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Advanced Fiber/Matrix Material Systems*

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Summary

Work completed in Phase I of the NASA-Advanced Composite Technology program is discussed. Two unique towpreg forms (commingled yarns and fused powder towpregs) are being characterized under the program. These towpregs will be used to evaluate textile fabrication technologies for advanced aircraft composite structures. The unique characteristic of both of these material forms is that both fiber and matrix resin are handled in a single operation such as weaving, braiding or fiber placement. The evaluation of both commingled and fused powder towpreg is described. A candidate matrix list has been proposed and is discussed. Various polymer materials were considered for both subsonic and supersonic applications. Polymers initially being evaluated include thermoplastic polyimides such as Larc-TPI and New-TPI, thermoplastics such as PEEK and PEKEKK as well as some toughened crosslinked polyimides. Preliminary mechanical properties as well as tow handling are evaluated.

Introduction

As part of the NASA Advanced Composite Technology (ACT) effort, whose primary effort is to bring about more affordable and damage tolerant composites for the aerospace industry, an effort was undertaken to explore the use of two unique composite prepreg concepts. The two concepts developed by BASF Structural Materials, Inc. address primary objectives of the ACT program. The concept of using these material forms to fabricate composite structures with through the thickness reinforcements results in improved damage tolerance and more cost effectiveness due to the reduction of the labor intensive traditional approach of laying down plies of prepreg. Of course, thermoplastics bring to the table simpler as well as faster manufacturing approaches versus thermoset materials. The range of polymers explored on the program address the current needs of subsonic and supersonic aircraft as well as the flexibility to explore materials for the future that may operate at temperatures as high as 700°F.

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Material Concepts

Commingled and Fused Powder Tow

In the commingled approach, thermoplastic yarns after being spun are commingled with an appropriate reinforcement. In this work carbon fiber is used exclusively but reinforcements such as glass and ceramic fiber have been evaluated. The ability to use the prescribed amount of filaments thus resulting in a net resin content can be easily achieved. The resulting tow which is very drapable is usually woven into numerous fabrics such as satin weaves, non-crimp style uni or bidirection styles for composite fabrication. Shown in Fig. 1 is a schematic of the commingled yarn. Typical polymer yarn size averages around 20 micron versus 5-7 micron for the carbon fibers.

The fused powder tow expands the technology to those polymers in which spinning is not practical due to technical or economic reasons. Thermosets, for example, are not capable of being spun. Additional benefits of fused powder eliminate the need for binders to contain the powder on the fiber. One of the primary objectives was to produce a towpreg with good powder distribution as well as good handling, such as drapability. This has been achieved with the BASF technology. Shown in Fig. 2 is a schematic of fused powder towpreg. Powder size requirements are a function of each individual polymer.

Fig. 1
Commingled Yarn Technology

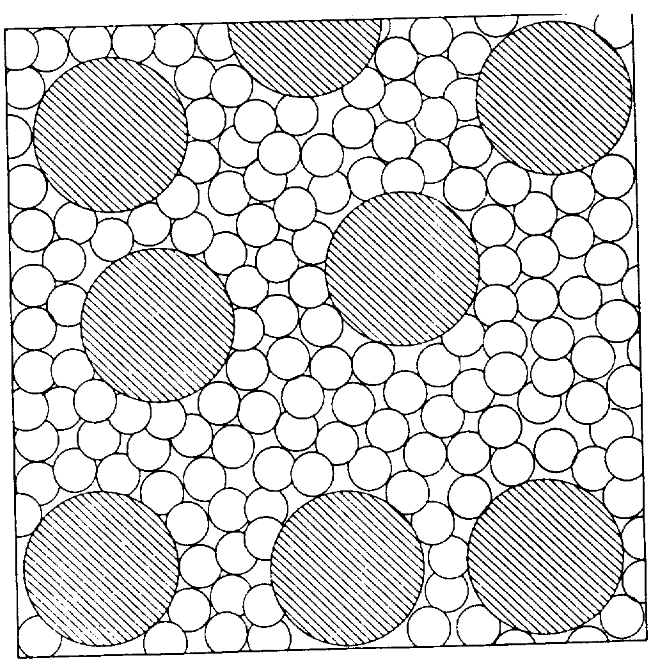
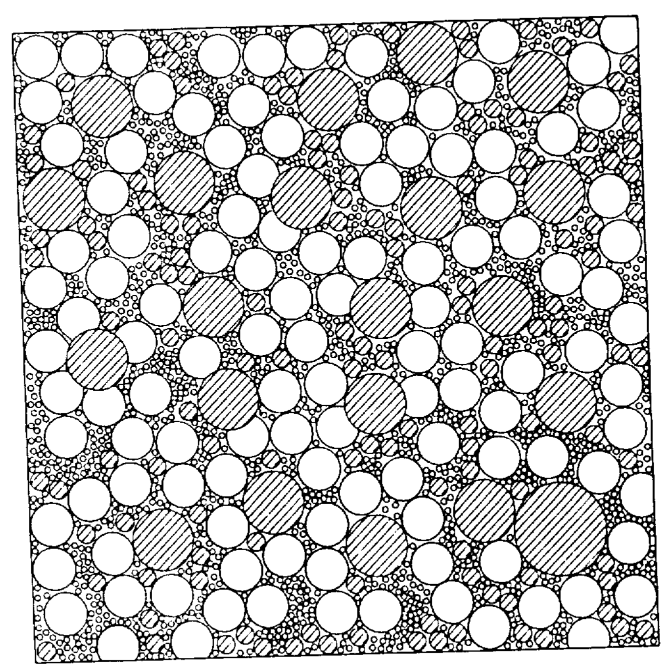


Fig. 2
Fused Powder Technology



Candidate Matrix List

Shown below in Table I is a list of polymers being explored in the program. The objective was to evaluate the commingled as well as the fused powder approach and also to address polymer systems that would have applications for subsonic and supersonic aircraft. Polymers such as PEEK and PEKEKK offer opportunities in the subsonic area. Both are semicrystalline in nature and offer exceptional toughness as well as moisture and solvent resistance. An established data base exists with PEEK. The PEKEKK offers a higher use temperature and somewhat greater toughness over PEEK based on CAI data.

New-TPI is a thermoplastic polyimide that has a use temperature in excess of 400°F. The commingled form is limited to the lower mol. wt. range. Initial mechanical properties indicate excellent potential for this system. Processing temperatures are high due to the high melt point of the polymer. Very little crystallinity remains after processing, and despite this the polymer has excellent solvent resistance.

Larc-TPI-1500 is also a thermoplastic polyimide. Recent modifications such as endcapping the polymer make it very melt stable. The medium molecular weight version has been chosen due to improved neat resin strain and toughness. As can be seen, a considerably lower melt point exists with this polymer, resulting in successful composite processing at 700°F versus 760°F for the New-TPI polyimide. NBI stands for norboreneimide and NBI #1 represents a toughened version of the fully imidized prepolymer. Only neat resin initial characterization has been accomplished.

Table I

Candidate Matrix List

Trade Name	Polymer	Tg°c	Tm°c	Comments
Victrix (ICI)	PEEK 450	143	343	Task 2 Powder
Ultrapek (BASF)	PEKEKK	175	380	Task 2 Commingle
New TPI-X	Polyimide	250	380	Task 1 Commingle
Larc-TPI-1500 (Mitsui Toatsu)	Polyimide	250	325*	Task 1 Powder
Toughened NBI #1	TP mod. Polyimide	350	- -	Task 1 Powder

*No crystallinity in processed composite

Fused Towpreg

Initial Mechanical Properties

Two thermoplastic powders, PEEK 150 and Larc-TPI-1500, were fused onto AS-4 (3K) unsized carbon fiber. Both towpregs were frame wrapped in a unidirectional pattern prior to molding with graphite tooling in a conventional press. The objective was to generate fiber and resin dominated properties as an initial attempt to evaluate the process. Shown below in Table II are initial mechanical properties on both materials as well as developed process cycles. Other than the low 90° tensile properties from the Larc-TPI, the properties are very good with a high percent translation. In both cases void free laminates were fabricated. Fracture toughness as measured by DCB specimens has been measured. The PEEK data is representative of literature values. The Larc-TPI medium mol. wt. is considerably better than the low mol. wt. data (1) reference.

Table II
FUSED TOWPREG
INITIAL MECHANICAL PROPERTIES

Property		PEEK-150 AS-4	LARC-TPI-150 AS-4
0°	- Flexural Strength* (Ksi)	350	296.6
	- Flexural Modulus (Msi)	16.2	17.7
90°	- Tensile Strength (Ksi)	11.96	4.82
	- Tensile Modulus (Msi)	1.32	1.17
Mode I	- DCB In.Lbs./In.^{2}	10.8	8.75
Fiber Volume %		57	61
Void Content		0	0

*Mod. ASTM D-790

Processing Cycle:

1. Rt. ---> 600°F, 10°F/min. contract pressure
2. 600°F apply 200 psi
3. 600°F ---> 700°F (750°F for PEEK) @ 10°F/min.
4. Hold 45 min.
5. Cool 10-20°F/min. under pressure
6. Remove when under 200°F

Fiber/Resin Distribution

Fused Towpreg

For both fused towpreg systems photomicrographs were taken. The pictures indicate excellent fiber/resin distribution with little or no voids present. What is somewhat unusual is the lack of discrete ply lines normally present with conventional prepreg. Fiber bundles can be made out but they seem to be unoriented. This would probably not affect composite properties except Modes I and II where crack propagation normally would run between discrete plies. Shown below in Figs. 3 and 4 are the respective photomicrographs from both systems.

Photomicrograph
Larc-TPI-1500/AS-4
100X

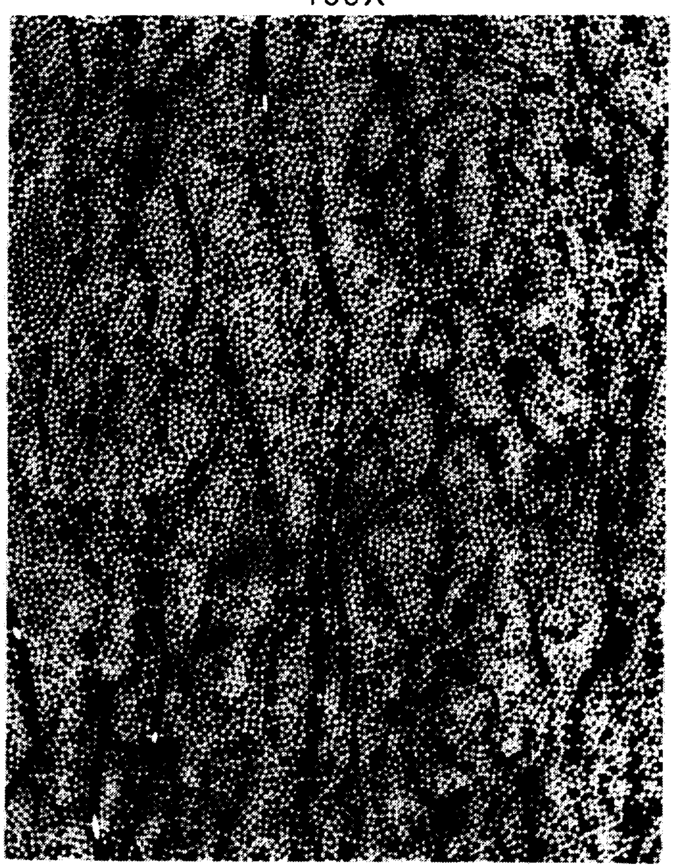


figure 3

Photomicrograph
PEEK-150/AS-4
100X

figure 4

Fracture Morphology

Observation of the fracture surface of composite specimens indicates good matrix resin adhesion. This can be observed with both PEEK and Larc-TPI-1500. Shown below in Figs. 5 and 6 are SEM's of both PEEK and Larc-TPI-1500 carbon fiber composite specimens. Little or no exposed carbon fiber can be seen for either system. Stress whiting can be observed on both systems which is indicative of a tough system. At this stage of development only simple process cycles have been explored. How changes in the process cycle, such as cooling rates, affect mechanical properties and thus fracture morphology has yet to be extensively explored.

SEM Fracture Surface
PEEK/AS-4

figure 5

SEM Fracture Surface
Larc-TPI/AS-4

figure 6

PEKEKK Neat Resin Properties

Shown below in Table III are neat resin mechanical properties. The overall properties are excellent for a thermoplastic polymer that is being used for an aerospace composite application. The tensile modulus is most noteworthy and helps translate into good compression and CAI properties.This polymeric resin system is semi-crystalline in nature. The crystallinity helps promote excellent chemical resistance, low moisture absorption and a high level of mechanical properties over a wide range of temperatures. It possesses very good adhesion properties which promote excellent carbon fiber interface development.

Table III

Ultrapec PEKEKK
Mechanical Properties

Property	Unit	Method	
Tensile Strength at Yield	Ksi	Din 53455	15.9
Tensile Modulus	Ksi	Din 53457	625
Elongation at Yield	%	Din 53455	5.3
Elongation at Break	%	Din 53455	40

Shown in figure 7 is a press molding cycle for PEKEKK composites. There is little or no restriction in heat up or cool down rate and there is an obvious advantage in shortening the cycle as much as possible. This is probably not an optimized cycle but represents the cycle which has generated the best mechanical properties to date. It is obvious that lowering the upper process temperature to 750°F would greatly benefit autoclave processing. The pressure has been established with the autoclave in mind. Compression molding above 200 psi may allow the upper process temperature to be reduced. Additional process studies to evaluate percent crystallinity and effect of mechanical properties after annealing will be accomplished as a part of the overall effort.

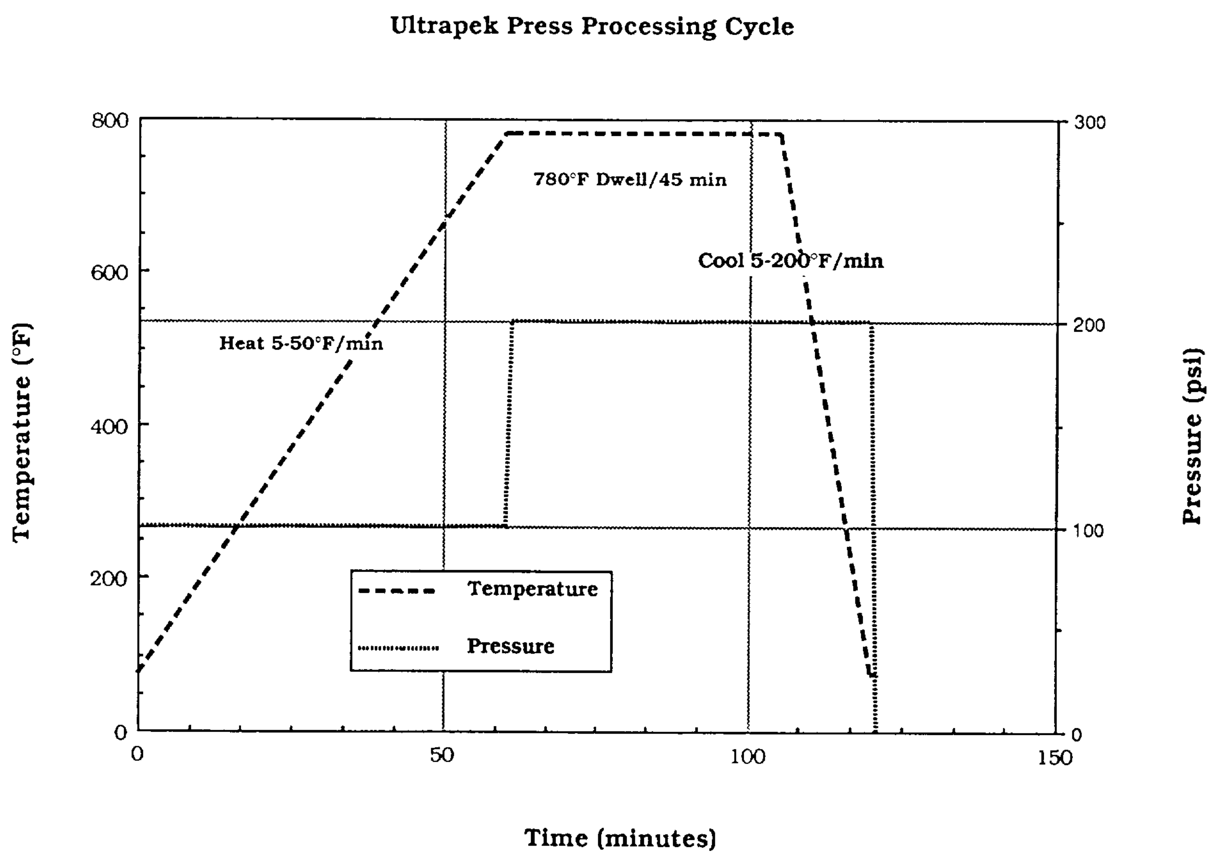


figure 7

PEKEKK Composite Properties

Shown in Table IV below are preliminary composite properties. Overall properties shown have excellent fiber translation. This is best understood by the good interface development between fiber and matrix as well as the neat resin toughness and high modulus. The CAI strength and strain values are some of the best for a thermoplastic matrix composite. A more extensive mechanical characterization will be completed in phase II of the program. Dynamic properties such as long-term fatigue as well as open-hole data are some of the additional information needed to be generated on this composite system.

Table IV

3K AS4/PEKEKK(ULTRAPEK) NCS 2381 UNIDIRECTIONAL NON CRIMP FABRIC (English Units)

TYPICAL FABRIC DATA

Carbon Fiber Volume 60.2 %		Areal Weight	334 g/m^2
Fiber Weight 67.5 %		Yield	1.40 yds/lb

TYPICAL COMPOSITE PROPERTIES

0° Properties	RT Dry	250°F Dry	325°F Wet	Unit	Test Method
Compression Strength	200			Ksi	ASTM
Compression Modulus	17.5			Msi	D695
Flexural Strength	255	219	133	Ksi	ASTM
Flexural Modulus	16.2	16.9	15.1	Msi	D790
Tensile Strength	250			Ksi	ASTM
Tensile Modulus	18.8			Msi	D3039

90° Properties	RT Dry	Unit	Test Method
Tensile Strength	13.0	Ksi	ASTM
Tensile Modulus	1.5	Msi	D3039
% Elongation	0.9	%	

+/- 45° Properties	RT Dry	Unit	Test Method
In Plane Shear Stress	17.0	Ksi	ASTM
In Plane Shear Modulus	0.87	Msi	D3518

Compression After Impact	RT Dry	Unit	Test Method
Ultimate Stress	49.9	Ksi	SACMA
Modulus	8.1	Msi	SRM
Strain To Failure	8300	µin/in	2-88
Impact Energy	1500	in lb/in	

Fracture Energy	RT Dry	Unit	Test Method
G_{IC}	12.9	in lb/in^2	NASA/DCB
G_{IIC}	13.9	in lb/in^2	PUB1092

Larc-TPI-1500 Neat Resin Mechanical Properties

Shown below in Table V are neat resin mechanical properties generated by BASF and Mitsui Toatsu. As can be observed the early testing of Larc-TPI differs from the later repeat testing.

Neat resin evaluation of two different mol. wts. of Larc-TPI-1500 indicates that the medium mol. wt. polymer possesses significantly higher properties than the lower mol. wt. This is most evident when toughness properties are compared. Strain-to-failure as well as Mode I fracture toughness indicate that the medium mol. wt. should be the resin of choice. Mechanical properties were generated from injection molded tensile dogbones and resin plaques. This technique results in high quality void free specimens. All specimens tested by BASF used an extensometer to measure tensile strain-to-failure and modulus values. Mode I fracture specimens were of the compact tension type as described in ASTM-E-399.

Table V

Larc-TPI-1500 Neat Resin Mechanical Properties

Property	Unit	Med. Flow Grade			High Flow Grade		
		Early BASF	Later BASF	Mitsui	Early BASF	Later BASF	Mitsui
Tensile Strength	Ksi	18.1	18.8	18.7	11.6	11.6	10.1
Tensile Modulus	Msi	0.310	0.650	0.625	0.330	0.680	0.625
Elongation	%	8.8	8.6	3.8	13.7	3.6	1.7
Mode I*, G_{1c}	in.lbs./in.^{2}	---	11.1	---	---	<3.0	---

*ASTM E-399

Larc-TPI-1500

Rheology

Characterization work on the apparent viscosity of the medium mol. wt. Larc-TPI indicates that the polymer is very stable at 370°C in air. As received material was run on the parallel plate Rheometrics in air. The choice of 370°C was chosen as a processing condition based on earlier viscosity studies as well as DSC work. Shown in figure 8 are two lots of material. It is understood that endcapping of the polymer has resulted in improved melt stability. Both were run at 370°C for 1 hr. as a worse case condition. For the most part, little or no air is present during consolidation. It is believed also that time for complete fiber wetout is considerably less than 1 hr. but consideration must be given to thick laminates where a thermal gradient through the thickness must be taken into consideration during molding.

Larc-TPI-1500 Med. Flow Powder (Time Sweep)

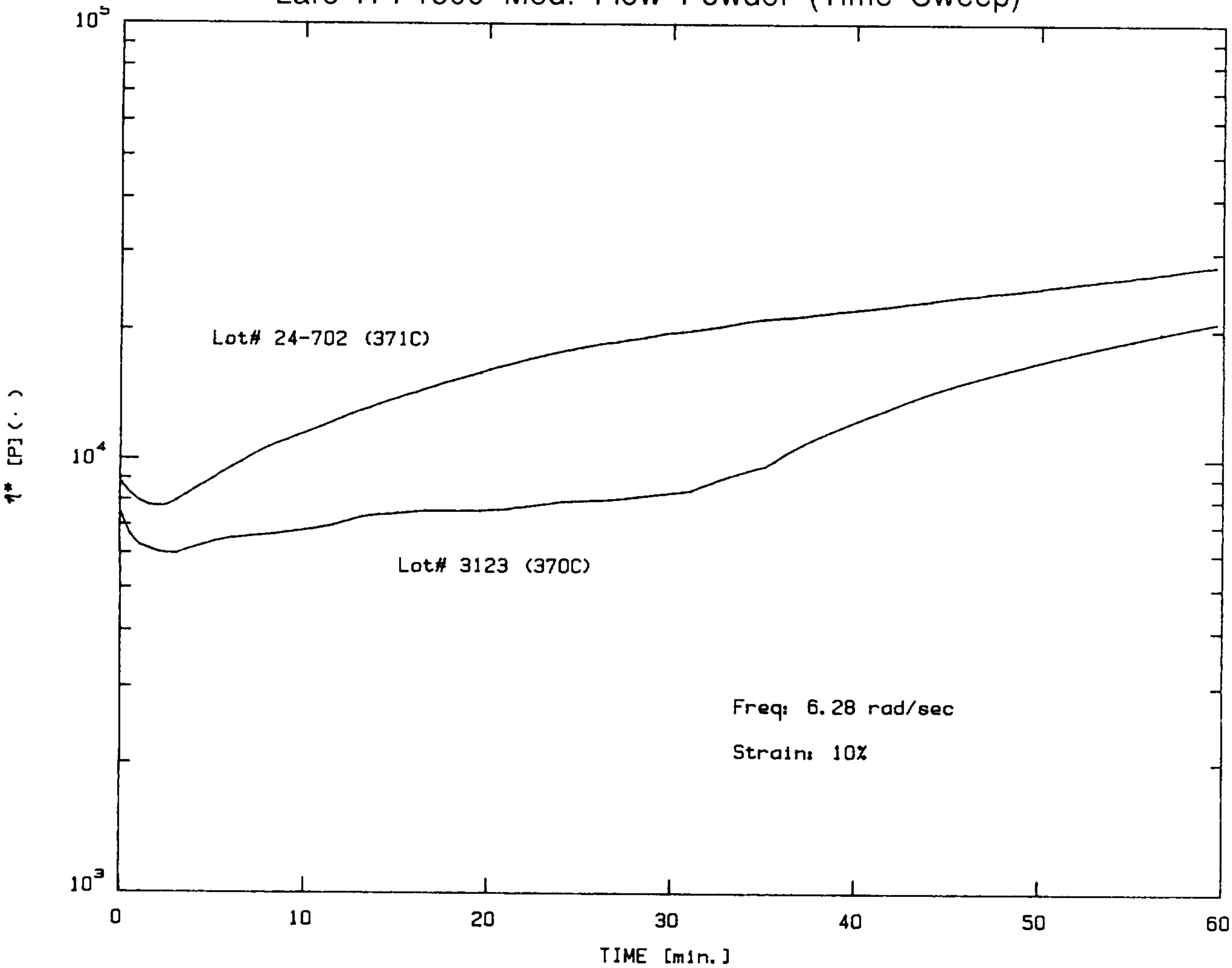


figure 8

Larc-TPI-1500

Differential Scanning Calorimetry (DSC)

A thermal analysis profile on the medium mol. wt. using DSC is shown in figure 9 below. The material was run twice as shown and exhibits a thermal profile as has been demonstrated before. A transient crystallinity is observed in the first run and disappears when the polymer is rerun. A slight shift in Tg is also noticed when one compares the first run to the second. This has also been reported in the literature.(1-2) No annealing studies have been completed on this polymer in the program to determine if Tg can be maximized. This study will be initiated.

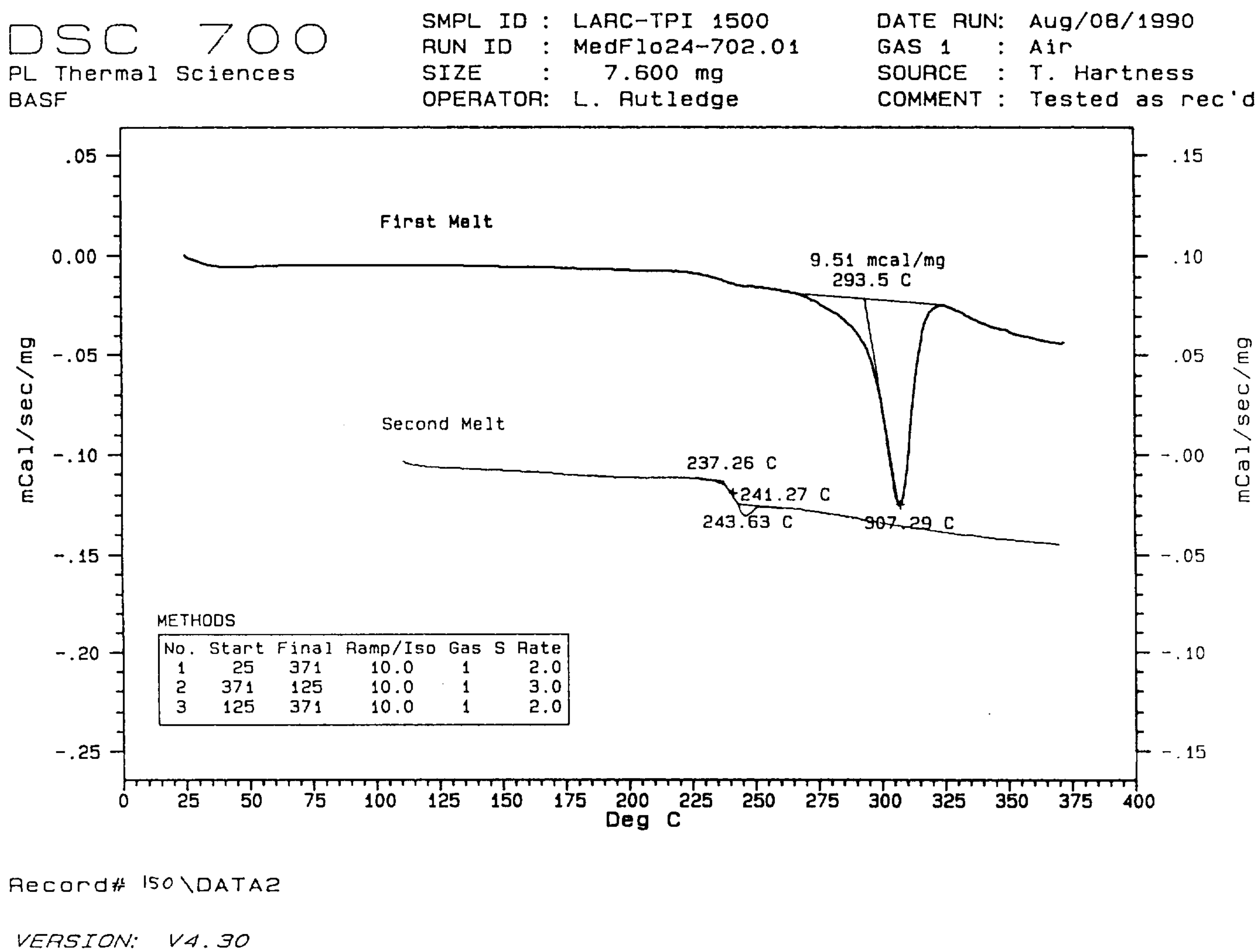


figure 9

Fused Towpreg

Consistency Study

A study was completed to evaluate the resin consistency of a 30 lbs. Larc-TPI-1500/G30-500 (6K) fiber run. Shown in figure 10 are the percent resin by weight measurements for each bobbin, 45 total, and the average. As can be observed a very consistent and tight control was achieved.

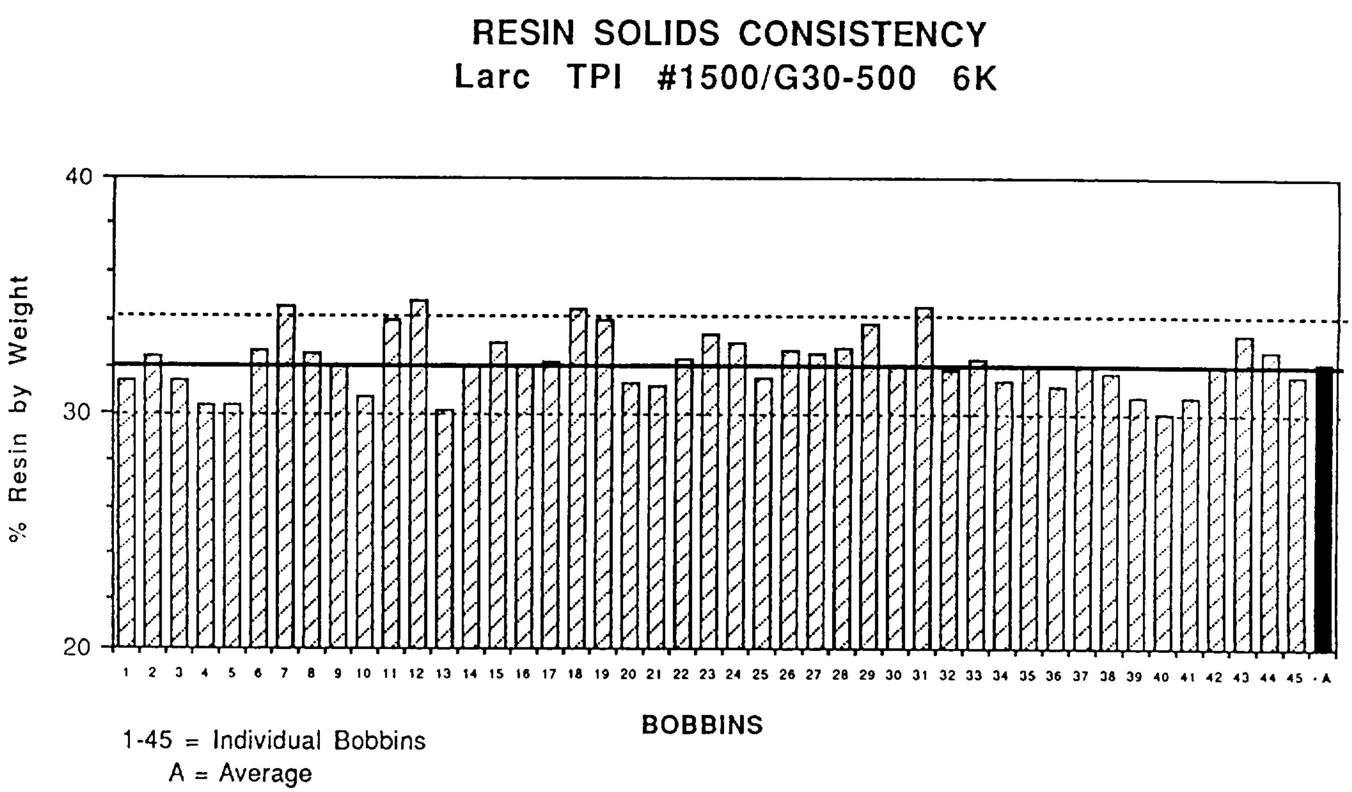


figure 10

Toughened Polyimide

Characterization was initiated on a toughened version of a fully imidized polyimide prepolymer. The objective was to develop a level of toughness in the composite where little or no microcracking occurs after thermal cycling. A neat resin target of fracture toughness was established based on work accomplished and reported on by Dr. Ruth Pater at NASA Langley Research Center[3] In this work a neat resin fracture toughness of 2 in. lbs./in.^{2} resulted in no microcracking in the composite. Shown below in Table VI are initial toughness values versus a 10% thermoplastic toughened polymer. Specimens were compression molded and then cut into compact tension specimens and tested following ASTM E-399.

Table VI

Neat Resin Fracture Toughness

	G_{Ic} in.lbs./in.^{2}	E- Modulus x10^5	Test Procedure ASTM
Standard PI	1.20	5.67x10^5	E-399
10% TP Toughened PI	1.74	5.66x10^5	E-399

Note: All samples postcured 24 hrs. @ 600°F cir. air oven

Thermoplastic Toughener Thermal Characterization

Shown in figures 11 and 12 are the thermal profiles of the TP used to toughen the polyimide. Torson rectangular samples were run on the molded neat resin as received and after a 24 hr. postcure at 600°F. The 24 hr. postcure was done as this may represent the required postcure for the polyimide. As can be observed, there was approximately an 11°C increase in Tg based on G' data. This is apparently due to some cross-linking in the polymer.

Thermoplastic No Postcure

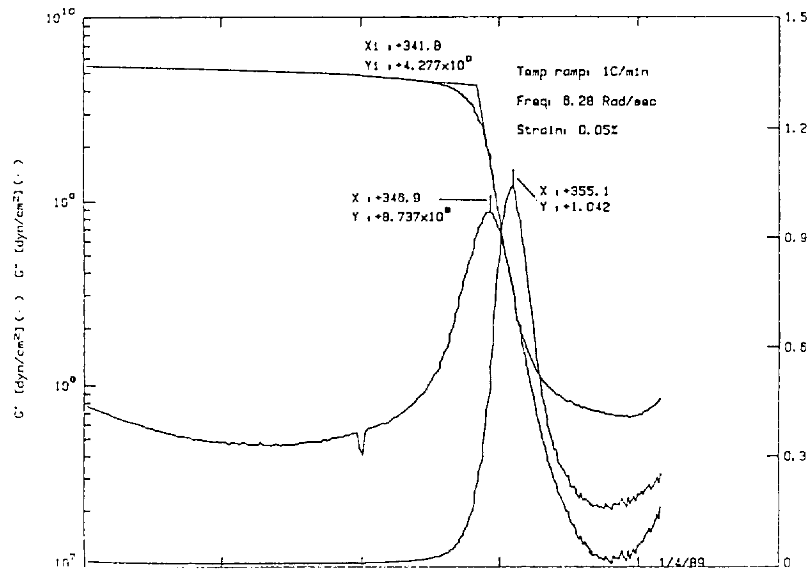


figure 11

Thermoplastic After 24 Hr. Postcure

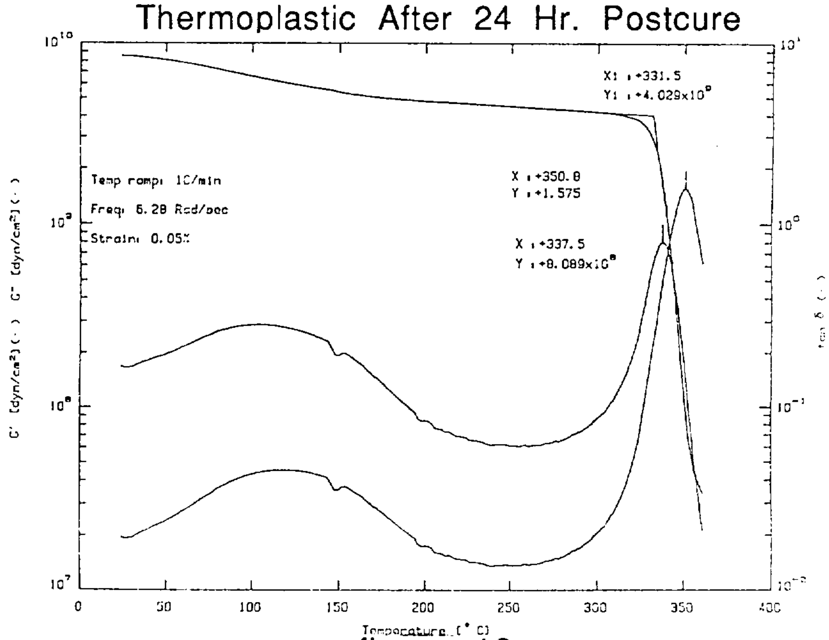


figure 12

Toughened Polyimide

Rheology

Shown in figure 13 is the apparent viscosity of the untoughened and toughened polyimide prepolymer. Obviously, some sacrifice is made in the process viscosity. It is hoped that an untoughened minimum viscosity less than 1,000 poise can be made available. This would possibly allow an increase in TP to 15%. It is believed that this level of TP would result in G_{1c} levels greater than 2 in.lbs./in.^{2}. Data WAS generated on a Rheometrics (RDA) using the parallel plate mode.

Apparent Viscosity Untoughened
vs. Toughened PI

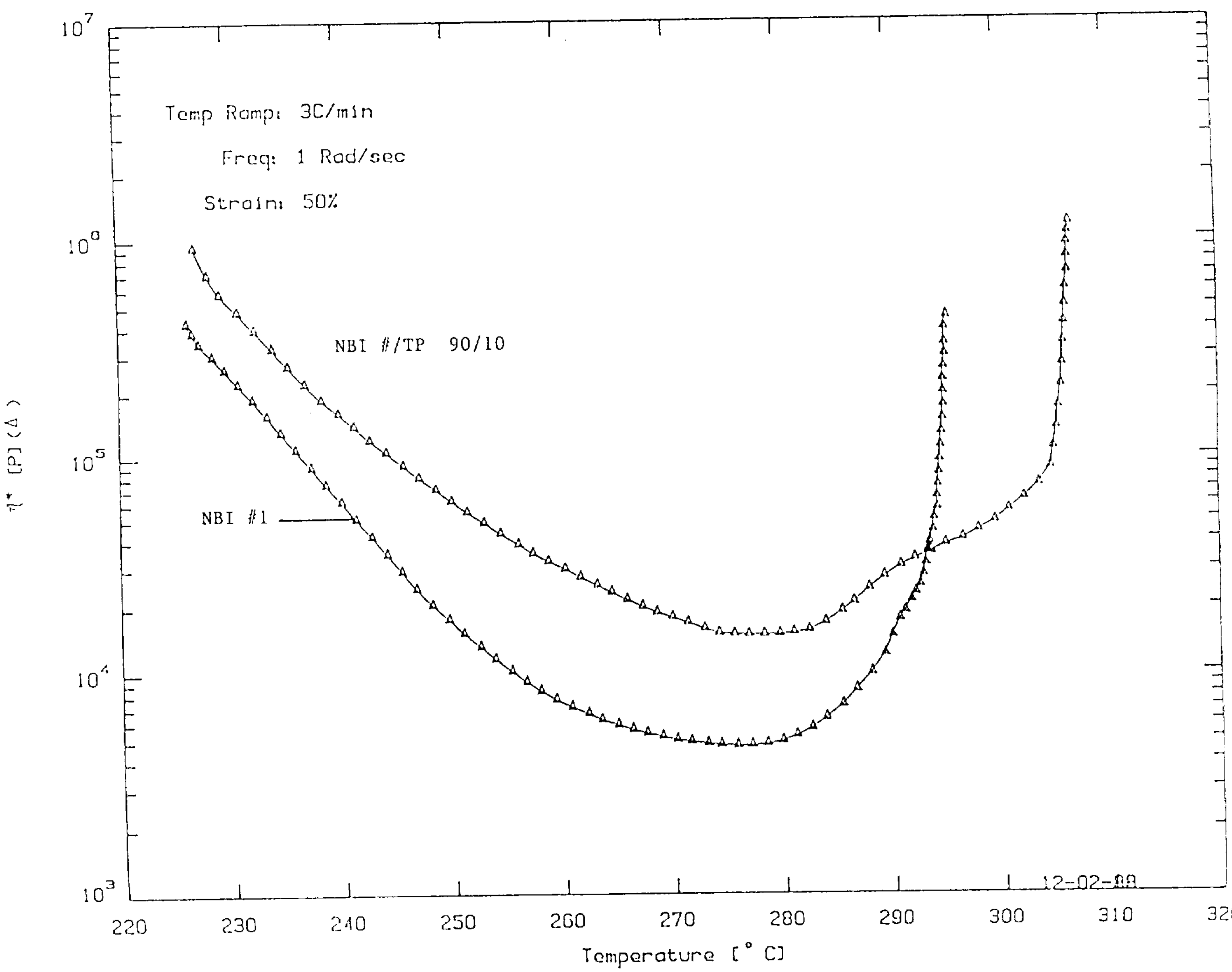


figure 13

Toughened Polyimide

Thermal Characteristics

Shown in figure 14 are Rheometric runs of the untoughened and toughened polyimide both after a postcure for 24 hrs. at 600°F. This was accomplished free standing in a circulating air oven. Specimens were rectangular torsion. Run parameters are shown on the thermal profile sheets. As can be observed there is a reduction in Tg based on G' of approx. 13°C. This is still considered an excellent Tg. There were no other apparent differences observed on the Rheometric runs. Plans in the future will evaluate a prepolymer with a lower melt viscosity. This will allow the exploration of higher TP loadings. The objective is to develop improved toughness and still maintain good processibility.

Thermal Profile of Untoughened vs. Toughened PI after 24 Hr. 600°F Post Cure

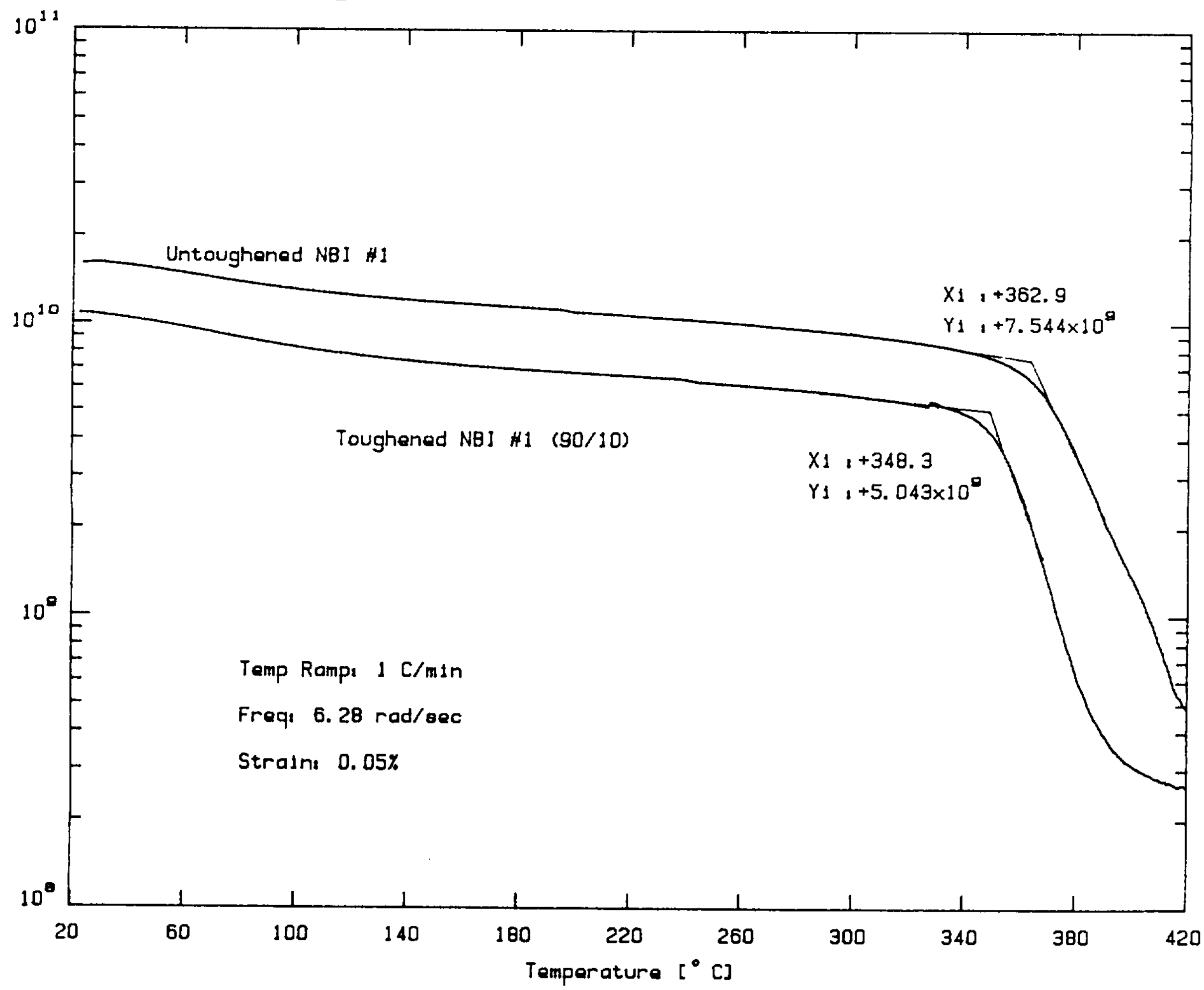


figure 14

Future Work

- Weaving trial of Larc-TPI-1500 8-harness satin bidir cloth
  - Complete mechanical characterization
- 3-D weaving trial PEKEKK/AS-4 (3K)
  - Three weave variations
  - Mechanical properties generation
- Toughened Epoxy fused towpreg characterization

References

(1) T. Towell, N. Johnston, T. St. Clair, Ohta, Tamai, 35th International SAMPE Symposium (April, 1990)

(2) J. T. Hartness, "An Evaluation of a High Temperature Thermoplastic Polyimide Composite", 32nd International SAMPE Symposium & Exhibition, Proceedings (April, 1987)

(3) R. Pater and C. Morgan, SAMPE Journal, Vol. 24, No. 5, Sept./Oct., 1988