NASA Contractor Report 159335

STUDY OF CATALYST CURED LARC-160/CELION 6000 COMPOSITES

Robert Edelman

Celanese Corporation
Celanese Research Company
Summit, New Jersey 07901

Contract NAS1-15749 - Task Assignment No. 2
September 1980

National Aeronautics and Space Administration

Langley Research Center
Hampton, Virginia 23665

NASA CONTRACTOR REPORT 159335

STUDY OF CATALYST CURED LARC-160/CELION 6000 COMPOSITES

ROBERT EDELMAN

CELANESE CORPORATION
CELANESE RESEARCH COMPANY
SUMMIT, NEW JERSEY 07901

CONTRACT NAS1-15749 - TASK ASSIGNMENT No. 2
SEPTEMBER 1980

National Aeronautics and
Space Administration

Langley Research Center
Hampton, Virginia 23665

TABLE OF CONTENTS

SUMMARY

LaRC 160 polyimide has been modified with a high temperature peroxide catalyst, USP-138, in an attempt to reduce the final cure temperature to below 316°C (600°F). This effort was directed at obtaining a material for 177°C (350°F) use that would cure at similar temperatures to a high performance epoxy while still maintaining the good moisture resistance of a polyimide material.

Prepreg was initially prepared from Celion® fiber and the modified LaRC 160 containing either zero, two and one half or five percent catalyst. These materials were cured at 193°C (380°F) and 0.59 MPa (85 psi) for eight hours. This was followed by stepwise free standing 20 minute post cures up to a maximum temperature of 246°C (475°F). The panel containing 5% catalyst had an interlaminar shear strength of 27.6 MPa (4,000 psi) at room temperature. The other two panels were both significantly foamed with the uncatalyzed laminate containing the higher level of voidiness. Increasing the catalyst level to ten percent resulted in only limited improvement in properties. Similarly, an increase in pressure to 1.0 MPa (150 psi) also had no appreciable effect.

Attempts were then made to cure the catalyzed LaRC 160 product at a final temperature of either 232°C (450°F) or 260°C (500°F). During this effort, various modifications of the cure cycle were examined in order to find the optimum procedure for curing the catalyzed product. Maximum properties were achieved using a variant of the conventional LaRC 160 two stage cure. The first stage was conducted under two to four inches of vacuum at a temperature of 163°C (325°F) for 30 minutes. The second stage was a matched metal die cure starting at 204°C (400°F). Application of 1.4 MPa (200 psi) was done immediately followed by heating to the desired final temperature. One bleeder ply per face plus CELGARD® microporous polypropylene film as a breather was used to achieve an optimum fiber volume.

Using this procedure with a maximum temperature cure of 232°C (450°F) for three hours, a laminate was obtained with only a moderate level of properties, i.e., ILSS = 55.2 MPa (8,000 psi) at 22°C. An uncatalyzed control cured under identical conditions was too soft to test.

When the final cure temperature was 260°C (500°F), shear strength at room temperature improved to 107 MPa (15,500 psi). The control laminate had a shear strength value of 57.2 MPa (8,300 psi). Shear strength for the catalyzed product at 177°C was 41.4 MPa (6,000 psi). Catalyst level in the prepreg for this latter effort was optimized at the five percent level.

The catalyzed LaRC 160 prepreg was also used to examine the possibility of shortening the conventional LaRC 160 cure at 316°C (600°F). Maximum properties were obtained using a 2.5% catalyzed product with a cure at 316°C (600°F) for fifteen minutes. The uncatalyzed control had similar room temperature properties to the catalyzed product but an extremely low level of elevated temperature properties. Differences in properties between catalyzed and uncatalyzed product disappeared, however, when the cure time at 316°C (600°F) was extended to 45 minutes.

INTRODUCTION

High performance epoxy prepregs have been used extensively to provide composites with a maximum use temperature of 132°C (270°F). Although nominally rated for use at 177°C (350°F), environmental exposure to moisture effectively reduces the use temperature to below 149°C (300°F). Polyimide prepregs are also available which yield composite materials with a use temperature of 260-316°C (500-600°F). Mechanical properties of these materials at 121-177°C (250-350°F) are less affected by water despite the fact that moisture pickup is frequently as high as is found with the high performance epoxy resins.[1] Polyimide prepregs (LaRC 160, PMR-15) currently available are cured at a temperature of 316°C (600°F) followed by a significant free standing post cure at the same temperature. Bismaleimide materials which are solely addition cured polyimides, such as the Kerimids,® * are cured at somewhat lower temperatures and are generally not used above 232°C (450°F).[2] These bismaleimide materials are also more prone to microcracking and reduced fatigue resistance than the higher temperature polyimide prepregs.

It would be very desirable to have a polyimide prepreg system, such as LaRC 160, which gave good elevated temperature properties[2] and moisture resistance at 177°C (350°F),[2] but which could be cured at significantly lower temperatures than are currently used. Ideally, a polyimide system that cured at 193°C (380°F) under 0.59 MPa (85 psi), very much like the current high performance epoxy systems such as Narmco's 5208, would be desired. Such a material would be useable at 177°C (350°F) and should not undergo the reduction in strength properties observed with epoxies after extended humidity exposure. It is preferred that cure take place at a maximum temperature of 193°C (380°F) in order to allow the continued use of inexpensive nylon bagging materials currently used in vacuum bag-autoclave layups with epoxy prepregs. Maximum temperature use for this material is ca. 199°C (390°F). Polyimide prepreg materials must be cured in high temperature polyimide (Armalon) bags which are considerably more expensive.

Cure of a polyimide material at temperatures of 204-260°C (400-500°F) would also be desirable since it would allow for the use of polyimides at temperatures of 177-232°C (350-450°F) without undergoing the excessively high 316°C (600°F) cure currently needed. However, such a cure would entail the use of the more expensive polyimide bagging material.

---

*Use of commercial products or names of manufacturers in this report does not constitute official endorsement of such products or manufacturers, either expressed or implied, by the National Aeronautics and Space Administration.

Two polyimide prepregging materials are available which when cured at 316°C (600°F) are suitable for final use at 260°C (500°F). These are LaRC 160 and PMR-15 as previously mentioned. Both materials are based on the same formulation concept; i.e., they are mixtures of monomers (polymerizable monomer reactants) mixed together in a paste form suitable for prepregging. The LaRC 160 contains significantly less solvent than PMR-15 and this feature renders it more desirable from a processing point of view.

LaRC 160 cures by a two stage procedure which involves an initial condensation reaction to form a polyimide prepolymer followed by an addition polymerization of the nadic group to form the final cross-linked product. The monomers found in LaRC 160 and their mode of reaction during cure is shown in Figure 1.

Prepolymerization to form low molecular weight oligomers (ca. 1600) results in the loss of ethanol from transamidation and residual solvent as well as significant quantities of water of imidization. This first stage is carried out under vacuum for one hour at 163°C (325°F). The second stage cure involves heating to a temperature of 274°C (525°F) at which point 1.4 MPa (200 psi) is applied. The application of pressure is necessary to prevent the evolution of cyclopentadiene which is a product of the reverse Diels-Alder reaction of the nadic moiety. Heating is then continued to 316°C (600°F) and held for two hours. The cure cycle is completed by a free standing post cure at 316°C (600°F) for four hours. This latter temperature is necessary since thermal polymerization of the nadic vinyl group does not take place until this temperature is reached.

The aim of our research effort was to examine the possibility of using an initiator to reduce the temperature at which the thermal homopolymerization occurred at an appreciable rate. If this could be done, a cross-linked polymer might be formed at a significantly lower temperature than currently used.

Our initial exploratory effort in this area revealed that one commercially available peroxide, USP-138 from Witco Chemical, U. S. Peroxygen Division, might be suitable in causing the lower temperature cure to occur. In addition to initiating a lower temperature cure, this catalyst would also have to be relatively dormant during the first stage prepolymer formation. While the USP-138 came closest of the materials commercially available to fulfilling this purpose, it was not completely suitable. Realistically, the highly complex reaction possibilities in the first stage of cure rendered it unlikely that any peroxide would completely survive the conditions that would be present. The peroxide would also have to be sufficiently non-volatile to withstand removal from the reaction mixture while under varying vacuum levels and finally it would have to be compatible with the polyimide resin.

LARC 160 CHEMISTRY

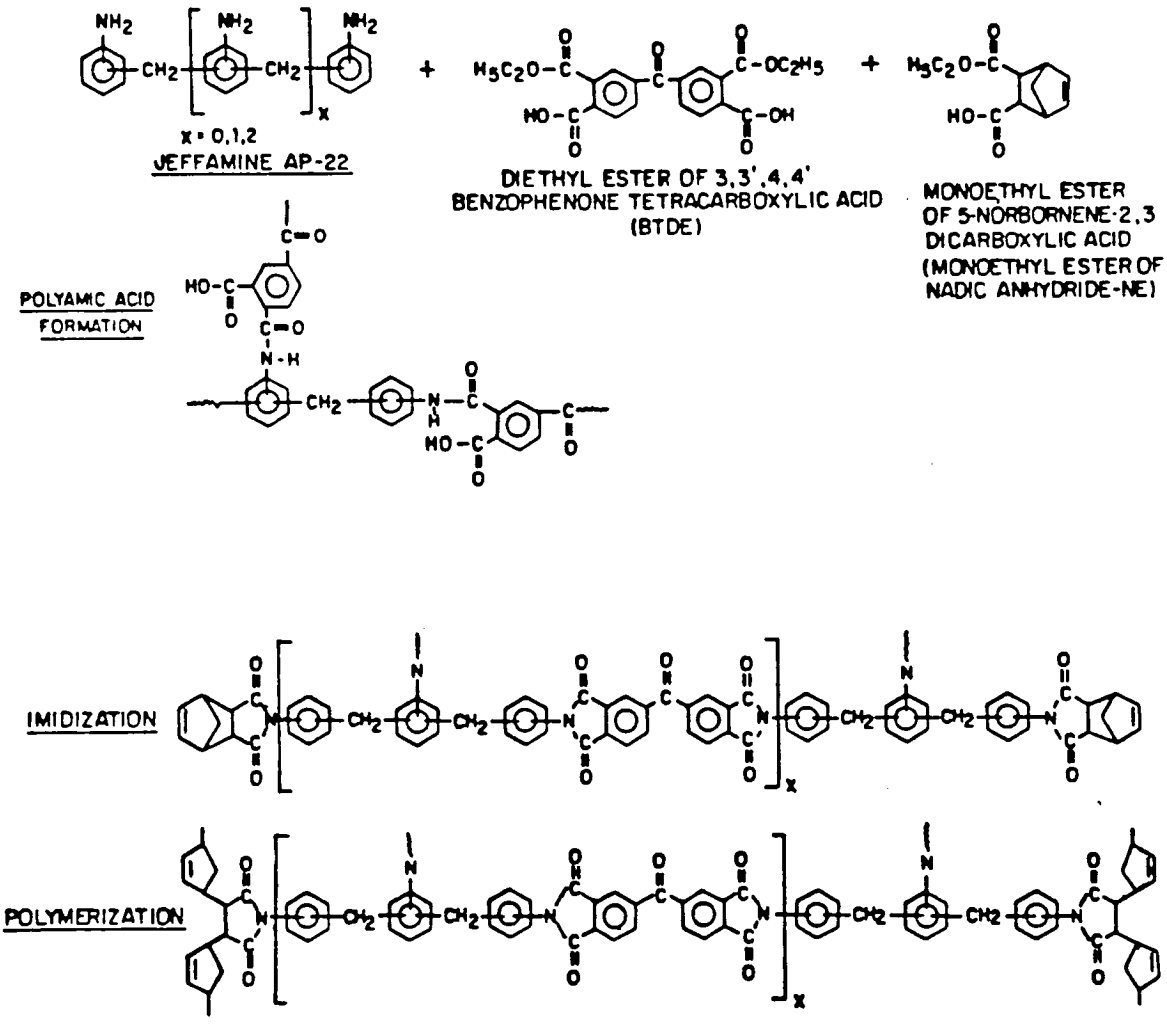
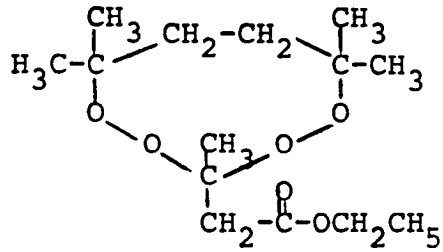


FIGURE 1. LaRC 160 CHEMISTRY

USP-138, whose structure is shown below, is a high temperature peroxyketal recommended for use in cross-linking polyethylene.[3]



3,6,6,9,9-Pentamethyl-3(ethyl acetate)-1,2,4,5-tetraoxycyclononane

Half life performance for the material is as follows:[4]

Half-Life Temperature (0.2M in benzene)

°C(°F)		
10 Hr.	1 Hr.	1 Min.
138(280)	160(320)	203(397)

Precisely how this material would perform in the presence of the LaRC 160 monomers was obviously unclear since it does have significant activity even at 163°C (325°F), the temperature used during the first stage cure. It does seem likely, however, that high levels of free radicals would be generated at 204°C (400°F) which might be suitable for initiating the nadic vinyl group polymerization.

The results discussed in the following section were obtained with the invaluable assistance of Hector Zabaleta, George Johnson, George Brenn and Stan Urbanski. Administrative chores were performed by Joseph R. Leal, Senior Staff Associate.

RESULTS AND DISCUSSION

DSC Study

An initial experiment was run to examine the effect that the USP-138 peroxide would have on the reactivity of the LaRC 160 material in the Differential Scanning Calorimeter (DSC). At the 5% level, USP-138 was mixed with the LaRC 160 resin without difficulty at a temperature slightly above room temperature. The mixture containing the catalyst was then subjected to a one hour treatment in a vacuum oven at 163°C (325°F) to simulate the first stage LaRC 160 cure procedure. The foamed product that formed was very friable and was readily pulverized by hand. This material was then analyzed by DSC to observe the point at which the exotherm generated by the cross-linking of the nadic residues would occur. Prepolymer formation and imidization had already taken place during the vacuum oven first stage treatment. A control LaRC 160 material was subjected to identical procedures as the catalyzed material for comparison purposes.

The DSC curves obtained are shown in Figures 2 and 3. A significant difference in exothermic activity is observed. The control material behaved as expected showing no significant exotherm peak until 316°C (600°F). The catalyzed product, on the other hand, showed the start of an exotherm at 170°C (338°F), reaching a maximum at 205°C (401°F) receding and then starting a slow continuing increase at 232°C (450°F). These interesting results prompted us to prepare LaRC 160 prepreg materials to which varying levels of USP-138 had been added. A wide variety of cure cycles was then examined with these catalyzed products.

Low Temperature Cures ("Epoxy Type" Cure at 177-193°C)

Initial effort in the catalyzed LaRC 160 project focused on achieving adequate cure of the material at a maximum temperature of 193°C (380°F). Pressure applied during the cure was at a maximum of 0.59 MPa (85 psi). These conditions are very similar to those currently used in industry to cure premium grade epoxy prepreg systems such as T300 and C6000/5208.

It was decided that two properties that were more responsive to resin cure would be examined. These were flexural strength and interlaminar shear strength. Properties were examined at room temperature and 177°C (350°F).

PART NO. 900326

DUPONT INSTRUMENTS

SAMPLE: 27000-19B LARC 160 + USP-138 ORIGIN: R. Coleman	SIZE 8.60 REF. PROGRAM MODE RATE 10 °C/MIN, START °C	ATM. N2 T: 50 °C/IN. ΔT: .2 °C/IN. SCALE SETTING	RUN NO. DATE 10.4.72 OPERATOR E.O TC 1499, 1500/78

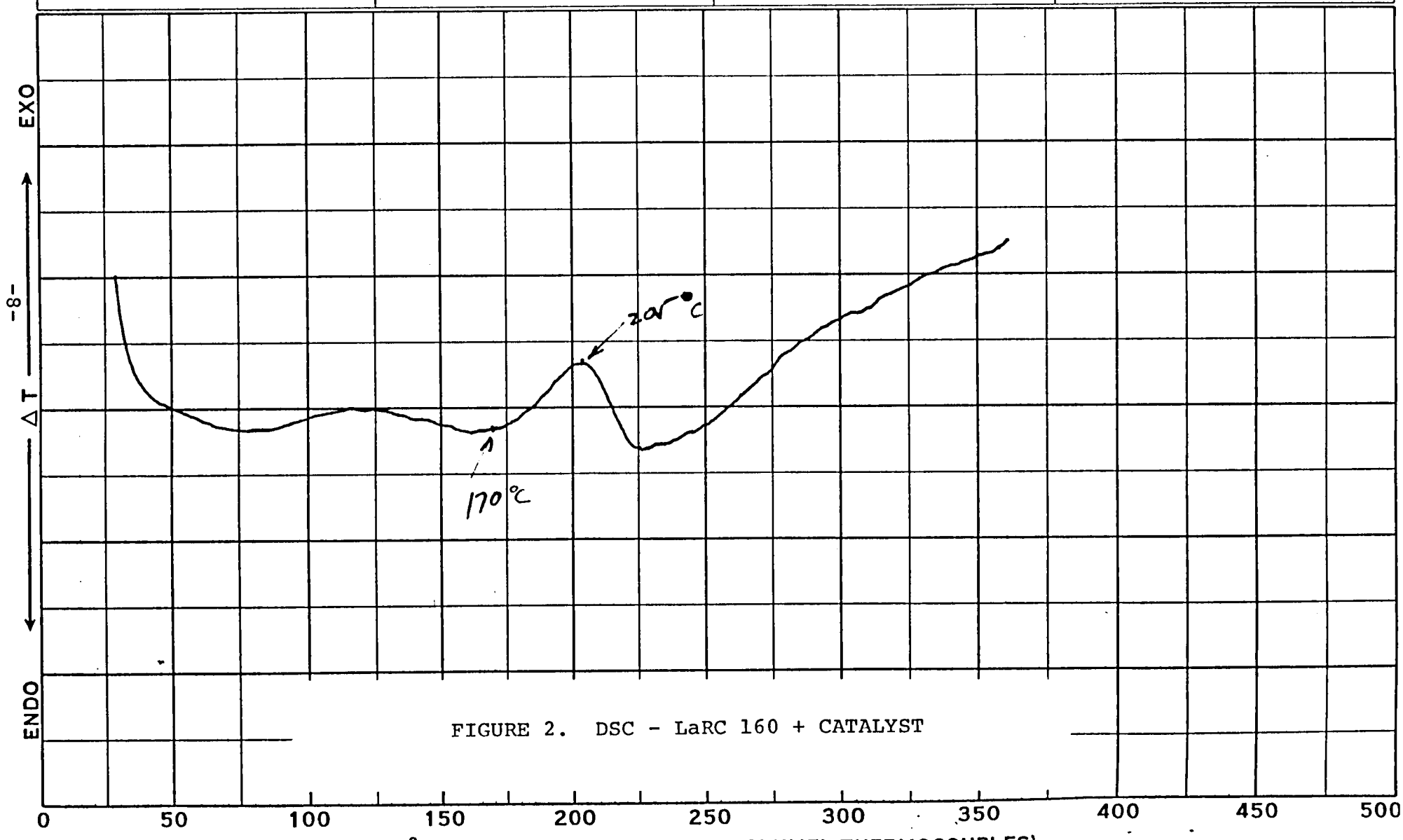


FIGURE 2. DSC - LaRC 160 + CATALYST

PART NO. 900326

DUPONT INSTRUMENTS

SAMPLE: 27000-19A LARC 160 Control ORIGIN: R. Coleman	SIZE 8.28 REF. PROGRAM MODE RATE 10 °C/MIN. START °C	ATM. T ΔT SCALE SETTING 50 °C/IN .2 °C/IN	RUN NO. DATE 10.5.78 OPERATOR E.O TG/1PPJ30/78

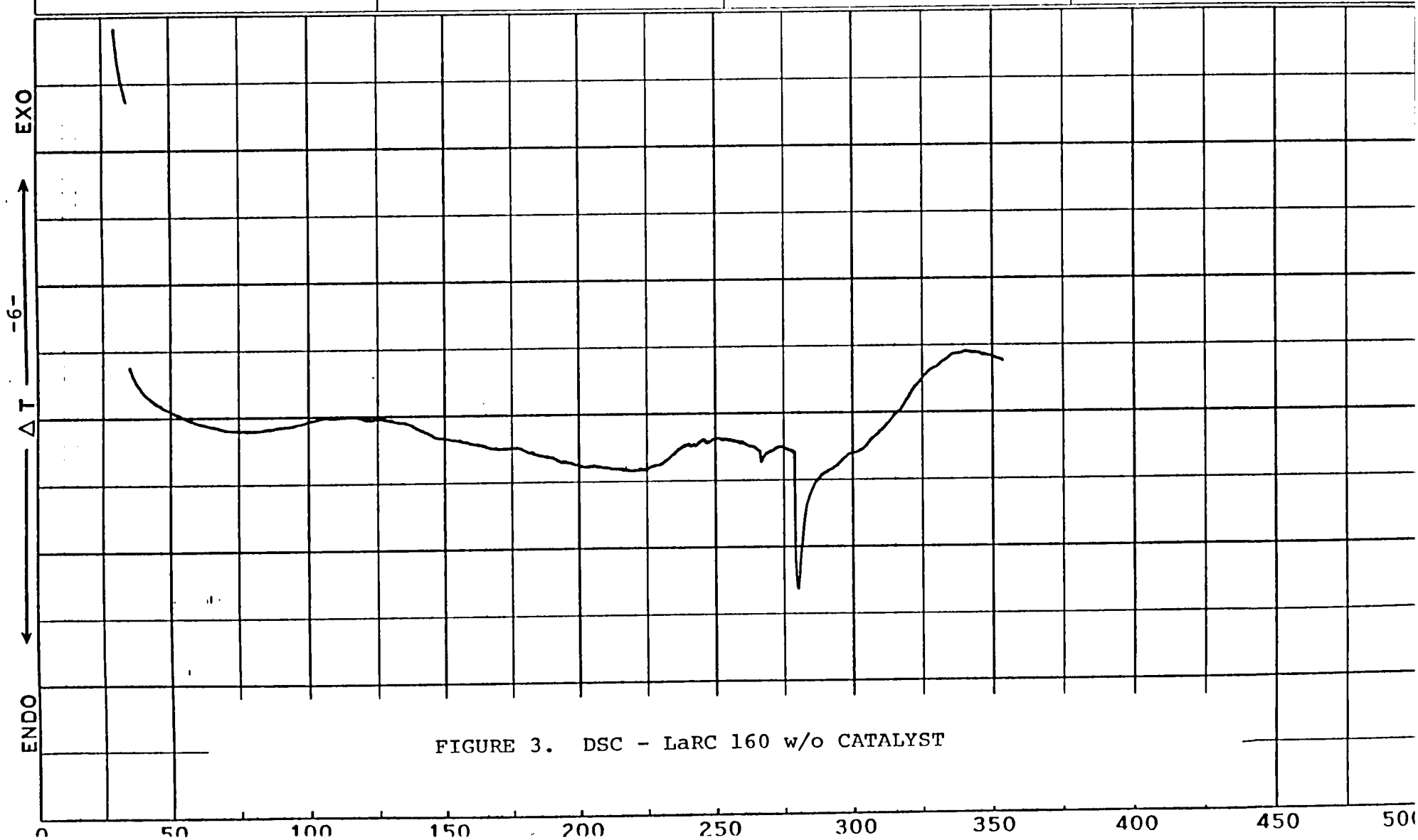


FIGURE 3. DSC - LaRC 160 w/o CATALYST

Laminates were prepared from LaRC 160 prepreg containing 0, 2.5 and 5% USP-138 catalyst. The cure cycle used was as follows:

1. Autoclave one hour at 163°C (325°F) under full vacuum.
2. Panels were then heated to 193°C (380°F) at 0.59 MPa (85 psi) for eight hours.

These panels were then subjected to a stepwise free standing post-cure. Heating was rapid (4°C/min.) to 193°C (380°F). This temperature was held for fifteen minutes before continuing at 2.5°C/min., with 30-minute holds at 10°C increments, up to the final temperature of 246°C (475°F). This temperature was held for 20 minutes. The 246°C (475°F) temperature was chosen as an upper limit to avoid excessive gassing from cyclopentadiene generation which occurs in the range of 260°-274°C (500-525°F).

Examination of the panels after this treatment indicated that the control panel containing no catalyst was badly foamed. The panel containing 2.5% catalyst showed significantly less foaming than the control. The panel containing 5% catalyst showed only minimal signs of voids. This panel, tested for short beam shear strength, gave a value of 27.6 MPa (4,000 psi) at room temperature. Although the value was low, this was the first evidence that a catalyzed LaRC prepreg could be made into a composite panel with some integrity using a low temperature "epoxy type" cure.

This initial effort indicated that higher levels of catalyst might effect a greater compaction of the laminate and subsequently result in reduced void content. Following this reasoning, prepregs containing 7.5% and 10% catalyst were prepared and subjected to the same cure cycle already described. Composite mechanical properties were measured at room temperature and at 177°C (350°F). Little difference in properties was observed between the panels containing the two different catalyst levels. Room temperature properties were improved over the panels prepared at lower catalyst levels, but elevated temperature properties were low (see Table I).

Two additional runs were made using procedures that differed from those originally followed. After the first stage autoclave cure at 163°C (325°F), the bleeder plies which lay adjacent to the prepreg layup were replaced. The reason for the replacement was the concern that the catalyzed LaRC material that flowed into the bleeders would cross-link and then impede the access of vacuum to the laminate. However, the new procedure yielded properties that were no better than when the bleeders were left unchanged. Indeed, elevated temperature properties were diminished.

TABLE I. COMPOSITE PROPERTIES OF CATALYZED LaRC 160 A3 POLYIMIDE USING LOW TEMPERATURE EPOXY (5208) CURE CYCLE

SAMPLE[2,6]	TEST TEMPERATURE (°C)	FLEXURAL[1,7,8] STRENGTH MPa	(ksi)	MODULUS GPa	(Msi)	INTERLAMINAR SHEAR STRENGTH MPa	(psi)
A							
7.5% Catalyzed[3]	22	1117	(162.0)	137	(19.9)	41.0	(5950)
Bleeders Unchanged	177[9]	320	(46.4)		-	25.5	(370)
Free Standing Post Cure							
B							
10% Catalyzed[3]	22	993	(144.0)	152	(22.0) (?)	37.2	(5400)
Bleeders Unchanged	177	565	(82.0)		-	26.9	(3900)
Free Standing Post Cure							
C							
7.5% Catalyzed[3,4]	22	855	(124.0)	131	(19.9)	39.6	(5740)
Bleeders Changed	177	183	(26.5)		-	8.1	(1170)
Free Standing Post Cure							
D							
10% Catalyzed[3,4]	22	821	(119.0)	150	(21.8)	40.7	(5900)
Bleeders Changed	177	572	(83.0)		-	24.8	(3600)
Free Standing Post Cure							
E							
7.5% Catalyzed[4,5]	22	662	(96.0)	145	(21.1)	38.6	(5600)
Bleeders Changed	177	124	(18.0)		-	11.6	(1680)
Matched Metal Die Contact Pressure During Post Cure							
F							
10% Catalyzed[4,5]	22	1696	(246.0)	160	(23.2) (?)	46.9	(6800)
Bleeders Changed	177	869	(126.0)		-	33.8	(4900)
Matched Metal Die Contact Pressure During Post Cure							

TABLE I - FOOTNOTES

1. All fiber volumes normalized to 62%.

2. Cure Cycle: 1st stage: one hour at 163°C under vacuum.
   2nd stage: eight hours at 193°C under full vacuum and 0.59 MPa (85 psi).
   Post Cure: (free standing) R.T. to 93°C. fast, 93°C→193°C ∿ 5°C/min.-hold 30 minutes, 193°C → 207°C ∿ 5°C/min.-hold 25 minutes, 207°C → 221°C ∿ 5°C/min.-hold 25 minutes, 221°C → 235°C ∿ 5°C/min.-hold 25 minutes, 235°C → 246°C ∿ 5°C/min.-hold 30 minutes. (Total post cure time ≈ 3 hours.)

3. Catalyst is U. S. Peroxygen 138.

4. Bleeder plies were changed after the first stage. Cure cycle was changed to six hours at 193°C under full vacuum at 0.59 MPa (85 psi).

5. Post cure was conducted in a compression mold under contact pressure .03 MPa (5 psi). Heating cycle is the same as outlined in footnote 2.

6.

	Appearance After Post Cure	% Volatiles Lost on Post Cure
A	Some Blisters	0.55
B	Blister-free	0.40
C	Blister-free	0.35
D	Blister-free	0.32
E	Blister-free	0.36
F	Blister-free (cracked on removal from mold)	0.56

7. Fiber volumes showed excessive variation (? - may be related to balance weighing problems) e.g., System F varied from 48.4 to 61.8%; System D varied from 51.7 to 59.2%.

8. All flex samples failed in interlaminar shear. (Bonding is poor, possibly related to lack of complete cure.)

9. Two minutes only at the test temperature.

The second set of changes that was made involved the replacing of the bleeder plies as well as using contact pressure on the laminate during the post cure. This procedure was done in a compression mold. Results obtained on panels prepared in this manner showed improved properties. Apparently even a minimal pressure application during the post cure is useful for reducing void content by aiding in removal of volatiles.

In a further attempt to improve the properties obtained with the 193°C catalyzed LaRC 160 cure, a higher pressure of 1.0 MPa (150 psi) was used. Results shown in Table II indicate no significant improvement in properties as compared to those obtained with the (0.59 MPa) 85 psi cure. If the first stage cure was done at 149°C (300°F) for two hours in place of the one hour at 163°C (325°F), no property improvement was observed (See Table III). This procedure was designed to allow the formation of prepolymer to take place while the catalyst was less active.

Thus our initial efforts with the catalyzed product indicated that a drastic change from the conventional LaRC 160 cure temperature of (316°C) 600°F to 193°C (380°F) could not be made by the addition of the USP-138 catalyst and still achieve adequate cure. From this evidence, it was concluded that the material cannot be cured as are current aerospace grade epoxies.

Low Temperature Cures (204-260°C)

Based on these early results, it was decided to examine the cure of catalyzed LaRC 160 at temperatures of 204°-260°C (400-500°F) to see if the material might provide acceptable properties at 177°C-232°C (350°F-450°F). Such a material might be of interest since its use temperature would fall in a range between that served by high performance epoxies and by PMR type polyimides. Such a temperature range could of course be satisfied by the current LaRC 160 polyimide. However, in order to be useful in this range, an elevated temperature cure of LaRC 160 at 316°C (600°F) is necessary. Lower temperature cures of uncatalyzed LaRC 160, such as 232-260°C (450-500°F), were also examined during the course of this work to see if they would provide materials with adequate levels of properties at 177°C (350°F). Thus, a catalyzed LaRC 160 material that underwent a cure at temperatures significantly lower than 316°C (600°F) would be desirable.

The initial attempt to test this hypothesis is shown in Table IV. Final cure temperature and time for the catalyzed material was 260°C (500°F) for a period of three hours. Properties obtained for the five percent catalyzed material were quite good, except for a low flex strength at 177°C (350°F). Void content of the prepared laminate was essentially zero (-.07%).

TABLE II. COMPOSITE MECHANICAL PROPERTIES OF CELION ® 6000/CATALYZED LaRC 160[5]

SAMPLE	TEST TEMPERATURE (°C)	(°F)	FLEXURAL STRENGTH MPa	(ksi)	FLEXURAL MODULUS GPa	(Msi)	INTERLAMINAR SHEAR STRENGTH MPa	(psi)
Control[1]	22	72	338	(49)[3,7]	139	(20.1)	-	-[6]
	177	350	117	(17)[3]	94.5	(13.7)		
10%[2] USP-138 Catalyst	22	72	827	(120)[4,7]	-		41.4	(6000)
	177	350	765	(111)[4,7]	-		24.5	(3550)

(1) Cf 5775 (No catalyst present in prepreg.)

(2) Cf 5776

(3) Fiber volumes normalized to 62% from 61.9%.

(4) Fiber volumes normalized to 62% from 43.8%. (This is questionable normalization.)

(5) Cure Cycle: First Stage: One hour under vacuum on the autoclave at 163°C.
Second Stage: Eight hours at 193°C under 1.0 MPa (150 psi)(autoclave).
Post Cure: Apply 1.0 MPa (150 psi); heat stepwise (from R.T.) with 15-20 minute holds at 10°C increments to 232°C. Hold for three hours.

(6) Material could not be tested.

(7) Failed in interlaminar shear.

TABLE III. COMPOSITE MECHANICAL PROPERTIES OF CELION® 6000/ CATALYZED LaRC 160[1]

SAMPLE[2]	TEST TEMPERATURE °C	FLEXURAL STRENGTH MPa	(ksi)	INTERLAMINAR SHEAR STRENGTH MPa	(psi)
10% Catalyzed	22	1717	(249)[3,4]	37.9	(5500)
	177	724	(105)[3,4]	28.3	(4100)

(1) Cf 5608.

(2) Cure Cycle Used: Vacuum bag for two hours at 149°C. Apply 1.0 MPa (150 psi) and heat to 193°C. Hold for 8 hours. Post cure was free standing using an incremental step cure with 20-30 minute holds ca. every 10°C. Maximum temperature was 232°C.

(3) Fiber volume ranged from 51.6 to 62.9%.

(4) All flex bars broke in an interlaminar shear mode.

TABLE IV. COMPOSITE MECHANICAL PROPERTIES OF CELION® 6000/CATALYZED LaRC 160[6]

SAMPLE[1]	TEST TEMPERATURE °C	FLEXURAL[2] STRENGTH MPa	(ksi)	MODULUS GPa	(Msi)	INTERLAMINAR SHEAR STRENGTH MPa	(psi)
2.5% Catalyst[4]	22	1675	(243)[3]	125	(18.1)	68.3	(9900)
	177	496	(72)			51.0	(7400)
5% Catalyst[5,7]	22	1937	(281)	128	(18.1)	110	(16000)
	177	1103	(160)			75.8	(11000)

(1) Cf 5851 - A+B.

(2) Flex values normalized to 62% fiber volume.

(3) Specimens broke in interlaminar shear.

(4) Fiber loading range was 67 — 73.3%.

(5) Fiber loading range was 68 — 72.2%.

(6) Cure Cycle: First Stage - one hour under vacuum in the autoclave at 163°C.
Second Stage - matched metal die mold at 204°C. Apply 1.4 MPa (200 psi) immediately: Heat at 2-3°C/min. to 260°C. Bumped at 260°C. No post cure.

(7) Void content determined on the laminate prepared gave a negative value of -.07%. For purposes of calculating the void content, the resin density is 1220 kg/m^3.

Laminates prepared from the 2.5 percent catalyzed LaRC 160 prepreg had significantly lower properties.

One significant change was made in the cure cycle used to prepare the laminates discussed above. This was done in order to maximize properties in the presence of the catalyst. In the conventional LaRC 160 cure cycle, during the second stage cure, 1.4 MPa (200 psi) is not applied until a temperature of (274°C) 525°F is reached. This is done in order to prevent cyclopentadiene evolution. The USP-138 catalyst has significant activity at temperatures as low as 163°C (325°F) over a period of one to two hours. Thus, if pressure is applied at too high a temperature during the second stage cure, the resin may have significantly reduced flow because of the presence of the catalyst which will have cross-linked the material. It was decided, therefore, to apply pressure immediately at the start of the second stage cure at 204°C (400°F).

Since the cure at a maximum temperature of 260°C (500°F) resulted in acceptable mechanical properties, it was necessary to examine this approach more fully. To this end, various cure cycles were tried to see if improved properties could be obtained. Of particular interest was variation in the first stage of the cure cycle. Initially a one hour treatment under full vacuum at 163°C (325°F) was used. Since it is known that the peroxide catalyst shows significant activity during this period, it was felt that a two hour treatment at 149°C (300°F) would be more suitable. With the latter treatment, it would be expected that peroxide activity would interfere less with prepolymer development. This approach was tried in an earlier effort without success.

Using this first stage cure, the second stage was kept as is or altered in regard to the temperature where pressure was applied. In the initial work, 200 psi had been applied at 204°C (400°F). The variation examined was the application of pressure at 232°C (450°F). This was done to try to reduce the fiber volumes from excessively high levels. The results obtained from these modified cure cycles are shown in Table V.

It is clear that using the two hour first stage cure at 149°C (300°F) did not improve properties but rather substantially reduced them at elevated temperature. Changing the temperature at which the pressure is applied in the second stage of the cure, had little effect. This alteration of the second stage cure was also tried using the original one hour treatment at 163°C (325°F), in the first stage of the cure cycle. The results obtained are shown in Table VI. They show clearly the positive effect of the 163°C (325°F) first stage cure. However, properties are still lower than those shown in Table IV.

TABLE V. COMPOSITE MECHANICAL PROPERTIES OF CELION® 6000/CATALYZED LaRC 160

SAMPLE	TEST TEMPERATURE °C	FLEXURAL[3] STRENGTH MPa	(ksi)	MODULUS GPa	(Msi)	INTERLAMINAR SHEAR STRENGTH MPa	(psi)
5% Catalyst[1,5,7]	22	1772	(257)[4]	129	(18.7)	99.4	(14400)
	177	1096	(159)			14.5	(2100)
5% Catalyst[2,6,8]	22	1765	(256)[4]			82.7	(12000)
	177	710	(103)			14.5	(2100)

(1) Cf 5886.

(2) Cf 5885.

(3) Flex values normalized to 62% fiber volume.

(4) Specimens broke in interlaminar shear.

(5) Fiber loading range was from 56.4 to 73.4%.

(6) Fiber loading range was from 64.6 to 73.3%.

(7) Cure Cycle: First Stage - two hours under full vacuum @ 150°C.
Second Stage - matched metal die mold at 204°C. Heat at 2.8°C/min. to 232°C and apply 1.4 MPa (200 psi). Heat at 2.8°C/min. to 260°C. Bump at 260°C. Hold for three hours. No post cure.

(8) Cure cycle is the same as in footnote seven except pressure is applied in the second stage at 204°C.

TABLE VI. COMPOSITE MECHANICAL PROPERTIES OF CELION® 6000/CATALYZED LaRC 160

SAMPLE[1]	TEST TEMPERATURE °C	FLEXURAL[2] STRENGTH MPa	(ksi)	MODULUS GPa	(Msi)	INTERLAMINAR[3] SHEAR STRENGTH MPa	(psi)
5% Catalyst	22	1744	(253)	127	(18.4)	101	(14700)
	177	1282	(186)			37.2	(5400)

(1) Cf 5888.

(2) Flex values normalized to 62% fiber volume from 68.6%.

(3) Shear specimens contained 71.2% fiber volume.

(4) Cure Cycle: First Stage - one hour under full vacuum at 163°C.
Second Stage - Matched metal die mold at 204°C. Heat at 2.8°C/min. to 232°C and apply 1.4 MPa (200 psi). Heat at 2.8°C/min. to 260°C. Bump at 260°C. Hold for three hours. No post cure.

Further work was done to examine if a still higher level of catalyst (7.5%) would have a significant effect on properties. The cure cycle used was that which produced optimum properties using the 5% catalyzed material. This consisted of a first stage cure of one hour under full vacuum at 163°C (325°F). This was followed by a second stage matched metal die cure at 204°C (400°F) with immediate application of 1.4 MPa (200 psi). Heating was continued to 260°C (500°F) where a hold was applied for three hours. No post cure was done. Results obtained are shown in Table VII. These values were also inferior to those observed previously with the 5% catalyzed product.

A variant cure cycle using a first stage of only thirty minutes at 163°C (325°F) was also tried. It appears that the shortened first stage cure improves the shear properties obtained although not substantially (see Table VIII).

Using the same cure cycles described, an altered fabrication procedure was tried. This involved using one glass bleeder ply per face instead of the usual two per face. This procedure was designed to reduce the removal of resin from the laminate resulting in lower fiber volumes. High fiber volumes have been a general problem throughout this effort. The results obtained are shown in Tables IX and X. The desired objective was achieved in that fiber volumes were reduced, but property levels were also lowered. It is not clear why this occurred.

All of the efforts discussed indicate that the desired amount of catalyst necessary in the prepreg is five percent. The results also indicate that the thirty minute first stage cure gave improved properties as compared to the longer times previously used. Thus it was necessary to investigate the five percent catalyzed product subjected to a first stage cure of only thirty minutes.

A series of runs were undertaken with the 5% catalyzed material using the shortened first stage cure. Included in these runs was the additional variant of using a limited vacuum of 50-108mm (two to four inches) of Hg during the first stage cure. It had been indicated from several sources that this level of vacuum is superior to the use of full vacuum in obtaining reduced porosity and void content in the final cured part.

Mechanical property test results are shown in Table XI. Void content obtained on the best panel was essentially zero (0.6%). It is clear that the combination of minimal vacuum and one half hour first stage cure gives virtually an equivalent level of properties to that observed in Table IV.

TABLE VII. COMPOSITE MECHANICAL PROPERTIES OF CELION ® 6000/CATALYZED LaRC 160[1,4]

SAMPLE	TEST TEMPERATURE °C	FLEXURAL[2,3] STRENGTH MPa	(ksi)	MODULUS GPa	(Msi)	INTERLAMINAR SHEAR STRENGTH MPa	(psi)
7.5% Catalyst	22	1779	(258)	127	(18.4)	91.7	(13300)
	177	1083	(157)		-	44.1	(6400)

(1) Cf 5918.

(2) Flex values normalized to 62% fiber volume.

(3) Specimens showed evidence of delamination during testing.

(4) Cure Cycle: First Stage - one hour under vacuum in the autoclave at 163°C.
Second Stage - matched metal die mold at 204°C (400°F). Apply 1.4 MPa (200 psi) immediately. Heat at 2-3°C/min. to 260°C (500°F). Bumped at 260°C. Hold three hours. No post cure.

TABLE VIII. COMPOSITE MECHANICAL PROPERTIES OF CELION ® 6000/CATALYZED LaRC 160[1,4]

SAMPLE	TEST TEMPERATURE °C	FLEXURAL[2,3] STRENGTH MPa	(ksi)	MODULUS GPa	(Msi)	INTERLAMINAR SHEAR STRENGTH MPa	(psi)
7.5% Catalyst	22	1827	(265)[3]	128	(18.6)	114	(16600)
	177	965	(140)		-	38.6	(5600)[5]

(1) Cf 5929.

(2) Flex values normalized to 62% from 71.2%.

(3) First failures were observed in the testing of each specimen. (At 93 and 94% of ultimate.)

(4) Cure Cycle: First Stage - one half hour at 163°C under vacuum.
Second Stage - matched metal die molded at 204°C. Apply 1.4 MPa (200 psi) immediately. Heat at 2-3°C/min. to 260°C. Bumped at 260°C. Hold three hours. No post cure.

(5) Plastic failure.

TABLE IX. COMPOSITE MECHANICAL PROPERTIES OF CELION® 6000/CATALYZED LaRC 160[1,5,6]

SAMPLE	TEST TEMPERATURE °C	FLEXURAL[2] STRENGTH MPa	(ksi)	MODULUS GPa	(Msi)	INTERLAMINAR SHEAR STRENGTH MPa	(psi)
7.5% Catalyst	22	1310	(190)[3]	134	(19.4)	61.4	(8900)
	177	676	(98)		-	29.6	(4300)[4]

(1) Cf 5919.

(2) Flex values normalized to 62% fiber volume from 66.9%.

(3) One specimen delaminated during testing.

(4) Several specimens underwent plastic failure.

(5) Cure Cycle: First Stage - one hour under vacuum at 163°C.
Second Stage - matched metal die molded at 204°C. Apply 1.4 MPa (200 psi) immediately. Heat at 2-3°C/min. to 260°C. Bumped at 260°C. Hold three hours. No post cure.

(6) One bleeder ply per face was used in place of two bleeders during laminate fabrication.

TABLE X. COMPOSITE MECHANICAL PROPERTIES OF CELION ® 6000/CATALYZED LaRC 160[1,4,5]

SAMPLE	TEST TEMPERATURE °C	FLEXURAL[2] STRENGTH MPa	(ksi)	MODULUS GPa	(Msi)	INTERLAMINAR SHEAR STRENGTH MPa	(psi)
7.5% Catalyst	22	1476	(214)	132	(19.2)	76.5	(11100)
	177	800	(116)[3]		-	44.8	(6500)

(1) Cf 5930.

(2) Flex values normalized to 62% fiber volume from 67.7%.

(3) Delamination occurred during testing.

(4) Cure Cycle: First Stage - one half hour under vacuum at 163°C.
Second Stage - matched metal die molded at 204°C. Apply 1.4 MPa (200 psi) immediately. Heat at 2-3°C/min. to 260°C. Bumped at 260°C. Hold three hours. No post cure.

(5) One bleeder ply per face used in place of two bleeders during laminate fabrication.

TABLE XI. COMPOSITE MECHANICAL PROPERTIES OF CELION® 6000/CATLAYZED LaRC 160

SAMPLE	TEST TEMPERATURE °C	FLEXURAL STRENGTH MPa	(ksi)	FLEXURAL MODULUS GPa	(Msi)	INTERLAMINAR SHEAR STRENGTH MPa	(psi)
5% Catalyst[1,2,3]	22	2055	(298)	125	(18.1)	114	(16600)
	177	841	(122)		-	57.9	(8400)
5% Catalyst[4,5,6]	22	910	(132)[7]		-	43.4	(6300)
	177	500	(72.5)[8]		-	34.5	(5000)
5% Catalyst[9,10,11]	22	1910	(277)[7]	125	(18.2)	103.4	(15000)
	177	558	(81)		-	28.3	(4100)[15]

(1) Cf 5959. Void content of the prepared laminate was equal to 0.6%.
(2) Fiber volume was normalized to 62% from 74.8%.
(3) Cure Cycle: First Stage - 30 minutes under vacuum 50.8-102mm Hg (2-4") at 163°C.
Second Stage - matched metal die molded at 204°C. Apply 1.4 MPa (200 psi) immediately. Heat at 2-3°C/min. to 260°C. Bumped at 260°C. Hold three hours. No post cure.
(4) Cf 5960.
(5) Fiber volume was normalized to 62% from 66.8%.
(6) Same cure cycle as in footnote No. 3 except full vacuum was used.
(7) Failed in interlaminar shear.
(8) Delamination occurred during testing.
(9) Cf 5958.
(10) Fiber volume was normalized to 62% from 74.2%.
(11) Same cure cycle as in footnote No. 3 except the first stage cure was done for one hour.

The final effort using the low temperature cure approach concentrated on obtaining an adequate cure of the five percent catalyzed LaRC 160 product using a maximum temperature of 232°C (450°F). A control resin containing no catalyst was included for comparison purposes. This latter material was cured in an identical manner to the conventional LaRC 160 prepreg except that the maximum temperature used was 232°C (450°F). Pressure was applied during the second stage cure at 204°C (400°F) instead of the usual 274°C (525°F). In addition, all of the runs were subjected to short post cures at 260°C (500°F).

Properties obtained from the catalyzed LaRC 160 laminates all gave low results. The maximum interlaminar shear strength obtained at room temperature for any of the procedures was 53.8 MPa (7,800 psi). The control material containing no catalyst was extremely soft and could not be tested. An attempt to post cure the catalyzed LaRC 160 laminate at 260°C (500°F) resulted in a blistered material. It is possible that further examination of curing and post curing conditions could result in improved properties. The results obtained, using a maximum cure temperature of 232°C (450°F), are shown in Table XII.

The cure cycles used to prepare the catalyzed LaRC 160 laminates were the usual two step procedures. The initial stage, conducted at 163°C (325°F), was for either 15 or 30 minutes under two to four inches of vacuum. The second stage was done in a matched metal die mold, initially at 204°C (400°F). A pressure of 200 psi was applied immediately followed by heating to 232°C (450°F). Two bleeder plies were used above and below the laminate. The use of this procedure resulted in fiber volumes of 68 and 71%. These loadings were not considered excessively high and probably did not contribute to reduced mechanical properties. A modified fabrication procedure using only one bleeder ply per face plus a CELGARD® breather (in place of the conventional glass fabric) was also tried. This reduced the fiber volume to 63.3%. Properties obtained were essentially unchanged using this procedure.

Laminates were also prepared using a final cure temperature of 260°C (500°F) to verify previously obtained results. The cure cycles used were similar to that described previously for the 232°C (450°F) cure. Properties obtained at room temperature were acceptable although a little low at elevated temperature. It is possible that an adequate post cure could improve the elevated temperature properties. When CELGARD® was used in the fabrication procedure (See Figures 4 and 5), fiber volume was substantially reduced from 75.5% to 64.9%. Although actual physical property values were not changed by this procedure, the tendency

TABLE XII. COMPOSITE MECHANICAL PROPERTIES OF CELION® 6000/CATALYZED LaRC 160 CURED AT 232°C

SAMPLE	TEST TEMPERATURE °C	FLEXURAL STRENGTH MPa	(ksi)	FLEXURAL MODULUS GPa	(Msi)	INTERLAMINAR SHEAR STRENGTH MPa	(psi)
5% Catalyzed[1]	22	1027	(149)[2]	138	(20.0)	53.8	(7800)
5% Catalyzed[3]	22	1061	(154)[4]	130	(18.8)	53.8	(7800)
Control[5]	22	Material too soft to test				-	-
5% Catalyzed[6]	22	1220	(177)[7]			42.1	(6100)

(1) Cf 6073. Cure Cycle: First Stage - Vacuum of 50.8-102mm of Hg (2-4") for 30 minutes at 163°C. Second Stage - Matched metal die molding at 204°C. Apply 1.4 MPa (200 psi) immediately. Heat to 232°C and hold three hours. No post cure.

(2) Fiber volume normalized to 62% from 67.9%.

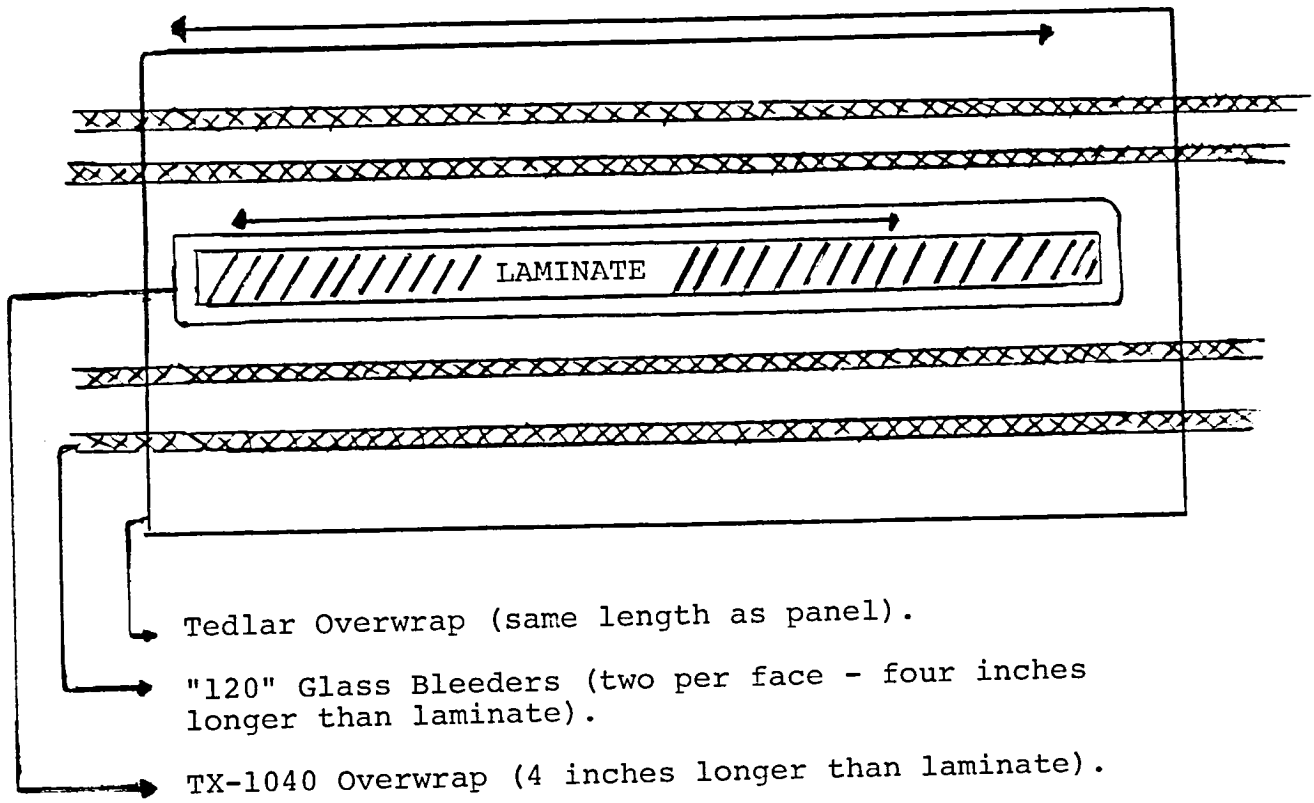
(3) Cf 6074. Same cure cycle as 6073 except the first stage was held for 15 minutes.

(4) Fiber volume normalized to 62% from 71.1%. Interlaminar shear failures were observed in all specimens.

(5) Cf 6076. Cure Cycle: First Stage - Vacuum of 50.8-102mm of Hg (2-4") for one hour at 163°C. Second Stage - matched metal die molding at 204°C. Heat to 232°C and apply 1.4 MPa (200 psi). Hold for three hours.

(6) Cf 6162. Same cure cycle as Cf 6073. Only one bleeder ply per laminate face was used. CELGARD® was used as a breather in place of glass fabric.

(7) Fiber volume normalized to 62% from 63.3%. Interlaminar shear failures were observed in all specimens.

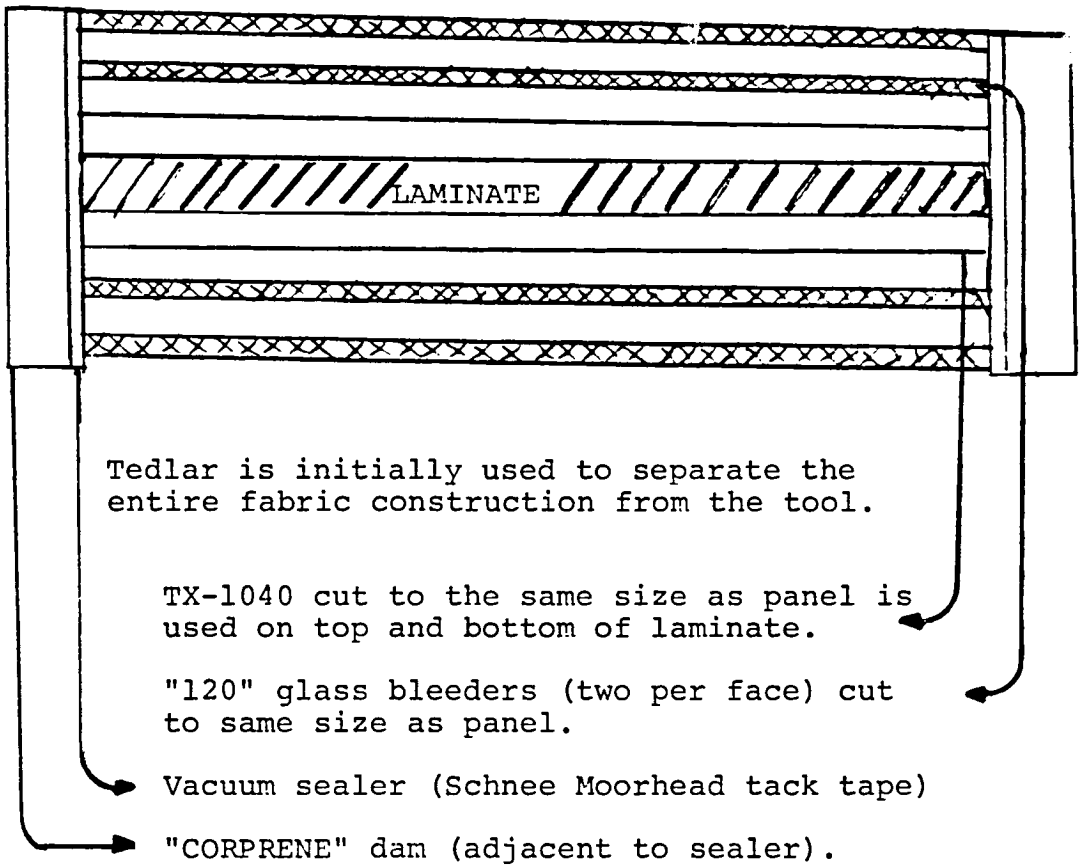


The above layup is covered with a 1581 glass cloth breather which is in contact with the ends of the bleeders at the end of the panel to allow bleeders to access vacuum more readily.

Finally, a nylon vacuum bag is used.

(No caul plate and no dams are used in the layup.)

FIGURE 4. LAYUP PROCEDURE FOR LAMINATE PREPARATION (FIRST STAGE)



CELGARD® is then used to cover layup. (The film is taped halfway on to the dam.)
A 1581 glass cloth breather is then placed over the layup.
Finally, a nylon vacuum bag completes the layup.

FIGURE 5. LAYUP PROCEDURE FOR LAMINATE PREPARATION USING CELGARD®FILM (FIRST STAGE)

for the flexural specimens to undergo interlaminar shear failure during testing was not observed. The results obtained are shown in Table XIII.

A control prepared from uncatalyzed LaRC 160 and cured at a maximum temperature of 260°C (500°F) for three hours gave significantly inferior properties to the catalyzed product. Fiber volume for the control laminate was 66.6%. CELGARD® was not used in the layup of the control.

An additional LaRC 160 control material was prepared using the conventional LaRC 160 cure, two hours at 316°C followed by a post cure of four hours at 316°C (600°F). The properties of this material were at the level normally expected for LaRC 160 confirming the quality of the control prepreg. All of these results are shown in Table XIII.

Shortened Elevated Temperature Cure at 316°C

In addition to the effort previously described on low temperature cure, work was also done examining cure cycles which used a maximum temperature of 316°C (600°F), but for a significantly shorter period than is used in curing uncatalyzed LaRC 160. This effort was directed at obtaining adequate 260°C (500°F) mechanical properties by use of a 316°C (600°F) cure for 15 to 45 minutes with the catalyzed LaRC 160 product. No post cure was done. This differs from the standard cure cycle, conventionally used with LaRC 160, which consists of a two hour cure at 316°C (600°F) plus a four hour free standing post cure at 316°C (600°F).

Introductory experiments involved the use of catalyzed LaRC 160 with a sharply curtailed cure cycle as discussed above. The total cure cycle used is given in Table XIV. The results obtained using laminates prepared with several catalyst levels are also shown in Table XIV.

The control material containing no catalyst gave the best room temperature properties. Values obtained at room temperature showed a high degree of scatter indicating uneven level of cure. Obviously the conditions used are not adequate to develop sufficient cure in the uncatalyzed LaRC 160 material. Of all the catalyzed systems, the one containing 5% USP-138 had the best balance of room temperature and elevated properties. Elevated temperature properties were not good but were significantly improved over those obtained with the uncatalyzed material.

TABLE XIII, COMPOSITE MECHANICAL PROPERTIES OF CELION® 6000/CATALYZED LaRC 160 CURED AT 260°C

SAMPLE	TEST TEMPERATURE °C	FLEXURAL STRENGTH MPa	(ksi)	FLEXURAL MODULUS GPa	(Msi)	INTERLAMINAR SHEAR STRENGTH MPa	(psi)
5% Catalyzed[1]	22	1855	(269)[2]	129	(18.7)	107	(15500)
	177	958	(139)			41.4	(6000)
	232	862	(125)			35.2	(5100)
5% Catalyzed[3]	22	1779	(258)[4]	133	(19.3)	97.9	(14200)
5% Catalyzed[5]	22	2124	(308)[6]	132	(19.2)	107	(15500)
	177	862	(125)			43.4	(6300)
	232		-			37.2	(5400)
Control[7]	22	1572	(228)[8]	128	(18.5)	57.2	(8300)
Control[9]	22	2027	(294)[10]	136	(19.7)	122	(17700)
	177	1655	(240)			77.9	(11300)
	232	1393	(202)			57.9	(8400)

(1) Cf 6071. Cure Cycle: First Stage - Vacuum of 50.8-102mm Hg (2-4") for 30 minutes at 163°C
Second Stage - Matched metal die molding at 204°C. Apply 1.4 MPa (200 psi) immediately. Heat to 260°C and hold three hours. No post cure.

(2) Fiber volume normalized to 62% from 75.5%. First failures were observed in two of three specimens tested.

(3) Cf 6072. Same cure cycle as Cf 6071 except first stage cure was done for 15 minutes.

(4) Fiber volume normalized to 62% from 72.6%. Interlaminar shear failures were observed in all specimens.

(5) Cf 6161. Same cure cycle as Cf 6071. CELGARD® film was used as the breather in place of glass fabric. One bleeder ply per face was used instead of two.

(6) Fiber volume normalized to 62% from 64.9%. No interlaminar shear failures or first failures were observed.

TABLE XIII. FOOTNOTES (continued)

(7) Cf 6153. Cure Cycle: First Stage - Vacuum of 50.8-102mm Hg (2-4") for one hour at 163°C.
Second Stage - Matched metal die molding at 204°C. Heat to 260°C and then apply 1.4 MPa (200 psi). Hold three hours. No post cure.

(8) Fiber volume normalized to 62% from 66.6%. Interlaminar shear failures were observed in all specimens. CELGARD® was used as a breather to prepare laminates.

(9) Cf 6075. LaRC 160 - Uncatalyzed.
Cure Cycle: First Stage - Vacuum of 50.8-102mm Hg. (2-4") for one hour at 163°C.
Second Stage: Matched metal die molding at 204°C. Heat to 274°C and apply 1.4 MPa (200 psi). Heat to 316°C and hold for two hours. Post cure at 316°C for four hours.

(10) Fiber volume normalized to 62% from 68.9%.

TABLE XIV. COMPOSITE PROPERTIES OF CELION® 6000/CATALYZED LaRC 160 USING A SHORT CURE CYCLE[1]

SAMPLE	TEST TEMPERATURE °C	FLEXURAL[2] STRENGTH MPa	(ksi)	MODULUS GPa	(Msi)	INTERLAMINAR SHEAR STRENGTH MPa	(psi)
Zero Catalyst	22	672-2192	(97.4-318)	137	(19.9)	99.3-122	(14400-17700)
	260	332	(48.1)	73.1	(10.6)	5.2-13.1	(750-1900)
5% Catalyst[3]	22	1786-1972	(259-286)	-		57.4-88.3	(8330-12800)
	260	652	(94.6)	125	(18.1)	23.8-37.6	(3450-5460)
7.5% Catalyst[3]	22	889-1427	(129-207)	-		40.7-51.7	(5900-7500)
	260	803	(116.4)	132	(19.1)	24.8-32.4	(3600-4700)
10% Catalyst[3]	22	876-972	(127-141)	-		34.5-41.4	(5000-6000)
	260	658	(95.4)	130	(18.9)	20-24.8	(2900-3600)
LaRC 160 Cured Using Standard Cycle	22	2069	(300)	-		110	(16000)
	260	1600	(232)	-		58.6	(8500)

TABLE XIV - FOOTNOTES

(1) Cure Cycle: First Stage - Vacuum bag devolatilize. Apply full vacuum at 22°C. Heat 2.5°C/min. to 163°C and hold one hour. Cool under vacuum.

Second Stage - Apply contact pressure and compression mold at 204°C (hot mold and press). Immediately heat to 274°C (2.5°C/min.). Apply 1.4 MPa (200 psi) and bump 10X. Heat to 316°C. Hold at 316°C for 15 minutes. No post cure. Cool under pressure.

Standard LaRC 160 cure calls for two hours at 316°C and four hour free standing 316°C post cure.

(2) Fiber loadings normalized to 62°.

(3) Catalyst used is U. S. Peroxygen 138.

Two additional approaches were tried in an attempt to obtain improved properties. The first involved examining lower catalyst levels, since it appeared from the initial experiments that the lowest level of catalyst used (5%) gave the best overall results. The inferior level of room temperature shear strength may also be improved by applying pressure in the cure cycle at an earlier temperature than is used with the conventional cure cycle. This approach was previously used with the lower temperature cure experiments and gave an improved level of properties.

As was discussed previously, the application of pressure at 274°C (525°F) may be at too high a temperature since sufficient cross-linking may already be developed prior to reaching this temperature to cause entrapment of volatiles and consequent reduction in properties. Properties obtained using a 2.5% USP-138 catalyst with pressure being applied at 204°C (400°F) are shown in Table XV. Interlaminar shear strength at 22°C and 260°C (500°F) are quite good. Flex values are good but first failures were observed. These are probably the result of incomplete cure.

It appears clear, however, that early application of pressure during the second stage cure is beneficial in developing adequate property levels. Void content of a laminate prepared in this manner was -0.6%. As seen in Table XV, application of pressure at 274°C (525°F) results in inferior laminate properties.

In order to check whether elevated temperature properties could be improved further, cure at 316°C (600°F) was extended to 45 minutes in place of a fifteen minute cure. A control was also run to see what level of properties the standard LaRC product would exhibit under this shortened polyimide cure.

Results, shown in Table XVI indicate that some improvement in elevated temperature properties is obtained with the catalyzed LaRC system by extending the cure from 15 to 45 minutes at 316°C (600°F). In addition, it is observed that the standard LaRC 160 product has achieved a good level of properties even after a 45 minute cure at 316°C (600°F). These results indicate that the catalyzed LaRC material does not offer any significant advantage over LaRC 160 in providing a shortened polyimide cure. At 316°C (600°F), even after only a relatively brief exposure of 45 minutes, LaRC 160 has achieved a similar level of properties to that of the catlyzed LaRC 160 product.

TABLE XV. COMPOSITE MECHANICAL PROPERTIES OF CELION® 6000/CATALYZED LaRC 160 USING A SHORT POLYIMIDE CURE

SAMPLE	TEST TEMPERATURE °C	FLEXURAL STRENGTH MPa	(ksi)	FLEXURAL MODULUS GPa	(Msi)	INTERLAMINAR SHEAR STRENGTH MPa	(psi)
2.5% USP-138[1,3,5]	22	2061	(299)	135	(19.6)	108	(15700)[9]
	260	1076	(156)		-	25.5	(3700)[9]
2.5% USP-138[2,4,6]	22	1841	(267)[7]	123	(17.9)	121	(17500)
	260	1241	(180)		-	43.4	(6300)

(1) Cf 5537.
(2) Cf 5538. Void content of the laminate was a negative value of -0.6%.
(3) Cure Cycle: 1st stage - one hour under vacuum at 163°C.
2nd stage - matched metal die molding at 204°C with heating at 2.5°C/min. up to 316°C. Apply 1.4 MPa (200 psi) at 274°C. Hold at 316°C for fifteen minutes. No post cure.
(4) Cure Cycle: 1st stage - one hour under vacuum at 163°C. Caul-plate used during first stage. No Tedlar wrap. Vacuum sealer used with dam.
2nd stage - matched metal die molding at 204°C. Apply 1.4 MPa (200 psi) at 204°C. Heat at 2.5°C/min. to 316°C. Bumped several times at 260°C. Hold at 316°C for fifteen minutes. No post cure.
(5) Flex values normalized to 62% from 64.1% (range 63.2-65.1%).
(6) Flex values normalized to 62% from 69.6% (range 67.1-72.9%).
(7) First failures observed in testing of each specimen. Average value = 1924 MPa (279 ksi) un-normalized.
(8) Time at test temperature = five minutes.
(9) Plastic failure.

TABLE XVI. COMPOSITE MECHANICAL PROPERTIES OF CELION® 6000/CATALYZED LaRC 160 USING A SHORT POLYIMIDE CURE

SAMPLE[3]	TEST TEMPERATURE °C	FLEXURAL STRENGTH MPa	(ksi)	FLEXURAL MODULUS GPa	(Msi)	INTERLAMINAR SHEAR STRENGTH MPa	(psi)
Control[1,4,6] (Zero Catalyst)	22	1882	(273)	121	(17.6)	111	(16100)
	260	1131	(164)			57.2	(8300)
2.5% Catalyst[2,5,7] (USP-138)	22	1558	(226)	123	(17.8)	108	(15600)
	260	1151	(167)			42.7	(6200)

(1) Cf 5806-B.

(2) Cf 5806-A.

(3) Cure Cycle: 1st stage - one hour under vacuum at 163°C.
2nd stage - matched metal die molding at 163°C. Apply pressure immediately and heat at 2.5°C/min. to 316°C. Hold for 45 minutes at 316°C. Bump several times at 260°C. No post cure.

(4) Flex values normalized to 62% from 73.5%.

(5) Flex values normalized to 62% from 69.5%.

(6) Delamination occurred in the testing of two of three specimens.

(7) Delamination occurred in the testing of one specimen.

CONCLUSIONS

The results of this exploratory effort indicate that the USP-138 catalyst can alter the curing behavior of LaRC 160 polyimide. Although some degree of cure was achieved by treating the catalyzed product at 177°C (350°F), properties were considered to be low. Catalyst utility appeared to improve substantially when the cure temperature was raised to 260°C (500°F).

The catalyst also showed some effect in curing the LaRC 160 product more rapidly at 316°C (600°F). However, property levels with the standard LaRC product were similar to those of the catalyzed material when the cure time was extended from 15 to 45 minutes.

Overall, the USP-138 catalyst appears to have only limited utility in modifying the cure behavior of LaRC 160 polyimide. It is recommended that no further effort be expended on this particular approach.

EXPERIMENTAL

The USP-138 catalyst, which is a liquid, was readily blended into the LaRC 160 resin by minimal heating of the resin to about 38°C. The catalyst was then added and mixed in thoroughly with the warm resin.

Prepreg was prepared using the Celanese three inch line by pulling the fibers through a molten pool of resin. This procedure is not the optimum one since the catalyzed material changes color during this procedure. This is presumably because of continuous exposure to a hot shoe temperature of 80°C. The hot plate temperature was 103°C. Prepregging rate was one meter/minute. Unsized Celion® 6000 was used. The prepreg contained 38% resin and had a fiber areal weight of 133.4 g/m^2.

REFERENCES

(1) Vinson, J. R., Pipes, R. B., Walker, W. J. and Ulrich, D. R., Ed., "The Effects of Relative Humidity and Elevated Temperature On Composite Structures." AFOSR TR-77-0030, 1976, p. 57.

(2) Rhodia Technical Bulletin "Kerimid 353," February 1975.

(3) Pastorino, R., Lewis, R. and Halle, R., Modern Plastics, September 1978, p. 86.

(4) USP-138 Preliminary Data Sheet, Witco Chemical Co.-U.S. Peroxygen Division, Richmond, California.

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
NASA CR-159335		

4. Title and Subtitle	5. Report Date
STUDY OF CATALYST CURED LARC-160/CELION 6000 COMPOSITES	September 1980
	6 Performing Organization Code
7. Author(s)	8. Performing Organization Report No.
Robert Edelman	
	10. Work Unit No.
9. Performing Organization Name and Address	11. Contract or Grant No.
Celanese Corporation Celanese Research Company Box 1000, Summit, NJ 07901	NAS1-15749 Task Assgt.2
	13. Type of Report and Period Covered
12. Sponsoring Agency Name and Address	Contractor Report JUN79 to AUG80
National Aeronautics and Space Administration Washington, DC 20546	14. Sponsoring Agency Code

15. Supplementary Notes

Langley technical monitor: James B. Nelson
Final Report, Task Assignment No. 2

16. Abstract

LaRC 160 polyimide has been modified with a high temperature peroxide catalyst, USP-138, in an attempt to reduce the final cure temperature to below 316°C. This effort was directed at obtaining a material for 177°C use that would cure at similar temperatures to a high performance epoxy while still maintaining the good moisture resistance of a polyimide material.

Attempts to prepare a laminate made from Celion ® 6000 fiber and 5% catalyzed LaRC 160 resin gave a material with minimal properties after curing at 193°C. Acceptable properties (ILSS=107 MPa at room temperature) were not obtained until a final cure temperature of 260°C was used. A control laminate containing no catalyst and cured under the same conditions had only half the level of shear strength.

The catalyzed LaRC 160 prepreg was also used to examine the possibility of shortening the conventional LaRC 160 cure at 316°C. Maximum properties were obtained using a 2.5% catalyzed product with a final cure temperature of 316°C held for fifteen minutes. Differences in properties between catalyzed and uncatalyzed product disappeared, however, when the cure time at 316°C was extended to 45 minutes.

17. Key Words (Suggested by Author(s))	18. Distribution Statement
Catalyzed LaRC 160 polyimide Celion 6000 Reduced temperature cure Shortened cure	Unclassified-Unlimited

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price*
Unclassified	Unclassified	40	

For sale by the National Technical Information Service, Springfield, Virginia 22161

End of Document