SOLVENTLESS LARC-160 POLYIMIDE MATRIX RESIN

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Abstract

The addition polyimide, LARC-160, which was originally synthesized from low-cost liquid monomers as a laminating resin in ethanol, has been prepared as a solventless, high viscosity, neat liquid resin. This resin was processed by hot-melt coating techniques into graphite prepreg with excellent tack and drape. Comparable data on graphite reinforced laminates made from solvent-coated and various hot-melt-coated prepreg have been generated. LARC-160, because of its liquid nature, can be easily autoclave processed to produce low-void laminates. Liquid chromatographic fingerprints indicate good reaction control on resin scale-ups. Minor changes in monomer ratios also have been made to improve the thermal aging performance of graphite laminates.

1. INTRODUCTION

Polyimide matrix resins exhibit excellent thermooxidative properties, and therefore, show potential for use in the aerospace industry. A major problem with this class of materials has always been the necessity for a solvent to keep the prepreg from being "boardy" or stiff. The presence of solvent leads to a problem later in processing, namely generation of volatiles and prepreg variability. A new polyimide system LARC-160, has been developed which overcomes these problems.[1] This resin is a modification of the well-known PMR-15 system which was developed at NASA-Lewis Research Center.[2] LARC-160 neat resin is a liquid at room temperature so, without the use of solvent, the resulting prepreg is not "boardy" but has both tack and drape (plies stick together and can be contoured to complex shapes). These properties are major requirements for a successful resin system. Production-scale runs of LARC-160 have been made and preliminary results of commercial prepregging, laminate preparation, and mechanical property testing are presented in this paper.

2. EXPERIMENTAL

2.1 RESIN PREPARATION

The low-cost materials necessary for the preparation of LARC-160 are the diethylester of benzophenone tetracarboxylic acid (BTDE), the ethylester of norbornene dicarboxylic acid (NE), Jeffamine AP-22, and ethanol.[1]

The BTDE (0.67 mole) and NE (1.22 mole) were prepared by refluxing the corresponding anhydrides with a slight (5%) excess of ethanol (2.69 mole). As the ethanol reacted in the esterification reaction, the the temperature of the mixture was controlled at 353K ± 5K (boiling point of ethanol is 351.5K). This temperature was maintained for one hour after all of the anhydrides had dissolved. The reaction mixture was then cooled to 313-323K and mixed with Jeffamine AP-22 (2.56 molar equivalents of amine). This mixture was further cooled to 295K and stored under nitrogen.

A modified version of LARC-160, LARC-160 A3, was prepared in the same manner as previously described except that the BTDE (0.735 mole) to NE (1.094 mole) ratio was adjusted to afford during B-staging a higher molecular weight oligomer. The amount of ethanol and Jeffamine AP-22 used remained the same. The LARC-160 A3 was formulated to improve 589K (600°F) stability.

All batches of resin discussed in this paper, in-house, contractual or commercial, were characterized by liquid chromatoraphy using a Waters Associates 202/R401 high pressure liquid chromatograph.

2.2 PREPREGGING

Graphite prepreg was prepared from the solventless resin system by either of two methods. The first was to cast a film of the resin onto release paper and then calender graphite tows into the resin. The second method was to use a hot-melt coating apparatus where the resin was heated both to lower its viscosity and to improve its wetting characteristics.

LARC-160 resin is also amenable to solvent coating. It can be prepared at any desired concentration in ethanol and subsequently applied to the fiber by either brush coating or immersion in a resin bath. After solvent evaporation the prepreg remains flexible and tacky.

A solution of LARC-160 A3 was prepared at 50% solids in ethanol and prepregged onto Hercules HT-S graphite by brush coating. After solvent evaporation this resin system left a flexible, tacky prepreg.

2.3 LAMINATE PREPARATION

The prepreg was cut into 7.6 cm by 17.8 cm laminae and stacked into unidirectional preforms and either autoclave processed or molded with matched metal dies. In both cases the first stage in the curing process (Figure 1) required the preform to be bagged in vacuum at 7-14 kPa,gauge (2-4 in. Hg, gauge), then heated from

ambient at a rate of 2.8K (5°F) per minute to 436K (325°F) and held at that temperature for one hour. This step allowed the monomeric reactants to form oligomeric imide chains. During this imidization step, condensation by-products were lost which amounted to 23% by weight of the resin. This left a consolidated billet averaging 36% resin by weight.

For press molded panels, the billet was trimmed to fit a matched-metal mold with open ends in the 0°-fiber direction. The mold was then preheated to 478K (400°F) and charged with the billet. Contact pressure was applied and a heating rate of 2.8K (5°F) per minute was established. At 547K (525°F), pressure was increased to 1.4 MPa (200 psi) over a one-minute span. A maximum curing temperature of 603K (625°F) was then attained and held for two hours. After cooling under pressure at 2.8K (5°F) per minute to a temperature below 366K (200°F), the panel was removed from the mold and postcured for 4 hours at 589K (600°F).

For autoclaved panels, the vacuum-bagged billet was heated at 2.8K (5°F) per minute from 436K (325°F) to 603K (625°F) with 1.4 MPa (200 psi applied at 547K (525°F). The same bag vacuum was maintained throughout the autoclave run. The same postcure conditions were used as for the molded laminates. The panel characteristics as well as aging and testing techniques were the same as previously reported.[1]

3. RESULTS AND DISCUSSION

3.1 SOLVENTLESS RESIN PREPARATION

The preparation of LARC-160 at the high solids level was accomplished by reacting the anhydrides with a five percent molar excess of ethanol. A slight excess of ethanol insured more complete conversion of anhydride to ester-acid. Because the ethanol is being used up in this reaction, the temperature must be controlled at or near the boiling point of ethanol 351.5K (173°F). Since reaction times vary depending on batch size and equipment (type of stirring, uniformity of heating, etc.), the conversion of anhydride to ester should be monitored by high pressure liquid chromatography.

LARC-160 prepared on contract for NASA by Riggs Engineering Corp., San Diego, CA and commercially by U.S. Polymeric, Santa Ana, CA, exhibits the same liquid chromatographic fingerprint in each case, indicating that approximately the same degree of reaction control was exercised in each preparation. The viscosity of the LARC-160 can be controlled by varying the amount of excess ethanol used in forming the ester-acid. The first scale-up of LARC-160 was a 190 liter (50 gallon) batch. This material contained 97% resin and 3% ethanol (excess used for anhydride conversion).

3.2 PREPREGGING

Seven commercial prepreggers were supplied with a 19-liter sample from a 190-liter batch of solventless LARC-160 prepared on contract to NASA by Riggs Engineering Corp. Most of the prepreggers indicated that the viscosity of this material was slightly lower than preferred. A subsequent 190-liter batch made by Riggs Engineering Corp. with only 1-2% excess ethanol was reported to be more viscous. This indicates that viscosity can be controlled during resin preparation to meet the various hot-melt prepregging requirements. Four commercial prepreggers have successfully hot-melt prepregged LARC-160 onto unidirectional graphite fiber: two of which were 7.6 cm (3 in.) wide HT-S and two which were 30.5 cm (12 in.) wide Celion tape. Because of the temperatures used, two of the processes left the prepreg leathery. The others, however, afforded a more desirable tacky, drapeable prepreg.

The LARC-160 A3 resin, when brushed onto HT-S graphite from a 50% ethanol solution, yielded a prepreg which was identical in all respects to LARC-160 prepreg.

3.3 LAMINATES

According to the data in Table I, LARC-160 laminates prepared according to the previously outlined procedure have similar properties regardless of how the prepreg is prepared (hot-melt or solvent-coated). The solvent-coated and hot-melt prepregs differed only slightly in behavior during B-staging, namely the hot-melt prepregs had less flow into the bleeder plies due to heat history. However, in the subsequent molding step, the same degree of flow was obtained from either prepreg.

The resin batch size did not appear to affect the quality of laminates as evidenced by the data in Table II.

TABLE I. MECHANICAL PROPERTIES OF LARC-160 GRAPHITE LAMINATES PREPARED FROM SOLVENT AND HOT-MELT PREPREG[1]

	Short Beam Shear, MPa(psi)		Flexural Strength, MPa(ksi)	
Prepreg	R.T.	561K	R.T.	561K
HT-S (Solvent)	95.7 (13,900)	48.2 (7000)	2060 (300)	1450 (210)
HT-S (Hot-melt)	84.7 (12,300)	50.3 (7300)	1850 (269)	1200 (175)
Celion (Solvent)	110.2 (16,000)	45.5 (6600)	1900 (276)	1050 (153)[2]
Celion (Hot-melt)	103.3 (15,000)	49.6 (7200)	1870 (272)	1380 (200)

[1] Sources and number of specimens are variable

[2] Interlaminar failure

TABLE II. SHORT BEAM SHEAR STRENGTHS OF LARC-160 GRAPHITE LAMINATES PREPARED FROM LAB-SCALE AND 190-LITER BATCHES OF RESIN

Prepreg	Aging Conditions	Short Beam Shear, MPa(ksi) R.T.	589K
HT-S (Lab-scale)	none	95.7 (13.9)	42.0 (6.1)
HT-S (Lab-scale)	250 hr/589K(600°F)	59.9 (8.7)	40.6 (5.9)
HT-S (190 liters)	none	92.9 (13.5)	46.1 (6.7)
HT-S (190 liters)	250 hr/589K(600°F)	60.2 (8.8)	40.6 (5.9)

Laminates made from LARC-160 A3 were more thermooxidately stable than those made from LARC-160. This modification involves a 10 mole percent decrease in nadimide content with a corresponding increase in BTDA content. Since nadic moieties contain aliphatic (or easily oxidized) carbon atoms, the use of less of this monomer should lead to a more thermooxidatively stable system. Comparative data of the mechanical properties of laminates made from LARC-160 A3 and LARC-160 are in Table III (Figures 2 and 3). The LARC-160 A3 had only a 8 percent drop in room temperature short beam shear strength after 500 hours at 561K compared to a 40 percent loss for the LARC-160. Better retention of initial strength was realized for LARC-160 A3 after each aging period at either temperature.

Both the LARC-160 and LARC-160 A3 as well as the other addition systems undergo a post-cure when aged at 561K (550°F) and 589K (600°F).[1] This is shown in Table III (Figures 2 and 3) where the 561K and 589K short beam shear values are lower initially than after aging for 125 hours at either temperature.

Laminates made from the previously described LARC-160 and LARC-160 A3 were well consolidated with less than two percent voids as calculated from density measurements. Ultrasonic "C"-scans showed the LARC laminates to be as well consolidated and have the same apparent void content as epoxy panels with negligible voids.

4. CONCLUSIONS

The LARC-160 system which is made from low-cost monomers has been successfully scaled-up as a solventless resin. A 190-liter batch has been made and distributed to prepreggers for evaluation. At present four of these prepreggers have made hot-melt graphite tape with this material. Liquid chromatographic fingerprints of the various batches indi-

TABLE III. Short Beam Shear Strengths of LARC-160 A3 and LARC-160 HT-S Graphite Laminates

Exposure Hrs @ K(°F)	Test Temp K(°F)	Average Short Beam Shear Strength, MPa (ksi) LARC-160	LARC-160 A3
None	RT	95.7 (13.9)	85.4 (12.4)
None	561 (550)	44.8 (6.5)	46.2 (6.7)
None	589 (600)	42.0 (6.1)	37.2 (5.4)
125 @ 561 (550)	RT	81.3 (11.8)	82.7 (12.0)
125 @ 561 (550)	561 (550)	60.6 (8.8)	56.5 (8.2)
500 @ 561 (550)	RT	57.1 (8.3)	78.5 (11.4)
500 @ 561 (550)	561 (550)	46.8 (6.8)	53.7 (7.8)
125 @ 589 (600)	RT	75.0 (10.9)	87.4 (12.7)
125 @ 589 (600)	589 (600)	47.5 (6.9)	51.0 (7.4)
250 @ 589 (600)	RT	59.9 (8.7)	65.4 (9.5)
250 @ 589 (600)	589 (600)	40.6 (5.9)	44.8 (6.5)
375 @ 589 (600)	RT	46.1 (6.7)	-
375 @ 589 (600)	589 (600)	33.0 (4.8)	-
500 @ 589 (600)	RT	Severely	55.1 (8.0)
500 @ 589 (600)	589 (600)	Oxidized	37.2 (5.4)

cate good control in and reproducibility of resin preparation. The hot-melt prepregs made from the large, solventless resin batch processed with the same ease as prepreg from previous smaller batches. The mechanical properties of graphite laminates prepared from these prepregs were also equal to or better than those prepared from lab-scale runs. A version of LARC-160 has been prepared which has considerably better retention of mechanical properties than the original LARC-160 as evidenced by tests after thermal aging in air at both 561K and 589K.

5. REFERENCES

1. T. L. St. Clair and R. A. Jewell, "LARC-160: A New 550°F Polyimide Laminating Resin", Preprints, 8th National SAMPE Technical Conference, Vol. 8, p. 82, Seattle, WA, October 12-14, 1976.
2. T. T. Serafini, P. Delvigs, and G. R. Lightsey; J. Appl. Polym. Sci., Vol. 16, no. 4, 905 (1972).

6. BIOGRAPHY

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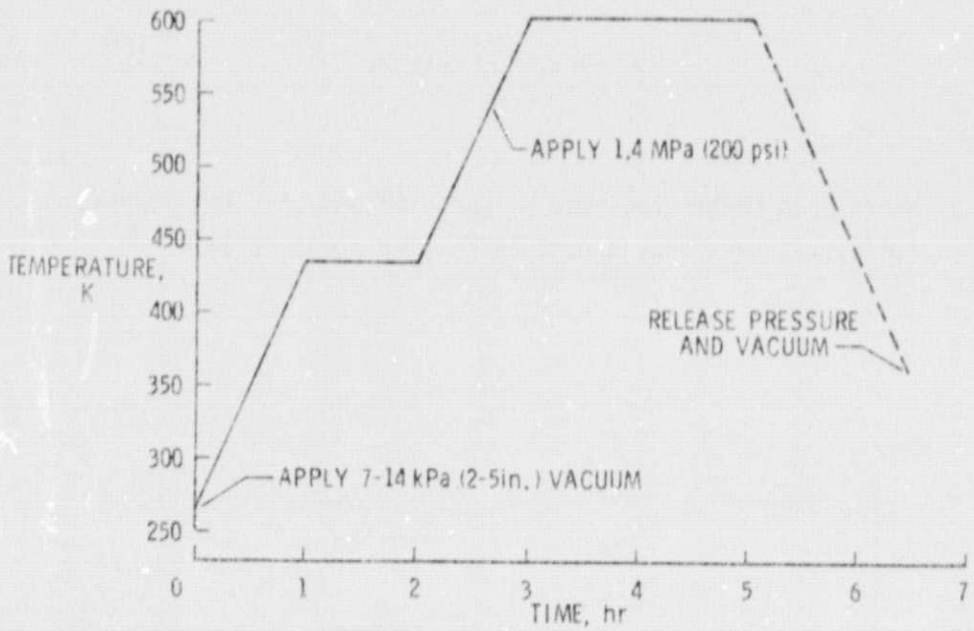

FIGURE 1. Cure cycle for LARC-160.

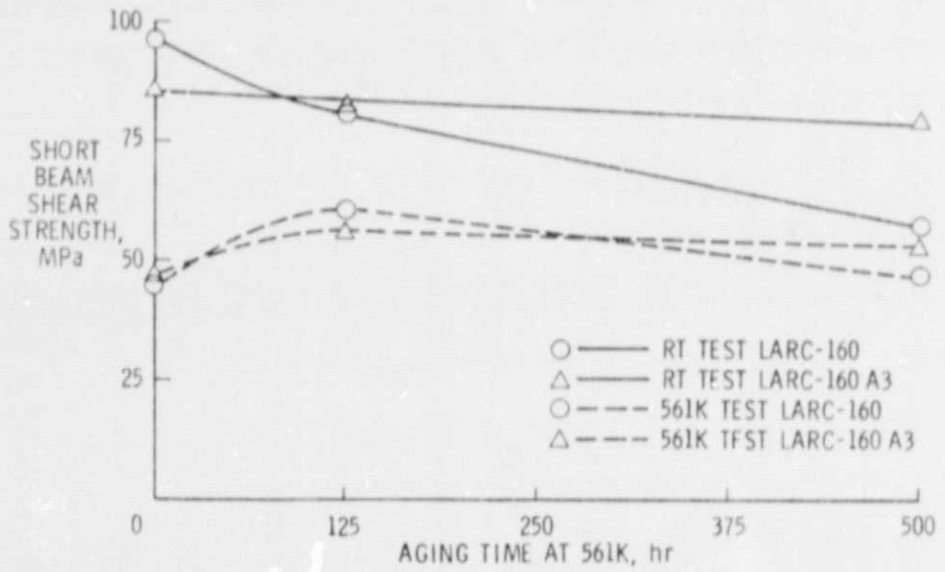

FIGURE 2. Short beam shear strengths of LARC-160 and LARC-160 A3/HT-S composites tested at RT and 561K after aging at 561K.

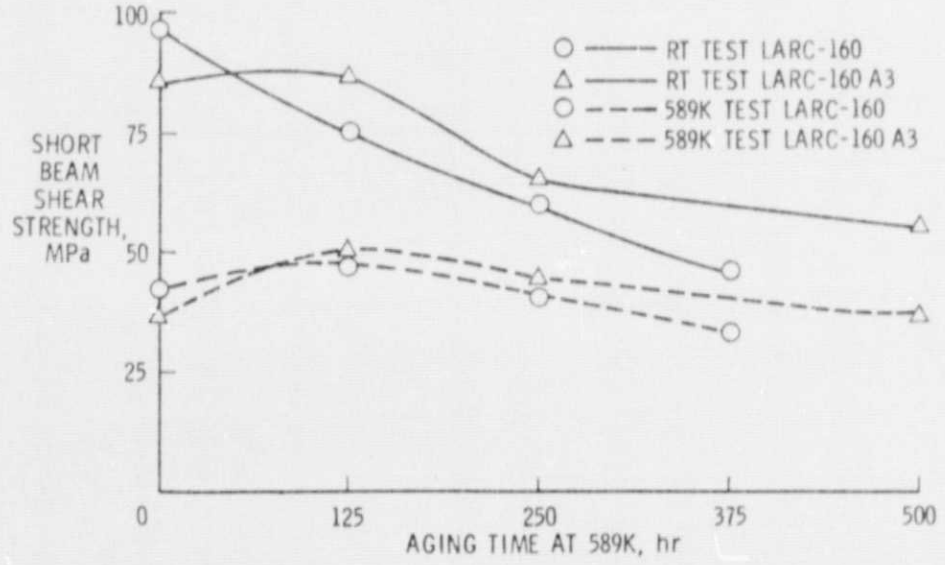

FIGURE 3. Short beam shear strengths of LARC-160 and LARC-160 A3/HT-S composites tested at RT and 589K after aging at 589K.