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## DEVELOPMENT OF RTM AND POWDER PREPREG RESINS FOR SUBSONIC AIRCRAFT PRIMARY STRUCTURES

Edmund P. Woo, and Michael R. Groleau  
The Dow Chemical Company  
Midland, Michigan

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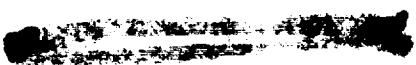
James L. Bertram, Paul M. Puckett, and Shawn J. Maynard  
The Dow Chemical Company  
Freeport, Texas

### SUMMARY

In task 1.3 of NASA Contract NAS-1-18841, Dow developed a thermoset resin which could be used to produce composites via the RTM process. The composites formed are useful at 200°F service temperatures after moisture saturation, and are tough systems that are suitable for subsonic aircraft primary structure. At NASA's request, Dow also developed a modified version of the RTM resin system which was suitable for use in producing powder prepreg. In the course of developing the RTM and powder versions of these resins, over 50 different new materials were produced and evaluated.

### INTRODUCTION

Historically, design engineers have selected metals for use in primary aircraft structures. Metals, which are isotropic, are well characterized and valued for their excellent strength, stiffness and ductility. The introduction of lighter anisotropic polymer-based composites into primary aircraft structures places certain demands on this class of materials. Many critical portions of an aircraft are subject to compressive forces, demanding that the composite possess excellent compressive strength and maintain good compressive properties following an impact. The ductility of metals, by contrast, insures that they suffer little damage from low energy impact and maintain most of their initial properties.



The substitution of polymer based composites for metal has proven to be problematic, especially in the area of damage tolerance. As composite technology has evolved over the years, state-of-the art prepreg materials (e.g. Toray T800/3900-2, Hercules IM-7/8551-7, Fiberite IM-7/977-2) have been developed which can provide very tough, damage tolerant composite products [1]. These impact resistant prepreg-based composites typically possess a resin-rich interlaminar region which has been toughened by the addition of relatively large elastomeric or thermoplastic particles. This type of composite micro-architecture is not easily transferable to applications where RTM is used to form the composite. Firstly, it is difficult to control the thickness of the interlaminar region in a dry preform into which a liquid is injected. Secondly, the use of large elastomeric or thermoplastic particles in an RTM formulation is unworkable, primarily because the preform acts as a filter, trapping particles as the resin flows through the fiber bundles. Furthermore, elastomeric or thermoplastic particles increase the resin viscosity to a level that prohibits saturation of the fibers during RTM.

Another approach to generating impact resistance in composites is the use of a three dimensional (3-D) preform [2]. On impact of a typical 2-D preform, one of the primary causes of failure is the development of interlaminar cracks and delamination. The use of through-the-thickness stitching (Z-axis) in a 3-D woven preform drastically reduces the possibility that failure can occur via delamination, since the plane of failure is constrained by the presence of reinforcement. Indeed, it has been demonstrated that composites made from brittle thermoset systems, that would typically have compression after impact values of 20-25 ksi, can exhibit CAI values of 30-35 ksi by stitching the preform through the thickness [3].

The use of these "tough" 3-D reinforced preform structures is compatible with resin impregnation via RTM. However, the use of a 3-D preform produces an unexpected side effect. The 3-D structure of the preform produces a triaxial stress on the polymer in the resin-rich interstitial pockets of the preform. The stress is generated by a combination of resin cure shrinkage and dissimilar thermal expansion coefficients between the polymer and fiber. Most of the relatively brittle polymers used in RTM relieve this stress by microcracking. However, there has been no reduction observed in static mechanical properties tested to date, which can be directly related to the presence of microcracks. Although the presence of microcracks does not typically result in a reduction in static mechanical properties, they do lead to increased moisture absorption and an increased probability of inter- and intra-laminar crack formation. These problems would most likely occur in an environment where thermal cycling of the composite is

anticipated. Therefore, an RTM resin that has a minimum tendency to microcrack when used with damage tolerant 3-D preforms would be desirable.

An alternative approach to forming tough, three-dimensionally reinforced composites is the use of powder prepreg. Following impregnation of fiber tows with a powder, these materials can be woven or braided into a 3-D structure. The consolidation of this type of 3-D preform with heat and pressure should provide a high quality composite via a process that could be economically competitive with RTM. However, as with RTM, it is the 3-D braiding, and not the processing method, which improves the toughness of the composite.

## DEVELOPMENT OF RTM RESINS

Task 1.3 called for the development of a tough, one-part resin suitable for RTM that can be processed at temperatures of less than 300°F (149°C). TACTIX\*695 epoxy resin [4], a resin originally developed for prepreg and adhesive applications, met the thermal and mechanical performance requirements of this task, but did not have the necessary processability. TACTIX\*695 is the original member of the CET (Crosslinkable Epoxy Thermoplastic) resin family. The resins described as CET materials are designed to cure with linear advancement of the epoxy, generating a thermoplastic-like structure, which then crosslinks in the last stages of reaction to form the final thermoset polymer. The crosslinking agent that is normally used in TACTIX\*695 formulations is diaminodiphenylsulfone (DDS). It is the addition of amines to TACTIX\*695, which contains both epoxy and phenolic components, that limits the RTM processability of this material. Because amines and phenolics act as catalysts for each other in the reaction with epoxy resins, the rate of reaction is increased, and the time available to mold the resin is significantly reduced.

Producing a formulation that was RTM processable began with the development of a non-amine curing agent substitute for DDS that increased the available pot-life and molding time. A key to the development was the identification of a catalyst package which would allow the resin and curing agent to be heated to temperatures of 200-250°F (93-121°C) for several

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hours before significant reaction and viscosity build began. This elevated temperature stability is essential to molding flexibility.

The absorption of moisture into a polymer plasticizes the matrix, causing a reduction in modulus and glass transition temperature [5]. Thus, the service temperature of a composite will be dependent on the initial polymer Tg and the amount of absorbed moisture. Our development efforts were guided by the concept that moisture absorption of the final polymer should be minimized.

Experimental resins XU-71992.00 and XU-71992.01 were identified as formulations that possessed the thermal, mechanical, and processing characteristics required for an RTM resin system. Experimental resin XU-71991.00, a modified, high molecular weight version of XU-71992.01, was developed for use in powder-prepregging applications. The data in Table 1 compares the unreinforced thermal and mechanical properties of TACTIX\*695 with experimental resins XU-71992.00, XU-71992.01 and XU-71991.00. This data shows that the experimental formulations provide increased toughness, equivalent modulus and moisture absorption, with slightly lower Tg's, as compared to TACTIX\*695.

The retention of flexural strength and modulus in unreinforced parts made from resins XU-71992.00, XU-71992.01 and XU-71991.00, tested at elevated temperatures following equilibrium moisture absorption obtained by 14 days water boil, is seen in Figures 1, 2 and 3 respectively. Note that the materials maintain greater than 80% of their initial modulus values at 200°F (93°C). In Figure 4, a comparison of the modulus retention of TACTIX\*695 and the three experimental resins is shown. TACTIX\*695 and all three experimental resins have equivalent moisture absorption values of 1.4-1.6%. The useful service temperature of each polymer, as defined by the break point in the modulus retention curve, can be correlated to the dry polymer glass transition temperature. The service temperature for each of the polymers (200-225°F / 93-107°C) is approximately 40-50°C below the Tg.

## **PROCESSING**

Figures 5 and 6 show DSC traces of XU-71992.01 and XU-71991.00, respectively. The cure energy profiles of the two RTM resins XU-71992.00 and XU-71992.01 are very similar,

liberating only 140-180 joules/gram. The resin for powder prepreg applications, XU-71991.00, which is a thermally advanced resin, liberates only 112 joules/gram of energy. In contrast, typical epoxy systems have a cure energy of approximately 300-400 joules/gram. Care must be taken to control the cure of epoxies because of the large amount of potential energy inherent in their chemistry. Problems normally associated with the release of this energy include generation of thermal stresses in a part during cure, and occasionally an uncontrolled adiabatic exotherm during the curing of thick composite parts. With the substantially reduced amount of energy liberated during the cure of CET resins, the problems associated with energetic cures are significantly reduced.

Figure 7 compares the viscosity of experimental resins XU-71992.00, XU-71992.01 and XU-71991.00 as a function of temperature. The RTM resins, XU-71992.00 and XU-71992.01, reach a pumpable viscosity at about 200°F (93°C) and a viscosity suitable for molding (500cps) at temperatures above 250°F (121°C). Temperatures of 200 -250°F are easily achievable in standard processing equipment and provide an excellent process window for these resins. Because it was developed for powder prepreg applications, experimental resin XU-71991.00 has a much higher molecular weight and therefore a much higher viscosity at 200-250°F.

Figures 8 and 9 show the viscosity increase with time at three isothermal temperatures (200, 250, 300°F) for XU-71992.00 and XU-71992.01, respectively. A comparison of Figures 8 and 9 shows these two RTM materials are very similar in terms of their processability, with the XU-71992.01 being slightly more viscous. This higher viscosity means that the material must be processed at slightly higher temperatures. Even at 275°F (135°C) the XU-71992.01 gives approximately two hours of molding life, while the XU-71992.00 has over three hours of molding life at 250°F.

Figure 10 shows the increase in viscosity with time at 300°F for XU-71991.00. The viscosity (at 300°F) is quite low (~1000 cps) for a thermally advanced epoxy resin, and the catalyst system apparently retains some latency. The latency of this resin is further seen in Figure 11. A dynamic viscosity profile obtained by heating experimental resin XU-71991.00 at a ramp rate of 2°C/min shows a minimum viscosity of ~300 cps at 350°F (177°C) for several minutes before the viscosity begins to rise.

The relationship between cure temperature and resin properties is shown in Table 2. Here, clear-castings of XU-71992.01 were cured at temperatures ranging from 248°F (120°C) to 392°F (200°C), and dynamic mechanical spectroscopy (DMS) was used to evaluate their  $T_g$ , shear modulus below  $T_g$ , and shear modulus above  $T_g$ . These three parameters are closely linked to the structure of the crosslinked network, which typically dominates the properties of the resin. As can be seen, the effect of cure temperature on the properties of the neat resin is insignificant. This should provide a substantial amount of flexibility in the design of cure schedules for different parts and processes.

## COMPOSITE PROPERTIES

Composite panels made with experimental resins XU-71992.00, XU-71992.01 and an unadvanced version of XU-71991.00 were produced via resin infusion molding. In this process, which is used by Dow for evaluating laboratory-scale quantities of resin, a plaque of degassed resin is placed into the bottom of a mold and a dry preform made of Celion G30-500, 3K, 8 Harness Satin fabric is placed on top. The mold is closed, and a vacuum, heat and pressure schedule is applied. In this process, the resin flows into the preform through the thickness direction. The typical consolidation pressure of 200 psi, combined with the vacuum on the mold cavity, allows for the formation of high quality, void-free panels. While resin infiltration was performed at temperatures ranging from 266°F (130°C) to 293°F (145°C), the cure schedule for these systems was 1 hour at 302°F (150°C), 1 hour at 347°F (175°C), and 2 hours at 392°F (200°C).

The data in Table 3 compares the composite performance of experimental resins XU-71992.00, XU-71992.01 and XU-71991.00. As would be expected, based upon their formulation, the materials have very similar properties. The short beam shear, compressive strength, and open hole compressive (OHC) strength values are very good and are comparable to values reported for standard prepreg systems (e.g. Fiberite 934). The 38-39 ksi compression strength after impact (CAI) values measured for these materials are outstanding. Such high CAI strengths are normally seen only in thermoplastic-modified prepreg-based materials, or in composites that are woven, braided or stitched through the third dimension (Z-axis reinforcement). The experimental CET resins provide sufficient matrix toughness to produce

composites with high impact resistance, without the aid of second phase toughening agents or Z-axis reinforcement.

Further, preliminary field trials using XU-71992.00 indicate a high resistance to microcracking in 3-D woven preforms. A study of the resistance of CET resins to microcracking is currently in progress.

## **CONCLUSIONS**

Two new RTM systems (experimental resins XU-71992.00 and XU-71992.01) have been developed for use in composites that have a 200°F/wet service temperature requirement. These materials are easily processed at temperatures of approximately 250°F (121°C) and provide a molding time of about 2 hours. The composites absorb very little moisture and have very good impact resistance.

A resin similar to these two has been produced by reaction advancement, forming a solid resin with a low melting point. This advanced epoxy system (experimental resin XU-71991.00) is useful in making prepreg via a powder process. While the composite properties of the powdered version of this resin have not been characterized, properties of the unadvanced resin have proven to be similar to those of the RTM resins.

## **NOTICE**

The information in this paper is presented in good faith, but no warranty is given, nor is freedom from any patent to be inferred.

## REFERENCES

- 1 a. C. B. Bucknall, Chapter 4, "Approaches to Toughness Enhancement," *Advanced Composites*, ed. Ivana K. Partridge, Elsevier Applied Science, NY, 1989, pp. 145-161.
- b. G. Almen, P. Mackenzie, V. Malhotra, and R. Maskell, "977: Characterization of a Family of New Toughened Epoxy Resins," 35th International SAMPE Symposium, April 2-5, 1990, pp. 419-431.
- c. Dodd H. Grande, Larry B. Ilcewicz, William B. Avery, Willard D. Bascom, "Effects of Intra- and Inter-laminar Resin Content on the Mechanical Properties of Toughened Composite Materials," First NASA Advance Composites Technology Conference, Seattle, WA, Oct. 29 - Nov. 1, 1990, 455-475, NASA Conference Publication 3104.
- d. F. W. Lee, Maureen A. Boyle, and Pierre Lefebvre, "High Service Temperature, Damage Tolerant Prepreg Systems Based on Cyanate Chemistry," 35th International SAMPE Symposium, April 2-5, 1990, pp. 162-174.
- e. H. G. Recker, V. Altstadt, W. Eberle, T. Folda, D. Gerth, W. Heckmann, P. Itemann, H. Tesch, T. Weber, "Toughened Thermosets for Damage Tolerant Carbon Fiber Reinforced Composites," *SAMPE Journal*, Vol. 26 (2), March/April 1990, pp. 73-78.
- f. Brian P. Rice and Ran Y. Kim, "Fracture Characterization of Toughened Bismaleimide/Graphite Composites," 35th International SAMPE Symposium, April 2-5, 1990, pp. 455-467.
- g. H. G. Recker, V. Altstadt, M. Stangle, "Rigidite 5276 - A Highly Damage Tolerant Epoxy System for Primary Aircraft Structure Applications," 37th International SAMPE Symposium, March 9-12, 1992, pp. 493-505.
- 2 a. Conference Proceedings: 3-D Composite Materials, ed. H. Benson Dexter, Eugene T. Camponeschi, Leighton Peebles, NASA Conference Publication 2420, Annapolis, MD, November 5-7, 1985.
- b. Joan G. Funk and Jerry W. Deaton, "The Interlaminar Fracture Toughness of Woven Graphite/Epoxy Composites," NASA Technical Paper 2950, November 1989.
- c. David S. Brookstein, "Interlocked Fiber Architecture: Braided and Woven," 35th International SAMPE Symposium, April 2-5, 1990, pp. 746-756.
- d. D. Brosius and S. Clarke, "Textile Preforming Techniques for Low Cost Structural Composites" *Advanced Composite Materials: New Developments and Applications Conference Proceedings*, Detroit MI, Sept 30 - Oct. 3, 1991, pp. 1-10.
- 3 a. M. B. Dow, D. L. Smith, S. J. Lubowinski, "An Evaluation of Stitching Concepts for Damage Tolerant Composites," *Fiber-Tex Conference*, Greenville, SC, Sept. 13-15, 1988, NASA Conference Publication 3038, June 1989.
- b. Raymond J. Palmer, Marvin B. Dow, Donald L. Smith, "Development of Stitching Reinforcement for Transport Wing Panels," First NASA Advanced Composites Technology Conference, Seattle, WA, Oct. 29 - Nov. 1, 1990, 621-646, NASA Conference Publication 3104.
- 4 a. James L. Bertram, Louis L. Walker, Jody R. Burman, James A. Clarke, US Pat. 4,494,291, June 16, 1988.
- b. James L. Bertram, Louis L. Walker, Van I. Stuart, US Pat. 4,725,652, Feb. 16, 1988.
- c. James L. Bertram, Louis L. Walker, John W. Muskopf, US Pat. 4,925,901, May 7, 1990.
- d. James L. Bertram, Louis L. Walker, Van I. Stuart, US Pat. 4,946,817, Aug. 7, 1990.
- 5 a. H. M. Clancy and D. E. Lufti, "Moisture in Composites - A Reminder," 18th International SAMPE Technical Conference, Oct. 7-9, 1986, 135-141.
- b. *Diffusion in and Through Polymers*, Wolf R. Vieth, Hanser Publishers/Oxford University Press, NY, 1991.



**TABLE 1. CET Resins: A Comparison of Clear Cast Properties<sup>#</sup>.**

Mechanical Test	Measurement	TACTIX*695	XU-71992.00	XU-71992.01	XU-71991.00
Fracture Toughness	K <sub>1c</sub> (psi √in)	650	835	835	711
	G <sub>1c</sub> (J/m <sup>2</sup> )	140	245	245	192
	G <sub>1c</sub> (in lbs/in <sup>2</sup> )	0.8	1.4	1.4	1.1
Density	Polymer (g/cc)	1.48	1.37	1.27	1.27
Tensile	Strength (ksi)	13	13	13	13
	Modulus (ksi)	445	440	425	410
	Elongation (%)	8.5	5.0	5.5	5
Flexural	Strength (ksi)	19	21	18.5	21
	Modulus (ksi)	455	495	450	450
	Strain (%)	>5	>5	>5	>5
Moisture Absorption	Weight %	1.6	1.4	1.6	1.4
Thermal	T <sub>g</sub> (Tan δ, °C)	165	155	156	164
	T <sub>g</sub> (DSC °C)	160	140	146	156

Cure Schedule: 4 hrs @ 150°C; Post Cure Schedule: 2 hrs @ 200°C

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<sup>a</sup>Compact tension geometry

<sup>b</sup>After two weeks in boiling water

<sup>#</sup>Typical properties, not to be construed as specifications

**TABLE 2. A Comparison of DMS Properties for Unreinforced Panels of Experimental Resin XU-71992.01 Cured Isothermally**

Initial cure T (°C)	G' @ 25°C (GPa)	T <sub>g</sub> from T at G'' = max (°C)	T <sub>g</sub> from T at tan δ = max (°C)	G' @ 200°C (dyn/cm <sup>2</sup> )
120	1.167	151	160	4.35e7
135	1.202	152	159	4.90e7
150	1.174	150	159	4.67e7
165	1.214	---	---	---
200	1.176	150	159	4.63e7

All clear-castings cured to 95% conversion at the temperatures shown above, followed by a post-cure for 2 hr. @ 200°C.

**TABLE 3. A Comparison of Composite Mechanical Properties<sup>#</sup> of Experimental CET Resins With G30-500 8HS**

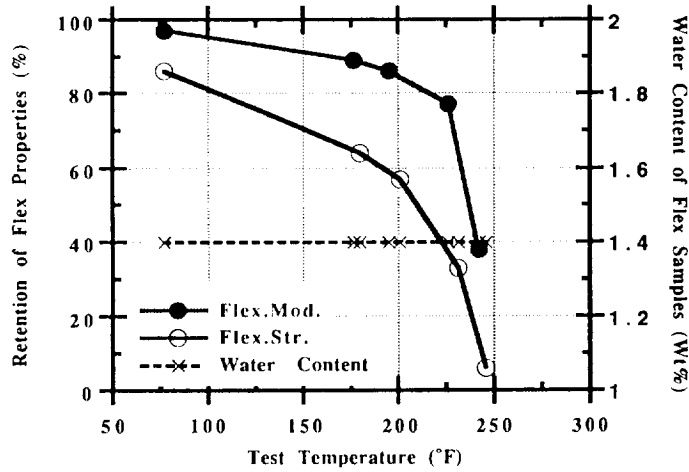
Mechanical Test	Measurement	XU-71992.00	XU-71992.01	XU-71991.00
0° Flex	<u>77°F-Dry</u> Strength (ksi)	152	138	137
	Modulus (ms)	8.0	8.8	8.3
Short Beam Shear	<u>77°F-Dry</u> Strength (ksi)	10	10	10
0° Compression	<u>77°F-Dry</u> Strength (ksi)	113	108	109
Open-hole Compression (OHC)	<u>77°F-Dry</u> Strength (ksi)	38	39	38
	180°F-Wet Strength (ksi)	34	33	34
Compression After Impact (CAI)	<u>77°F-Dry</u> Strength (ksi)	39	39	38

The cure schedule on all composite panels is 1 hr @ 150°C, 1 hr @ 175°C; followed by a post cure schedule of 2 hrs @ 200°C.

All tests were conducted according to SACMA recommended test methods.

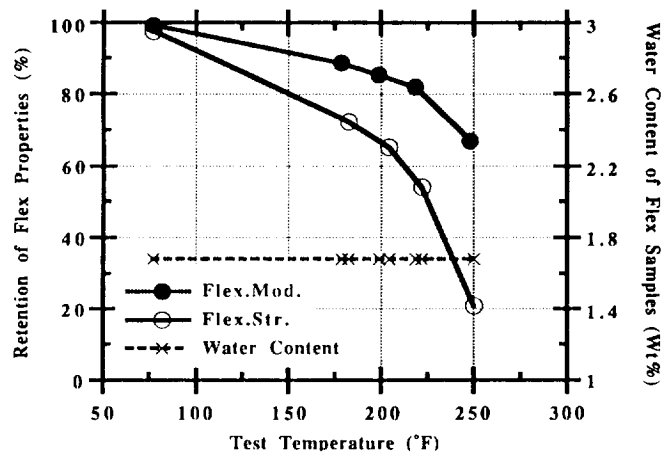
<sup>#</sup>Typical properties, not to be construed as specifications

**FIGURE 1. Effects of Moisture Absorption and Elevated Temperature on Unreinforced Flexural Properties of Experimental Resin XU-71992.00**



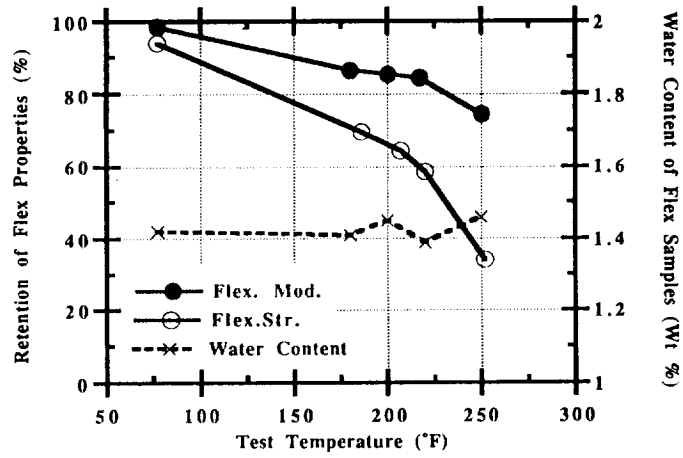
Cure Schedule: 4 hrs @ 150°C: Post Cured 2 hrs @ 200°C  
 Equilibrium Moisture Absorption Obtained by 14 Days Water Boil

**FIGURE 2. Effects of Moisture Absorption and Elevated Temperature on Unreinforced Flexural Properties of Experimental Resin XU-71992.01**



Cure Schedule: 4 hrs @ 150°C: Post Cured 2 hrs @ 200°C  
 Equilibrium Moisture Absorption Obtained by 14 Days Water Boil

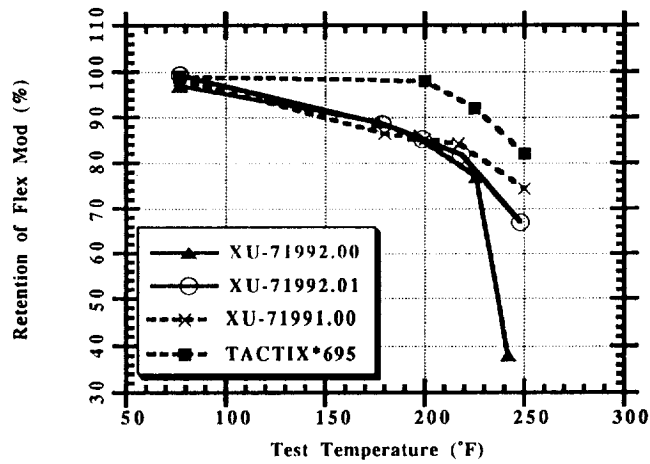
**FIGURE 3. Effects of Moisture Absorption and Elevated Temperature on Unreinforced Flexural Properties of Experimental Resin XU-71991.00**



Cure Schedule: 4 hrs @ 150°C: Post Cured 2 hrs @ 200°C

Equilibrium Moisture Absorption Obtained by 14 Days Water Boil

**FIGURE 4. A Comparison of Flexural Modulus Retention of Unreinforced Panels Made With CET Resins**

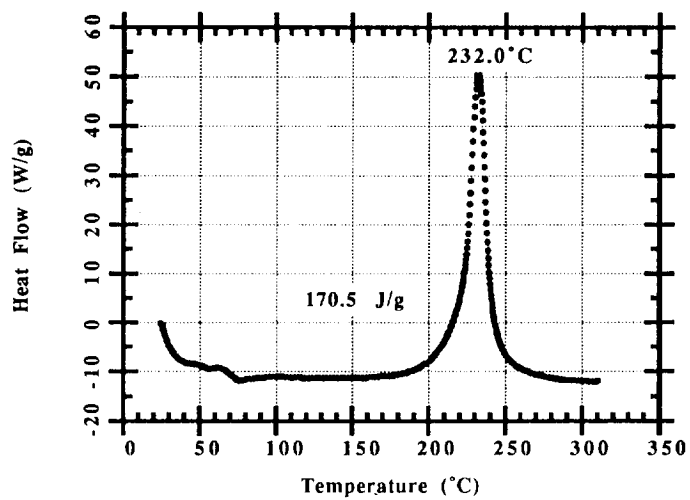


Cure Schedule: 4 hrs @ 150°C: Post Cured 2 hrs @ 200°C

Equilibrium Moisture Absorption Obtained by 14 Days Water Boil

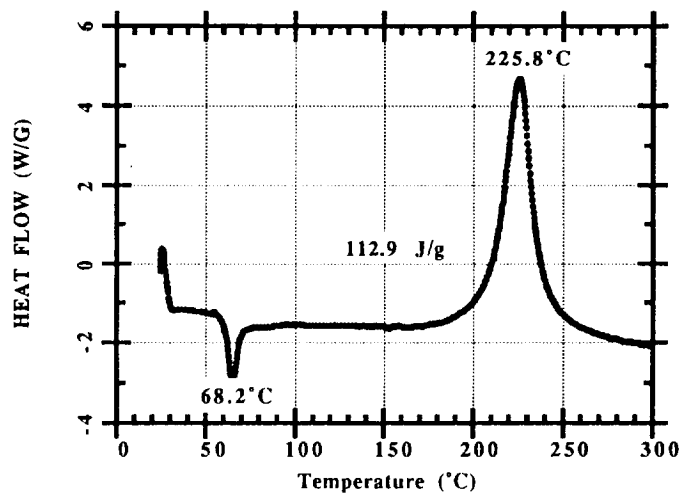
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FIGURE 5. DSC of XU-71992.01 (Uncured)



Ramp 10°C/min

FIGURE 6. DSC of XU-71991.00 (Uncured)



Ramp 10°C/min

FIGURE 7. Effect of Temperature on the Viscosity of Experimental CET Resins

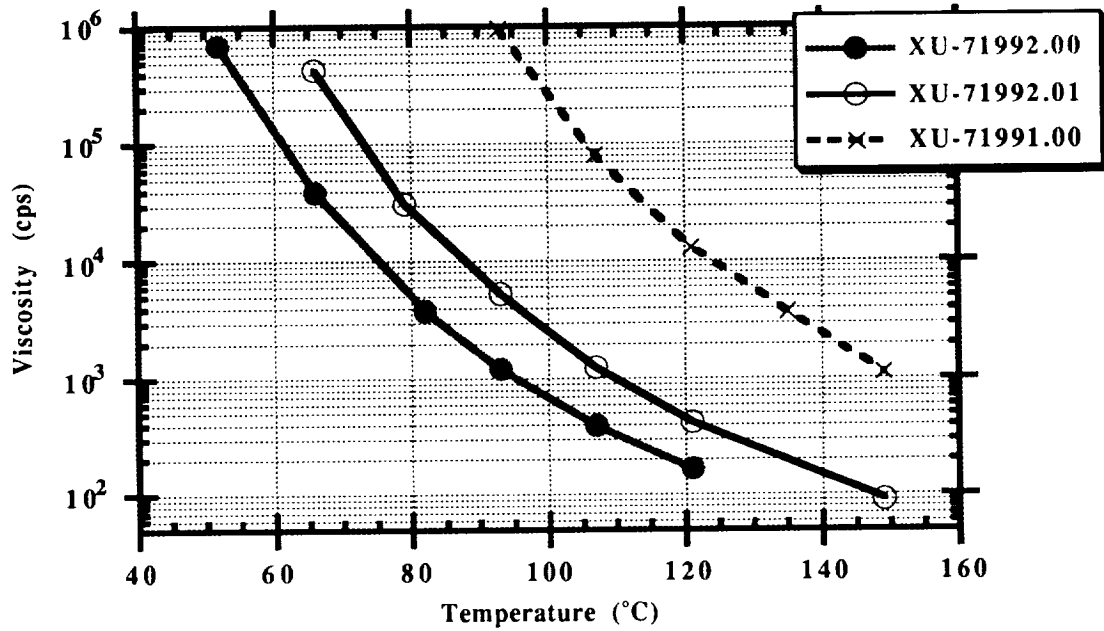


FIGURE 8. Isothermal Viscosity Profiles of Experimental Resin XU-71992.00

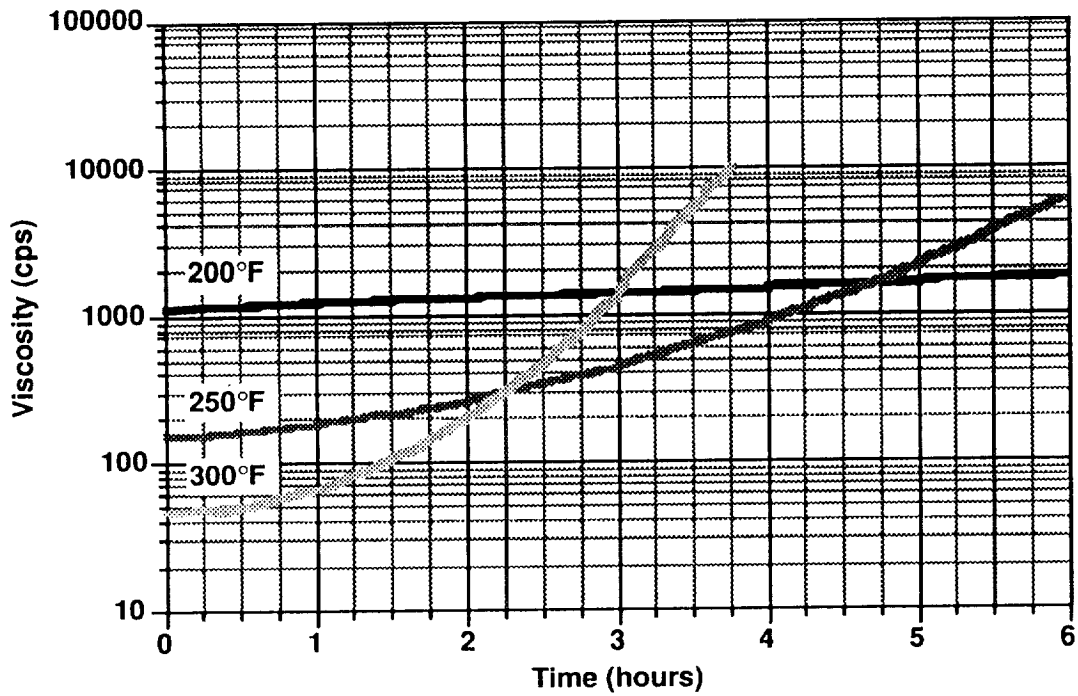


FIGURE 9. Isothermal Viscosity Profiles of Experimental Resin XU-71992.01

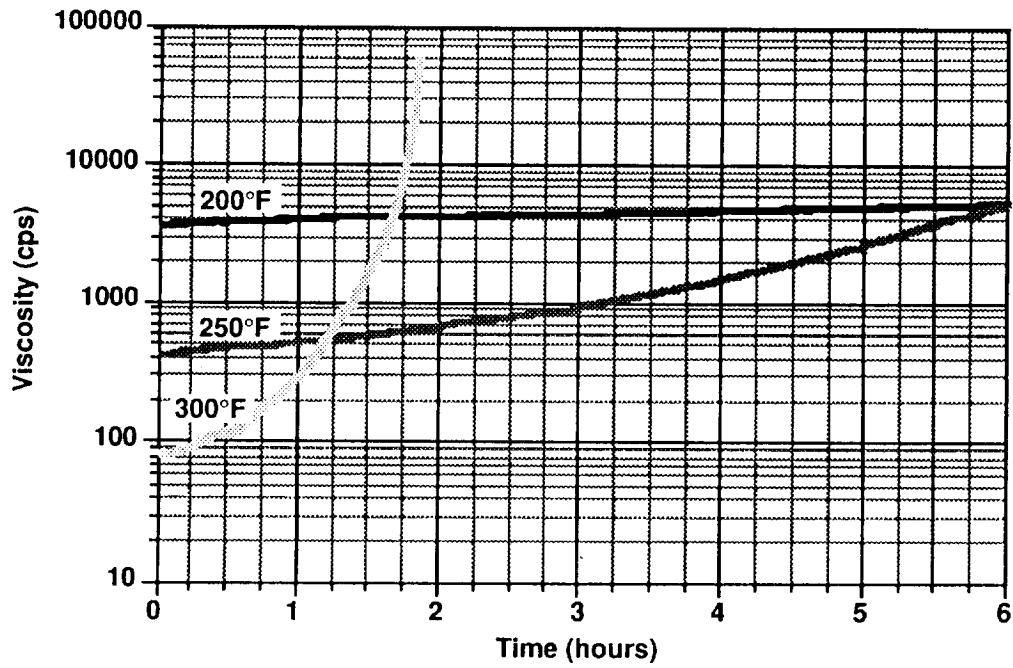
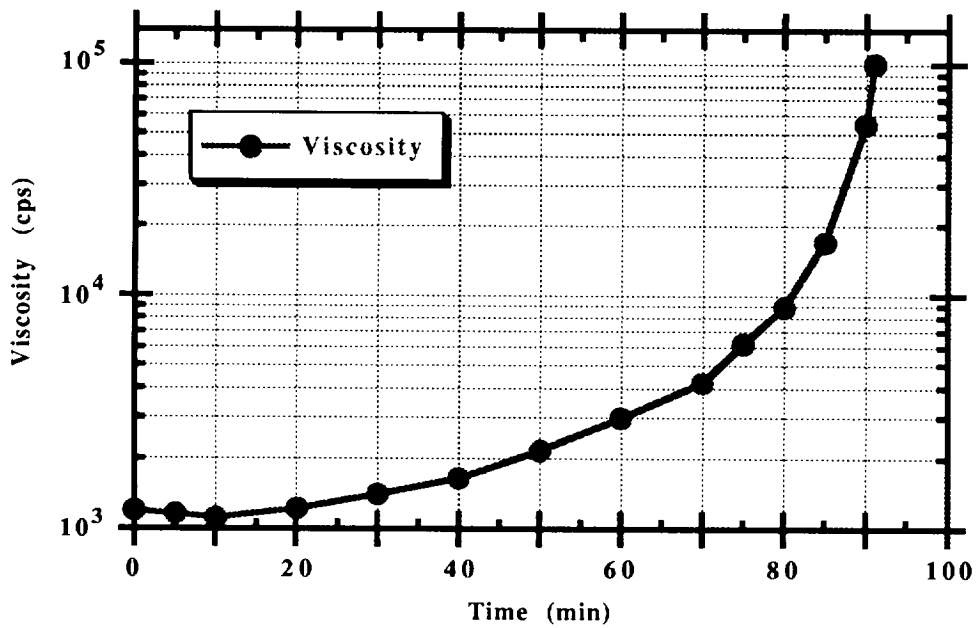
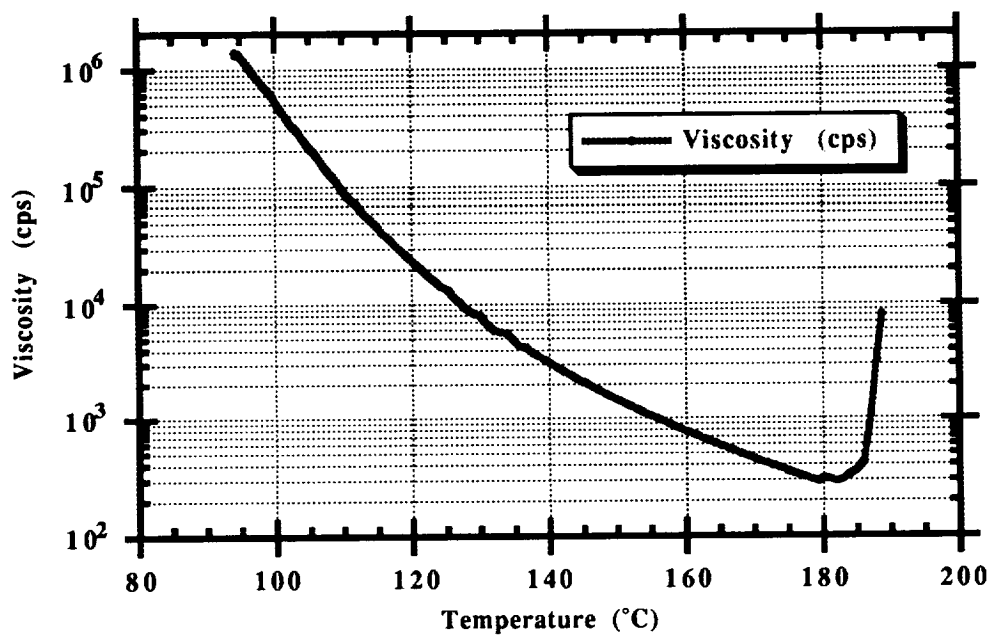


FIGURE 10. Isothermal Viscosity Profile of XU-71991.00 at 300°F (150°C)



**FIGURE 11. Dynamic Viscosity Profile of Experimental Resins XU-71991.00**



Heating Rate 2°C/min  
Parallel Plate - 50 mm: 0.5 mm Gap