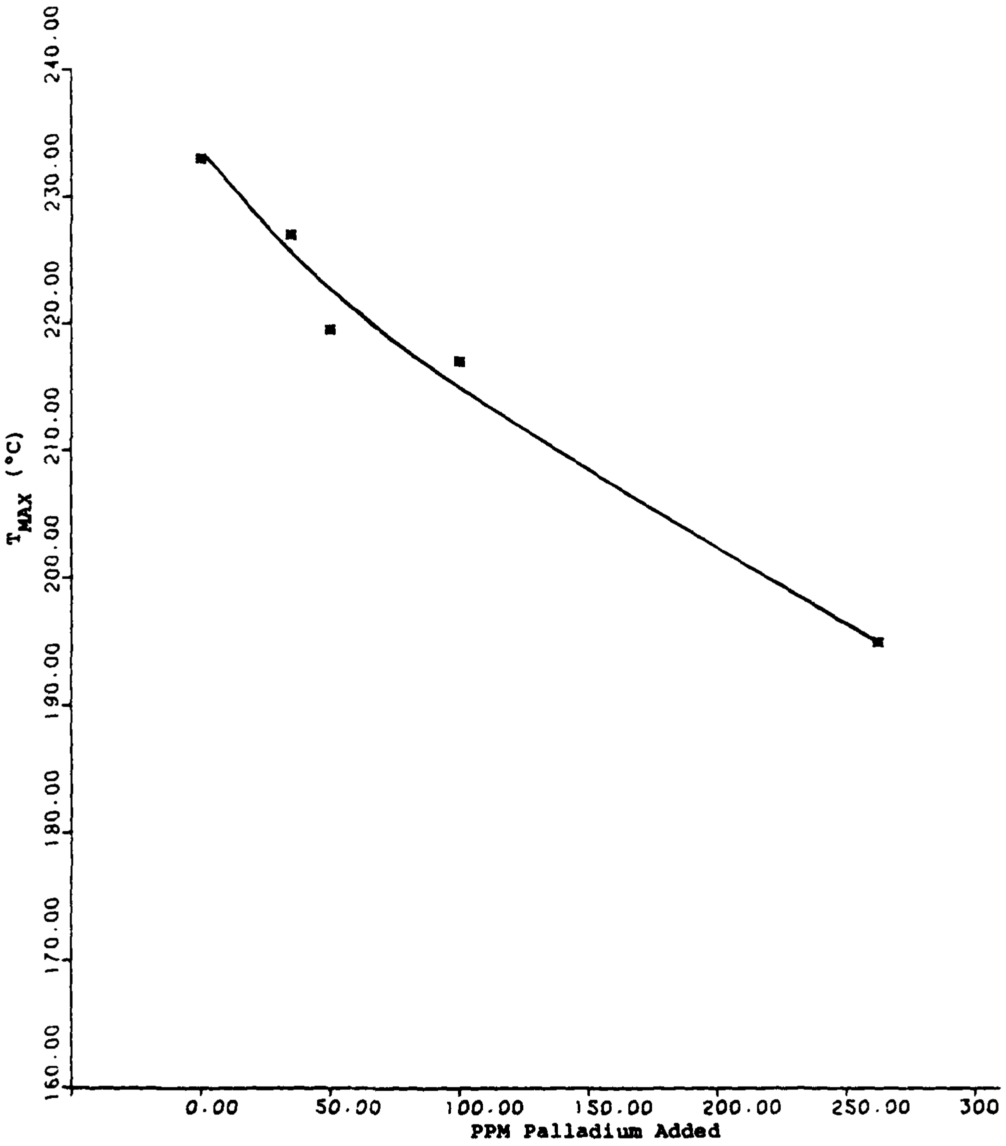


Figure 10. Change in Temperature of Exotherm Cure Peak with Addition of Palladium Catalyst.

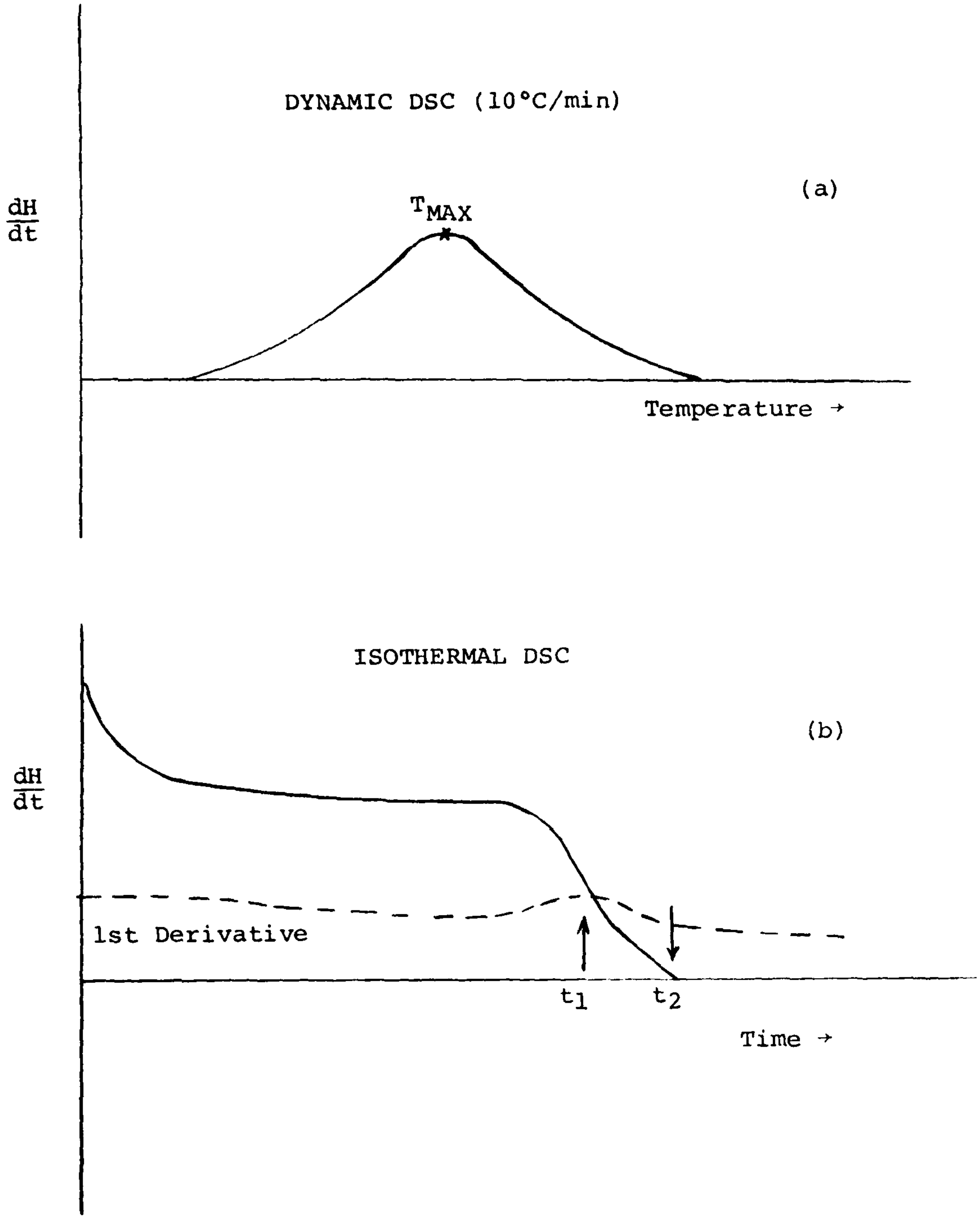


Figure 11. Schematic Diagram Illustrating Dynamic and Isothermal DSC Curves.

runs were carried out by ballistically heating the samples to the isothermal hold temperature at a rate of 320°C/min. The time for complete exotherm was estimated from the first derivative curve maximum occurring near the end of the exotherm (Figure 11b). These are the values listed in Table 2 for actual time to completion. The percent conversion values listed there are based on the residual ΔH_p values.

TABLE 2

ISOTHERMAL CONVERSION TIME VALUES

Temperature (°C)	% Conversion*	Time (Est.)†	Time (Actual)
150	59	90	94.0
158	60	66	71.2
168	57	38	38.0
172	57	36	28.4
177	62	28	21.8
182	65	27	17.6
186	72	27	13.8
205	80	15	6.0

* Measured by DSC.

† Estimated from reaction window plot.

Using the percent conversion values obtained we compared the measured values of conversion time to those estimated from the reaction window plot as diagrammed in Figure 12. The procedure involved is illustrated by the 150°C isotherm extended to the 59 percent isoconversion line. The time corresponding to that cure is then read from the abscissa. The values of time determined in this way are similar to those measured from the isothermal DSC tests.

Discrepancies in the two time values at higher temperatures are attributed to our estimated exotherm end points to be the first derivative maxima (t_1) rather than taking the actual time from the completion of the dH/dt exotherm curve itself (t_2).

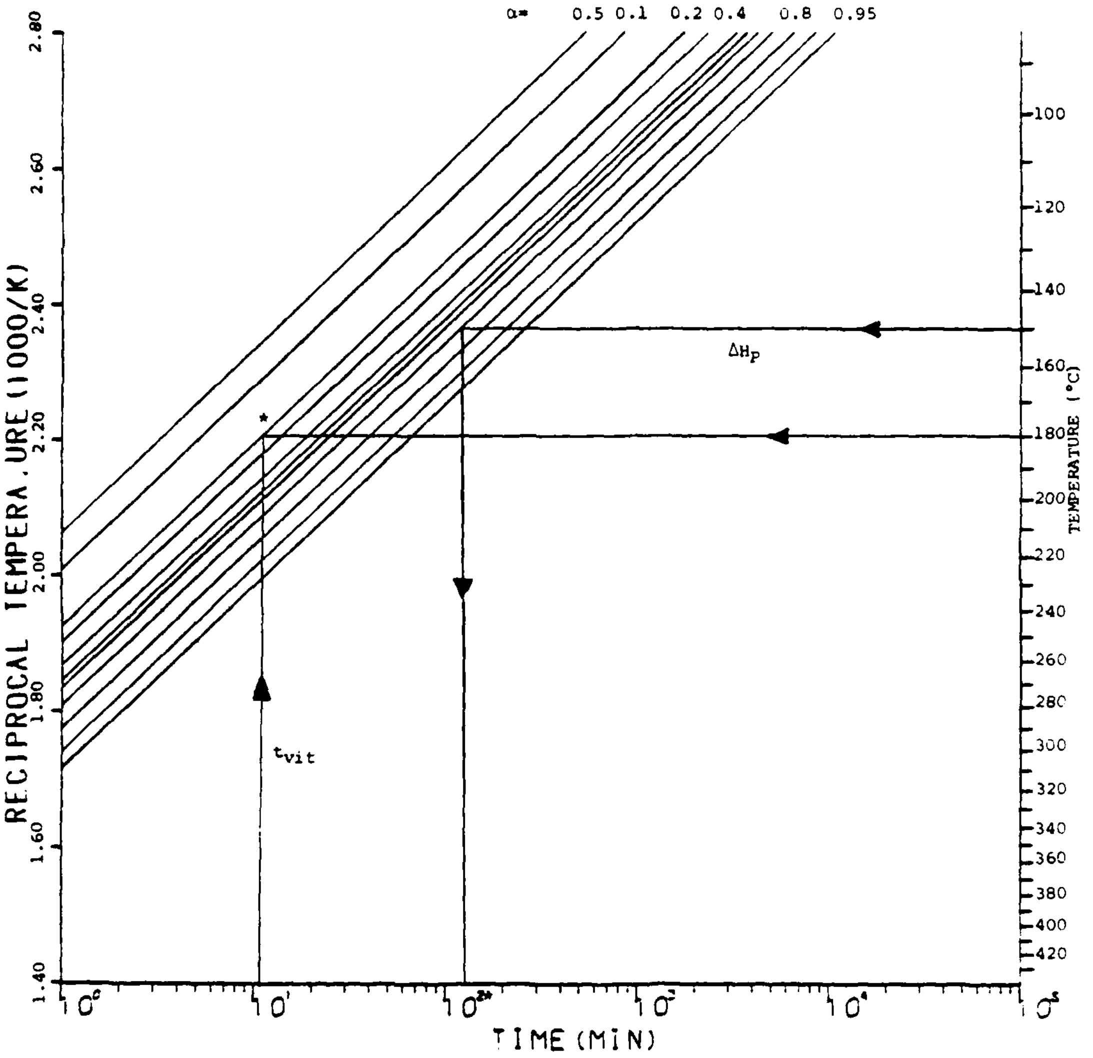


Figure 12. Reaction Window Plot Showing Methods for Estimating Cure Time From DSC Conversion Data and Degree of Conversion (%) From DMA Vitrification Data.

The data indicate, however, that the reaction window plot does predict conversion times in accord with reality. We find also that isothermal cures at temperatures below 205°C result in incomplete cures with conversions in the range of 60 to 80 percent based on ΔH_P.

Residual ΔH_P values were measured for a series of samples taken from ATS_{G-2} tensile bars cured isothermally. The cure times used for these bars at each temperature were the same as those determined by DSC for completion of exotherm (t_2). The time required to reach isothermal temperature in each casting also was added to the total time used for fabrication of these samples. The residual ΔH_P values found are listed in Table 3. These are in the 70-80 percent conversion range as predicted. Based on this it appears that the isothermal DSC data and the reaction window plot can be used to reach a desired cure level in ATS castings.

TABLE 3

DSC EXOTHERM FOR TENSILE DOGBONES

Cure	ΔH_P (cal/gm)	% Conversion
4 hrs. 20 min. @ 140°C	30.2	69.7
1 hr. 37 min. @ 168°C	30.3	69.6
1 hr. 12 min. @ 186°C	19.6	80.3
1 hr. 4 min. @ 204°C	30.7	69.2

Additional isothermal scans were carried out at selected temperatures for cure times longer than those measured for dissipation of the reaction exotherm. The times selected were picked by drawing a line parallel to the exotherm completion line on a cure time versus 1/T plot as shown in Figure 13. The values obtained for ΔH_P listed in Table 4 indicate that cure does advance slightly beyond the 60 to 70 percent range but may not go much beyond 80 percent even at longer cure times.

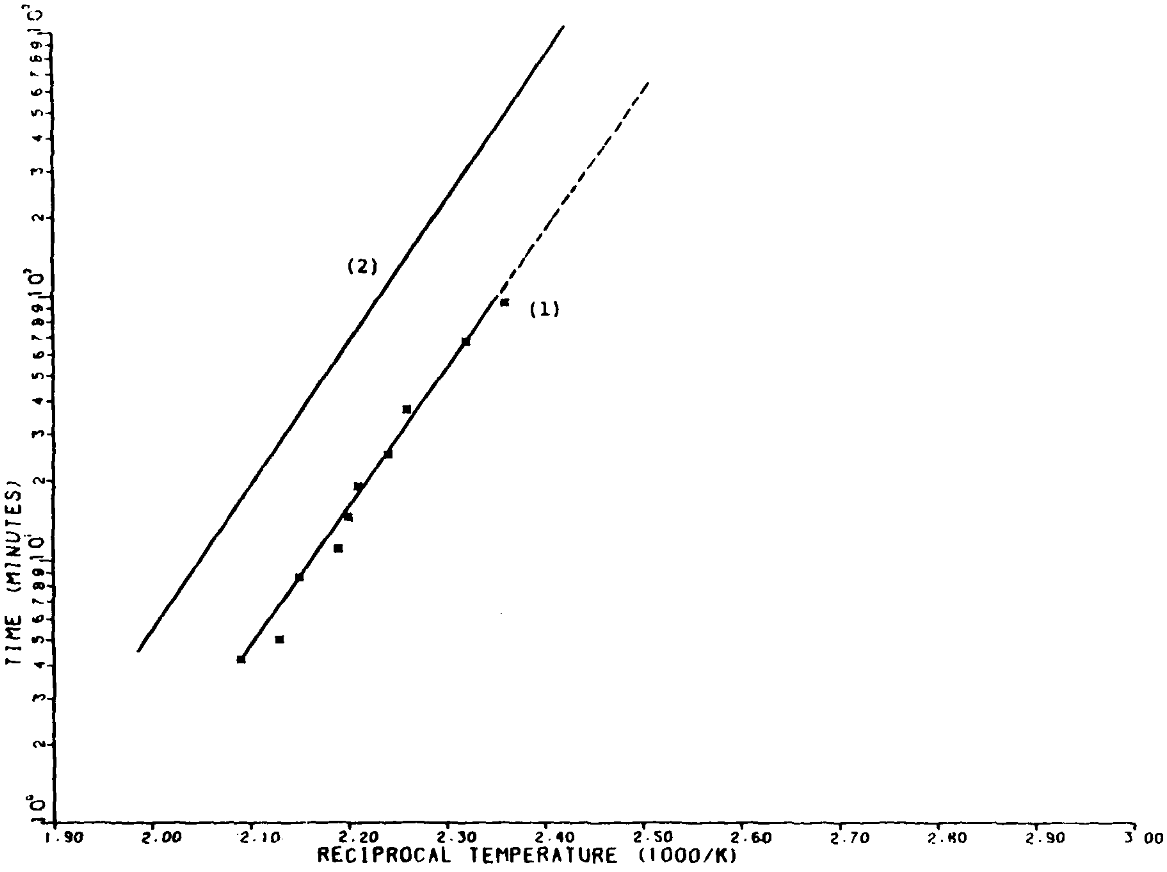


Figure 13. DSC Exotherm Isothermal Cure Times; Line 1 is Locus of Exotherm Completion Times, Line 2 Represents Times Picked for Extended Cures of Table 4.

TABLE 4

RESIDUAL ΔHp VALUES FOR EXTENDED
ISOTHERMAL CURES AT FOUR TEMPERATURES

Temperature (°C)	Cure Time (min.)	ΔHp	% Conversion
145	734	21.2	79.5
168	133	16.6	83.9
186	43.8	18.9	81.7
205	16	22.1	78.6

3. DYNAMIC MECHANICAL ANALYSIS (DMA) OF ATS CURE

The cure reaction of ATS_{G-1} was followed by Dynamic Mechanical Analysis (DMA) using an impregnated cloth technique where the resin is coated onto a fiberglass cloth support. The data of Figure 14, taken at 180°C, are typical of those taken isothermally at any given temperature. The curves are similar in shape to those obtained for other types of resins such as epoxies and clearly distinguish two important events that are referred to as gelation and vitrification[8,9]. As time proceeds, during cure the gelation point is the first maximum in the loss tangent curve and the vitrification point is the second maximum. This corresponds also to the maximum value of the loss modulus (E").

After developing the appropriate techniques for following ATS cure, isothermal DMA studies were carried out to determine the gelation and vitrification characteristics of ATS_{G-2}. This series of DMA measurements was performed in the shear mode with the ATS_{G-2} supported on fiberglass cloth containing about 55 percent resin. Figure 15 represents a typical isothermal DMA scan for ATS_{G-2} showing glation and vitrification events on both storage modulus and loss modulus curves. The point of incipient gelation is taken to be at the first shoulder in loss modulus and the vitrification point is the maximum in loss modulus (corresponding to the time to reach a glass transition).

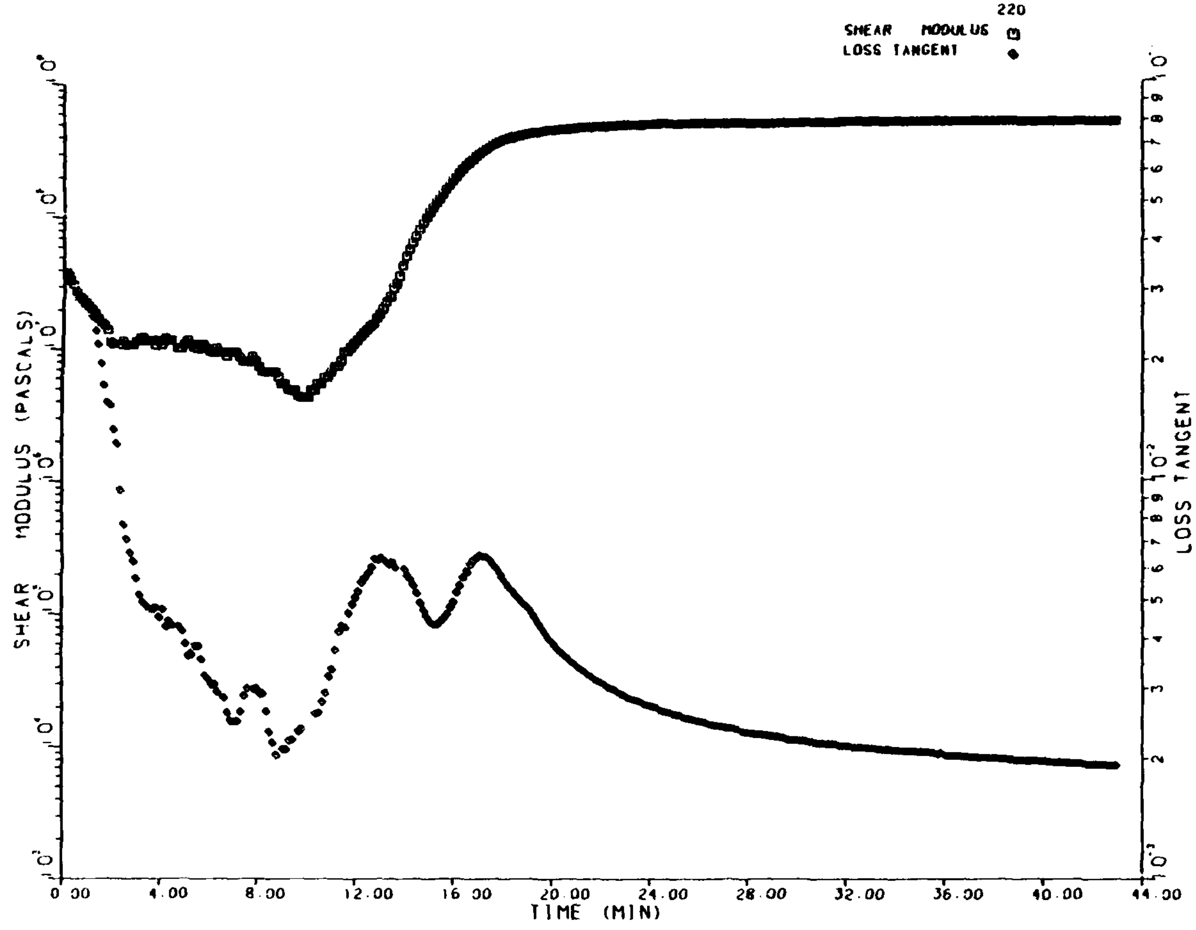


Figure 14. Isothermal DMA Scan for ATS_{G-1} Cured at 180°C; Sample Supported on Fiberglass Cloth.

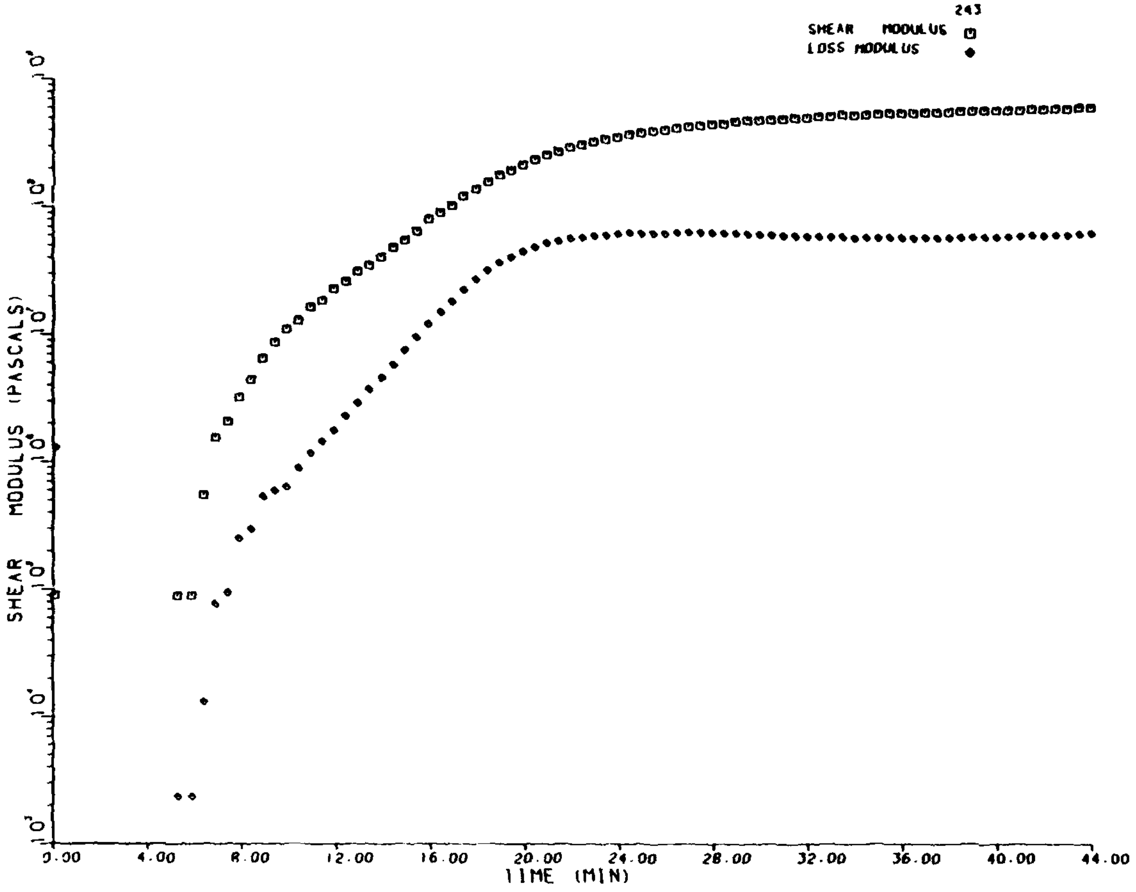


Figure 15. Isothermal DMA Scan for ATS_{G-2} at 158°C; Sample Supported on Fiberglass Cloth.

Gel and vitrification times for various temperatures are plotted in Figure 16. DMA vitrification times also are listed in Table 5 and are compared there with the time to reach completion of the reaction exotherm (determined by DSC) as discussed in Paragraph 2. It is apparent from the data that the reaction, as measured by heat evolution, continues for some time beyond the vitrification point.

That the cure reaction continues beyond vitrification in the glassy state is suggested also by the percent conversion values estimated from the reaction window plot. Using the vitrification times determined by DMA, the intersection with each isotherm on Figure 12 falls at about 20 percent as indicated in Table 6. This value is considerably below the 60 to 80 percent conversion level that is reached after the exotherm is complete.

4. DYNAMIC MECHANICAL ANALYSIS OF CURED ATS_{G-2}

DMA scans were carried out on ATS_{G-2} castings cured isothermally for the appropriate times determined from our isothermal DSC studies. The cure times selected were those listed in Table 7. This table illustrates the fact that samples with comparable ΔH_P values have different dynamic mechanical properties.

In Figure 17 DMA scans for samples 2 and 4 (Table 7) are compared. Sample 2 has a nominal T_g value of 155°C. Beyond this temperature the sample undergoes further cure, vitrifies at 200°C, and passes through a new T_g at 280°C. Below 155°C sample 2 has a higher modulus and loss tangent value than sample 4. Sample 4 exhibits a secondary transition at 160°C probably corresponding to the major transition in sample 2. The major T_g transition for sample 4, however, is in the 280°C range. While the two samples have the same degree of conversion according to the ΔH_P values in Table 7, sample 2 appears to have a more flexible chain molecular structure. This is probably indicative of less crosslinking.

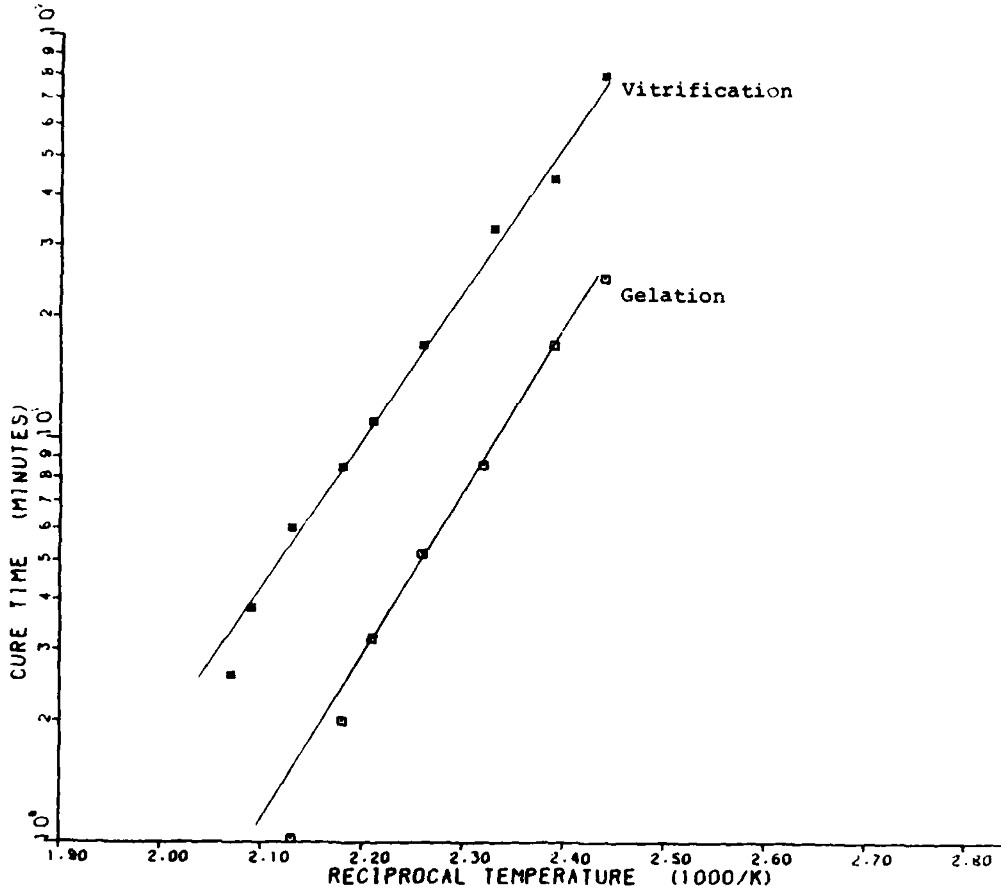


Figure 16. Gel and Vitrification Times Taken From Isothermal DMA Scans.

TABLE 5
VITRIFICATION vs. DSC EXOTHERM

Temperature (°C)	Time (Vit.)	Time (DSC)
145	43.6	--
150	--	94.0
158	27.4	71.2
168	17.3	38.0
172	--	28.4
177	11.1	21.8
186	8.5	13.8
205	4.8	6.0

TABLE 6
CONVERSION AT VITRIFICATION

Temperature (°C)	Time	% Conversion*
136	80	20
145	43	18
158	27	19
168	17	20
177	11	19
186	8.5	20
197	6	20
205	4.8	28

* Estimated from reaction window plot.

TABLE 7

RESIDUAL DSC EXOTHERM FOR TENSILE DOGBONES AND DMA BARS*

Sample	Cure	ΔH_P (cal/gm)
1	4 hrs. 20 min. @ 140°C	30.2
2	1 hr. 37 min. @ 168°C	30.3
3	1 hr. 12 min. @ 186°C	19.6
4	1 hr. 4 min. @ 204°C	30.7

---

* Both types of specimens cast simultaneously in silicone rubber molds as described in Paragraph 2, Section III.

Figure 18 is an additional comparison of samples 3 and 4 with another sample (sample 5) post-cured at 260°C. Sample 3 has a noteworthy loss dispersion at 180°C, while sample 4 has one that is lower and sample 5 has none. ΔH_P values in cal/gm for the three samples are: sample 3 -- 19.6, sample 4 -- 30.7, and sample 5 -- 0.

5. CHANGE IN ACETYLENE CONCENTRATION DURING CURE BY INFRARED SPECTROSCOPY (IR)

The rate at which the acetylene concentration decreases while ATS cures confirms that reaction continues in the glassy state. Such data confirm as well that reaction continues well beyond the point at which heat evolution can be detected by DSC.

Experiments were conducted to follow the disappearance of acetylene groups by using IR. ATS_{G-2} films were cast on NaCl crystals and were cured in a nitrogen atmosphere at 205°C and 140°C.

The $C\equiv C$ band absorbance at 3300 cm^{-1} was matched to constant band absorbance at 1600 cm^{-1}. An IR was taken every 10 minutes for the first three hours and every hour for the remaining 24 hours.

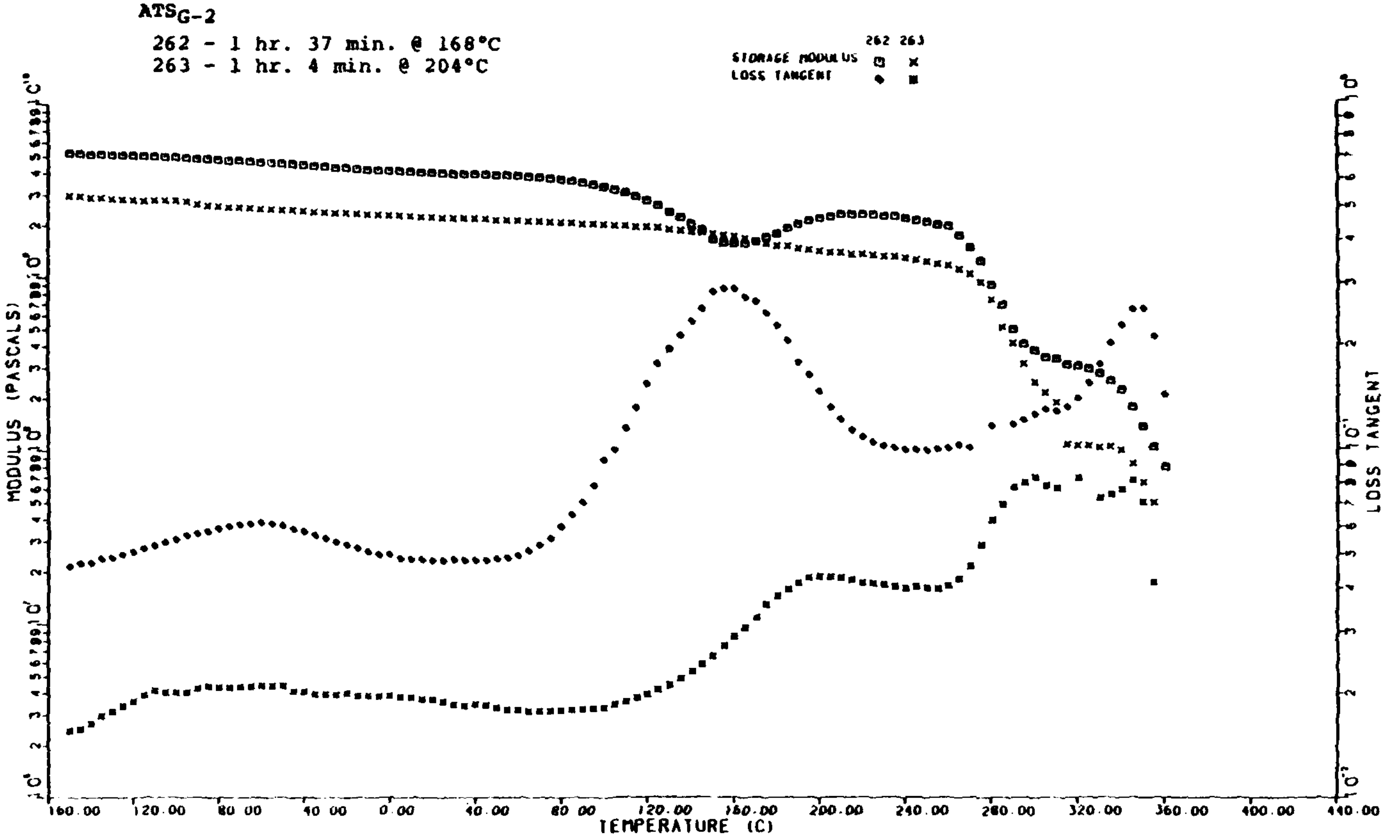


Figure 17. Comparison of DMA Scans for ATS_{G-2} Samples 2 (Run 262) and 4 (Run 263).

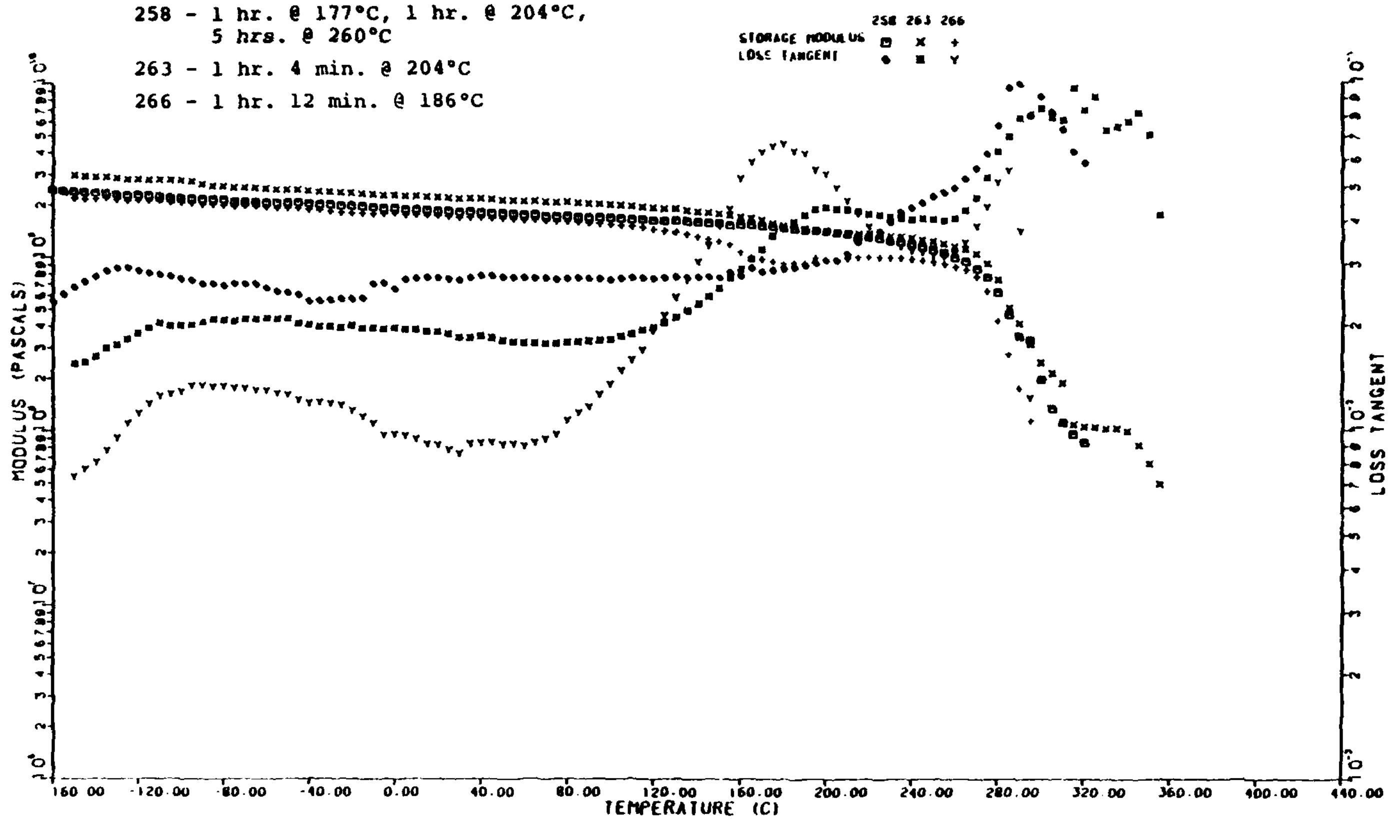


Figure 18. Comparative DMA Scans for ATS_{G-2} Samples 3 (Run 266), 4 (Run 263), and 5 (Run 258).

The ratio A_{3300}/A_{1600} for samples cured at each temperature is plotted in Figure 19. It is evident from the data that acetylene functionality is retained for extended time periods and only disappears gradually with time. Previously we found that vitrification occurs at 205°C in about four minutes. The IR data, however, indicate (as shown in Figure 19) that the acetylene group concentration remains appreciable for several hours after vitrification. This is consistent with a cure mechanism involving limited crosslinking at low temperatures followed by more extensive crosslinking during post-cure at higher temperatures.

6. DEGREE OF CONVERSION AT VITRIFICATION

It was estimated from the ATS_{G-2} Reaction Window plot that the conversion at vitrification based on DMA cure times is approximately 20 percent. This value is lower than one might expect from estimates made in previous AFWAL contract work on pure ATS.[2,5]

For this reason we performed additional isothermal cures with the DSC to approximate the cure during isothermal DMA scans. For each temperature two conditions were run. These were (a) ballistic heating to T_{iso} and (b) heating at a rate equal to that actually experienced in the DMA. The isothermal hold times in each case were t_{vit} determined from the DMA isothermal tests. After the isothermal hold period samples were cooled at a rate as close to ballistic conditions as possible.

The ΔH_P data for these cured samples presented in Table 8 are consistent with the notion that vitrification occurs at low conversions. The lower values of ΔH_P at 197°C and 205°C probably are a result of additional cure taking place during the cooling process following the isothermal cure period.

The various studies in this program involving DSC and DMA, as well as viscosity measurements, and HPLC analyses (discussed

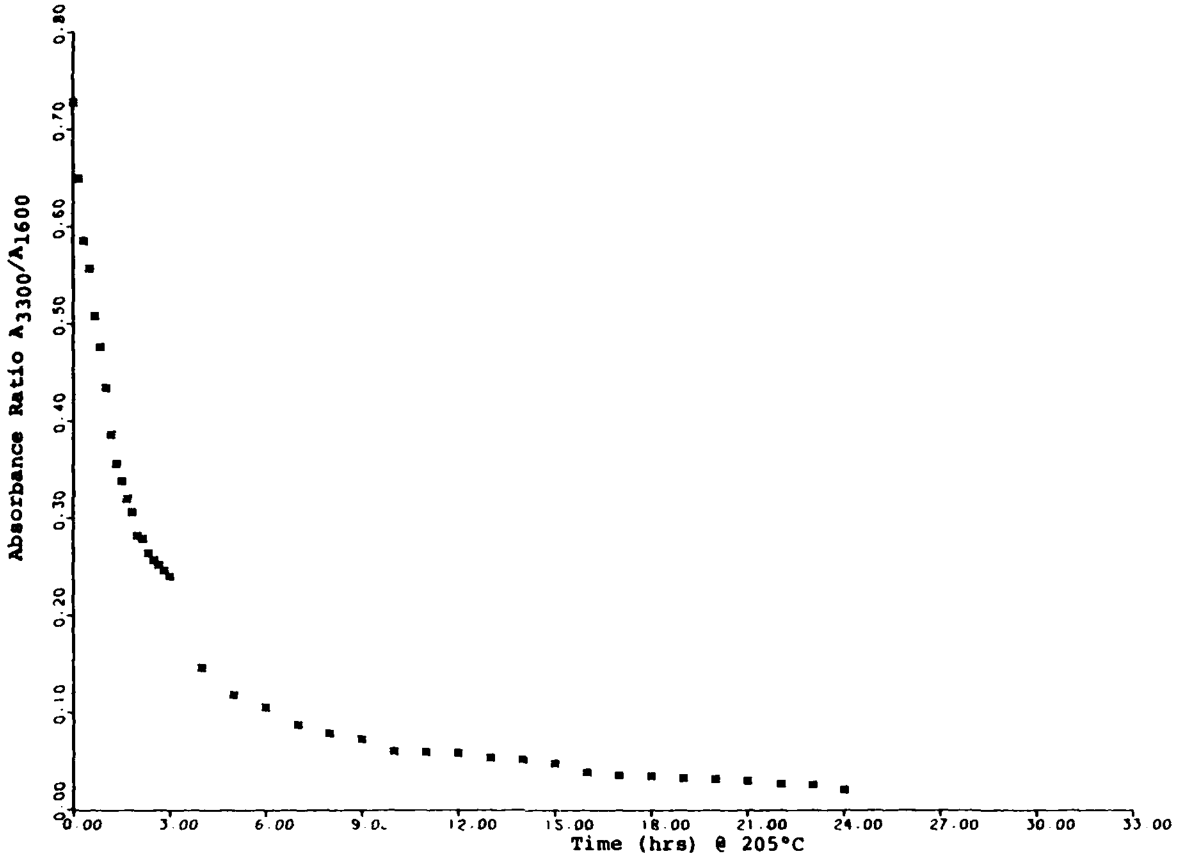


Figure 19(a). Infrared Absorbance Band Ratio for ATS_{G-2}, A_{3300}/A_{1600}, As Function of Cure Time; (a) 205°C, (b) 140°C.

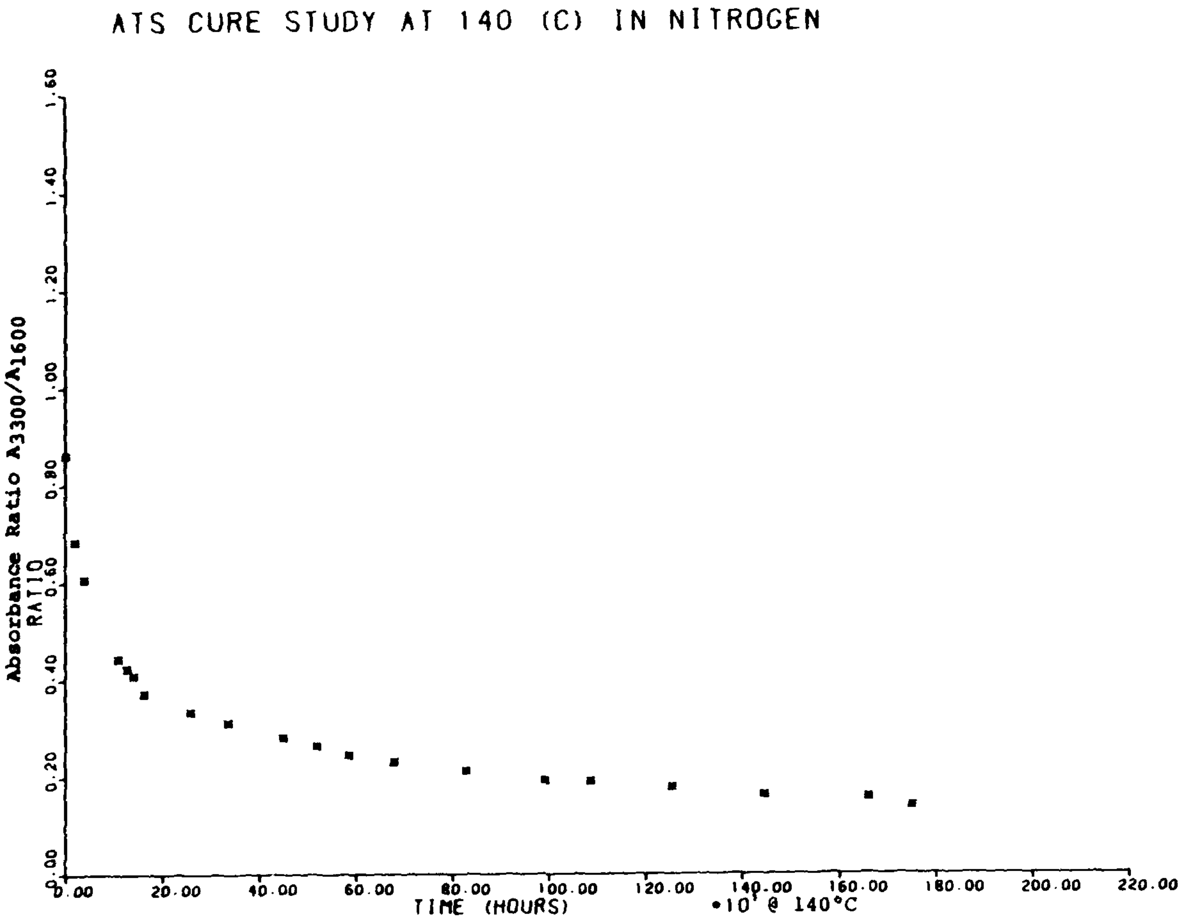

ATS CURE STUDY AT 140 (C) IN NITROGEN
Absorbance Ratio A_{3300}/A_{1600}
RATIO
0.00
0.20
0.40
0.60
0.80
1.00
1.20
1.40
1.60
0.00
20.00
40.00
60.00
80.00
100.00
120.00
140.00
160.00
180.00
200.00
220.00
TIME (HOURS)
•10' @ 140°C

Figure 19(b)

TABLE 8

ISOTHERMAL DSC CURES APPROXIMATING DMA VITRIFICATION TIMES

Temperature (°C)	% Conversion		ΔH_p (cal/g)	
	1†	2*	1†	2*
136	16.4	8.9	87.2	93.8
145	11.3	10.0	91.3	92.7
158	22.8	22.8	79.5	79.5
168	32.0	19.9	70.0	82.5
177	24.3	7.8	78.0	95.0
186	48.2	19.3	53.4	83.1
197	56.2	52.4	45.1	49.0
205	67.4	32.6	33.6	69.4

---

† Samples heated to cure temperature at 320°C/min.

* Samples heated to cure temperature at a rate similar to heat-up in the DMA instrument.

in Paragraphs 7 and 8) indicate that the critical degree of conversion for incipient gelation in ATS_{G-2} is approximately 20 percent. Using the two different approaches suggested by Carothers[10] and Flory-Stockmayer[11,12] for calculating conversion at the gel point we note that a total functionality of 8 per molecule yields an average value for the critical extent of conversion $p_c \approx 0.20$ (Carothers $p_c \approx 0.25$; Flory-Stockmayer $p_c = 0.14$).

This corresponds to a number average degree of polymerization $\bar{x}_n = 5$ or $\bar{M}_n = 2250$ (based on ATS monomer m = 450). However, assuming that the starting material contains 75 percent monomer and 25 percent dimer as well as higher molecular weight species, $\bar{M}_n$ at gelation should exceed 3,000.

An important point to note concerning the nature of the network formed during ATS polymerization is that a total functionality of 8 implies formation of tetrafunctional branches. This is not consistent with cyclization as a potential cure mechanism.

7. LIQUID CHROMATOGRAPHY

a. HPLC Analysis of ATS

HPLC separation of ATS_{G-1} was achieved successfully using a reverse phase gradient technique with dioxane-H_2O as the mobile phase. Two major components and several minor components are present in ATS_{G-1}. A chromatogram for ATS_{G-1} is shown in Figure 20. Integration of areas under the peaks indicates that the relative amounts of the two major components is 78 percent and 22 percent. This is the ratio expected for monomer to dimer. However, it is important to note that the several additional components, mostly higher oligomers, make up a significant portion of the total sample. For ATS_{G-1} the breakdown is approximately 60 percent ATS monomer, 15 percent dimer, and 25 percent other components. For ATS_{G-2} we find 59 percent ATS monomer, 16 percent dimer, and 25 percent other components.

A chromatogram for ATS_{G-2} taken at greater detector sensitivity is shown in Figure 21. It is clear that ATS_{G-2} itself has several components present in minor amounts. The two major components are monomer (component 4) and oligomer (component 7) in the ratio of about 79:21. However, the total percentage of these two components in ATS_{G-2} is considerably less than 100 percent. We note also that the monomer peak is a doublet probably consisting of meta and para isomers.

The technique used for separation of ATS was a general method for oligomer separations developed at UDRI. A Spectra-Physics Model 8000 high performance liquid chromatograph with a Tracor variable wavelength ultraviolet detector was used. The detector was set at 254 nm. Injections were made with a Valco ten part flow-thru injector equipped with a 25 µl loop. A 4.6 mm ID x 25 cm Zorbax ODS and Spectra Physics RP-8 column (Dupont) was used to perform the separation. Both types are packed with C-18 treated silica. The solvents used were HPLC Grade dioxane and water. The flow rate was 1.0 ml/min.

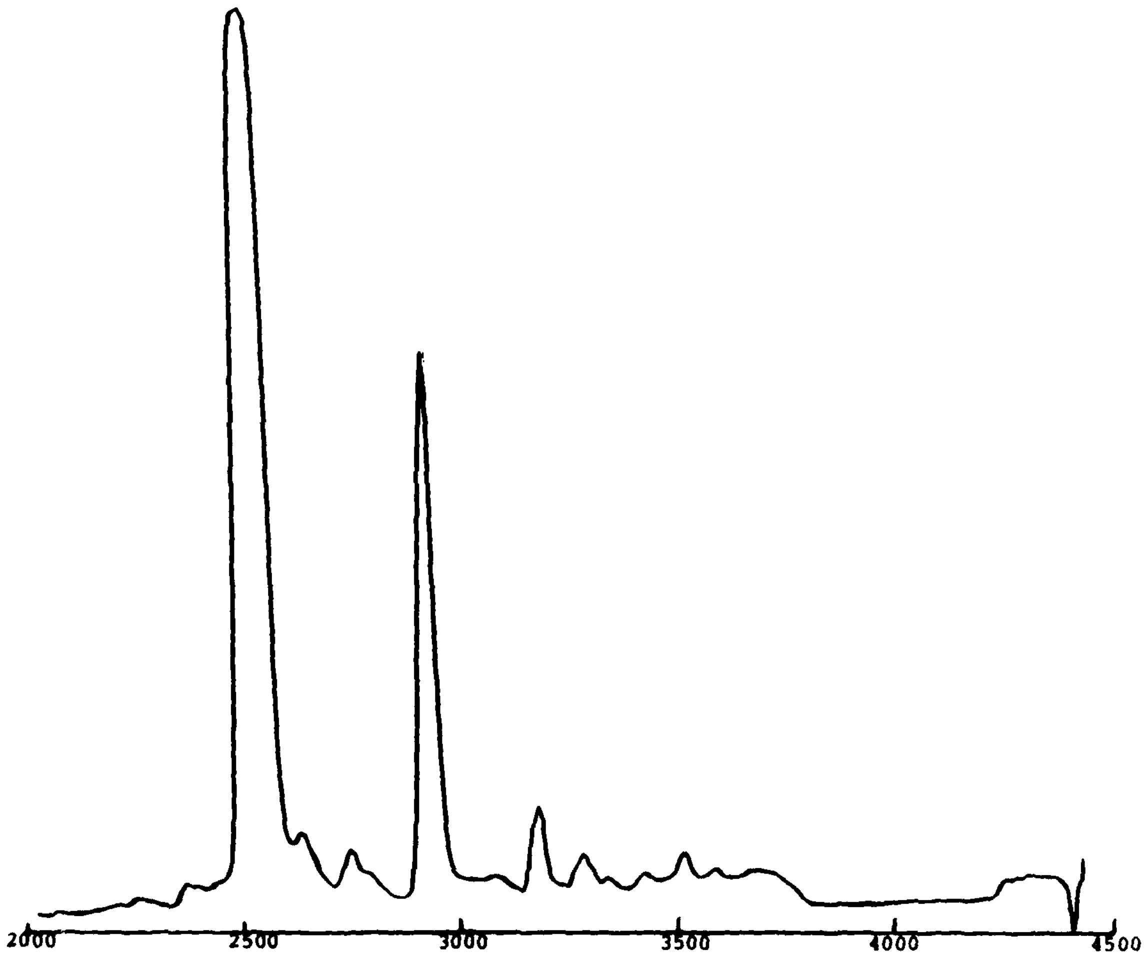


Figure 20. HPLC Chromatogram of Gulf ATS_{G-1} Showing Major and Minor Components.

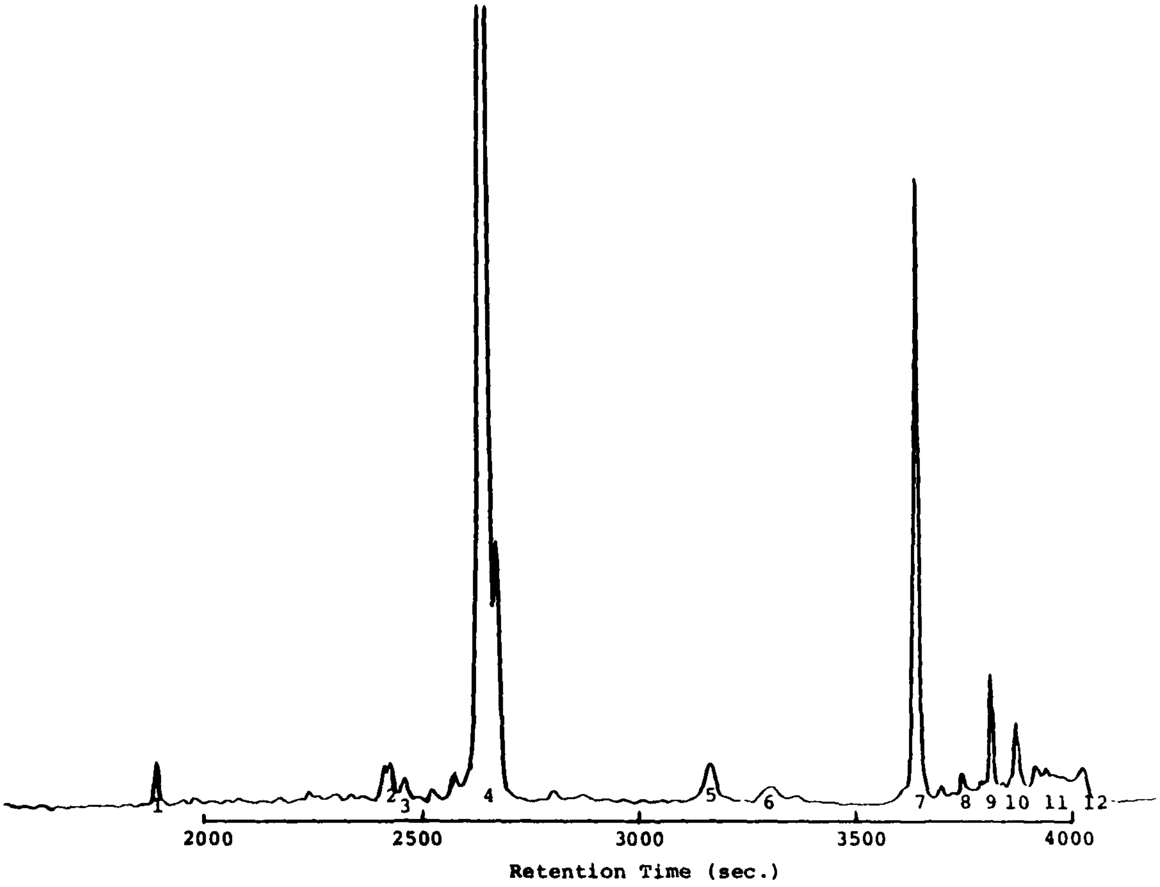


Figure 21. HPLC Chromatogram for Unreacted ATS_{G-2} by a Reverse Phase Gradient Elution Technique; Dioxane-H_2O Mobile Phase.

ATS samples were dissolved in pure dioxane to make a 0.13 percent solution by weight. The solution was filtered and injected into the column at 30°C. The column was also maintained at 30°C. The gradient profile is listed in Table 9.

Using this method we completed HPLC analyses of several different batches of ATS obtained from different sources. For each sample different monomer/dimer ratios were found, indicating the potential for variations from one batch to another. Table 10 contains a summary of the quantitative data obtained.

b. HPLC Analysis of ATS Cure Advancement

Reverse phase gradient elution HPLC separations of ATS_{G-2} and selected samples of partially cured ATS_{G-2} were carried out using dioxane and water as the mobile phase. We find that our technique gives good resolution of the individual species in each sample and that changes in species during curing are apparent. In Figures 21 and 22 we have chromatograms for ATS_{G-2} and a sample cured for 60 minutes at 140°C. The greatest differences in the two chromatograms are found in the region beyond 4,000 sec. retention time indicating a noteworthy increase in higher molecular weight species in the partially cured specimen.

Additional HPLC analyses were completed on ATS_{G-2} samples cured for various times up to the gel point. A cure temperature of 140°C was selected and a series of samples was considered. The percentages of ATS monomer and all other higher molecular weight components (various oligomers) were calculated from the peak areas under the chromatograms. These percentages are represented in Figure 23 where we see a steady decrease in monomer concentration and a steady increase in total oligomer concentration.

The gel point of 80 min. is taken as the point where the first insoluble material appeared. This time corresponds exactly to the gel points determined by both viscosity

TABLE 9
HPLC ANALYSIS GRADIENT PROFILE

Time (min)	% Water	% Dioxane
0.0	100.0	0.0
5.0	60.0	40.0
29.0	36.0	64.0
55.0	36.0	64.0
60.0	25.0	75.0
65.0	20.0	80.0
70.0	0.0	100.0
75.0	0.0	100.0

TABLE 10
SUMMARY OF HPLC QUANTITATIVE ANALYSES OF VARIOUS ATS SAMPLES

Sample Origin	Soln.Conc. (Wt. %)	Monomer (Area %)	Dimer (Area %)	Column
Gulf ATS_{G-1}	0.13	80.5	19.5	Zorbax ODS (DuPont)
Gulf ATS_{G-2}	0.13	78.9	21.1	Zorbax ODS (DuPont)
UDRI-B	0.18	98.8	1.2	RP-8 (Spectra-Physics)
AFWAL-H	0.17	83.9	16.1	RP-8 (Spectra-Physics)
AFWAL-BY	0.14	100.0	0	Zorbax ODS (DuPont)
AFWAL Monomer/Dimer 33.3/66.7	0.13	33.8	66.2	Zorbax ODS (DuPont)

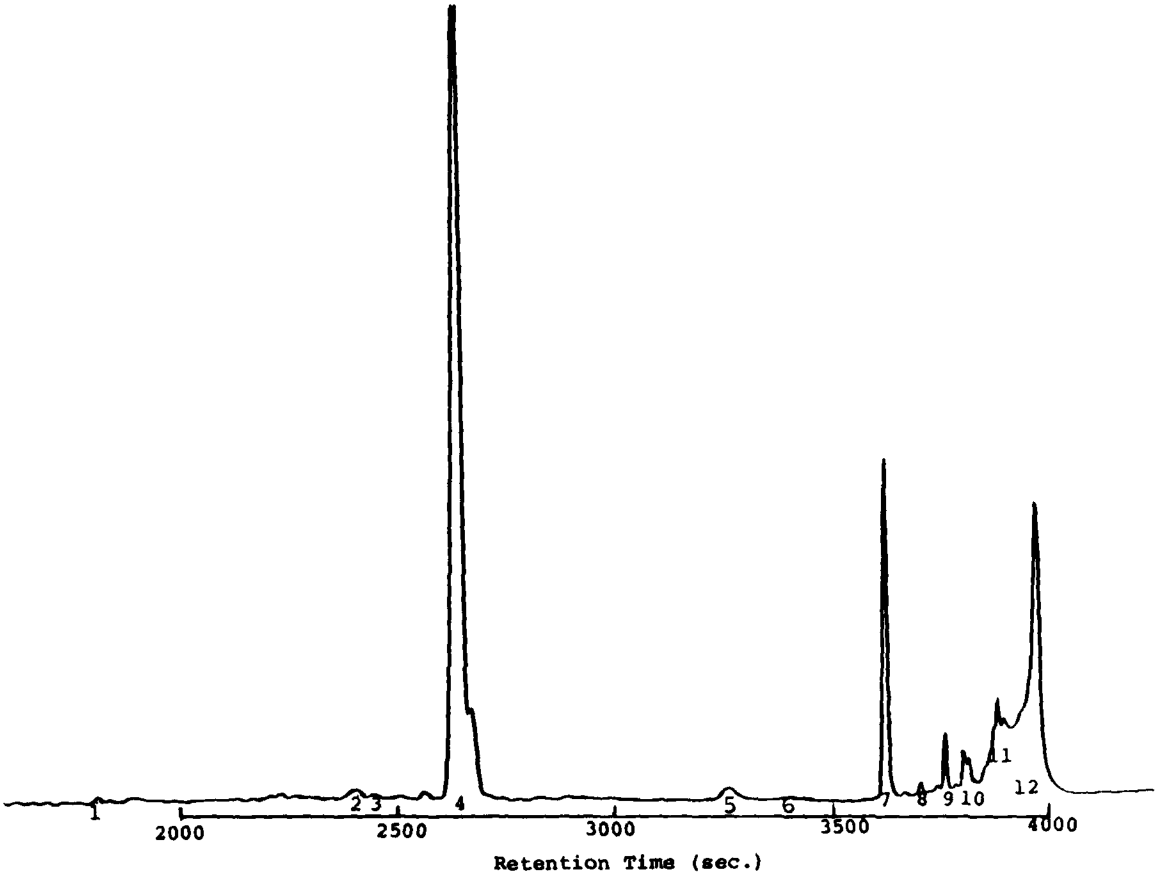


Figure 22. HPLC Chromatogram for ATS_{G-2} Cured 60 Minutes at 140°C; Note Buildup of Components 11 and 12.

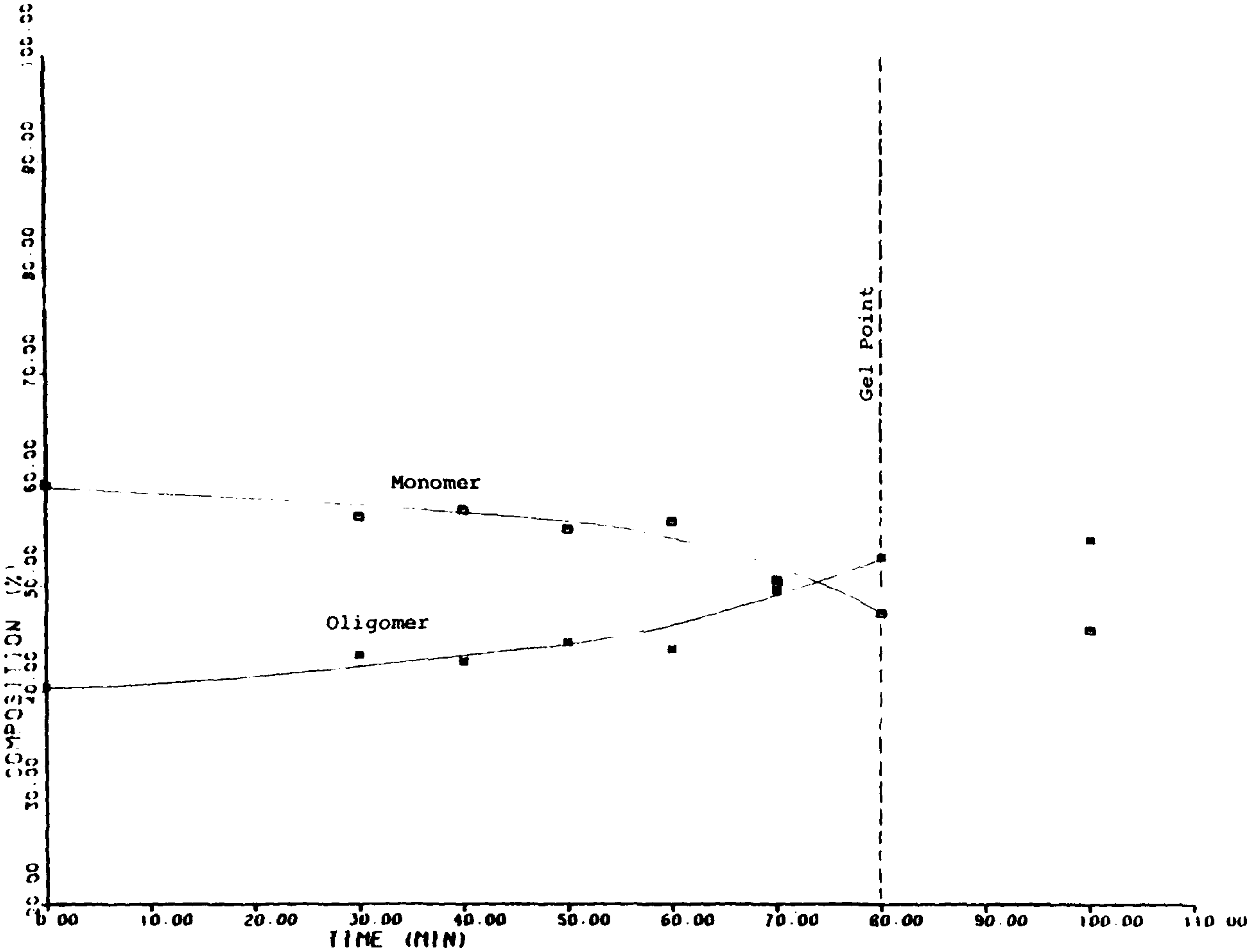


Figure 23. Concentration of ATS Monomer and Total Oligomers vs. Time During Early Stages of Reaction of ATS_{G-2}; Temperature is 140°C.

(Paragraph 8) and DMA measurements (Paragraph 5). At this point 20.5 percent of the original ATS monomer had disappeared. The data at 100 min. do not follow the projected conversion curves because only a limited portion of the total polymer mass was soluble by this time.

8. VISCOSITY PROFILES FROM THE UDRI PARALLEL PLATE RHEOMETER

The UDRI parallel plate rheometer is an accessory designed for use with the Perkin-Elmer thermomechanical analyzer (TMA). It operates by squeezing a resin from between two parallel plates and measuring the change in thickness with time (dh/dt). In the test a sample is subjected to a constant force. For isothermal resin cure studies we take a series of measurements on individual samples cured in the rheometer for various time periods. The amount of sample required for each measurement is approximately 50 mg. A more detailed description of the instrument is provided in Appendix A.

a. The Viscosity-Temperature Curve

At temperatures below 130°C our studies indicate that ATS_{G-2} does not react at an appreciable rate. Thus a single viscosity-temperature plot is sufficient to characterize the flow properties in this temperature range. The data obtained are shown in Figure 24, covering the range from 60-130°C.

Each data point on the plot was recorded after 11 minutes at the test temperature. The viscosity data above 130°C are increasing because of resin cure. Assuming that prepreg processing can be carried out at a viscosity level of 30,000-50,000 cpoise, a processing temperature of about 100°C is called for.

b. Viscosity-Gelation Curves

Figure 25 is a plot of isothermal viscosity-time curves for ATS_{G-2} at several different cure temperatures. Certain features of these data are of particular interest.

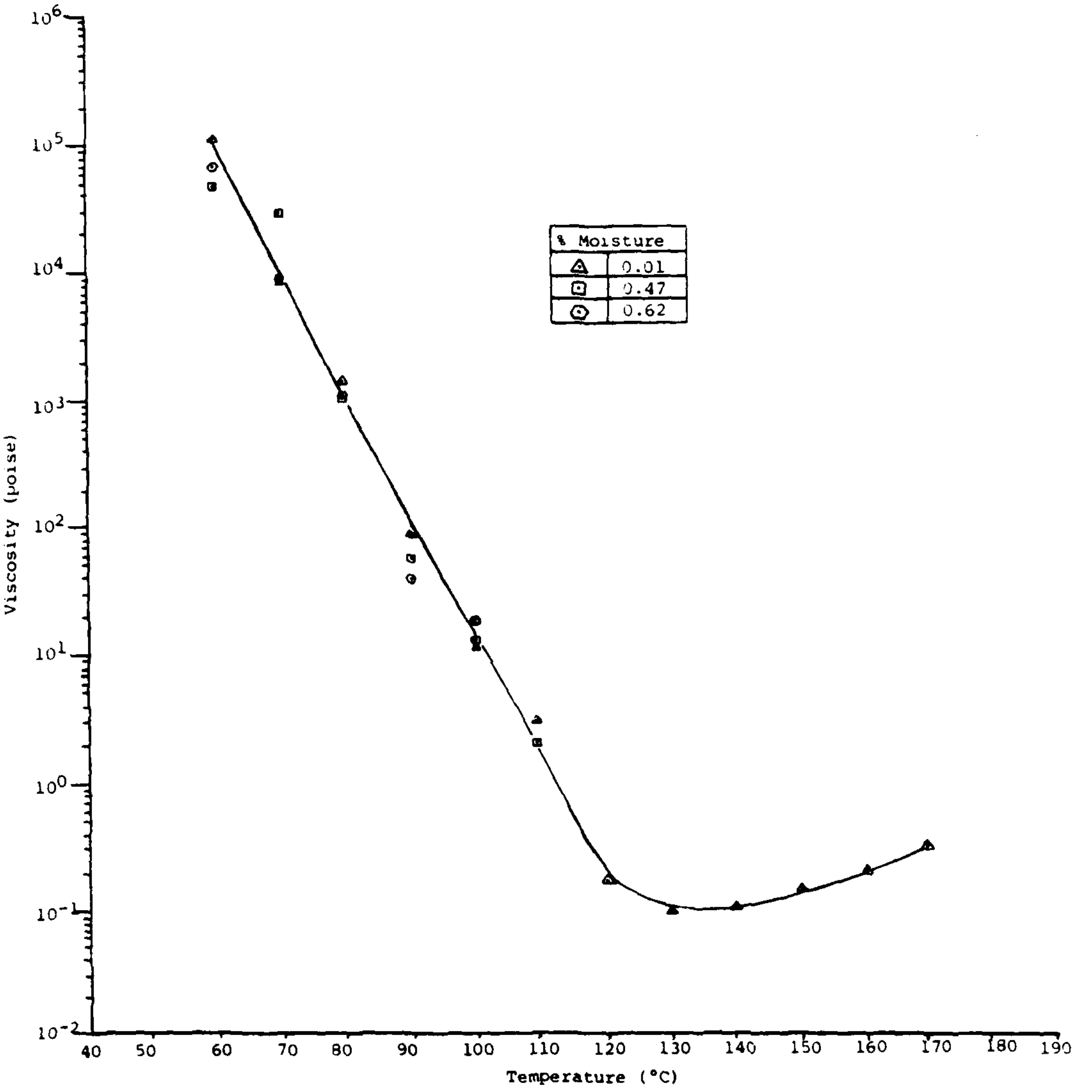


Figure 24. ATS_{G-2} Temperature Variation of Flow Viscosity; Data Taken with the UDRI Parallel Plate Rheometer.

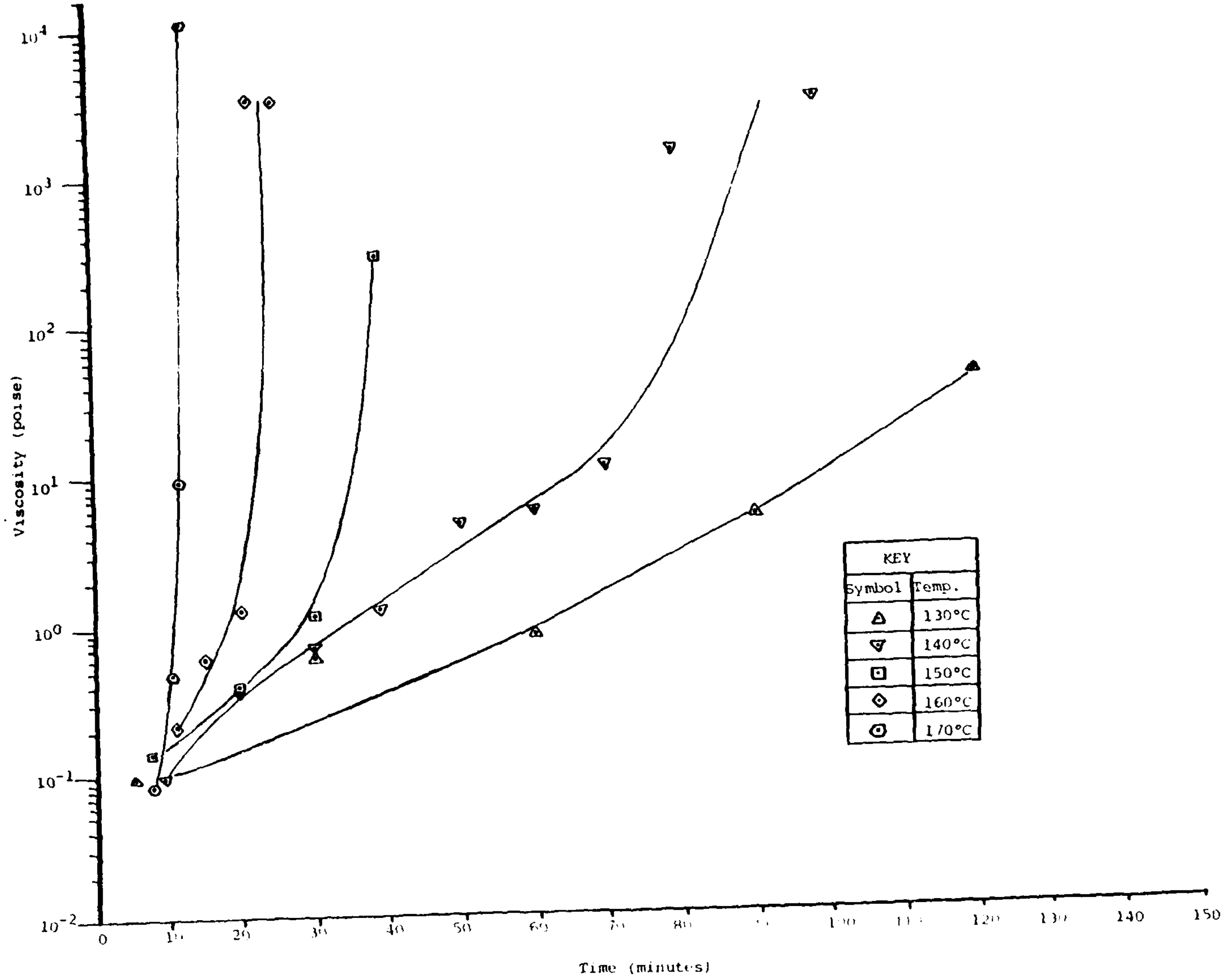


Figure 25. Isothermal Viscosity-Time Curves for ATS$_{G-2}$ Showing Onset of Gelation; Data Taken with the UDRI Parallel Plate Rheometer (PPR).

Each curve shows the characteristic sharp increase in viscosity associated with gelation and the gel times are short at temperatures above 150°C. The initial viscosity of the resin is on the order of 10 cpoise at these temperatures.

If the gel times specified by these viscosity-time curves are compared with the isothermal vitrification times determined by DMA, we find a good match as shown in Figure 26. The fact that the gel times measured by viscosity match the DMA vitrification times indicates that the so-called "gelation" times measured from the DMA may have no particular physical significance. The viscosity values at the DMA "gelation" times are less than 1000 cpoise.

9. HPLC ANALYSES ON PARTIALLY CURED ATS SAMPLES

HPLC analyses were carried out on ATS_{G-2} samples partially cured under isothermal conditions at several temperatures. The various samples had similar viscosities after thermal exposure. The object of this experiment was to determine whether a similar reaction mechanism was apparent at each temperature.

The results listed in Table 11 indicate that within experimental precision conversion in terms of percent ATS monomer reacted is about the same for each sample. These percentages were calculated from peak areas on the HPLC chromatograms. Moreover, the HPLC chromatograms also indicated similar populations of various ATS oligomers at this level of conversion. On a cure time versus 1/T plot such as Figure 27 the iso-viscosity data points fall on a line parallel to the vitrification line. These factors suggest that in the initial stages reaction proceeds by a similar mechanism at each of the temperatures considered. Moreover, since the population of various ATS oligomers increases and ATS monomer decreases steadily up to the gel point (ref. Figure 23), chain extension as well as crosslinking appears to be involved.

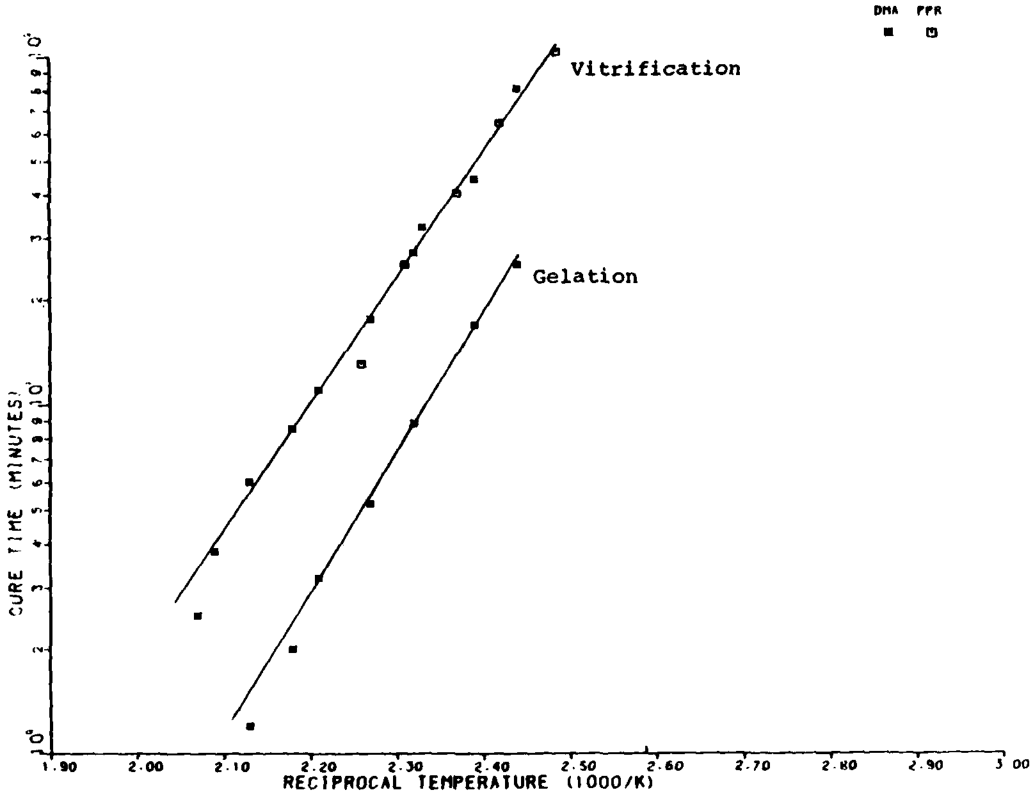


Figure 26. Plot of ATS_{G-2} DMA Vitrification and Gelation Times For Various Cure Temperatures; Data Show That Viscosity Gelation Times Match DMA Vitrification Times; Viscosity Data by Parallel Plate Rheometer (PPR).

TABLE 11

HPLC CONVERSION VALUES FOR ATS$_{G-2}$ SAMPLES PARTIALLY CURED UNDER ISOTHERMAL CONDITIONS AS INDICATED

Sample	η(poise)	% ATS Monomer	% Conversion
Neat ATS	---	60.6	0
40 min. @ 140°C	1.40	56.1	7.1
30 min. @ 150°C	1.30	54.2	10.6
20 min. @ 160°C	1.42	54.4	10.2
12 min. @ 170°C	1.80	53.9	11.1

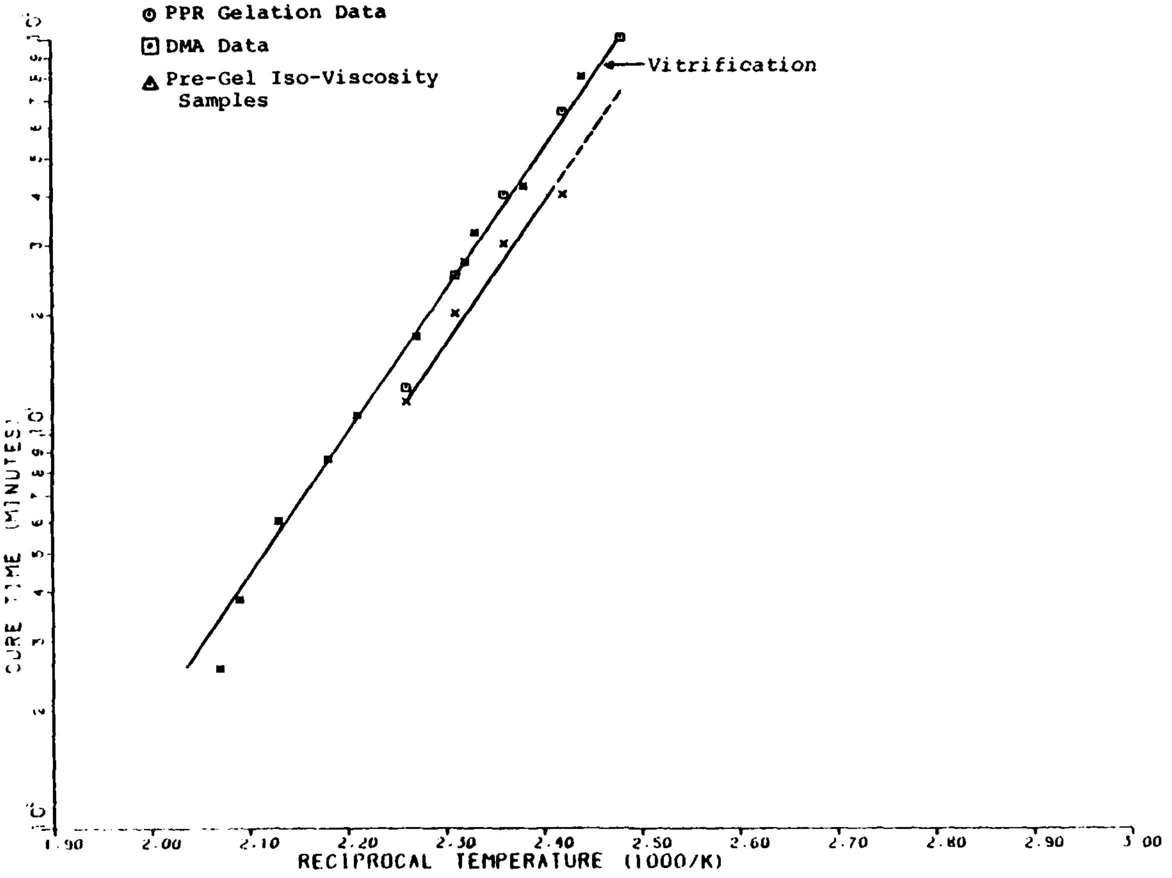


Figure 27. Plot of ATS$_{G-2}$ DMA Vitrification and Viscosity Gelation Times for Various Cure Temperatures Along With Iso-Viscosity Cure Times Referred to in Table 11.

SECTION III

MECHANICAL AND PHYSICAL PROPERTIES OF NEAT ATS RESIN

1. APPEARANCE AND QUALITY OF ATS$_{G-2}$ RESIN

A 45-lb quantity of ATS resin was delivered to UDRI by Gulf R&D Corporation at the end of October 1980. This new ATS was designated ATS$_{G-2}$. It differed in appearance from the several previous batches of ATS characterized by UDRI. Its physical state at ambient temperature was a solid, slightly tacky to the touch. It was easily cracked and chipped into small bits so that it could be transferred to different containers. Its color was dark brown with a red tinge.

A microscopic examination of this batch of ATS showed that two types of impurities were present. One was in the form of small black particles approximately 50-100 μm in size scattered randomly through the material. The other consisted of long thin fibers similar to those obtained from a filter or laboratory wipe. These impurities were subsequently observed in the neat resin castings referred to in subsequent paragraphs.

2. PREPARATION OF CAST ATS TEST SPECIMENS FOR TENSILE AND DMA EXPERIMENTS

A method for fabricating void-free castings of ATS$_{G-2}$ for tensile and DMA testing was developed for this program utilizing a variation of AFWAL procedures involving molds cast from an RTV silicone elastomer. The samples were dogbone ASTM types microtensile bars and rectangular DMA bars approximately 1-1/2 x 1/2 x 0.040.

The casting procedure adopted is as follows:

(1) The silicone RTV molds are held in the vertical position in a spring loaded clamping device. Two holes are provided in the top; one for filling the mold and one for air escape. The one for filling has additional volume outside

the mold area to provide for continuous filling and to hold ATS during evacuation after filling.

(2) The molds are preheated at 125°C for one hour prior to pouring to prevent solidification of the ATS during the pour.

(3) ATS is heated to 125°C in a vacuum oven for 15 minutes at 29 in. H_2O vacuum and poured into the molds. The molds are then held at 125°C and 29 in. H_2O vacuum for an additional 45 minutes.

(4) The molds are transferred to another oven held at the desired cure temperature. Total hold time in the cure oven is the sum of time required to heat molds to T_{cure} plus actual isothermal cure time.

(5) The partially crosslinked samples are next stripped from the molds and postcured in nitrogen or air atmosphere.

3. TENSILE EXPERIMENTS

a. Preliminary Tests

Dogbone tensile specimens of ATS_{G-2} were fabricated by casting in silicone rubber molds as discussed previously. The tensile bars were cured isothermally at various temperatures and postcured at selected time and temperature intervals. The amount of time and the cure temperatures selected were guided by our DSC and DMA cure studies. Five samples were prepared for each cure condition selected.

In order to establish an appropriate testing technique some preliminary tensile bars were tested at room temperature. Only one sample for each cure condition was submitted. The data, listed in Table 12, indicate that our results are similar to those obtained for ATS previously by AFWAL/MLBC. Crosshead speed was 0.05 in/min. Modulus and elongation were taken from a 1/2-inch extensometer.

TABLE 12

PRELIMINARY TENSILE DATA†

Cure Time* (hrs.)	Ult. Strength (psi)	Modulus (ksi)	% Max. Elongation
2	3,600	434.8	0.85
3	3,900	463.8	0.86
4	4,200	455.9	0.98
5	4,500	464.3	1.00

---

† Testing was performed at ambient temperature, crosshead speed 0.05 in/min., elongation measured by 1/2-inch extensometer.

* Times listed are for final postcure at 260°C, initial cure was 1 hr. @ 125°C, 1 hr. @ 177°C, 1 hr. @ 204°C.

b. Systematic Series of Tensile Tests on ATS_{G-2} Effects of Cure Temperature and Time on Tensile Properties

Microtensile dogbone castings of ATS_{G-2} cured under various conditions were tested at ambient temperature. These tests were completed at a crosshead rate of 0.05 in/min and elongation data were taken from a 1/2-inch extensometer. A summary of the data obtained is presented in Table 13. For each cure condition a minimum of three dogbones was tested and the results reported are average values.

The trend observed in the data is interesting. A maximum elongation in the range of 1.25 percent with single specimens in a group ranging up to 1.35 or 1.4 percent was noted at cure temperatures of 168°C and 186°C. It was decided to check these data by tests on separate sets of samples cured at the same conditions. In addition, cure temperatures of 158°C and 177°C also were considered. The results of these further tests are listed in Table 14. The objective in evaluating this group was to reproduce the results obtained previously for 168°C, 186°C, and 204°C cures and to consider whether longer time and/or higher temperature were beneficial to properties.

TABLE 13

TENSILE DATA FOR ATS_{G-2} CASTINGS CURED UNDER SELECTED CONDITIONS

Cure Conditions	Ultimate Strength (psi)	Ultimate Strength Pascals (10^7)	Ultimate Strength S.D. (psi)	Modulus of Elasticity (psi)	Modulus of Elasticity Pascals (10^9)	Modulus of Elasticity S.D. (psi)	Elongation (%)	Elongation S.D.
1 hr. 37 min. @ 168°C	3,483	2.4	850	572,669	3.95	34,298	0.64	0.16
1 hr. 12 min. @ 186°C	4,240	2.9	1,121	551,750	3.8	19,932	0.87	0.25
1 hr. 4 min. @ 204°C	4,863	3.4	966	518,625	3.6	47,776	0.80	0.20
4 hr. 20 min. @ 145°C 1 hr. 25°C to 300°C	5,098	3.5	888	433,886	3.1	39,721	1.19	0.20
1 hr. 37 min. @ 168°C 1 hr. 25°C to 300°C	5,119	3.5	534	415,750	2.9	20,104	1.27	0.12
1 hr. 12 min. @ 186°C 1 hr. 25°C to 300°C	4,988	3.7	894	418,400	2.9	19,194	1.15	0.32
1 hr. 4 min. @ 205°C 1 hr. 25°C to 300°C	4,154	2.9	1,037	435,450	3.0	19,696	0.93	0.25

NOTES:

All samples were exposed to a vacuum for 1 hr. @ 125°C for degassing prior to cure. Post-cures were carried out in an N_2 atmosphere.

Crosshead speed was 0.05 in/min.; test temperature, R.T.

TABLE 14

TENSILE DATA FOR ATS$_{G-2}$ CASTINGS CURED UNDER SELECTED CONDITIONS

Cure Conditions	Ultimate Strength			Modulus of Elasticity			Elongation	
	(psi)	Pascals (10^7)	S.D. (psi)	(psi)	Pascals (10^9)	S.D. (psi)	(%)	S.D.
2 hr. 15 min. @ 158°C	5,006	3.45	499	451,917	3.12	41,588	1.16	0.21
1 hr. 37 min. @ 168°C	5,185	3.575	1,515	462,607	3.19	29,847	1.15	0.38
1 hr. 20 min. @ 177°C	4,313	2.97	1,496	516,100	3.56	20,128	0.86	0.34
1 hr. 12 min. @ 186°C	4,627	3.19	986	451,125	3.11	16,180	1.05	0.24
1 hr. 4 min. @ 204°C	5,030	3.47	2,028	469,900	3.24	27,082	1.10	0.50
1 hr. 10 min. @ 225°C	5,073	3.50	733	480,458	3.31	18,373	1.07	0.20
4 hr. @ 168°C	4,505	3.11	1,452	500,900	3.45	21,811	0.93	0.38
16 hr. @ 168°C	5,094	3.51	1,212	511,950	3.53	21,466	1.03	0.27
1 hr. 37 min. @ 168°C 1 hr. @ 300°C	5,071	3.50	927	493,083	3.40	16,094	1.05	0.20
1 hr. 37 min. @ 168°C 2 hr. @ 300°C	5,341	3.68	1,185	498,333	3.44	22,959	1.08	0.38

NOTES:

All samples were exposed to a vacuum for 1 hr. @ 125°C for degassing prior to cure. Heating from 25°C to 300°C was accomplished over a 1 hr. period. Post-cures were carried out in an N_2 atmosphere.

Crosshead speed was 0.05 in/min.; test temperature, R.T.

In general, the results shown in Table 14 have more "scatter" than those in the previous test group. Average elongation values are not as great and ultimate strength and modulus values are somewhat lower also.

However, the data do indicate that strength, modulus, and elongation values are of the same order of magnitude as the first group of samples. The data also suggest that additional cure at a low temperature and/or postcure at a high temperature have no particular benefit in terms of property enhancement.

The particular cure and postcure conditions selected for these experiments were chosen for the following reasons. First of all, it was thought that maximizing chain extension at the expense of some crosslinking was most desirable for improving elongation. The most likely temperatures for this are at the lower end of the cure temperature range as determined by DSC. Thus we studied this range systematically to determine isothermal cure profiles. Also we found that isothermal cures in this temperature range did not result in a complete cure. However, DSC and DMA studies showed that a complete cure could be achieved by continuous heating to 300°C at a programmed rate. This yields a polymer with a T_g value of about 290-310°C. Another advantage of the cure cycles selected that we found promising is that they require relatively low temperatures and short times compared to cure cycles used previously for ATS.

As noted, all postcures used in generating these data were carried out at temperatures up to 300°C. It was established based on these results that the best combination of properties (strength, modulus, and elongation) were obtained using a cure temperature of 168°C. Reasonable properties cannot be achieved without a postcure.

In order to test the effect on properties of longer cure times and a 250°C postcure, an additional set of tensile tests were completed as reported in Table 15. According

TABLE 15

ADDITIONAL TENSILE DATA FOR ATS$_{G-2}$ CASTINGS CURED UNDER SELECTED CONDITIONS

Cure Conditions	Ultimate Strength			Modulus			Elongation	
	(psi)	Pascals (10^7)	S.D. (psi)	(psi)	Pascals (10^9)	S.D. (psi)	(%)	(S.D.)
1 hr. 37 min. @ 168°C 1 hr. 25°C-300°C 25 min. 300°C-25°C	5,547	3.824	1,127	464,919	3.205	59,096	1.14	0.28
1 hr. 20 min. @ 177°C 1 hr. 25°C-300°C 15 min. 300°C-25°C	5,514	3.801	1,462	440,346	3.036	27,595	1.31	0.35
1 hr. 37 min. @ 168°C 1 hr. 25°C-300°C N_2 1 hr. 300°C 15 min. 300°C-25°C	4,120	2.840	1,269	437,999	3.019	16,847	0.97	0.36
16 hr. @ 168°C 1 hr. 25°C-300°C 15 min. 300°C-25°C	5,746	3.961	953	424,241	2.925	20,089	1.38	0.31
1 hr. 37 min. @ 168°C 1 hr. 25°C-250°C 15 min. 250°C-25°C	4,926	3.396	1,090	492,725	3.397	37,821	1.03	0.23
1 hr. 37 min. @ 168°C 1 hr. 25°C-250°C 1 hr. 250°C 15 min. 250°C-25°C	5,716	3.941	936	460,199	3.173	42,653	1.29	0.26
1 hr. 12 min. @ 186°C 1 hr. 25°C-250°C 15 min. 250°C-25°C	4,121	2.841	1,027	467,660	3.224	28,172	0.87	0.34
1 hr. 12 min. @ 186°C 1 hr. 25°C-250°C 1 hr. 250°C 15 min. 250°C-25°C	4,399	3.033	1,648	449,096	3.096	27,147	1.03	0.42

NOTES:

All samples were exposed to a vacuum for 1 hr. @ 125°C for degassing prior to cure. Post-cures were carried out in an N_2 atmosphere.

Crosshead speed was 0.05 in/min.; test temperature, R.T.

to these data an extended cure time (16 hours) at 168°C may give a slight improvement in properties but similar property levels can be achieved by a short cure followed by a one hour postcure at 250°C.

The data in Table 16 were developed using the standard 168°C cure followed by a 250°C postcure for various lengths of time up to four hours. Also we considered alternative N_2 and air cure atmospheres. The results show that similar properties are achieved in air and N_2 and that some improvement in properties might be achieved by extending the postcure at 250°C over a two or three hour period. No particular advantage is achieved by extending the postcure beyond three hours.

c. Preferred Cure Cycle for ATS Laminates

Based on the data accumulated to date the following cure cycle is suggested for obtaining the most favorable combination of properties from ATS_{G-2}: degas at 125°C followed by cure for 40 minutes at 168°C, postcure at 250°C for three hours. It is important to note that these times do not include heat-up periods so that additional time must be added to account for heating the resin sample/laminate to the specified cure/postcure temperature. This cure cycle was implemented in the prepreg and composite process development phases of the program. These will be discussed in later sections of the report.

d. A Relation Between ATS Tensile Strength and Elongation

Figure 28 represents a correlation plot that relates tensile strength and elongation for ATS_{G-2} castings. Each data point on the diagram represents an individual tensile specimen. In contrast, the values listed in Tables 13 through 16 are average values taken for a number of specimens at each cure condition. The trend in data clearly indicates that one can expect strength and elongation to increase simultaneously, while the expected modulus values are in the $4 \cdot 10^5$ to $5 \cdot 10^5$ psi range.

TABLE 16

TENSILE DATA FOR ATS_G-2 CASTINGS CURED AT 168°C AND POSTCURED AT 250°C

Cure Conditions	Ultimate Strength			Modulus of Elasticity			Elongation
	(psi)	Pascals (10^7)	S.D. (psi)	(psi)	Pascals (10^9)	S.D. (psi)	(%)
0 hr. @ 250°C (Air)	5,956	4.11	898	484,376	3.34	31,707	1.29
2 hr. @ 250°C (Air)	5,394	3.72	225	471,964	3.25	16,045	1.20
4 hr. @ 250°C (Air)	6,137	4.23	935	469,326	3.24	17,626	1.39
3 hr. @ 250°C (N_2)	6,184	4.26	1,250	496,434	3.42	100,463	1.45
4 hr. @ 250°C (N_2)	4,985	3.44	1,046	452,614	3.12	13,573	1.17

NOTE: All samples were exposed to a vacuum for 1 hr. @ 125°C for degassing prior to cure. Cure was 168°C for 1 hr. 37 min. Postcure was initiated by heating from 25°C to 250°C over 1 hr. After postcure samples were cooled from 250°C to 25°C over 15 min.

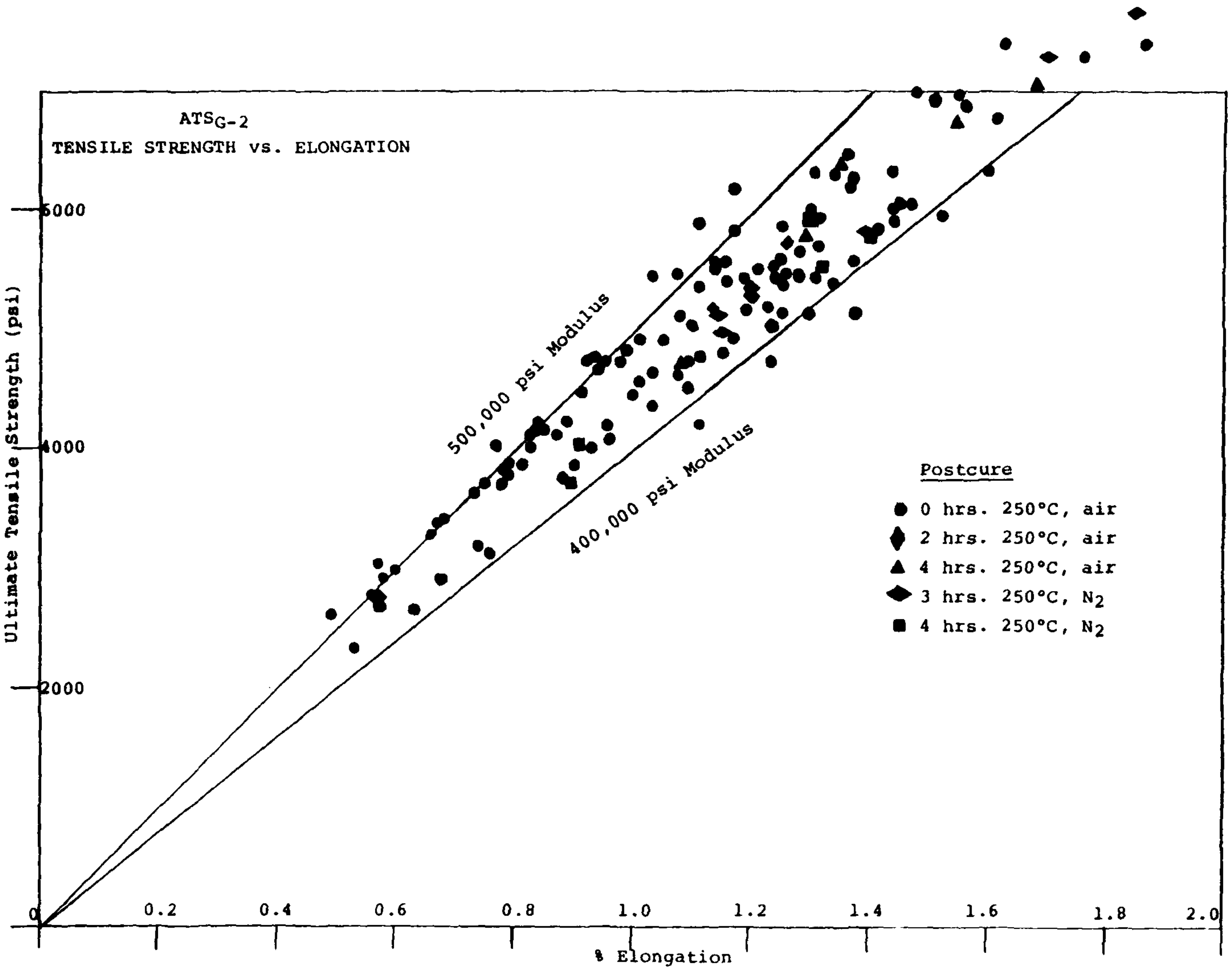


Figure 28. Relationship Between Tensile Strength and Elongation for Various ATS Tensile Castings.

e. Effect of Humidity on Tensile Properties

Tensile dogbone specimens cured under various conditions were exposed at 100 percent relative humidity for four weeks. Room temperature tensile tests at 0.05 in./min. were completed on all the samples and compared to results for comparable dry specimens. These data are tabulated in Table 17. The moisture content listed is based on dry sample weight.

The data in Table 17 clearly indicate that moisture generally causes a reduction in tensile properties. However, this reduction is slight as illustrated in Figure 29. On the correlation plot relating tensile strength and elongation we note that the data for individual wet specimens (■) fall within the 4-500,000 psi limits as indicated.

f. Reduced Crosshead Speed Tensile Results

A series of specimens cured under various conditions were tested at a lower crosshead rate, 0.02 in./min. These data are listed in Table 18 along with results for comparable specimens previously tested at 0.05 in.m/min. While the averaged data show no clear trend for values taken at a reduced strain rate, the individual data points in Figure 29 (▲) are shifted toward the upper portion of the diagram. This is contrary to an expected trend toward greater elongation and lowered modulus with decreasing strain rate.

4. RELATIONS BETWEEN TENSILE AND DMA DATA

Figure 30 shows a series of DMA plots for castings cured according to the four cycles in Table 13 that include postcures. The trend noted here is that loss tangent values over the entire temperature range scanned are greater for the higher elongation tensile series. This difference is particularly noticeable in the region around T_g. T_g values are about 290-310°C.

The same trend is observed for samples postcured at 250°C (refer to Table 17). Figure 31 contains DMA plots for samples

TABLE 17

TENSILE DATA COMPARISON FOR WET AND DRY ATS$_{G-2}$ CASTINGS CURED UNDER VARIOUS CONDITIONS

• Cure Conditions	Ultimate Strength		Modulus		% Elongation	% Moisture
	(psi)	(Pascals·10^7)	psi	(Pascals·10^9)		
177°C 1 hr. 20 min.	4630	3.17	438,000	3.02	1.26	1.52 (Wet)
+ 300°C (no hold)	4310	2.97	516,000	3.57	0.86	(Dry)
186°C 1 hr. 12 min.	4140	2.85	410,000	2.83	0.94	1.41 (Wet)
+ 300°C (no hold)	4920	3.39	451,000	3.11	1.11	(Dry)
204°C 1 hr. 4 min.	4450	3.07	442,000	3.05	1.07	1.44 (Wet)
+ 300°C (no hold)	5030	3.47	470,000	3.24	1.11	(Dry)
225°C 1 hr. 10 min.	5040	3.47	438,000	3.02	0.98	1.40 (Wet)
+ 300°C (no hold)	5070	3.50	480,000	3.31	1.07	(Dry)
168°C 4 hrs.	3930	2.71	480,000	3.31	0.88	1.49 (Wet)
+ 300°C (no hold)	4500	3.10	501,000	3.45	0.93	(Dry)
168°C 16 hrs.	4010	2.76	460,000	3.17	0.90	1.48 (Wet)
+ 300°C (no hold)	5090	3.51	512,000	3.53	1.02	(Dry)
168°C 1 hr. 37 min.	4250	2.93	421,000	2.90	0.99	1.46 (Wet)
+ 300°C 1 hr.	5070	3.50	493,000	3.40	1.05	(Dry)
168°C 1 hr. 37 min.	3100	2.14	427,000	2.94	0.76	1.36 (Wet)
+ 300°C 2 hrs.	5340	3.68	498,000	3.43	1.08	(Dry)
168°C 1 hr. 37 min.	4460	3.08	485,000	3.34	0.97	1.45 (Wet)
+ 250°C (no hold)	4930	3.40	493,000	3.40	1.03	(Dry)
168°C 1 hr. 37 min.	3280	2.26	447,000	3.08	0.75	1.62 (Wet)
+ 250°C 1 hr.	5720	3.94	460,000	3.17	1.29	(Dry)
186°C 1 hr. 12 min.	3880	2.68	465,000	3.21	0.88	1.46 (Wet)
+ 250°C (no hold)	4120	2.84	468,000	3.23	0.87	(Dry)
186°C 1 hr. 12 min.	4590	3.16	502,000	3.46	0.97	1.31 (Wet)
+ 250°C (no hold)	4400	3.03	449,000	3.10	1.03	(Dry)

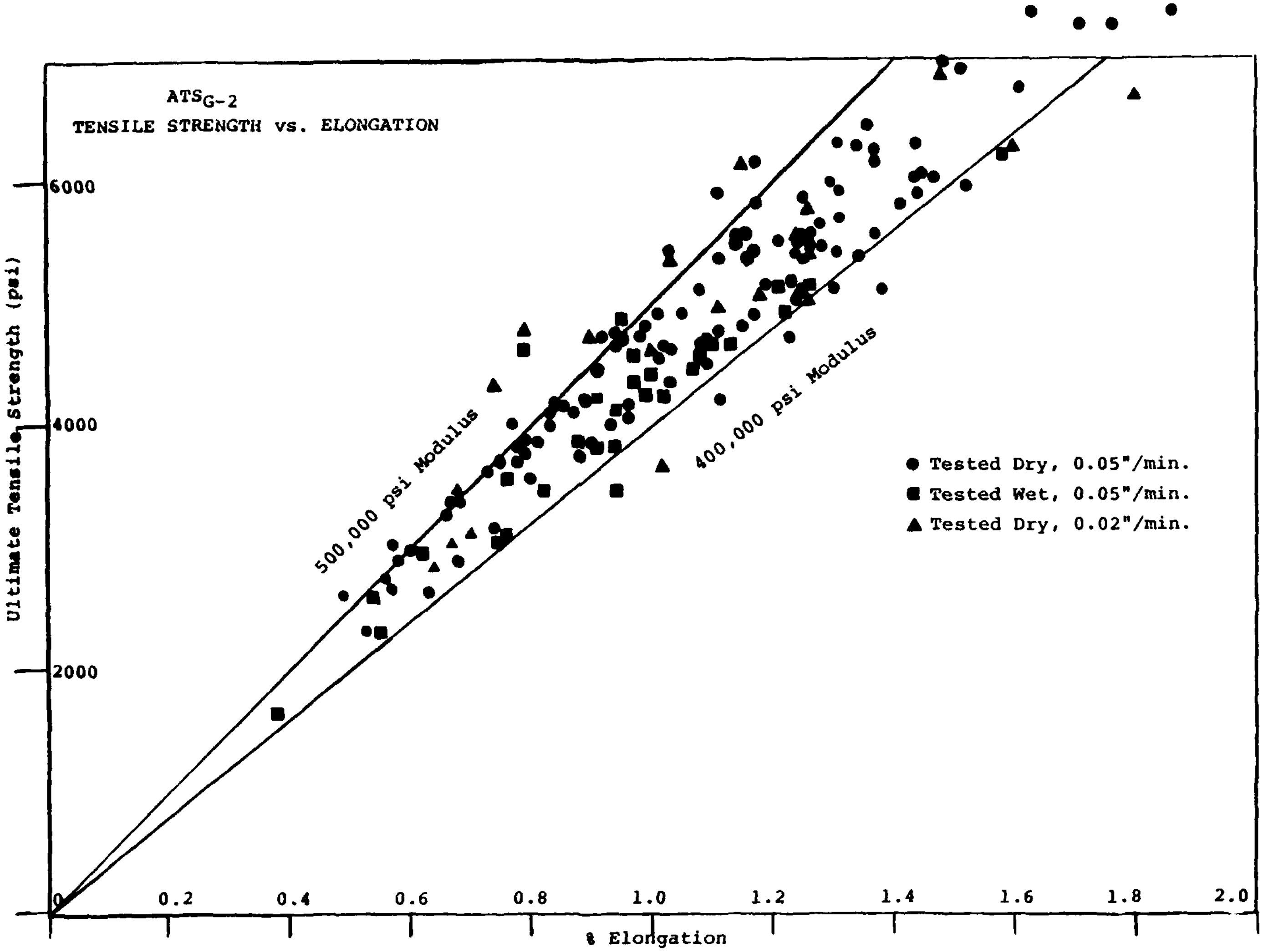


Figure 29. Tensile Strength versus Elongation Relationship for ATS$_{G-2}$ Dogbone Specimens.

TABLE 18

TENSILE DATA COMPARISON AT TWO DIFFERENT CROSSHEAD RATES, ATS_{G-2} CASTINGS CURED UNDER VARIOUS CONDITIONS

Cure Conditions	Ultimate Strength		Modulus		% Elongation	Crosshead Speed (in/min)
	(psi)	(Pascals·10^7)	(psi)	(Pascals·10^9)		
168°C 1 hr. 37 min.	4040	2.79	446,000	3.08	0.88	0.02
+ 300°C (no hold)	5550	3.83	465,000	3.21	1.14	0.05
177°C 1 hr. 20 min.	5320	3.67	456,000	3.14	1.17	0.02
+ 300°C (no hold)	5510	3.80	440,000	3.03	1.31	0.05
168°C 1 hr. 37 min.	6050	4.17	470,000	3.24	1.29	0.02
+ 300°C 1 hr.	4120	2.84	438,000	3.02	0.97	0.05
168°C 16 hrs.	4450	3.07	433,000	2.99	0.95	0.02
+ 300°C (no hold)	5746	3.96	424,000	2.92	1.38	0.05
168°C 1 hr. 37 min.	6520	4.50	386,000	2.66	1.70	0.02
+ 250°C (no hold)	4930	3.40	493,000	3.40	1.03	0.05
168°C 1 hr. 37 min.	5550	3.83	446,000	3.08	1.24	0.02
+ 250°C 1 hr.	5720	3.94	460,000	3.17	1.29	0.05
186°C 1 hr. 12 min.	4130	2.85	483,000	3.33	0.86	0.02
+ 250°C (no hold)	4400	3.03	449,000	3.10	1.03	0.05

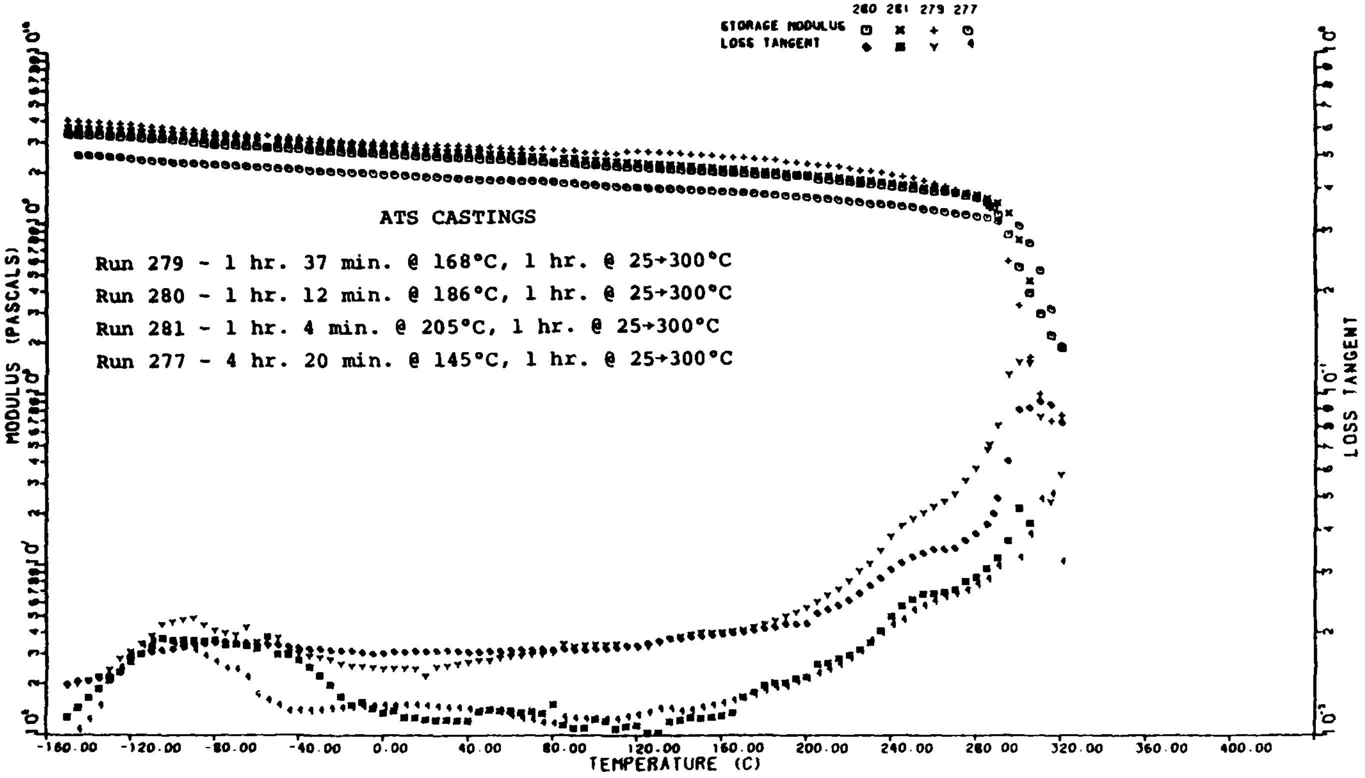


Figure 30. DMA Modulus and Loss Tangent Profiles for ATS_{G-2} Castings Cured by Various Routes; Cures Correspond to Those for Tensile Data in Table 13.

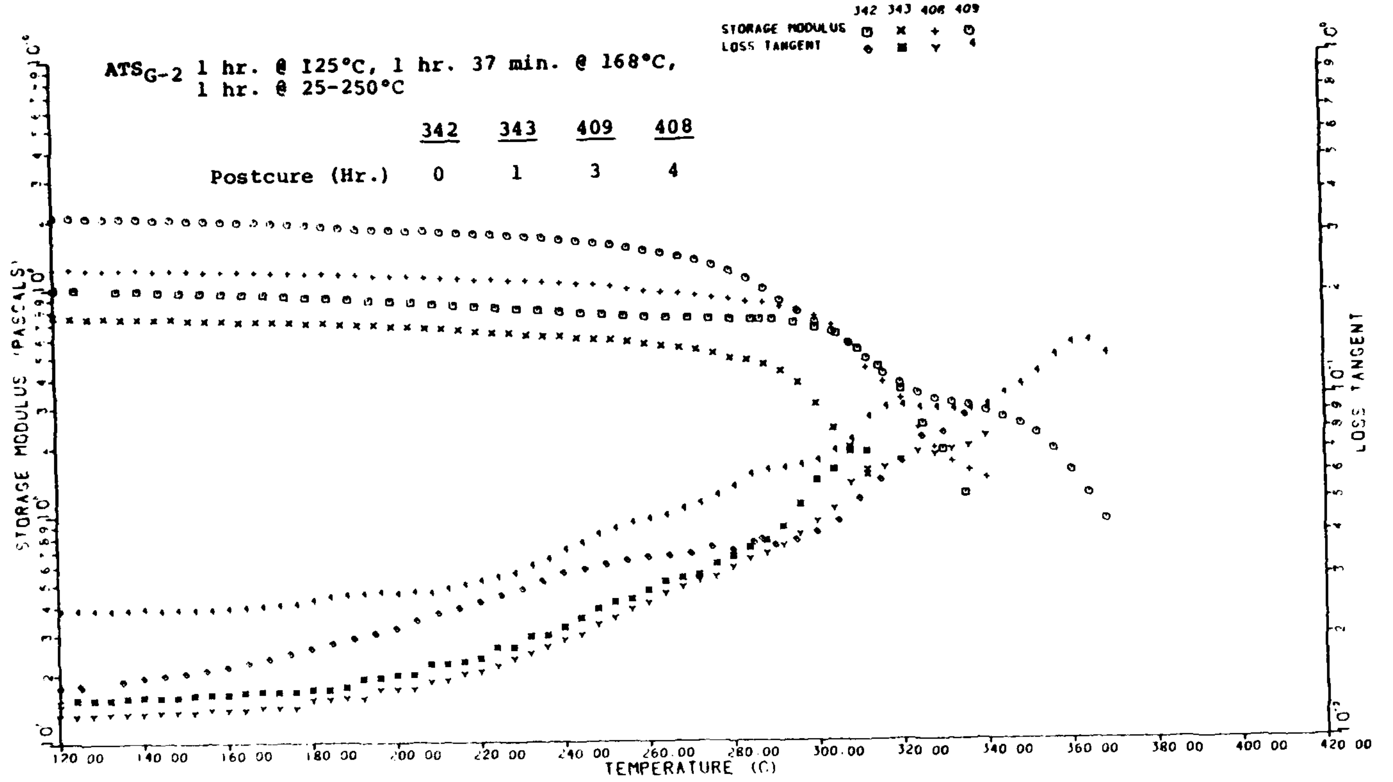


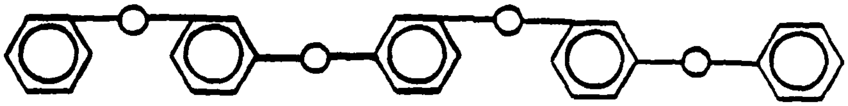
Figure 31. DMA Modulus and Loss Tangent Profiles for ATS$_{G-2}$ Castings Postcured in N_2 for Various Times.

postcured for various time periods in N_2. The actual DMA specimens studied were cut from tensile bars. An expanded view of the T_g region for each of these samples is shown in Figure 32. Figure 33 compares 250°C postcures in air and N_2. In each case the comparison indicates that the tensile samples with highest elongation also have greatest area under the loss tangent curve. Moreover, these preferred samples also tend to have higher modulus and ultimate strength values.

5. PLASTICIZED ATS COMPOSITIONS

a. Properties of OS-124 Plasticizer

Experiments were initiated to test the viability of plasticizing ATS_{G-2} with the nonvolatile, thermostable oligomer, pentaphenylether (PPE). PPE is a viscous, transparent liquid at ambient conditions, having a consistency similar to corn syrup. Its chemical structure is depicted below. The PPE compound is also referred to by its laboratory designation, OS-124.



Plasticizer Pentaphenylether (OS-124)

OS-124 has a T_g value of -33°C. Mixed with ATS_{G-2} it causes a reduction in T_g that is approximately linear with the percentage added. For example, ATS_{G-2} has a T_g value of 12°C; with 15 percent OS-124 added T_g falls to 5°C and with 30 percent OS-124 T_g is 2°C. The low volatility and thermostable characteristics of OS-124 are demonstrated by the TGA thermographs of Figure 34. By itself OS-124 begins to vaporize at 250°C but is not appreciably volatile until 300°C. When it is incorporated into cured ATS formulations no weight loss is observed until about 300°C.

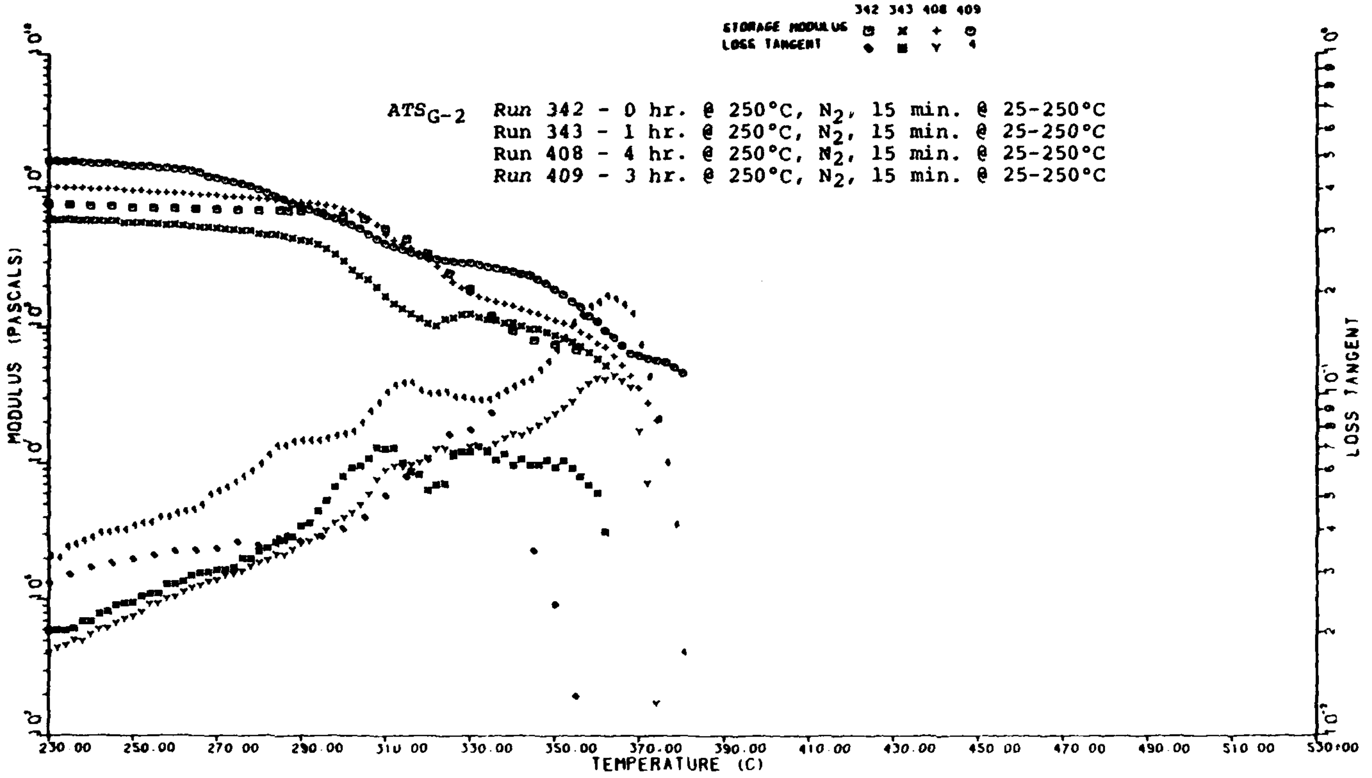


Figure 32. Expanded Graph of DMA Modulus and Loss Tangent Data of Figure 31.

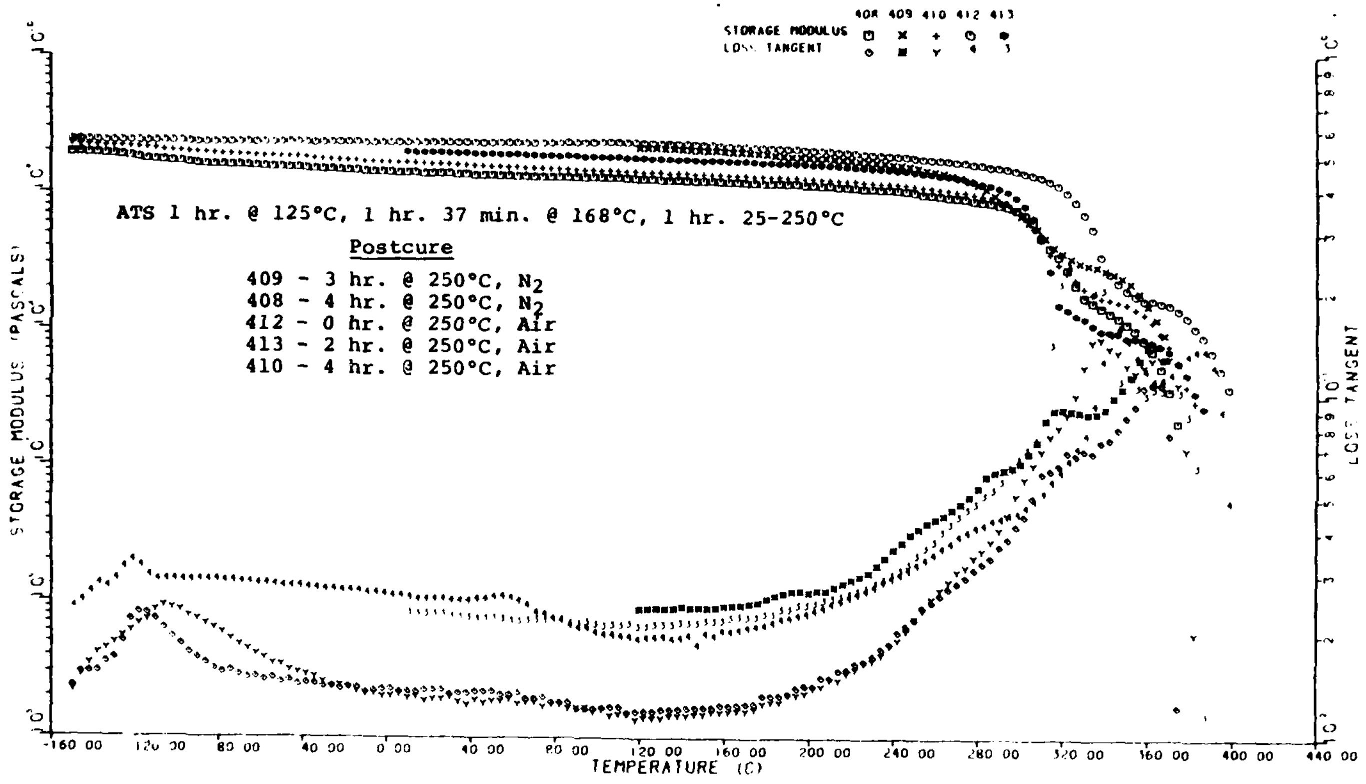


Figure 33. DMA Modulus and Loss Tangent Profiles for ATS_{G-2} Castings Postcured at 250°C; Comparison of Results in N_2 and Air Atmospheres.

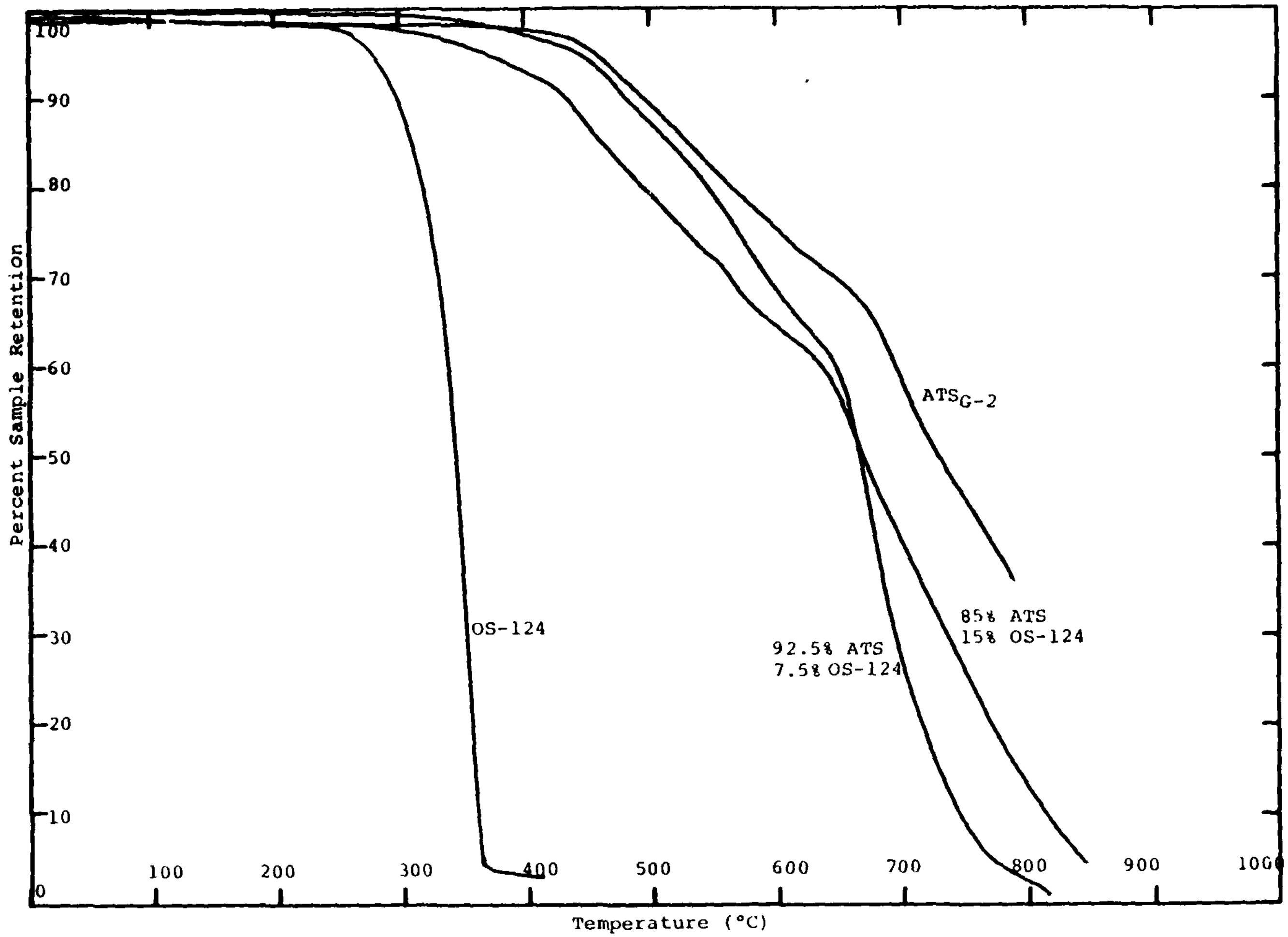


Figure 34. TGA Thermographs Showing Relative Weight Loss Characteristics of Cured Formulations of ATS$_{G-2}$/OS-124 Compared With Those for the Pure Materials.

b. Dynamic Mechanical Properties

As a means for comparing the thermomechanical properties of plasticized ATS_{G-2} and unplasticized ATS_{G-2} we prepared neat resin DMA specimens containing various amounts of OS-124, all cured using our standard processing schedule (precure 168°C, postcure 250°C). These specimens were then tested by DMA at a heating rate of 2°C/min.

The dynamic mechanical data of Figure 35 show that increasing the level of OS-124 plasticizer raises the magnitude of loss tangent in the range of ambient up to T_g. Over this range modulus values decrease slowly so that the plasticized formulations have slightly lower values than does unplasticized ATS_{G-2}. We noted previously in the program that such increases in loss tangent correlate with increased elongation and tensile strength in neat resin tensile specimens.

c. Tensile Properties

A series of neat resin microtensile dogbone specimens was fabricated from ATS_{G-2} containing 7.5, 15, 20, and 25 percent OS-124. Again the standard processing cycle (1 hr. 37 min. at 168°C followed by 3 hrs. at 250°C) was used for curing. The data obtained for these specimens are shown in Figure 36 where each point represents an individual tensile specimen.

The plot shows the correlation between ultimate strength and elongation developed earlier in the program. The locus of data obtained for unplasticized ATS_{G-2} (100 samples) is on the lower part of the diagram bounded by 6,500 psi strength and 1.6 percent elongation. Seven pure ATS_{G-2} neat specimens denoted by X had values above these levels. However, these samples were processed differently by curing to various degrees. The results were not reproducible.

The data for the plasticized samples (20 of 27 samples) fall on the upper part of the diagram and tend to increase in value as the plasticizer level increases. This trend is shown

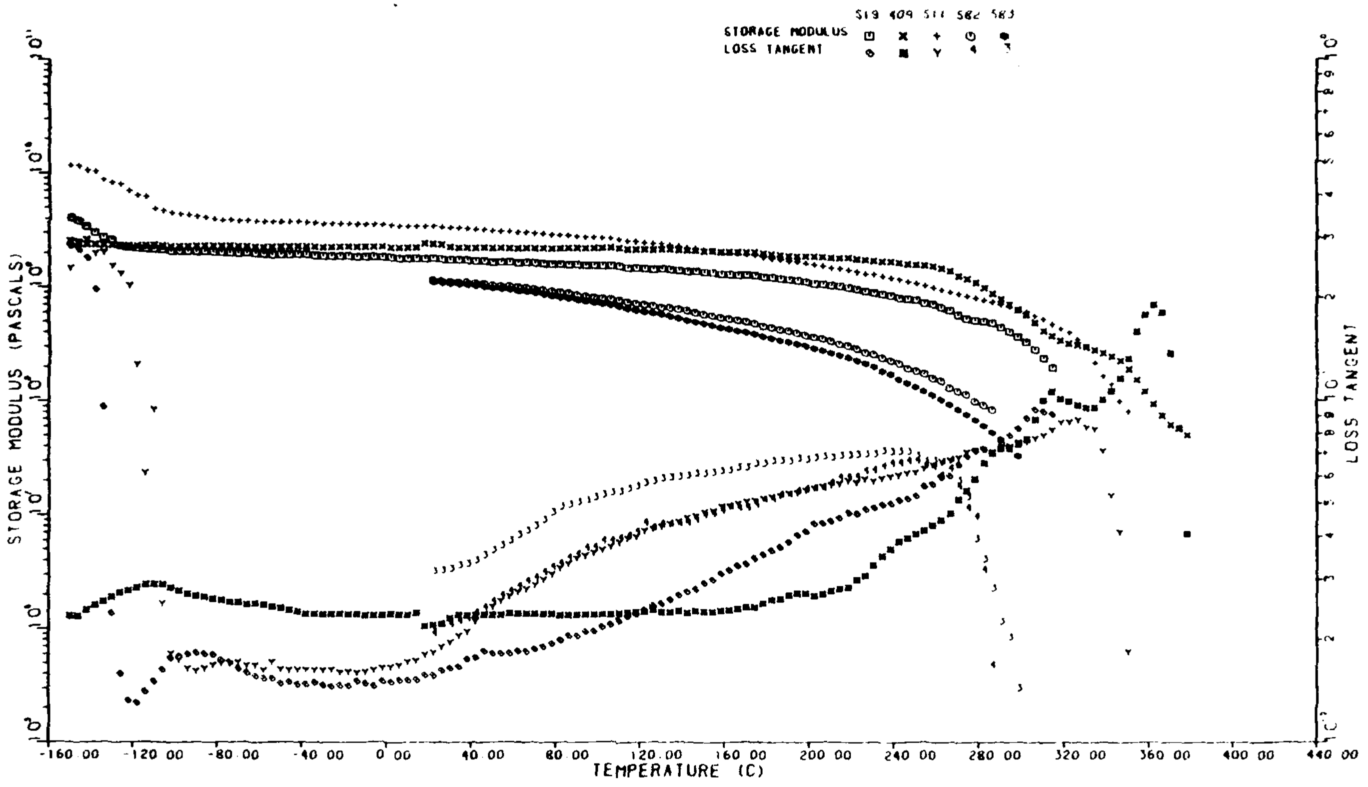


Figure 35. Dynamic Mechanical Properties of Various ATS_{G-2}/OS-124 Formulations Compared to ATS_{G-2}, All Cured Under Standard Conditions.

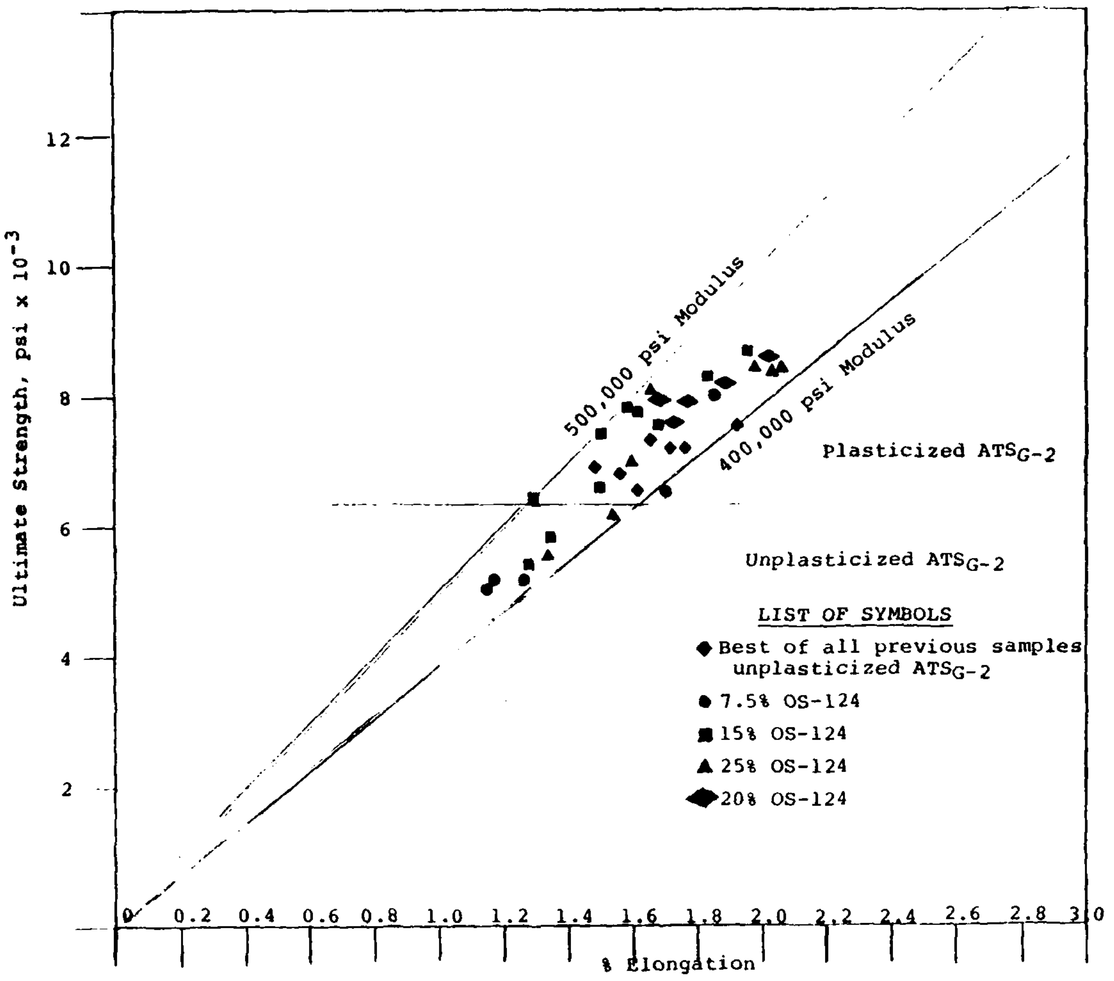


Figure 36. Correlation for Ultimate Strength and Elongation of ATS$_{G-2}$/ OS-124 Formulations.

also by the average values listed in Table 19. To this point values in the range of 8,500 psi and 2 percent elongation have been obtained. Moreover, these values are consistent and reproducible and the standard deviation figures for each set of specimens are relatively low.

Two important observations about the plasticized specimens suggest the possibility that improved results can be obtained from these formulations. The first of these is that the plasticizer was not uniformly distributed in samples fabricated for our preliminary tests. For example, the transmission of high intensity light through a sample cross-section is not uniform in many cases. Secondly, we observed that many of the specimens had some degree of dimensional distortion indicating that residual strains probably exist within. It is likely that such cooling stresses can be relieved by allowing a longer time for cooling the molded specimens both before stripping from the mold and after the postcure has been completed. This is suggested by the results in Table 19 where results from the first two sets of samples were improved by allowing a longer cooling period after postcure.

Finally, it is of interest to note that the tensile bars containing OS-124 are much less brittle to the touch than are pure ATS samples. The plasticized bars are quite flexible and can be bent and handled with no particular danger of breaking.

d. Prepreg and Laminate Processing

ATS_{G-2} and OS-124 can be mixed at slightly elevated temperatures (60-80°C) the mixtures have lower viscosities than pure ATS_{G-2}. UDRI is preparing to make enough 3-inch tape from a mixture of 75/25 ATS/OS-124 to characterize the interlaminar shear and flex properties of test laminates fabricated by methods used previously in this program. The prepreg will be produced by a hot melt technique using AS-4 fiber.

We anticipate that the prepreg produced will have superior tack and drape properties compared to those produced

TABLE 19

TENSILE PROPERTIES OF PLASTICIZED ATS_{G-2} CASTINGS

Plasticizer Content (wt. %)	Ultimate Strength			Modulus			Elongation	
	(psi)	Pascals (10^7)	S.D. (psi)	(psi)	Pascals (10^9)	S.D. (psi)	(%)	S.D.
7.5[1]	4,953	3.41	1,438	481,409	3.32	37,499	1.04	0.27
15[1]	6,959	4.80	1,093	527,891	3.64	15,366	1.52	0.17
7.5	6,060	4.22	1,400	469,000	3.27	16,000	1.38	0.35
15	6,990	4.88	1,300	482,000	3.37	37,000	1.54	0.27
20	7,630	5.32	1,200	505,000	3.49	25,000	1.69	0.34
25	7,510	5.24	1,170	480,000	3.36	46,000	1.75	0.28

All samples processed by degassing 1 hr. at 125°C prior to cure; First stage cure was 1 hr. 37 min. at 168°C followed by postcure of 3 hrs. at 250°C; Cool down period after postcure was 15 min. in case of samples designated by [1]; All others were cooled to ambient over a 45 minute interval.

Values listed are averages from 6 or more samples.

previously from pure ATS or ATS/ethanol. This is based on our observations of ATS/OS-124 mixtures at ambient temperatures. Such mixtures are quite "sticky" to the touch and are flexible when coated onto a fiberglass cloth.

SECTION IV
PROCESS DEVELOPMENT

1. RESIN-FIBER COMPATIBILITY

An effort was made in this program to use surface free energy analysis to match the surface energy of ATS_{G-2} to that of a particular graphite fiber in order to optimize interfacial wetting and bonding. In doing so, one should:

a. Use the wetting criterion--that the matrix resin should have a lower total surface energy than the fiber; and

b. Choose the fiber such that its polar component of the surface energy γ^p matches that of the resin almost exactly, while the dispersive component γ^d is the same order of magnitude, matching as closely as possible (but not exactly).

With this objective the following experiments were carried out.

a. Surface Free Energy Analysis of ATS_{G-2}

Contact angles were measured for ATS_{G-2} cured for one hour at 125°C in vacuum followed by isothermal holds at 204°C for one hour and 316°C for two hours in N_2. The data for nine reference liquids are listed in Table 20. We used the least squares method to fit the data and calculated polar and dispersive components of the surface energy following the procedure of Drzal[10] and Kaelble.[11] These are:

$$\gamma_s^p = 8.6 \text{ mj/m}^2, \gamma_s^d = 29.9 \text{ mj/m}^2, \gamma_s^T = 38.5 \text{ mj/m}^2 \quad (2)$$

Additional descriptive material on the experimental procedures for these measurements and the fiber surface energy measurements cited in the following paragraph (b) are described in Appendix B.

TABLE 20

CONTACT ANGLES FOR NINE REFERENCE FLUIDS ON ATS_{G-2}*

Solvent	Contact Angle, θ (Degrees)
water	74.2 ± 1
n-octane	2.1 ± 1
bromonapthalene	14.4 ± 1
hexadecane	4.2 ± 1
formamide	48.1 ± 1
PG-1200	7.3 ± 1
ethylene glycol	43.8 ± 1
glycerol	57.5 ± 1
tricresylphosphate	12.3 ± 1

* ATS_{G-2} sample was cured by heating 1 hour at 125°C in vacuum followed by isothermal holds in N_2 at 204°C for 1 hour and 316°C for 2 hours.

b. Surface Free Energy Analysis of Graphite Fibers

Contact angles were measured first for Celion 12000 fibers by dipping single fibers into various liquids and recording the surface tension forces with a microbalance. The average force over a period of 15 to 120 seconds was used to calculate contact angles by the formula $F = \gamma_L \pi d \cos \theta$, where γ_L is the surface tension of the liquid and d is the fiber diameter. The fiber diameters were determined by taking three readings at 3,000X magnification on the actual fiber end tested using the scanning electron microscope. Each contact angle reported in Table 21 is an average value for three separate fibers.

The polar and dispersive surface free energy components calculated using the contact angle are $\gamma_s^p = 19.8$ mj/m^2 and $\gamma_s^d = 23.7$ mj/m^2. The total surface free energy is $\gamma_s^T = 43.5$ mj/m^2.

Using the same method polar and dispersive surface free energy components were calculated for several other types of graphite fibers based on contact angle measurements performed on single fibers. The results of these measurements are presented in Table 22 and are compared with the corresponding values for ATS. Based on the data, AS-4 was judged to be the most compatible with ATS in terms of wettability. This was considered the most likely candidate for prepreg processing. However, if it proves necessary to select a sized fiber for subsequent prepregging, then Celion with an epoxy finish would be the recommended choice.

2. CHEMICAL INTERACTION BETWEEN RESIN AND FIBERS

The possibility that the reaction rate of ATS_{G-2} might be affected by presence of graphite fibers was considered by measuring ΔH_p values of mixtures of ATS_{G-2} with graphite fibers. The basic DSC thermograms for various amounts of ATS_{G-2} mixed with AS-1 fibers are not influenced by the fibers. Within experimental error both the location of the reaction exotherm

TABLE 21

CONTACT ANGLES FOR CELION 12000 GRAPHITE FIBERS IN VARIOUS LIQUIDS

Liquid	Contact Angle(degrees)
Water	52 ± 8
Glycerol	60 ± 4
Ethylene glycol	34 ± 3
Polypropylene glycol PG 1200	0
Formamide	31 ± 1
n-hexadecane	27 ± 8
bromonaphthalene	3 ± 5
n-octane	0

TABLE 22

SURFACE FREE ENERGY

Fiber	Polar	Dispersive	Total
ATS neat resin	8.6	29.9	38.5
Celion 1200/unsized	28.8	23.0	51.8
Celion 1200/epoxy	19.8	23.7	43.5
T300/unsized	29.6	22.7	52.3
T300/309 finish	20.6	22.8	43.4
AS-1	28.3	24.0	52.3
AS-4	17.4	26.5	43.9

peaks and the ΔH_p values (accounting for weight of fiber) are unaffected for the samples measured. This is shown in both Figure 37 and Table 23.

In Figure 37 we note that for the samples tested the values of ΔH_p for various fiber concentrations fall on the expected linear plot (dotted line). In Table 23 the temperatures for the beginning (T_1), maximum (T_2), and finish (T_3) of sample exotherms are listed.

TABLE 23

CHARACTERISTIC TEMPERATURES FOR ATS/AS-1
COMPOSITE DSC EXOTHERMS

AS-1 Fiber %	ΔH_p(cal/g)	T_1(°K)	T_2(°K)	T_3(°K)
0	105.6	423	497	556
21	79.2	404	496	566
24	76.6	422	496	549
26	79.8	418	496	550
54	54.1	414	496	557

T_1, T_2, and T_3 are, respectively, temperatures for the beginning, maximum, and finish of DSC exotherm.

3. NEAT ATS MOISTURE SORPTION AND VOLATILE RELEASE

TGA thermograms illustrating volatile release from ATS_{G-2} are shown in Figures 38 and 39. In Figure 38 we compare weight loss profiles for a sample of ATS_{G-2} as received (undried) and a sample dried for one hour at 90°C under vacuum. We note that even after one hour at 90°C there remained approximately 2 percent volatiles. Figure 39 is an isothermal TGA scan taken at 125°C. This shows that after heating for approximately 30 min. at 125°C most of the volatiles have been released. It is likely that this time will be much shorter if a vacuum is applied.

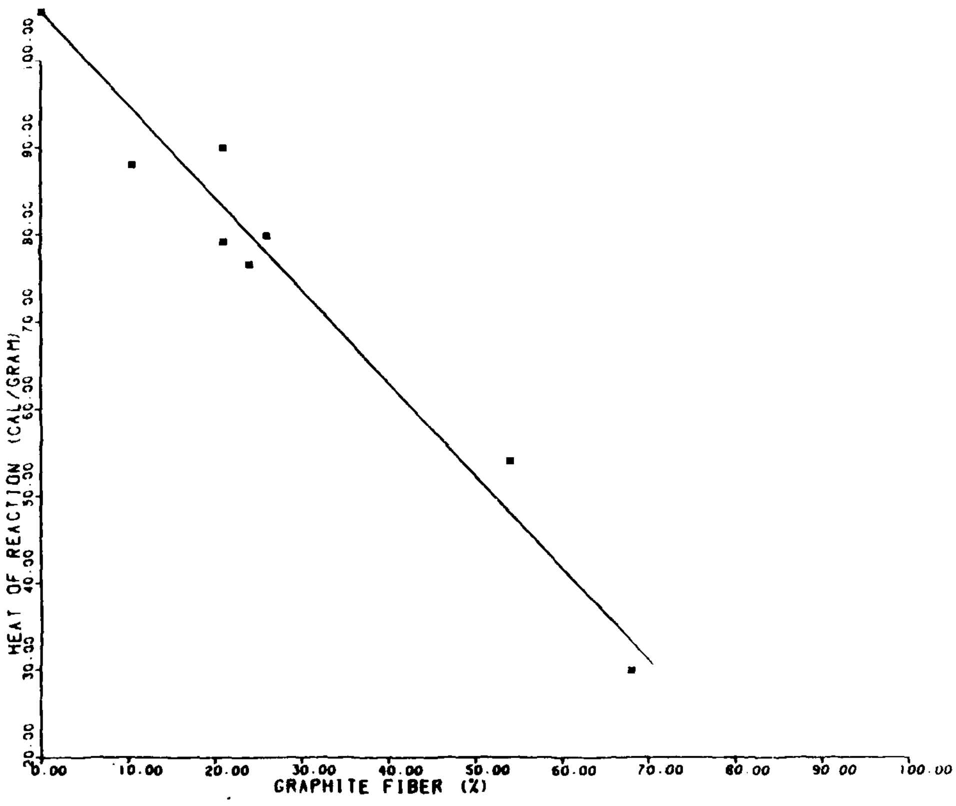


Figure 37. ATS$_{G-2}$ Heat of Reaction with Various Amounts of Graphite AS-1 Fiber Added.

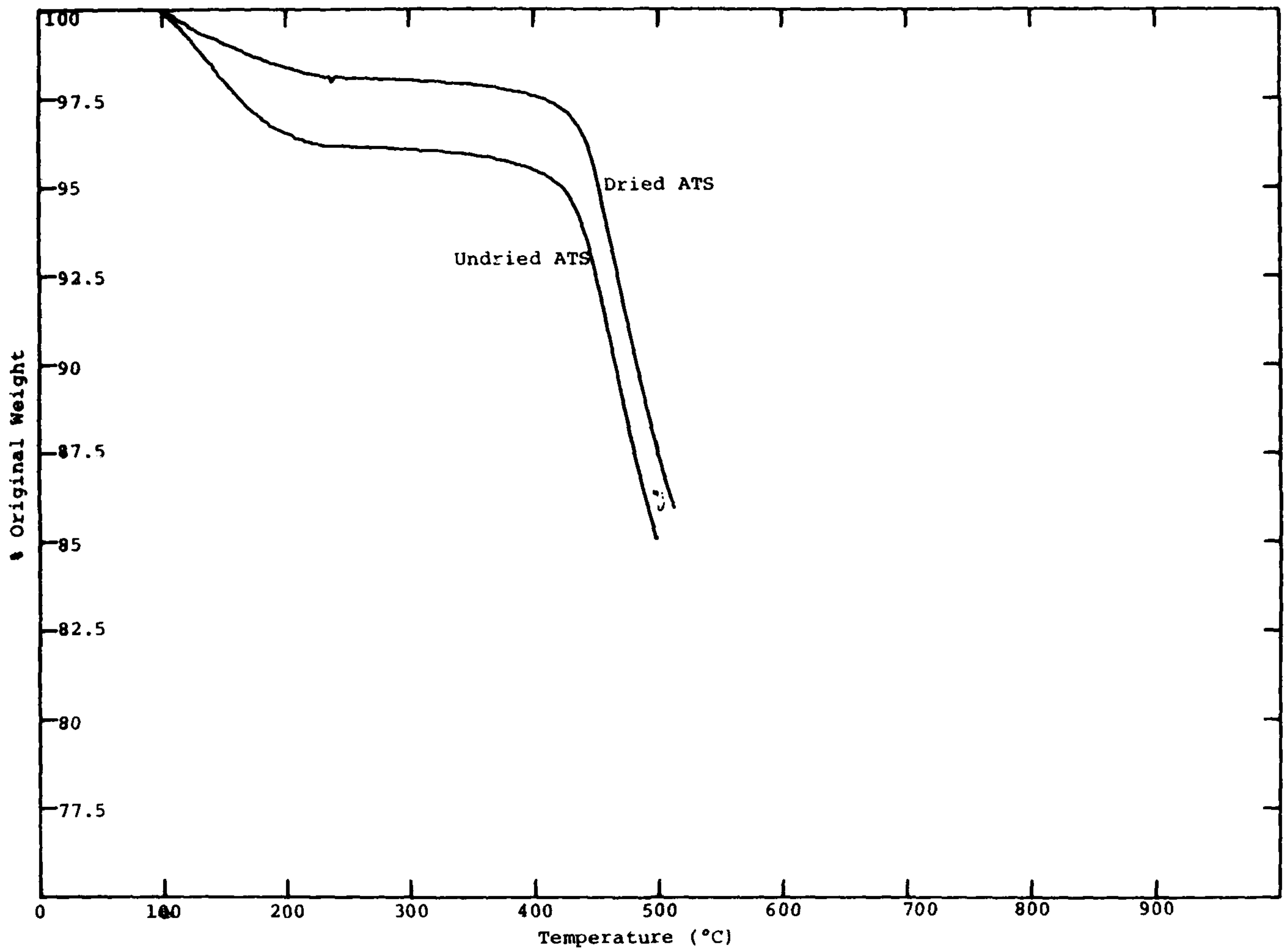


Figure 38. TGA Curves for As-Received (Undried) ATS_{G-2} and a Sample Treated in Vacuum 1 Hr. at 90°C; Heating Rate 10°C/min; 25% Scale.

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APR 82 R P CHARTOFF, D R ASKINS, J M BUTLER F33615-80-C-5029
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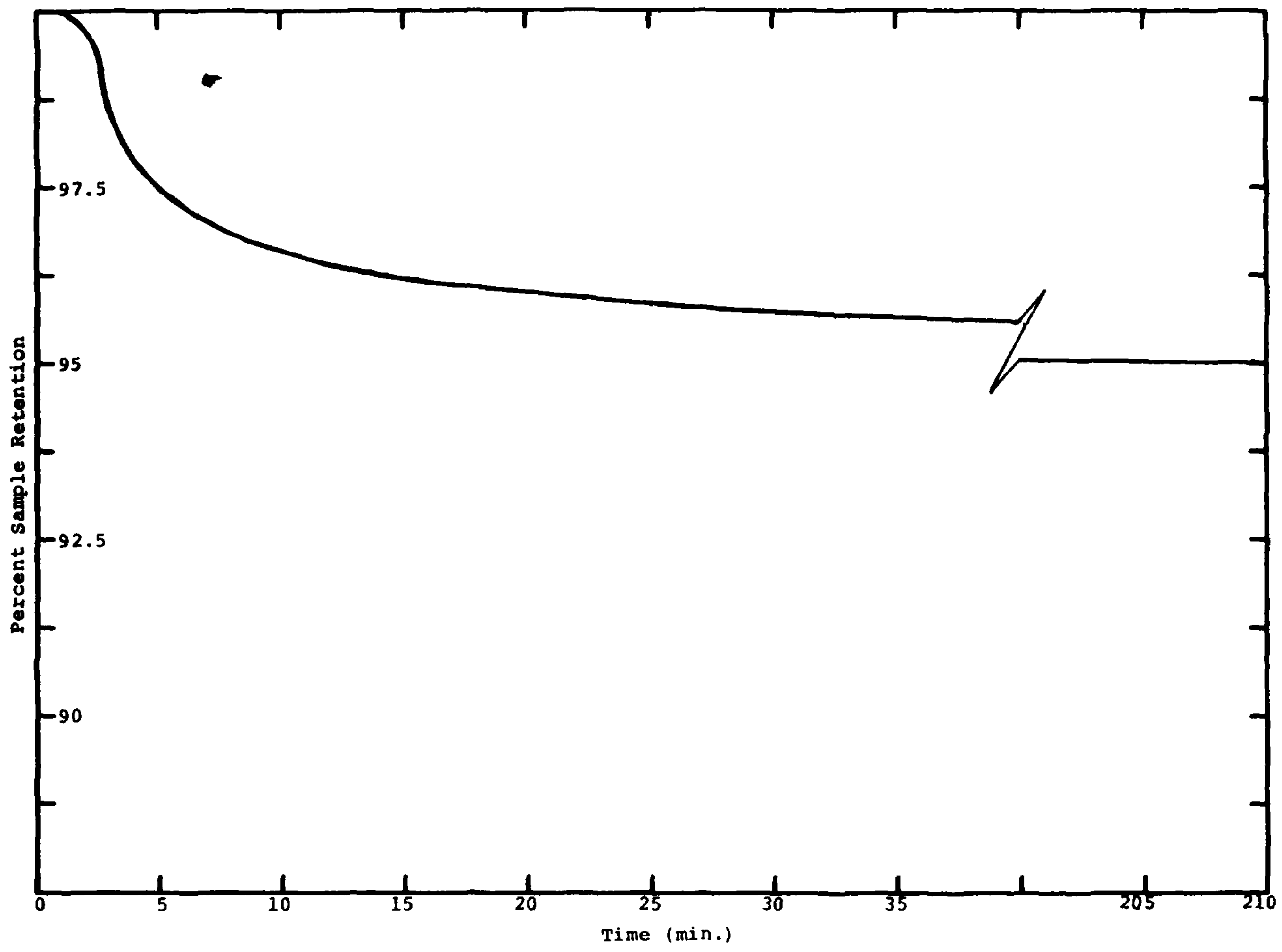


Figure 39. Isothermal TGA Scan on ATS_{G-2}; T=125°C; 25% Scale; Purge Gas N_2.

These results indicate that approximately 4 percent total volatiles are released from ATS. About half of this amount is released even after vacuum degassing at 90°C. The nature of these additional volatiles is not known. However, it is likely that low molecular weight diluents such as toluene (residual solvent) and diethynylbenzene, DEB, (impurity) are released during vacuum degassing. This is suggested by the vaporization TGA profile for DEB shown in Figure 40. Subsequent TGA/mass spectrometer data obtained by AFWAL/ML show that ATS monomer also is volatilized.

In order to learn more about moisture sorption, uncured ATS_{G-2} was aged in humid air at room temperature and at 50°C (120°F). Using the DuPont moisture analyzer we found that starting with a dry sample of <0.01 percent H_2O, exposure to 95 percent relative humidity at 25°C and 50°C result in 0.47 percent and 0.62 percent absorbed H_2O, respectively. The extent of moisture sorption by ATS is illustrated in the series of TGA curves shown in Figure 41. Curve 1 is for a sample of dry ATS, curve 2 is for a sample exposed at room temperature (R.T.) for several hours, while curve 3 represents the equilibrium sorption condition attained over long times at ambient conditions.

ATS that had attained equilibrium moisture sorption at both 25°C and 50°C had essentially the same DSC thermogram as dry ATS, with $\Delta H_P \simeq 99$ cal/g.

It is important to note that at this point the origin of volatiles in ATS_{G-2} has not been specified. Most likely a mixture of components is liberated when the uncured resin is heated. While it is important to remove volatiles prior to laminate processing, this does not appear to be difficult in the case of ATS_{G-2}. The preliminary data presented here suggest that sufficient devolatilization to insure void-free laminates possibly could be accomplished during prepregging. While subsequent prepreg and laminate processing studies seemed to confirm

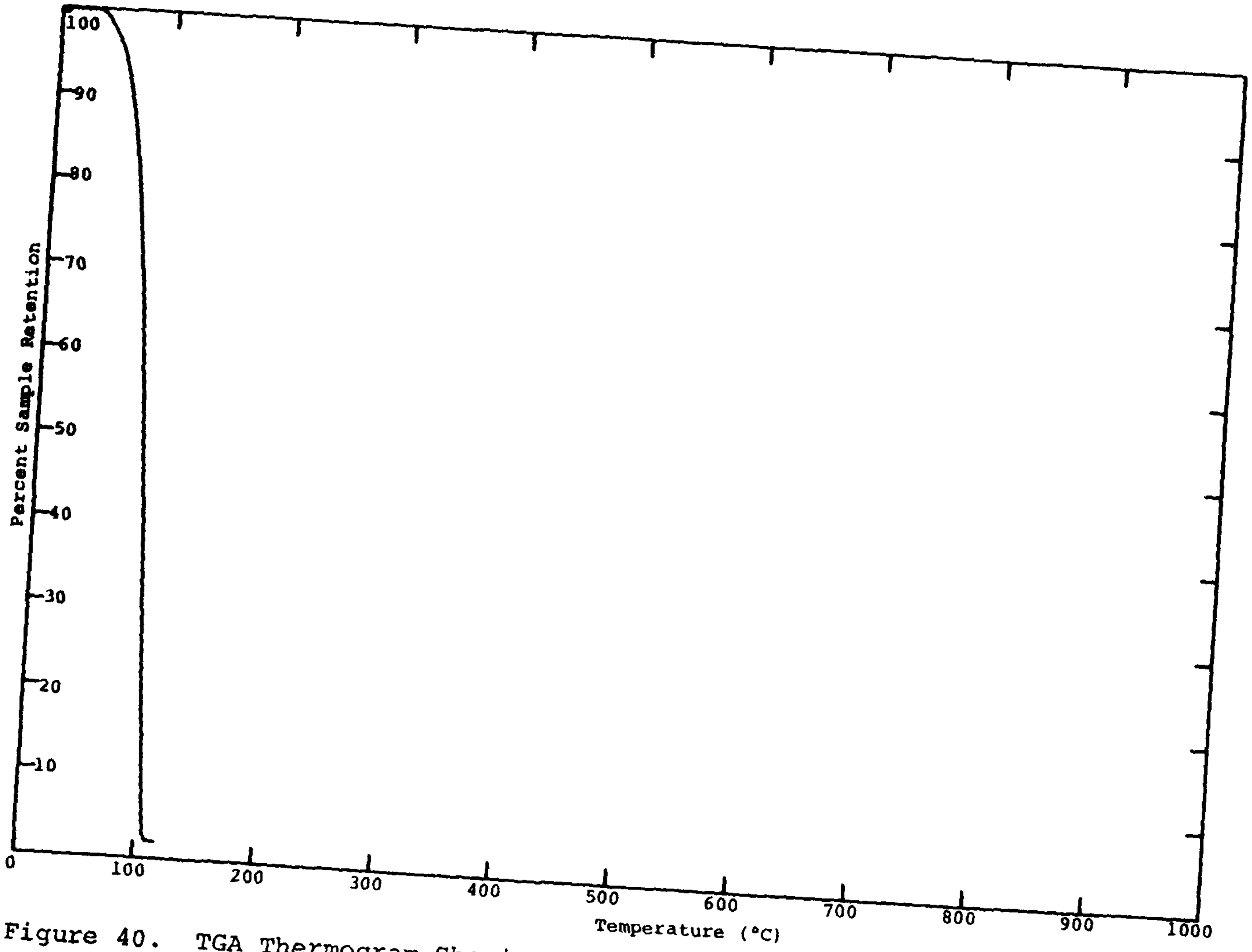


Figure 40. TGA Thermogram Showing Volatilization of Diethynylbenzene.

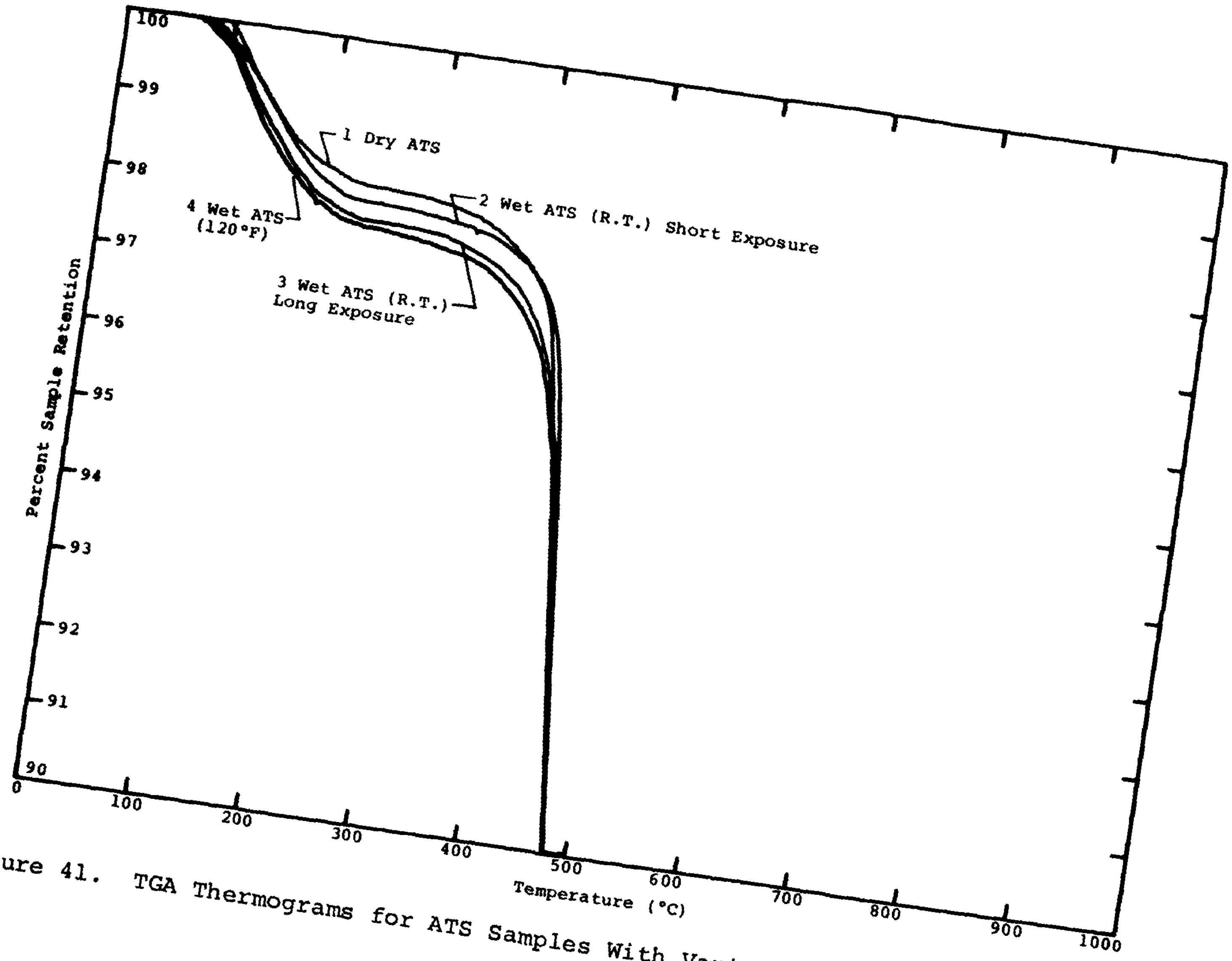


Figure 41. TGA Thermograms for ATS Samples With Various Amounts of Absorbed H_2O.

this conclusion, additional study of this problem is justified. Because of the possibility that ATS monomer may be volatile a venting step during laminate processing seems desirable.

4. PREPREG DEVELOPMENT

a. Prepreg Processing

Prepreg process development for this program was carried out by U.S. Polymeric Division of HITCO (USP), under direction of Mr. Don A. Beckley. All prepreg trials were made on USP's industrial scale equipment using a hot melt technique with in-line direct casting of resin onto the fiber. Three-inch prepreg tapes were produced using a melt temperature of 200°F (for neat resin) or 140°F (for ATS_{G-2}-1 percent ethanol mixtures) and a fiber feed rate of 7 fpm. In total six batches of prepreg were fabricated with three different fibers. These are listed in Table 24. AS-1 and Celion fibers were used before the final selection of AS-4 was made as described in Paragraph 1.

The processing studies demonstrated that ATS_{G-2} was readily prepregged on commercial unidirectional tape making equipment. The resin displayed poorer fiber wet-out capability than standard epoxy and polyimide resins. The first two prepreg batches contained resin starved areas. The prepreg produced was still and lacking in surface tack. The addition of 1 percent ethanol to the resin added flexibility to the prepreg tape but did not substantially improve tack. Prepreg process development work has terminated before any investigation of removing volatiles from the resin during impregnation.

USP has noted that there were particles in the ATS_{G-2} resin that do not liquify during impregnation. These particles accumulate and eventually clog the hot melt applicator, requiring periodic cleaning. This in turn results in a non-uniform resin distribution of approximately ± 3 percent across the 3-inch tape width. The presence of such particles in ATS_{G-2} was considered previously in this report.

TABLE 24

DESCRIPTION OF GRAPHITE/ATS PREPREG

USP Run No.	Reinf. Fiber	Fiber Finish	Solvent in Resin	Final Prepreg Physical Characteristics[1]			
				Resin Content (% by wt.)	Volatile Content (% by wt.)	Roll No.	Lot
1	AS1	Bare	None	31.4	0.8	1	2W5061
2	Celion	Polyimide	None	Received none of this material		---	---
3	AS1	Bare	Ethanol	30.2	1.5	2	2W5144
4	AS4	Bare	None	37.5	1.3	4	2W5144
5	AS4	Bare	Ethanol	44.8	2.1	5	2W5173
6	AS4	Bare	None	38.1	1.0	6	2W5169

[1] All values in this table were determined by UDRI.

b. Volatile Release From Prepreg

A TGA scan on the initial USP prepreg sample (Roll No. 1) is compared in Figure 42 with the neat resin volatile data previously cited in Figure 41. In comparison the volatile level is similar to that of sample No. 3 of neat ATS (wet) aged at room temperature. This indicates that 2% volatiles (based on resin weight) is released up to 140°C and from 140-240°C another 1% is released.

Figure 43 shows comparative TGA curves for prepreg from rolls 5 and 6. Total volatiles in each by the TGA method are approximately 1.9% for roll 5 and 0.8% for roll 6. In Figure 44 the TGA curves for rolls 5 and 6 are compared with those of the other prepreg batches.

5. LAMINATE PROCESSING AND CHARACTERIZATION

a. Fabricating Test Laminates From Prepreg Rolls 1, 3, and 4

Several eight-ply test laminates were fabricated from three rolls of USP prepreg (Rolls 1, 3, and 4). In working with Roll 1 a variety of different processing schedules were used (with only limited success) in an effort to fabricate void-free composites. These included vacuum-bag-only to vacuum-plus-30-psi-positive-pressure cures with and without holds at various temperatures in the cure schedules. In each case, substantial interply void concentrations resulted. These could not be eliminated. Since very few of the voids were present within the fiber bundles and very little flow was observed during the cures, it was concluded that the prepreg simply contained too little resin to permit voids to be washed out during cure. As the cure conditions were changed to force increased flow, the laminates became resin starved. Similar problems were encountered in efforts to make laminates from Roll 2. However, markedly increased flow was observed during laminate fabrication with prepreg from Roll 4.

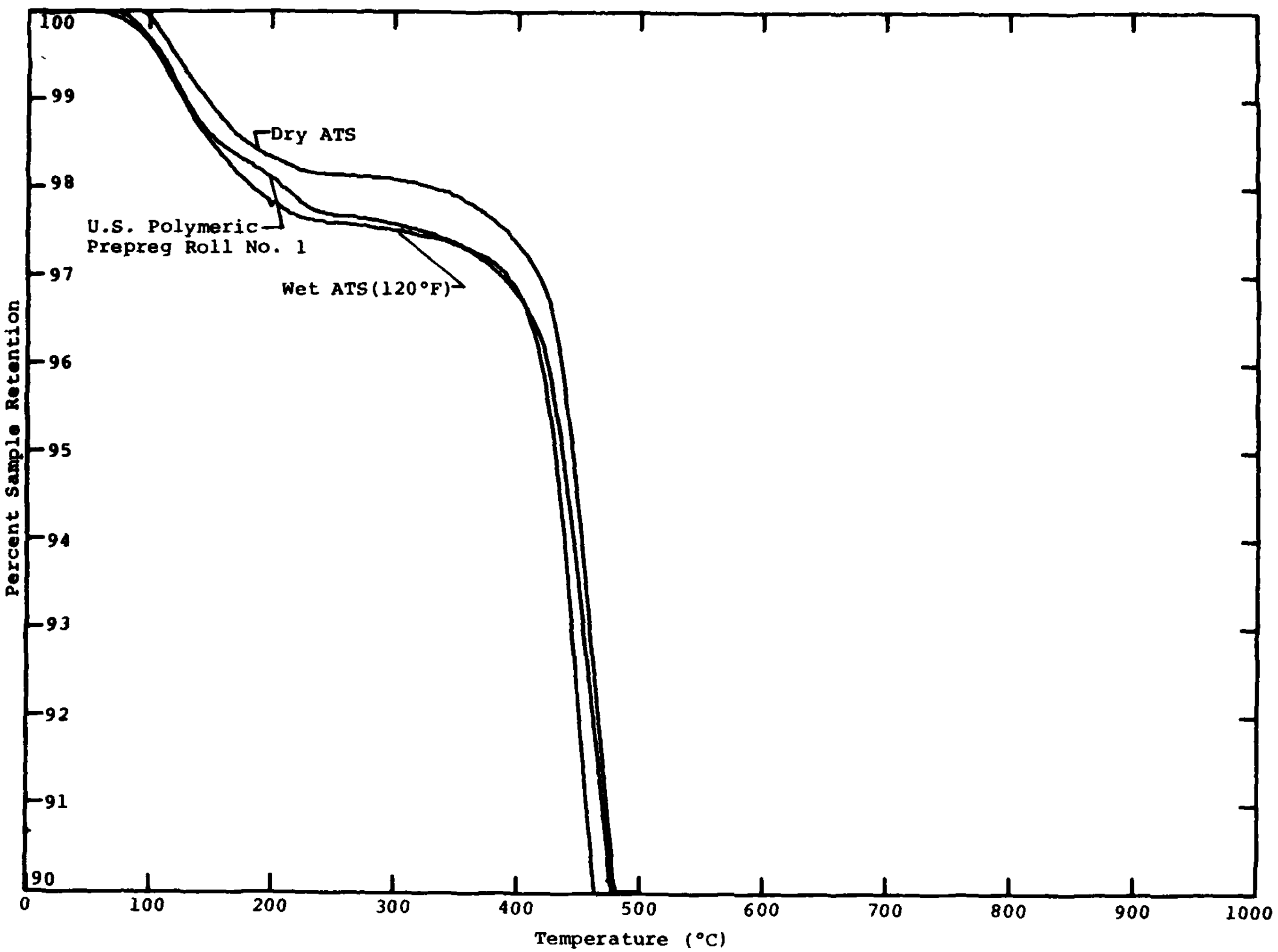


Figure 42. Comparison of TGA Thermograms for Neat ATS and U.S. Polymeric ATS Prepreg.

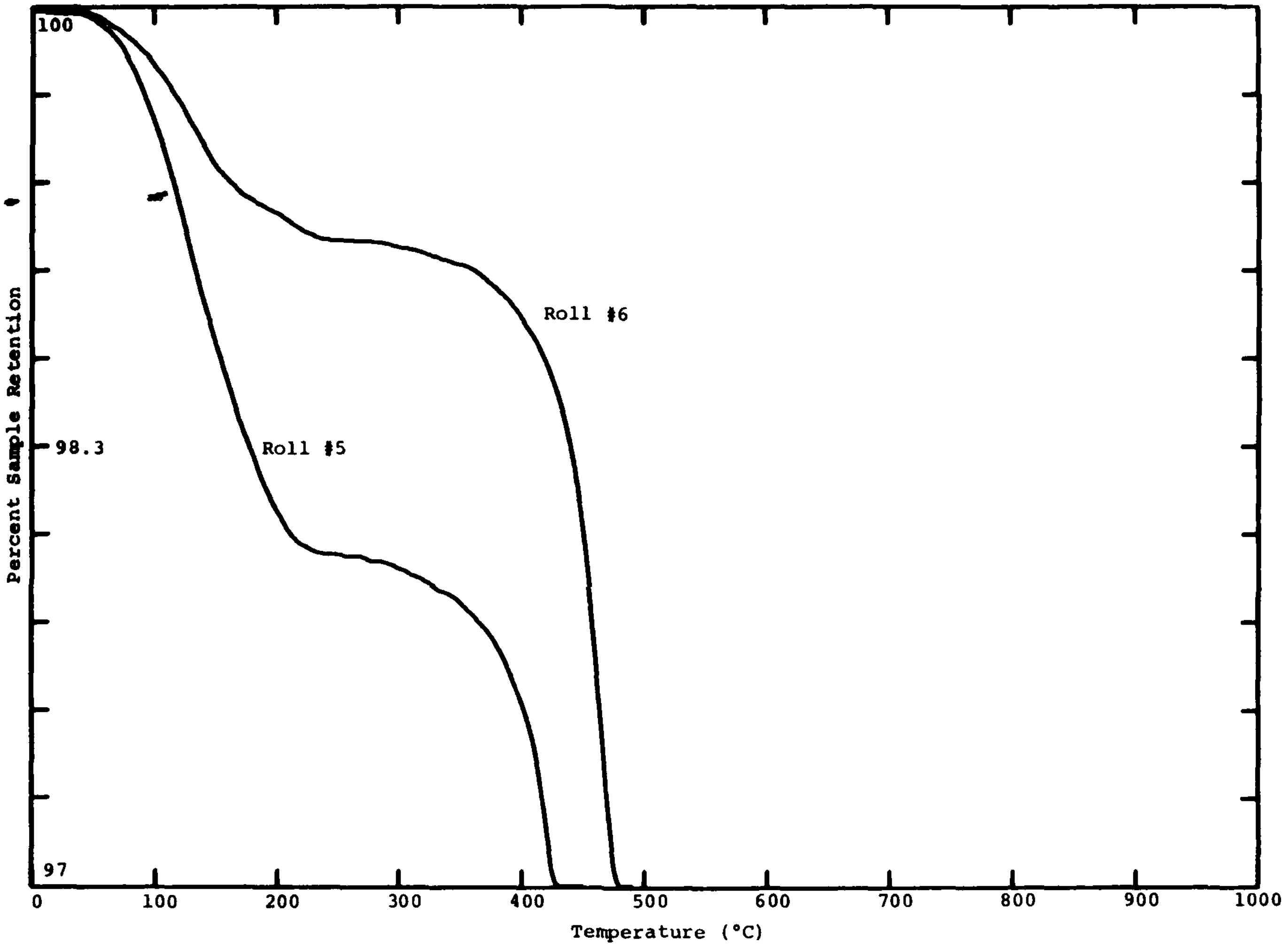


Figure 43. TGA Weight Loss Curves for Devolatilization of ATS Prepreg From Rolls 5 and 6.

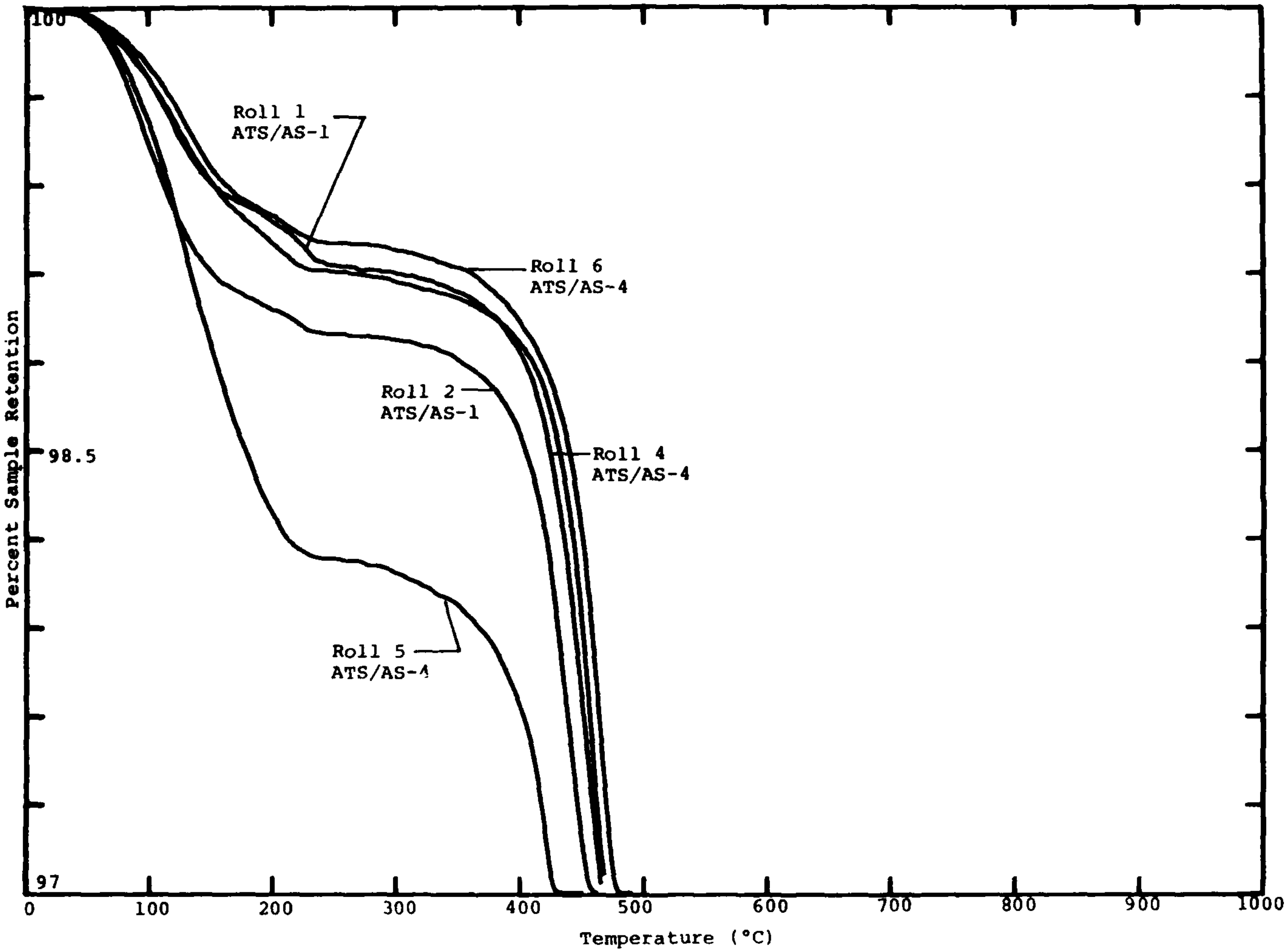


Figure 44. Comparison of Devolatilization TGA Curves for Various ATS Prepregs Listed in Table 24.

The initial laminate panels produced were too porous (based on photomicrographs) to merit mechanical property testing. However, the cure cycles employed were altered to those summarized in Table 25 and void content was greatly reduced. Laminates produced from Rolls 1, 3, and 4 subsequent to panel ATS-15 were essentially void free.

TABLE 25

CURE CYCLES USED FOR ATS COMPOSITES

#1	Apply full vacuum. Heat from R.T. to 125°C (258°F) at 3°C (5°F)/min. When 125°C (258°F) is reached, apply 30 psi positive pressure and hold at this pressure and temperature for one hour. After the hold, raise the temperature to 168°C (355°F) at 3°C (5°F)/min. Hold at 168°C (355°F) for 40 minutes. After the hold, cool under pressure and vacuum to below 66°C (150°F) and remove.
#2	Apply full vacuum. Heat from R.T. to 125°C (258°F) at 3°C (5°F)/min. Hold at 125°C (258°F) for 30 min. then apply 30 psi positive pressure and hold for another 30 min. After the second hold raise the temperature to 168°C (355°F) at 3°C (5°F)/min. and hold for 40 minutes. After the hold, cool under pressure and vacuum to below 66°C (150°F) and remove.

b. Property Characterization of Test Laminates From Rolls 1, 3, and 4

Four types of mechanical tests were conducted on specimens cut from the various graphite/ATS composites made from Rolls 1, 3, and 4. These are as follows:

(1) three-point flexure on 0° specimens at 32:1;

(2) four-point flexure on 90° specimens at 32:1;

(3) four-point interlaminar shear (flexure) on 0° specimens at 16:1; and

(4) three-point short beam shear on 0° specimens at 4:1.

Tables 26 and 27 present the mechanical and physical properties obtained on these graphite/ATS composites. It was difficult to

TABLE 26

FLEXURAL PROPERTIES OF GRAPHITE/ATS COMPOSITES AT ROOM TEMPERATURE

Panel No.	Roll No.[1]	Fiber Orient.	Flexure Strength[2]		Flexure Modulus		Specific Gravity	Fiber Content (% by vol.)	Void Content (% by vol.)	Cure Cycle[3]
			10^3 psi	MPa	10^6psi	GPa				
ATS-5	1	0°	245.2±32.4	1689±223	15.6±0.2	107±2	1.64	78.1	2.8	1
-8	1	0°	169.2±6.3	1166±44	19.1±1.3	132±9	1.55	65.2	4.9	1
-10	2	0°	197.8±24.2	1363±167	20.8±0.9	143±6	1.58	68.2	3.1	1
-12	4	0°	162.0±7.1	1116±49	17.0±0.3	117±2	1.53	60.3	6.4	1
-16	4	0°	209.5±9.1	1444±63	17.4±0.4	120±3	1.65	64.6	0	2
-17	4	0°	213.6±4.1	1472±29	18.4±0.3	127±2	1.60	62.7	2.0	2
ATS-9	1	90°	3.38±0.31	23.3±2.1	1.635±0.07	11.3±0.4	1.57	67.3	3.6	1
-11	2	90°	2.75±0.19	18.9±1.3	1.182±0.06	8.1±0.4	1.53	63.4	5.5	1
-13	4	90°	3.52±0.35	24.2±2.4	1.190±0.03	8.2±0.2	1.52	59.9	7.0	1

[1] See Table 24.

[2] Determined at a span-to-thickness ratio of 32:1.

[3] See Table 25.

TABLE 27

INTERLAMINAR SHEAR PROPERTIES OF
0° ATS/GRAPHITE COMPOSITES AT ROOM TEMPERATURE

Panel No.	Roll No.	Span to Thickness Ratio[1]	Ult. Strength		Specific Gravity	Fiber Content (% by vol.)	Void Content (% by vol.)	Cure Cycle[2]
			10^3psi	MPa				
ATS-5	#1	4:1	7.91±0.44	55 ± 3	1.64	78.1	2.8	1
ATS-8	#1	16:1	3.71±0.12	26 ± 1	1.55	65.2	4.9	1
ATS-10	#2	16:1	4.23±0.17	29 ± 1	1.58	68.2	3.1	1
ATS-12	#4	16:1	4.35±0.38	29 ± 3	1.53	60.3	6.4	1
ATS-16	#4	16:1	5.77±1.51	40 ± 10	1.65	64.6	0	2
ATS-17	#4	16:1	7.12±0.78	49 ± 5	1.60	62.7	2.0	2

[1] Panel ATS-5, tested in short beam shear. All subsequent panels tested in flexure with four-point loading.

[2] See Table 25.

interpret the data at this point because the laminate fiber and void contents were not yet optimal. This is discussed in the following paragraphs.

Photomicrographs of cross-section views of laminate panels ATS-12 and ATS-17 are shown in Figures 45 and 46, respectively. Both laminates were fabricated from prepreg Roll No. 4, which contains 37.5 percent resin. Panel 12 contains considerable interlaminar voids as reflected in its specific gravity value of 1.53. Panel 17, however, appears to be void free with a specific gravity of 1.60. This improvement in morphology was achieved through allowing greater time for release of volatiles during processing, before pressure application.

While panel 17 showed a marked improvement, it is apparent from the photographs that relatively little resin remains between individual fibers. In order to improve the laminate resin distribution we considered it necessary to have a higher prepreg resin content and at this point ordered additional prepreg from U.S. Polymeric with a minimum of 42 percent resin content.

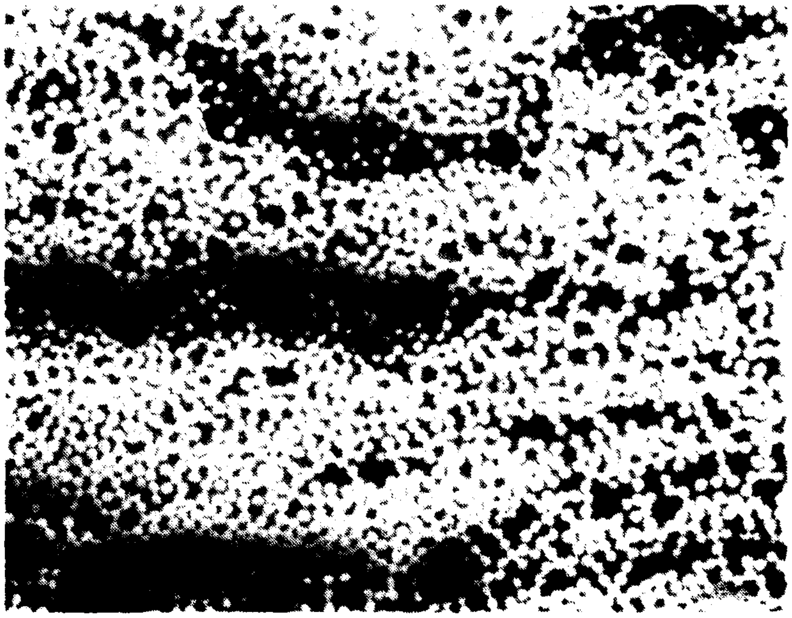
c. Fabricating Test Laminates From Prepreg Roll 6, ATS/AS-4

Initial difficulties were encountered in fabricating void-free laminates from USP prepreg Roll No. 6. Thus alterations in cure cycle were made until void-free panels were produced. The most successful cure cycle involved predrying the prepreg prior to subsequent processing. This cure cycle is listed in Table 28. The importance of a predry step with ATS/AS-4 prepreg was first suggested by processing studies performed by AFWAL/MLBC on prepreg from Roll No. 6.

d. Property Characterization of ATS/AS-4 Laminates From Prepreg Roll No. 6

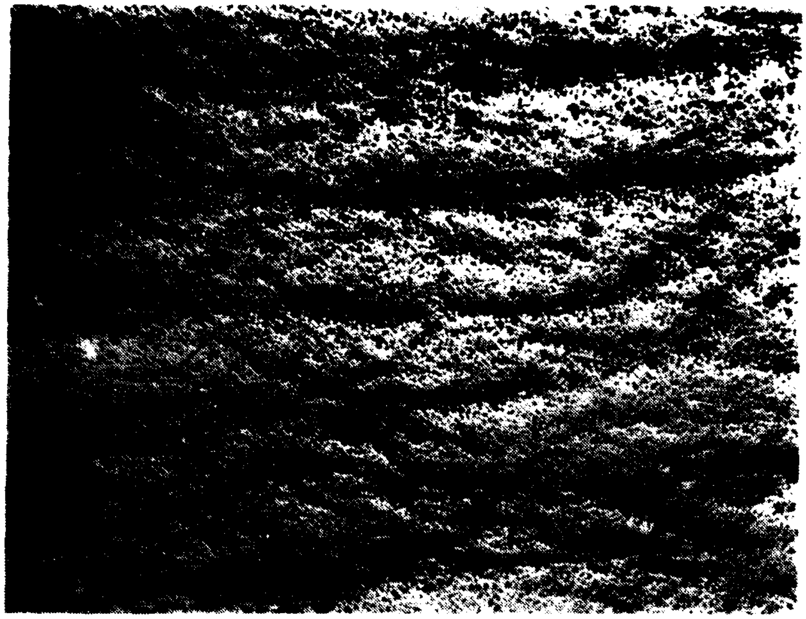
The quality of the laminates produced using the cure cycle cited in Table 28 is illustrated by the photomicrographs in Figure 47. Based on photomicrographs and densities (values approx. 1.60) these panels were judged to be void free.

(a) 100X



(b) 250X

Figure 45. Cross-sectional Photomicrographs of ATS-12 Laminate Panel.



(a) 100X

(b) 250X

Figure 46. Cross-sectional Photomicrographs of ATS-17 Laminate Panel.

TABLE 28

FINAL CURE CYCLE EMPLOYED FOR LAMINATES FROM PREPREG ROLL NUMBER 6

Cure Cycle

(1) Predry prepreg in vacuum oven for 2 hours at 210°F (100°C).

(2) Layup using heat gun (or hotplate).

(3) Place in autoclave and apply full vacuum pressure.

(4) Heat from R.T. to 210°F (100°C) @ 5°F/min. and hold for 1 hour.

(5) After hold at 210°F (100°C), apply 45 psi then vent vacuum.

(6) Increase temperature to 350°F (177°C) @ 5°F/min. and hold for 1 hour.

(7) After hold, cool down slowly (≤5°F/min.), under pressure, to below 125°F.

(8) Release pressure and remove.

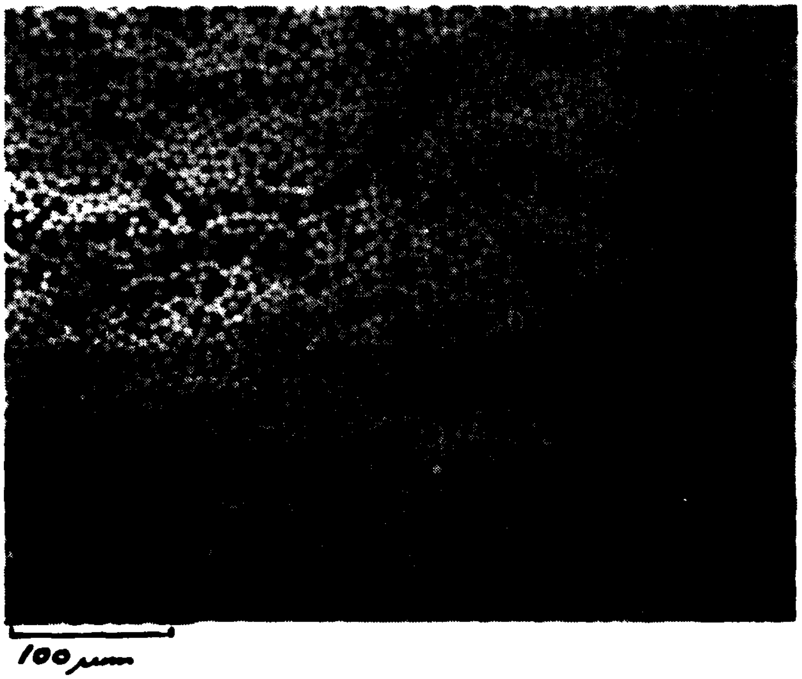
Postcure Schedule

(1) Place panel in air-circulating oven (free-standing) and heat up to 480°F (250°C) at 5°F/min.

(2) Hold at 480°F (250°C) for 2 hours.

(3) Cool panel down slowly (≤5°F/min.) to below 125°F, and remove.

(a) Cross-section View Photomicrograph (100X)



(b) Enlarged Cross-section View Photomicrograph (250X)

Figure 47. ATS/AS-4 Graphite Fiber Laminate Number 26.

The mechanical property test matrix used for screening ATS/AS-4 laminate properties is listed in Table 29. The test results obtained are presented in Table 30. The property values determined are considered representative of ATS/AS-4 laminates. They are clearly inferior to those of comparable epoxy systems.

TABLE 29

MECHANICAL PROPERTY TEST MATRIX FOR ATS SCREENING

Property	Test	Comments
0° Flexure	3 point at 32:1	---
90° Flexure	4 point at 32:1	Load at quarter points
Interlaminar Shear	4 point at 16:1	Load at quarter points
$(+30,+30,-30,-30,90,90)_s$, Tension	Straight-sided specimens, tabbed	Note load when longitudinal splitting occurs at midplane.

TABLE 30

MECHANICAL AND PHYSICAL PROPERTIES FOR AS4/ATS-RESIN LAMINATES (Roll #6, Lot #2W5169)

Type of Test	Panel No.	Ultimate Strength		Modulus		Strain to Failure (%)	Delamination Strength 10^3psi/(MPa)	Specific Gravity	Fiber Content (% by vol.)	Resin Content (% by wt.)	Voids* (% by vol.)
		10^3psi	MPa	10^6psi	GPa						
0° Interlaminar Shear (Flex, L/D = 16/1) 4-point loading	ATS-25	8.23± 0.8	56.9 ± 5.3	---	---	---	---	1.59	61.89	29.29	1.92
0° Interlaminar Shear (Short beam, L/D = 4/1)	ATS-27	11.5± 0.6	79.3 ± 4.4	---	---	---	---	1.60	64.04	27.17	1.39
0° Flexure (L/D = 32/1) 3-point loading	ATS-27	226.2± 6.2	1559.6±42.6	17.0± 0.7	117.6± 5.1	---	---	1.60	64.04	27.17	1.39
90° Flexure (L/D = 32/1) 4-point loading	ATS-26	6.0± 0.4	41.6 ± 2.6	2.0± 0.17	13.6± 1.2	0.33±0.06	---	1.58	56.59	34.96	0.51
$[+30_2,-30_2,90_2]_{sym}$ Straight-sided tension	ATS-28	25.6± 0.6	176.4 ± 4.0	6.0± 0.4	41.6± 2.6	---	10.9±1.8/ (75.2±12.5)	1.55	66.29	22.35	---

*Calculated from reported fiber and resin specific gravity values; measured laminate specific gravity and photomicrographs indicate zero voids.

SECTION V

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APPENDIX A

UDRI PARALLEL PLATE RHEOMETER DESCRIPTION

APPENDIX A

UDRI PARALLEL PLATE RHEOMETER DESCRIPTION

The flow geometry which was used for ATS viscosity characterization closely duplicates the melt experience in compression molding in that the flow in each case is a pressure flow rather than a drag flow. In the microparallel plate rheometer the material to be tested is placed between parallel circular plates and a constant force is applied perpendicularly to the plates to cause them to approach each other. The rheological behavior of the test material may be determined from the measurement of the displacement of one plate with respect to the other as a function of time.

Dienes and Klemm[A-1] developed a theory for the parallel plate plastometer starting from the equation of motion of an incompressible viscous fluid. A Newtonian liquid completely fills the space between the plates as shown in Figure A.1. Ignoring edge effects, the final relation in this case is

$$\eta = (2h^3F/3\pi R^4)/(-dh/d\theta) \qquad \text{(A.1)}$$

where F is the applied force, h is the clearance between the two plates, R is the radius of the plates, η is the viscosity of the fluid between the plates, and θ is the time. Equation A.1 can be rewritten as

$$\log(-dh/d\theta) = 3 \log h + \log(2F/3\pi R^4\eta) . \qquad \text{(A.2)}$$

Thus, if $\log(-dh/d\theta)$ is plotted against log h, a straight line of slope 3 should be obtained for Newtonian liquids. From the intercept on the ordinate, the value of η can be found. Alternatively, Equation A.1 may be integrated with respect to θ to give

$$1/h \;= (4F/3\pi R^4\eta)\theta + 1/h_o{}^2 \qquad \text{(A.3)}$$

[A-1] G. H. Dienes and H. F. Klemm, J. Appl. Phys., <u>17</u>, 458, 1946.

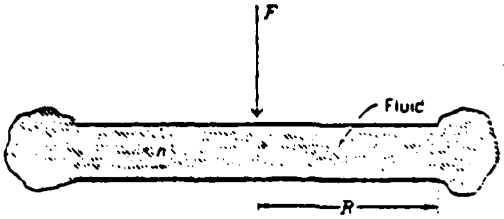

Figure A.1. Microparallel Plate Compression Rheometer.

where h_0 is the plate separation at the start of the experiment. Thus, when $1/h^2$ is plotted against θ, the viscosity can be calculated from the slope.

The University has constructed a microparallel plate rheometer for use with the Perkin-Elmer TMS-2 thermomechanical analyzer. This type of geometry is well suited to moderately low shear rate measurements particularly in the compression molding range and comes very close to duplicating the shear history experienced in compression molding. In particular it operates at a constant pressure exerted on the melt. Using the LVDT sensor of the TMA instrument, it is possible to follow continuously the viscosity change which normally occurs during the cure of thermosets.

In the parallel plate instrument data on non-Newtonian liquids should be measured over a wide range of applied force, F. Then, for each value of F, a value of η may be obtained from Equation A.1, A.2, or A.3 for a selected fixed value of h by getting $-dh/d\theta$ at that fixed value from a plot of h or any function of h against θ. Since the shear stress is proportional to F, the shape of the flow curve may be found by plotting F versus η/F. At the fixed value of h, the detailed pattern of flow for a given non-Newtonian will be independent of stress above the yield value.

A typical viscosity trace (schematic) for cure of a thermoset in the PPR is shown in Figure A.2. This is obtained from a TMA thermogram showing the change in h with time at constant temperature. The data also can be obtained for a variable temperature scan duplicating the heating schedule during the molding operation. Sample size is a 30 to 50 mil disk, 0.375 in. in diameter. Thus only very small amounts of material are required.

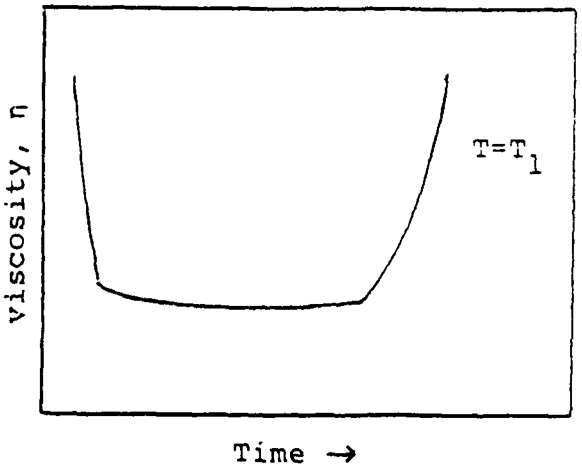

Figure A.2. Typical Parallel Plate Rheometer Scan for a Thermoset (Schematic).

APPENDIX B

SURFACE FREE ENERGY CHARACTERIZATION OF RESINS AND FIBERS

APPENDIX B

SURFACE FREE ENERGY CHARACTERIZATION OF RESINS AND FIBERS

Interfacial Considerations

While there are many factors which affect fiber-matrix interactions, ultimately the surface free energy (γ_S) of the graphite fiber determines the wetting behavior of the matrix and the thermodynamics of the matrix-fiber interface. In the case of polymer-fiber interactions, the values of surface free energy provided by measurements of ambient conditions have been found to be relevant to interfacial adhesion studies, even though interfacial bonds may be formed or broken under nonambient atmospheric conditions.[B-1,B-2]

Kaelble[B-1] has shown that for low energy surfaces, the surface free energy can be taken as the sum of two parts, γ_s^d, a dispersive or nonspecific interaction component, and γ_s^p, a specific polar interaction component such that $\gamma_S = \gamma_s^d + \gamma_s^p$. A major emphasis in surface energy analysis for judging fiber-matrix compatibility is to isolate the values of γ_s^d and γ_s^p based on wettability measurements with liquids of known values of surface tension, $\gamma_{LV} = \gamma_L^d + \gamma_L^p$.

These quantities can be measured for a solid surface by measuring the contact angle, θ, for a series of liquids of known dispersive (γ_L^d) and polar (γ_L^p) surface tension components. γ_s^d and γ_s^p are then evaluated by using the relationship:[B-1]

$$\frac{\gamma_{LV}(1+\cos\theta)}{2(\gamma_L^d)^{1/2}} = (\gamma_S^d)^{1/2} + \left(\frac{\gamma_L^p}{\gamma_L^d}\right)^{1/2} (\gamma_s^p)^{1/2} \quad . \qquad \text{(B-1)}$$

This is a linear equation of form $y = mx + b$. The slope and intercept of the best straight line through the data points give, respectively, $(\gamma_s^p)^{1/2}$ and $(\gamma_s^d)^{1/2}$.

Experimentally the contact angle measurement on a matrix resin is straightforward. However, the measurement on a single graphite fiber (diameter 8 to 10μ) requires a special method. The easiest way to do this is a micro-Wilhelmy technique such as that described by Drzal, et al.[B-3] In this method, a single fiber is partly immersed in the liquid of interest and the contact force F between a fiber of circumference C and the liquid is described by

$$F = C\,\gamma_{LV}\cos\theta \ . \qquad \text{(B-2)}$$

If F and γ_{LV} are measured by microbalance and C is determined optically or by the force developed when the fiber is dipped into a wetting liquid, where $\cos\theta = 1.0$, the contact angle θ can be evaluated.

Polymeric surface coatings are now commonly applied to graphite fibers used in polymer matrix composites. Application of the coatings is made by melt impregnation or sometimes by varnish techniques with the fiber surface exposed to a dilute solution of resin in a solvent. The primary purpose of a fiber coating is considered to be for better handling of the fiber to minimize breakage and introduction of flaws and cracks during processing.

Matching the fiber surface characteristics to the matrix resin is also of interest but it is generally assumed that matching the fiber coating type to the matrix-resin type (e.g., epoxy-epoxy) is sufficient for assuring good interfacial bonding. Relatively little has been done to use surface energy data to match fiber and resin surface energies in order to optimize interfacial bonding.

In doing so for ATS as a matrix resin one should:

(a) Use the wetting criterion--that the matrix resin should have a lower total surface energy than the fiber;

(b) Choose the fiber such that its polar component of the surface energy γ^p matches that of the resin closely, while the dispersive component γ^d is the same order of magnitude, matching as nearly as possible (but not as closely as γ^p); and

(c) Consider that the fiber surface treatment should have sufficient thermal stability to resist degradation and off-gassing, at temperatures around that of the probable curing temperature range of ATS composites (up to 250°C).

REFERENCES - APPENDIX B

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B-3. L. T. Drzal, J. A. Mescher, and D. L. Halb, Carbon, 17, 375, 1979.

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