CHARACTERIZATION OF POLYIMIDE

MATRIX RESINS AND PREPREGS

M. G. Maximovich and R. M. Galeos
Lockheed Missiles and Space Company (LMSC)

Graphite/polyimide composite materials are attractive candidates for a wide range of aerospace applications. They have many of the virtues of graphite/ epoxies, i.e. high specific strengths and stiffness, and also outstanding thermal/ oxidative stability. Yet they are not widely used in the aerospace industry due to problems of processability.

By their nature, modern addition PI resins and prepregs are more complex than epoxies; the key to processing lies in characterizing and understanding the materials.

Chemical and rheological characterizations were carried out on several addition polyimide resins and graphite reinforced prepregs, including those based on PMR-15, LARC 160 (AP 22), LARC 160 (Curithane 103) and V378A. The use of a high range torque transducer with a Rheometrics mechanical spectrometer allowed rheological data to be generated on prepreg materials as well as neat resins. The use of prepreg samples instead of neat resins eliminated the need for pre-imidization of the samples and the date correlates well with processing behavior found in the shop. Rheological characterization of the resins and prepregs found significant differences not readily detected by conventional chemical characterization techniques.

INTRODUCTION

A great deal of interest has been expressed in graphite/polyimide composite materials for applications where outstanding thermal/oxidative stability is a prime requirement. These materials also exhibit excellent mechanical properties, low specific gravities, and other attractive properties, yet they are only occasionally used in actual production programs.

The factor limiting the use of G/PI composites is processability. High quality, reproducible hardware is difficult to fabricate, due to lack of understanding and control of the various physical and chemical changes that occur during the processing of these materials. Many modern addition PIs, such as PMR-15 and LARC 160, are based on the Ciba-Geigy P-13N chemistry. Figure 1 shows the temperature ranges over which several different phenomena occur during the processing of P-13N. Small changes in structure can shift these temperature ranges and so alter the processing window for these materials. By understanding the chemistry and rheology of these materials, we hope to define and optimize the processing windows for the reliable, reproducible fabrication of high quality composite hardware. The purpose of this work was to further identify and develop techniques to chemically and rheologically

characterize and understand the behavior of G/PI prepreg material during processing.

Experimental

1. Materials. The prepregs based on LARC 160 (AP-22) and PMR-15 were obtained from Fiberite Corp. The V378 prepreg material were obtained from U.S. Polymeric, Inc. PMR-15 and LARC 160 (AP-22) neat resins were prepared at LMSC using the procedures well documented in the literature (1,2). The Curithane 103 version of LARC 160 was prepared using a simple one-to-one substitution of Curithane 103 for Jeffamine AP-22 in the LARC 160 procedure. The LARC-160 (Curithane 103) based prepreg was prepared from the resin synthesized at LMSC.

2. Chemical Characterization.

2.1 I.R. Studies

As previously reported, (3) IR spectroscopy and liquid chromatography were employed. Samples of both LARC 160 batches appear to show no significant differences in IR absorption peaks.

As synthesized, the volatile content of each LARC 160 batch was running about 48%. This was determined by inserting a resin sample into a preheated oven at 316°C for 30 minutes and then calculating the sample weight loss. This figure includes both solvent and condensation by-products. In order to be more representative of resin found in a prepreg, it was decided that a realistic volatile to resin ratio should be determined and also that the as-synthesized resin should be dried to this level. The dry resin content (after 30 minutes at 316°C) and volatile content (same conditions) of fabric LARC 160 prepreg used at LMSC runs around 36% and 12%, respectively. This gives a ratio of 1:3 or in other words 25% of the net resin weight is volatile. Drying conditions of 50°C for 2 to 3 hours in a vacuum oven seem to be appropriate and IR data shows no side reaction products. The infrared spectra of the three synthesized resins are shown in Figures 2-4.

2.2 HPLC Studies

HPLC traces were run using established test procedures (4). In our case the aqueous portion of the gradient mobile phase was not buffered with KH_2PO_4. However, the change did not appear to affect the quality of the component separations. Figures 5-7 show the chromatograms of the LARC on IMR resins.

General identification of specific peaks is made in a few instances. Lack of chromatogram complexity as compared to that obtained by Rockwell (5) may be attributed to two factors. First, our syntheses were carried out in fairly pure ethanol whereas Rockwell's esterification was conducted using an industrial alcohol mixture. Second, our resins were prepared under dilute solvent conditions. According to the 9th Quarterly Report (June - September 1980) from Rockwell (6), high viscosity during the co-esterification of the starting anhydride materials results in incomplete conversion of BTDA to the BTDE diester and, thus, the presence of the BTDA tetra-acid (BTA) and BTDE monoester will be evident.

To determine the effects of staging on the separated peaks, staged resins were analyzed by HPLC. The chromatogram comparison is shown in Figure 8. Keep in mind that the resin staged 1 hour at 121°C was not completely soluble in acetonitrile. Thus, the curve represents resin that was soluble and prefiltered through a 0.45 fluoromembrane filter. As can be seen, there are obvious effects on all peaks as the result of staging. Slight changes are evident even for the resin drying period of 2 hours at 50°C. The significance of these differences is not known at this time. Radical variations are seen in the extreme case of 1 hour staging at 121°C. The main reaction peak predominates in this curve.

2.3 DSC Characterization

DSC studies were carried out on both unstaged resin and resin staged ½ hour at 120°C. Only minor differences were noted between the two LARC 160 versions. A set of curves was also run on a PMR-15 batch prepared at LMSC and is included for comparative purposes. Figure 9 through 14 show this data.

As noted previously (3), the main conclusion to be drawn from the chemical characterization studies were the little difference found between the two versions of LARC 160, which, in turn, differed significantly from the PMR-15 resin.

2.4 Rheological Characterization

2.4.1 Resin Studies

The first attempt to generate rheological data on the LARC 160 and PMR-15 resins were not entirely satisfactory. Although samples could be dried 2 hours at 50°C to remove solvent without significantly changing the resins, excessive volatiles were evolved during the cure. These volatiles, with condensation products and residual solvent, caused bubble formation in the Rheometrics mechanical spectrometer (RMS) sample cavity. The bubble formation led to excessive scatter in both the apparent viscosity (η^*) and the tan δ data.

In order to avoid the problem, a pressure cell transducer was obtained from Rheometrics. The cell had 500 psi pressure capability and was designed for use with resin systems that outgas during cure. Unfortunately, little improvement was found in the data generated while using the pressure cell. Inspection of the samples showed bubbling still occurred within the samples and the resin was forced out from between the parallel plates. An extensive effort was made to overcome the problem, including modifications of the plates, the fixtures and the test geometry. When these efforts proved unsuccessful, work with the pressure cell was discontinued.

Our next approach was to use preimidized samples of PMR and LARC resins in our study. This greatly reduced the amount of volatile material to be eliminated during the rheological testing.

Data was gathered on samples which were oven imidized at 121°C for 60 minutes prior to characterization. After imidization, samples were pulverized and desiccated. Prior to measurement, samples were further dried in a desiccated vacuum oven (RT/380-510 mm Hg) overnight.

In order to form a sample in the environmental chamber of the rheometer, the chamber was preheated to 200°C and a pre-weighted amount of imidized resin (fine powder) was introduced between opened parallel plates. The chamber was then closed and

when the indicated temperature again reached 200°C, a sample was formed by closing the plates to a predetermined gap (0.6 mm). The chamber was then again opened and excess resin was removed from the edges of the plate. The chamber was reclosed and heating was resumed when the chamber reached 200°C.

Complex viscosity as a function of temperature is shown in Figure 15 for LARC 160 (AP 22 and Curithane 103 versions) and PMR 15 (ethanol solution) at heating rates of 2 and 4°C/min. There appear to be distinct differences between all of the resins. The greatest difference was between the two types of LARC 160. Because of the greater amount of 4,4'-MDA in Curithane 103, one might logically expect this version of LARC 160 to have a higher minimum viscosity than its AP-22 counterpart. However, the data shows the opposite. Furthermore, if the AP-22 version of LARC 160 is compared to earlier data obtained from preimidized LARC 160 prepreg the viscosity profiles of the two resins are significantly different. The resin from the prepreg reaches a minimum viscosity in the neighborhood of 400 poise at 292°C as compared to around 7,000 poise at 250°C for freshly synthesized resin. Although the heating rates were the same, i.e., 4°C/min, the prepreg resin was scanned and started at 239°C while the current material resin was scanned from 200°C. The additional time at higher temperatures tends to explain the observed differences and also presents another problem. The viscosity measured in a characterization run might not reflect the true viscosity during a process. It clearly points out the need for parallel heat histories of samples being compared.

Note that an improved viscosity characterization procedure would be desirable to eliminate the initial peak in complex viscosity during the first 10-20 minutes of a run. The resin is not very fluid at 200°C. The lower temperature was used to minimize any reactions during sample formation and hence give better reproducibility. This higher initial viscosity requires a low shear stress and low shear rate because of the transducer limitations. However, the deflection of the transducer shaft must exceed 0.001 of the radius in order to give reliable results. The shear strain of 3 used to generate the data in Figure 15 was later found to be slightly less than required by calculation (γ = 5). The data is thus questionable. The effect of shear strain was examined in subsequent tests and the data appears in Figure 16.

For the AP-22 version of LARC 160, shear strains of 3, 5, 10 and 50 were examined. A starting temperature of 230°C was required to get the initial viscosity low enough to accept the higher shear strains. The data shows a scatter band but no systematic variation as a function of shear strain. The only large difference occurs in the case of γ = 3. Similar data for the Curithane 103 version of LARC 160 at shear strains of 3, 10 and 50 are also shown in Figure 16. In this case, the largest difference occurs in the case of γ = 50. It would appear that a shear strain of 10 might be the best choice. Despite the scatter, it is clear that in all cases the Curithane 103 version of LARC 160 has a lower minimum viscosity in the process critical range as compared to AP-22.

Note also that the curves for PMR-15 and AP-22 based LARC 160 resemble each other far more than they resemble that of the Curithane 103 based LARC 160.

2.4.2 Prepreg Viscosity Studies

A problem encountered throughout the work with the addition polyimide systems was that of sample preparation. Almost any technique for preparing a neat resin sample from prepreg can significantly change the nature of the resin. Solvent techniques

can pose serious problems in removing residual polar solvents that interact strongly with the polymer. Small amounts of such solvents, if not removed, act as plasticizers and reduce Tg of the resin. Heating to remove solvent will stage or alter the resin. Even physically scraping or grinding off resin flash can result in a sample contaminated with fiber or debris.

Another serious question must also be addressed. Laminates are fabricated from prepreg, not resin. How does the rheological response of the resin in the presence of the reinforcement differ from that of the neat resin? The presence of the fiber with its large surface area and the presence of active chemical species on the fiber surface can certainly affect the resin, both physically and chemically.

It was therefore decided to attempt to develop techniques for determining the rheological characteristics of reinforced prepreg samples on the Rheometrics mechanical spectrometer. Techniques were successfully developed, using well characterized graphite/epoxy materials and are reported elsewhere. (7) LARC 160/woven T300 prepreg samples were investigated, but initial efforts proved unsuccessful. The imidized systems were too high in viscosity to study with the torque transducers available to us at the time.

A high range torque transducer was obtained from Rheometrics. Prepreg samples were next pre-imidized using a 2 hour, 121°C hold, as for the neat resin samples. Unfortunately no additional LARC 160 (Curithane) prepreg was available. Figures 17 and 18 show the curves generated as preimidized LARC 160 (AP-22) and PMR-15 prepreg, and compare the dates with that generated on the neat resin. Note the significant difference in minimum viscosity (nearly an order of magnitude) of resin vs. prepreg samples. Minimum viscosity also occurs at a higher temperature for the prepreg than for the neat resin specimens.

Recent work on epoxy systems by Brown (8) has shown that volatiles in laminates escape out the sides of the layup rather than diffuse through the top and bottom. The bubbles follow the fibers to the edge of the panel, rather than working their way through the plies. It seemed possible that the RMS prepreg samples would behave in a similar manner, allowing good data to be obtained on prepreg without the need for an imidization step.

Samples were dried at 50°C, then placed in the RMS cavity. The runs were started at 60°C and cured to over 380°C. Little or no problems were encountered with bubble formation and data scatter and good, reproducible curves were obtained. Figure 19 compares the apparent viscosity curves of LARC 160 (AP-22) prepreg and PMR-15 prepreg, imidized versions, while Figure 20 shows the same data for samples run without imidization. The curves on the non-imidized versions appear to agree best with laboratory experience, as the low temperature, low viscosity behavior of the PMR is seen. The imidized and non-imidized data is consistent at higher temperatures as one would expect. LARC 160 shows lower viscosity (higher flow) at the usual processing temperatures (i.e. 270 - 320°C) for these systems.

Samples of another commercial addition polyimide, U.S. Polymeric V378A, were available. Rheometrics curves were successfully run on V378A resin reinforced with Celion 3000 and T300 fibers. Although rheological curve of the neat resin from each batch showed little difference, a significant difference in the prepreg viscosity curves were observed as can be seen in Figure 21. The Celion reinforced prepreg has a significantly lower minimum apparent viscosity, and therefore higher flow. This is consistent with the processing characteristics for these prepregs

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observed in the LMSC shop and elsewhere in the industry.

2.4.3 Solid State Rheometrics Studies

In order to run solid state rheological studies on the two LARC 160 resins, it was necessary to prepare neat resin moldings. This was not an insignificant task, as a staging cycle was required that allowed the powdered resin to be cured under pressure. Simple casting and curing or pressing to stops resulted in high void moldings or moldings with incomplete consolidation. After several attempts, we developed cycles for both resin systems. The Curithane based LARC 160, however, required significantly more staging than the AP-22 version to achieve the low flow characteristics required to produce satisfactory moldings. The staging cycles shown in Table 1 were used. The staged powders were then molded at 320°C, 0.83 MPa pressure for 1 hour. Satisfactory moldings were produced, samples were machined for rheological testing. Figures 22 and 23 give the solid state curves for the two LARC 160 polymers. The peak in Tan δ occurred at 367°C for the AP-22 LARC 160, while the curve went off-scale (at 397°C) for the Curithane 103 version. This data is consistent with TMA results that indicate a possibly higher Tg for Curithane LARC 160.

2.5 Laminate Fabrication

Prior to obtaining our high range torque transducer for polyimide prepreg studies, data generated on the neat resin systems was used as a basis for fabricating LARC 160 matrix laminates.

Standard commercial Fiberite prepreg was used in the AP-22 based laminate. Here LARC 160 is used to impregnate woven T-300 (8 harness satin) epoxy finish graphite cloth. The following cure schedule was used:

(1) Heat at 2°C/minute to a temperature of 121°C.

(2) Hold 90 min at 121°C, then heat at 2°C/min.

(3) Pressurize to 1.2 MPa at 260°C.

(4) Continue heating at 2°C/min to 330°C.

(5) Hold 90 min at 330°C, 1.2 MPa, then cool under pressure to below 100°C.

A well consolidated laminate was made by this procedure.

From the rheological data generated on the LARC resin it was apparent that the AP-22 cycle would need to be modified to successfully produce a Curithane based laminate. If the $\eta*$ curves are compared, the Curithane LARC 160 must be heated to 290°C to achieve a viscosity equivalent to that of the AP-22 LARC 160 at 260°C (pressurization point). It was, therefore, decided to use the AP-22 LARC 160 cure schedule listed above, but to pressurize at 290°C rather than 260°C.

A sample of Curithane 160 was applied to woven T-300 (8 HS), epoxy finish cloth reinforcement by a "dip and squee-gee" technique. The prepreg was air dried at ambient temperature overnight, followed by 4 hours at 93°C in a circulating air oven. The purpose of this bake was to eliminate solvent and thereby minimize plasticization and flow during cure. The resulting prepreg has a resin content of 46.8%. The laminate was laid up in a matched metal mold and press cured using the standard LARC 160 (AP-22) cycle, but applying pressure at 290°C. An apparently

high quality laminate was successfully molded by this procedure.

CONCLUSIONS AND RECOMMENDATIONS

Several important results were obtained and conclusions reached during the course of the work:

o Although only small differences were found between LARC 160 (AP-22) and LARC 160 (Curithane 103) by conventional chemical characterization techniques, major differences were found during rheological characterization.

o Imidized Curithane 103 based LARC 160 has significantly lower viscosity and therefore higher flow than AP-22 based LARC 160 during processing. PMR-15 behaves much more like LARC 160 (AP-22) than does LARC 160 (Curithane 103).

o Rheological studies can be used to develop processing cycles for Curithane 103 based LARC 160 resin and prepreg.

o Techniques were successfully developed to generate rheological data on LARC 160 and PMR-15 prepreg samples. Pre-imidization is not required with prepreg samples, but is necessary with neat resin samples.

o Rheometrics rheological data was generated on V378A prepreg systems. The type of woven graphite was found to significantly affect the rheological characteristics of the prepreg and was consistent with their observed processing behavior.

o Fully cured Curithane based LARC 160 may have a Tg that is higher than that of AP-22 based LARC 160.

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5. Young, Philip R., and Sykes, George F., "Analysis of Aromatic Polyamine Mixtures for Formulation of LARC-160 Resin".

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7. Maximovich, M. G. and Galeos, R. M., "Rheological Characterization of Advanced Composite Prepreg Materials", 28th National SAMPE Symposium, Anaheim, Calif., April, 1983.

8. Brown, G. G. and McKague, G. L., "Processing Science of Epoxy Resin Composites", AFML Contract F 33615-80-C-5021, Fifth Quarterly Report, February, 1982.

TABLE 1 LARC 160 STAGING FOR MOLDING COMPOUNDS

AP-22 LARC 160 CYCLE		CURITHANE LARC 160 CYCLE	
STEP: 1.	140°C - 90 MIN.	1.	140°C - 90 MIN.
2.	140°C - 30 MIN.	2.	140°C - 30 MIN.
3.	180°C - 60 MIN.	3.	180°C - 60 MIN.
4.	210°C - 30 MIN.	4.	210°C - 60 MIN.
5.	250°C - 60 MIN.	5.	220°C - 60 MIN.
	4.5 HOURS TOTAL	6.	250°C - 75 MIN.
			6.25 HOURS TOTAL

* RESIN WAS GROUND BETWEEN STAGING STEPS TO FACILITATE VOLATILE REMOVAL.
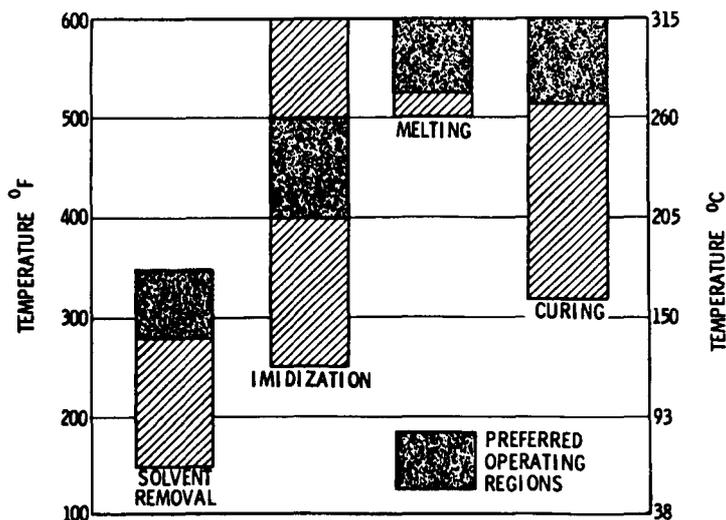
FIGURE 1 PROCESSING PARAMETERS FOR TYPICAL ADDITION PI
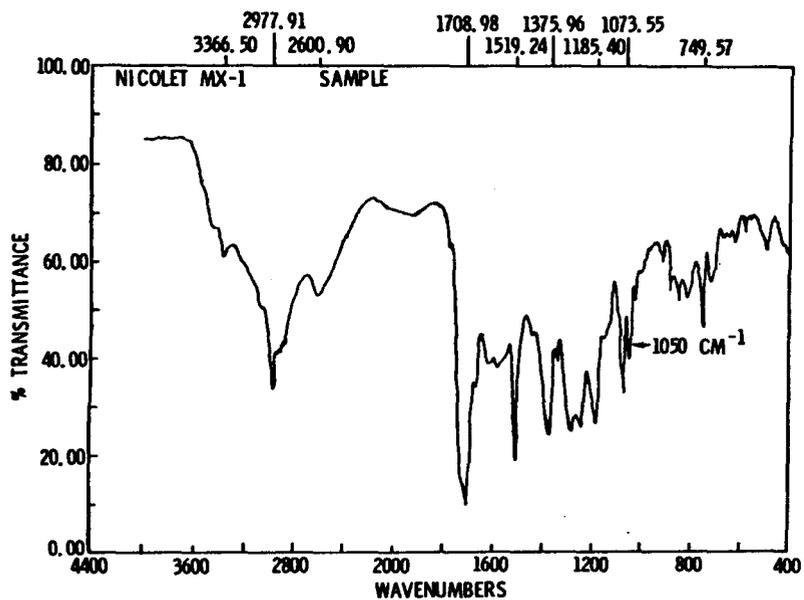
FIGURE 2   IR OF SYNTHESIZED LARC 160 WITH JEFFAMINE AP-22
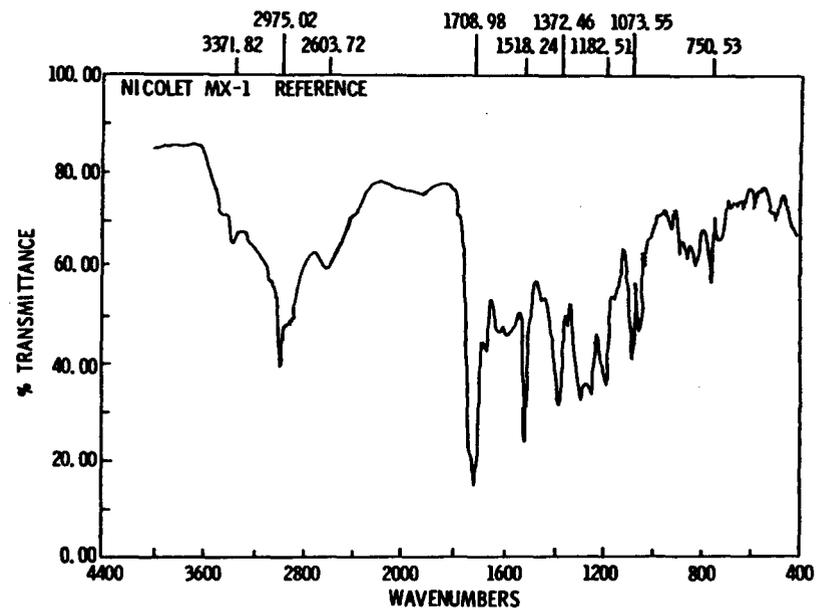
FIGURE 3   IR OF SYNTHESIZED LARC 160 WITH CURITHANE 103
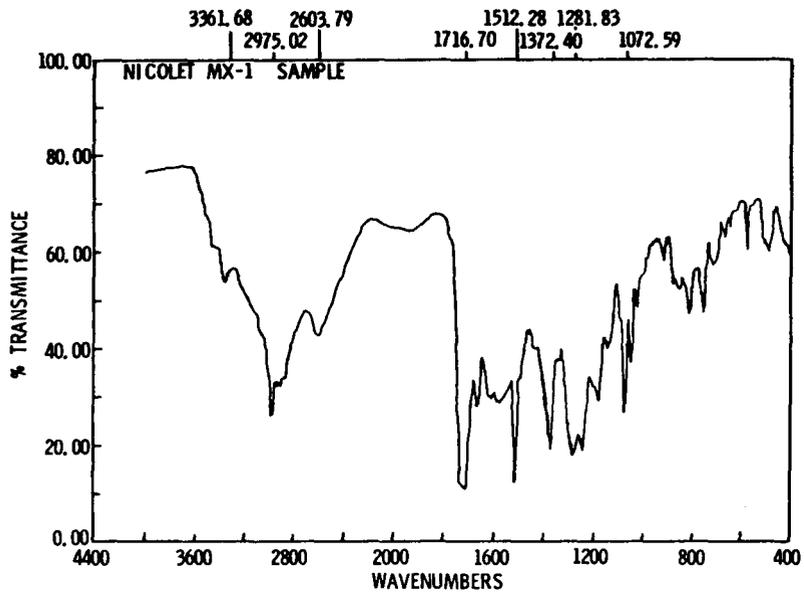
FIGURE 4   IR OF SYNTHESIZED PMR-15
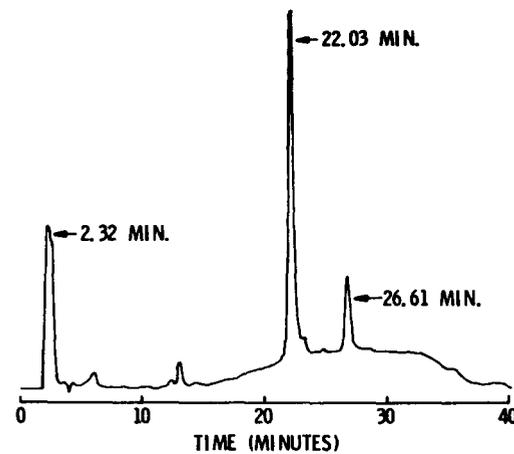
FIGURE 5   CHROMATOGRAM OF PMR-15
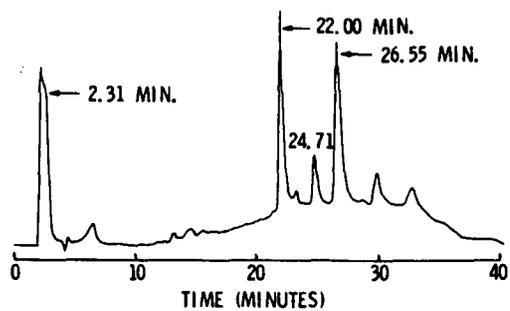
FIGURE 6 CHROMATOGRAM OF LARC 160 WITH AP-22
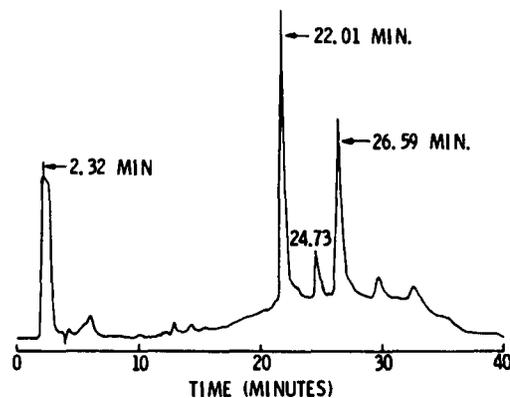
FIGURE 7   CHROMATOGRAM OF LARC 160 WITH CURITHANE 103
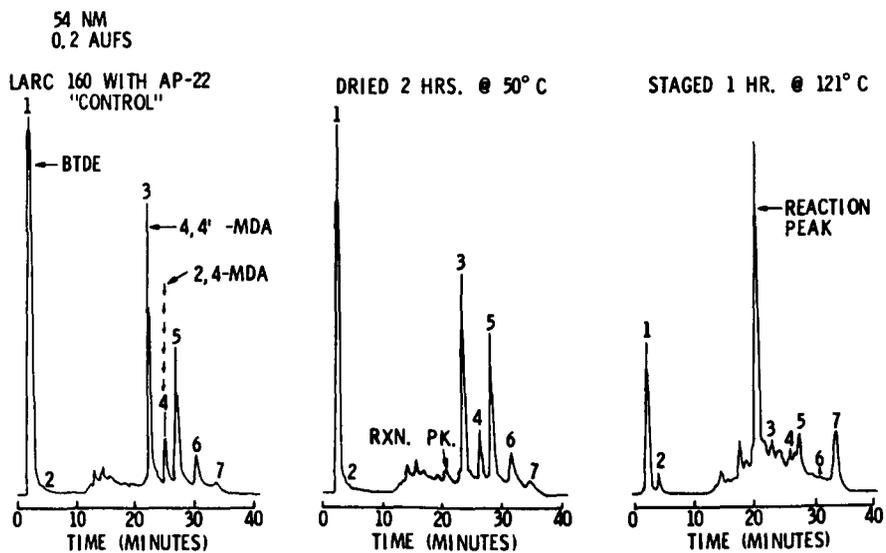
FIGURE 8 EFFECTS OF STAGING ON HPLC CHROMATOGRAMS

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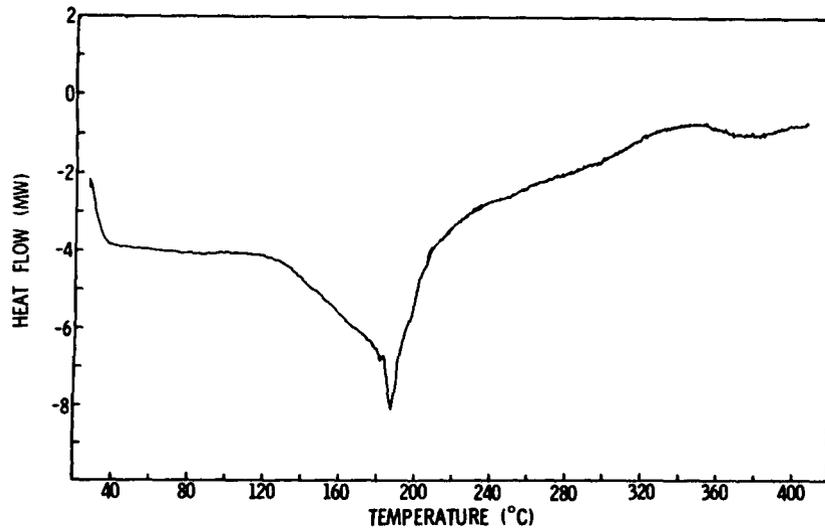
FIGURE 9   DSC OF PMR-15 UNSTAGED
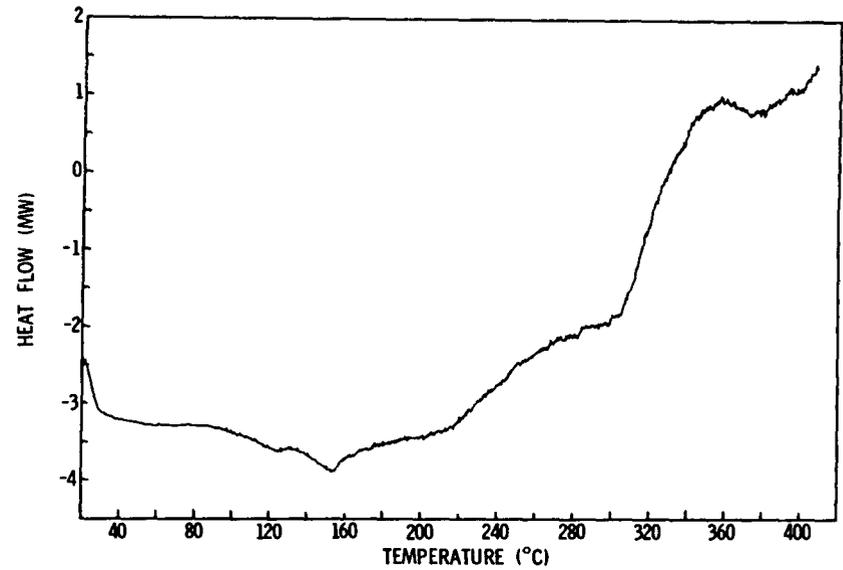
FIGURE 10   DSC OF PMR-15 STAGED .5 HR/120 C
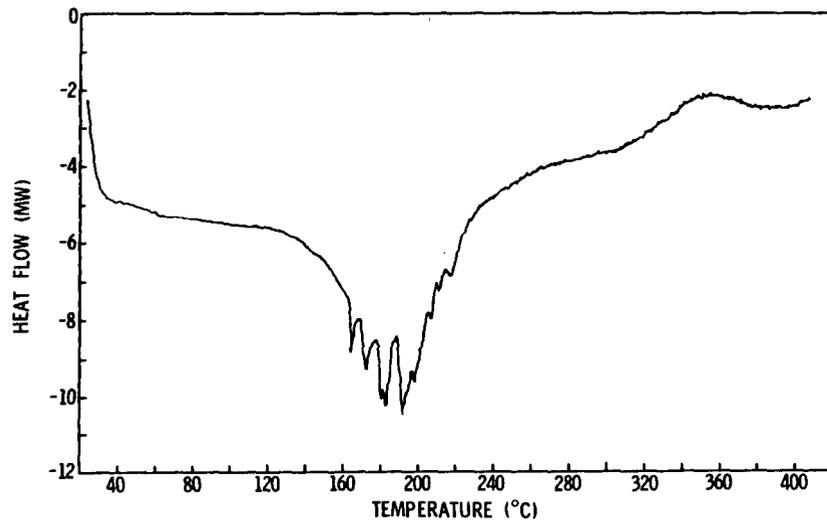
FIGURE 11   DSC OF LARC 160/22 UNSTAGED
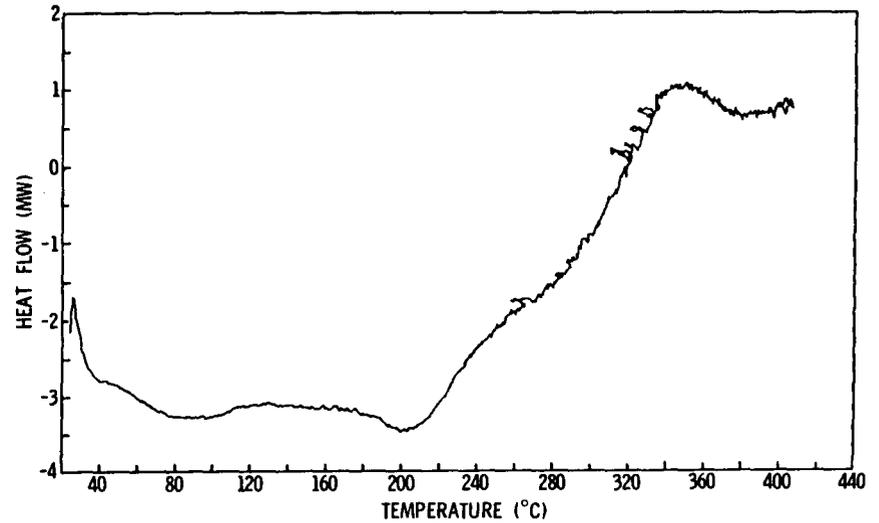
FIGURE 12   DSC OF LARC 160/22 STAGED .5 HR/120 C

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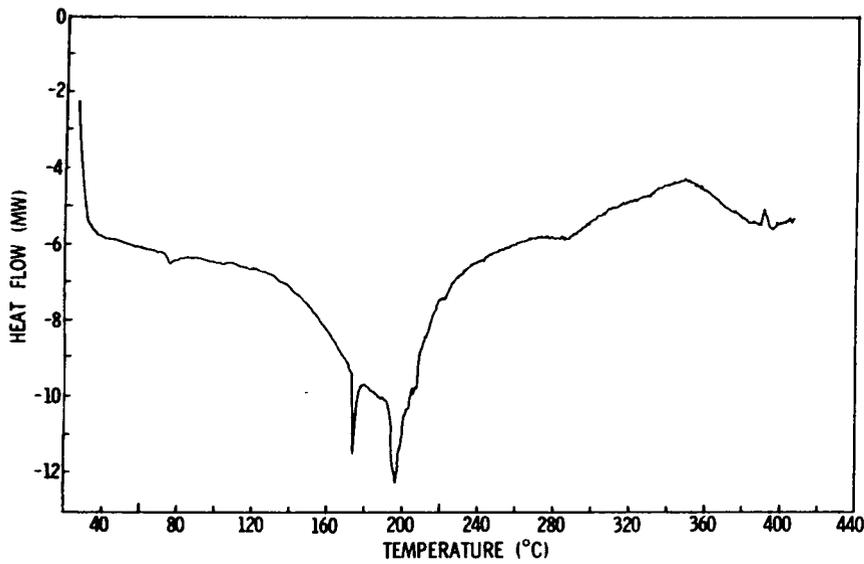
FIGURE 13   DSC OF LARC 160/103 UNSTAGED
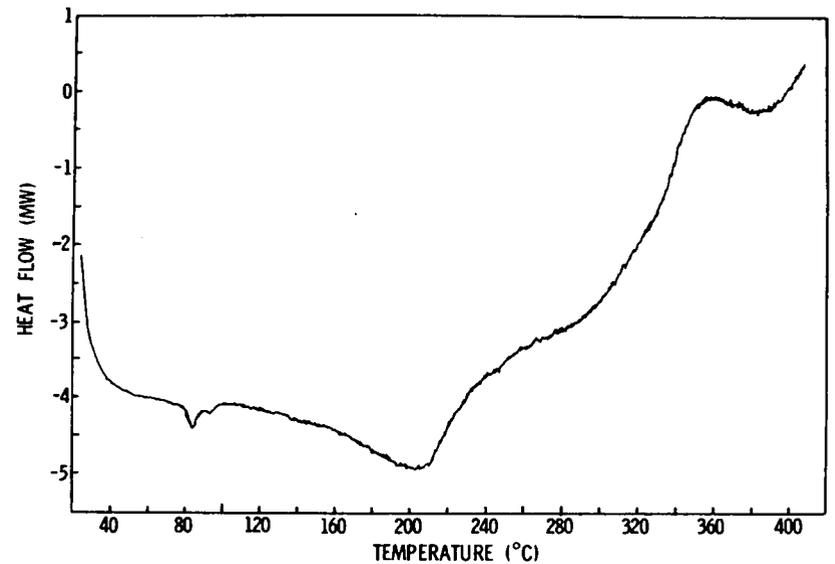
FIGURE 14   DSC OF LARC 160/103 STAGED .5 HR/120 C
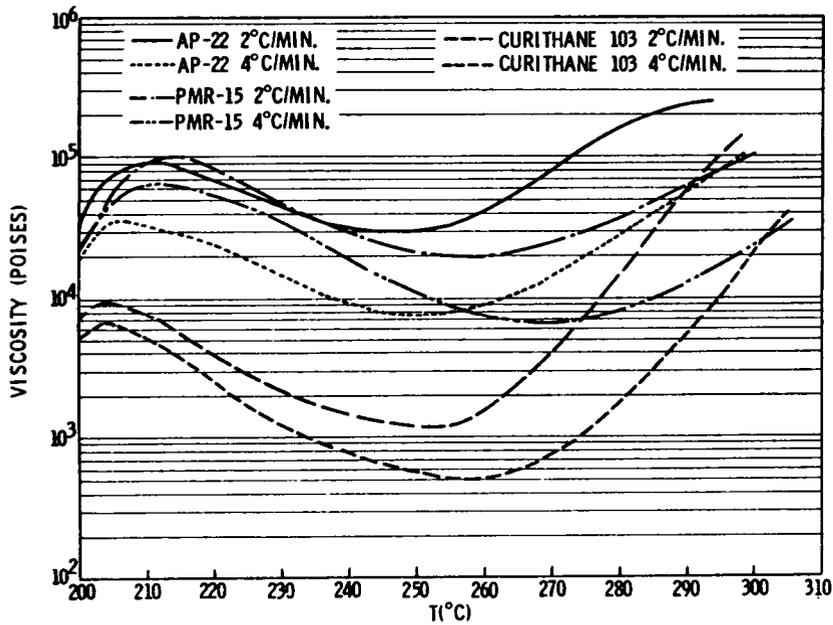
FIGURE 15   COMPLEX VISCOSITY VS TEMPERATURE
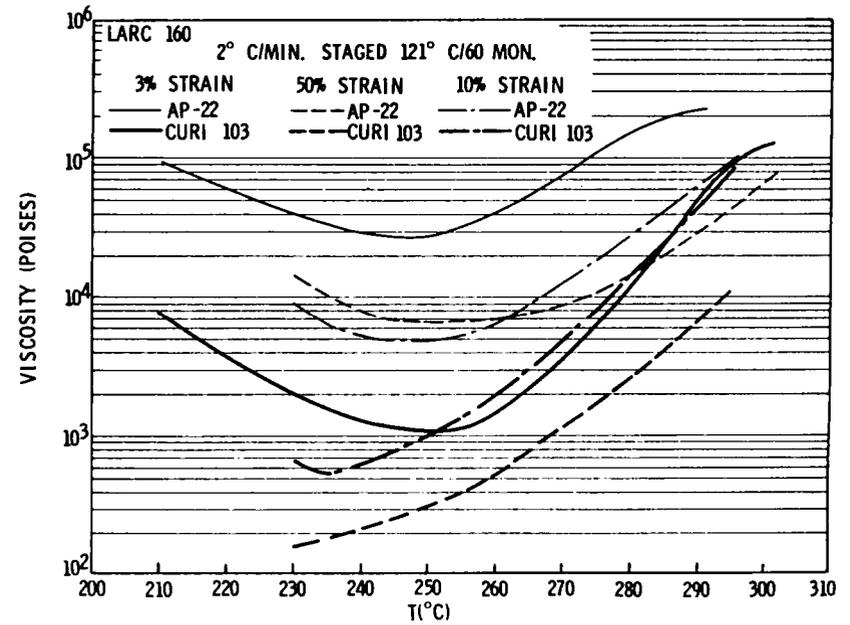
FIGURE 16 EFFECT & OF SHEAR STRAIN

FIGURE 17 (graph)

CURE CYCLE:
1) START AT 150°C
2) STRAIGHT HEAT-UP @ 4°C / MIN. TO 360°C

LARC 160 (AP22) PREPREG PRE-IMIDIZED @ 121°C 60 MIN.

LARC-160 (AP-22) NEAT RESIN PRE-IMIDIZED 121°C 60 MIN.

η^* (POISE) vs TIME (MIN.)
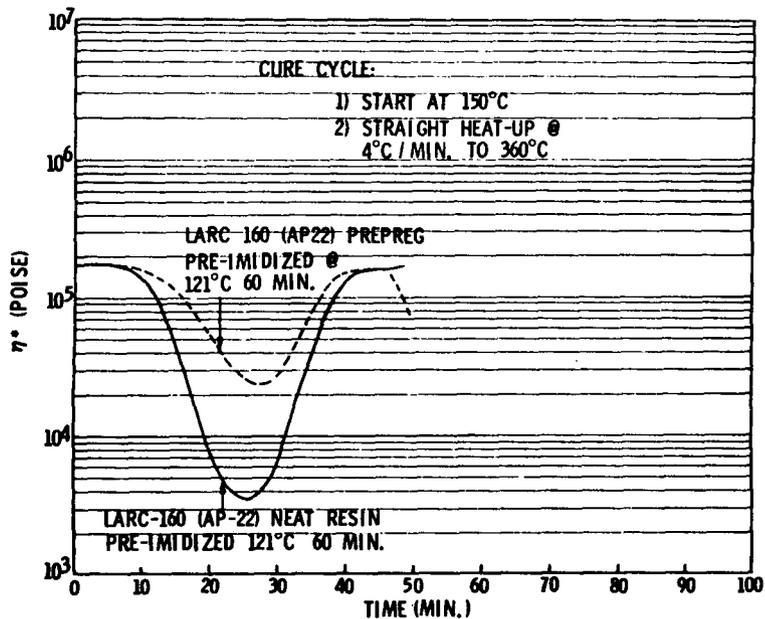
FIGURE 17 LARC-160 PREPREG & NEAT RESIN PRE-IMIDIZED @ 121°C, 60 MIN.

FIGURE 18 (graph)

CURE CYCLE:
1) START AT 150°C
2) STRAIGHT-HEATUP @ 4°C / MIN. TO 367°C

PMR-15 PREPREG

PMR-15 NEAT RESIN

η^* (POISE) vs TIME (MIN.)
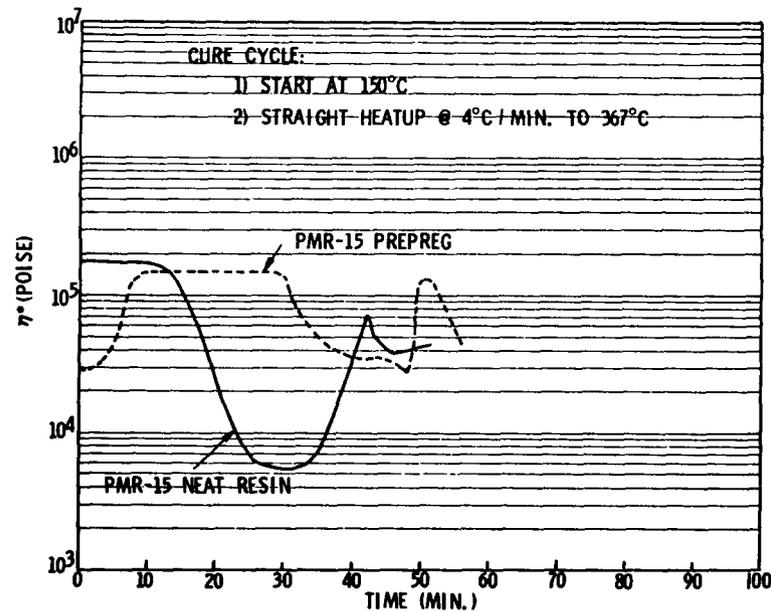
FIGURE 18 PMR-15 PREPREG & NEAT RESIN PRE-IMIDIZED @ 121°C, 60 MIN.

FIGURE 19 (graph)

PMR-15 PREPREG (PRE-IMIDIZED)

LARC-160 PREPREG (PRE-IMIDIZED)

270°C

START @ 150°C
STAIGHT HEAT UP RATE @ 4°C / MIN. TO 367°C

VISCOSITY (POISE) vs TIME (MIN.)
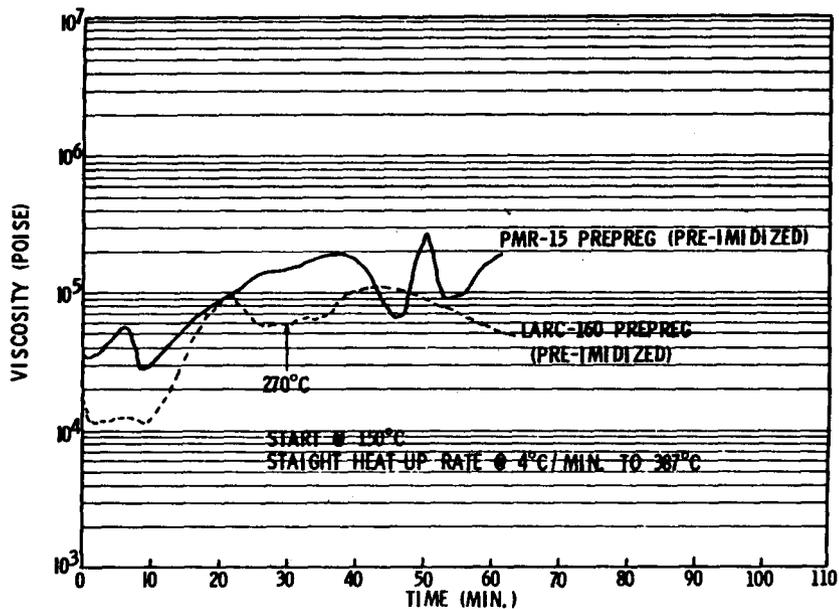
FIGURE 19 PMR-15 PREPREG (PRE-IMIDIZED) VS. LARC-160 PREPREG (PRE-IMIDIZED)

FIGURE 20 (graph)

LARC-160 PREPREG (NOT IMIDIZED)

PMR-15 PREPREG (NOT IMIDIZED)

270°C

START @ 60°C
STRAIGHT HEAT-UP RATE @ 4°C / MIN. TO 382°C

VISCOSITY (POISE) vs TIME (MIN.)
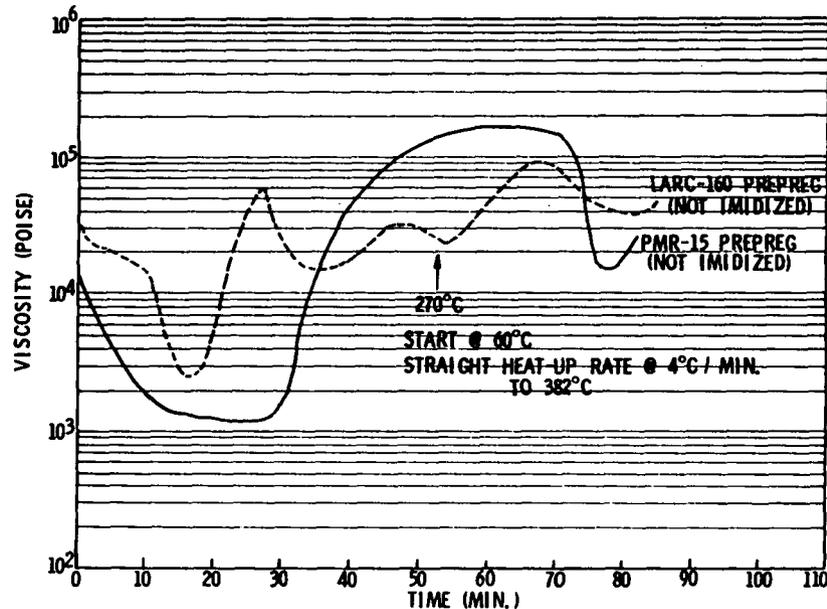
FIGURE 20 LARC-160 PREPREG (NOT IMIDIZED) VS. PMR-15 PREPREG (NOT IMIDIZED)
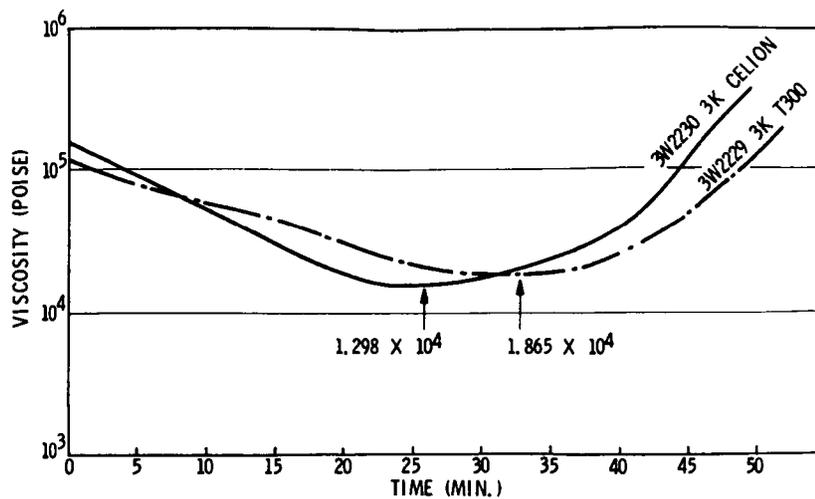
FIGURE 21 V378 PREPREG VISCOSITY VS TIME
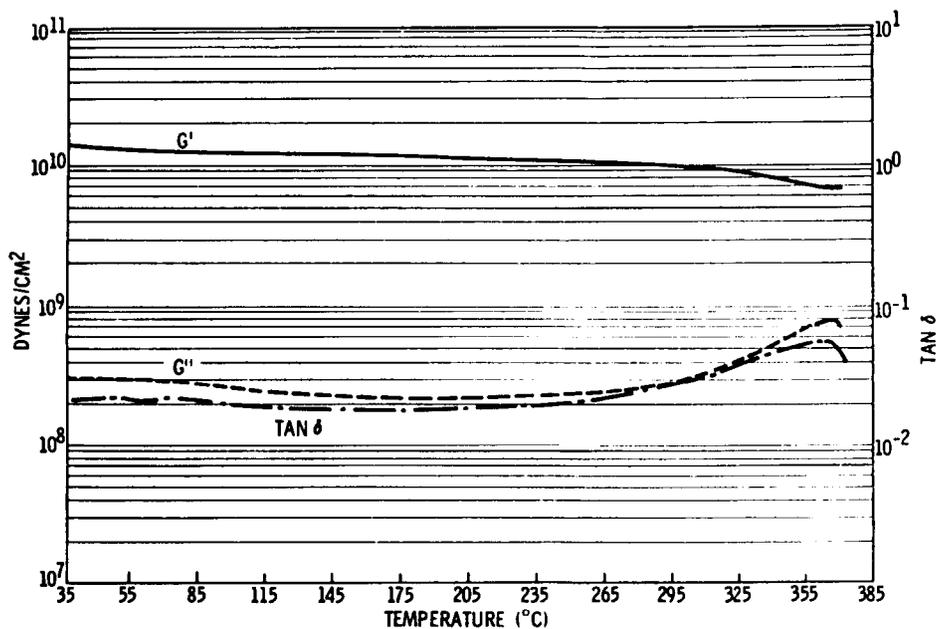
FIGURE 22 LARC 160, AP-22 (NEAT RESIN CASTING)
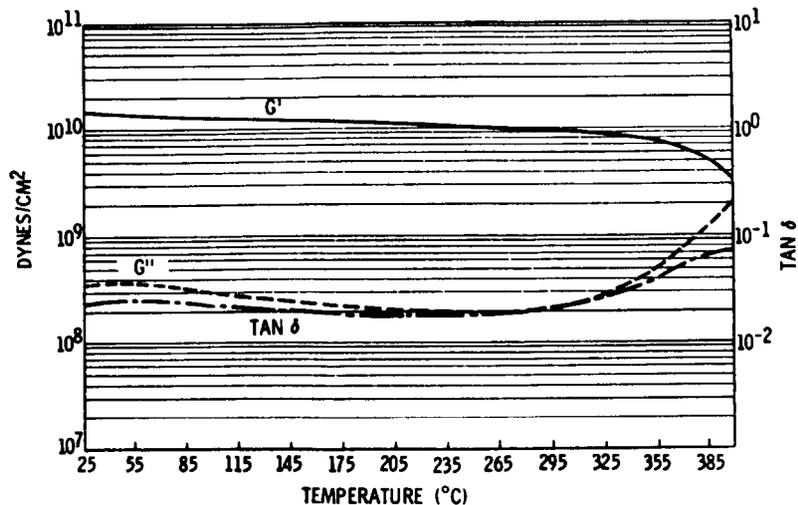
FIGURE 23 LARC 160, CURITHANE 103 (NEAT RESIN CASTING)

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