Composite Properties of Polyimide Resins Made From "Salt-Like" Solution Precursors[1]

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ABSTRACT

Recent work in high temperature materials at NASA Langley Research Center (LaRC™) have led to the development of new polyimide resin systems with very attractive properties. The majority of the work done with these resin systems has concentrated on determining engineering mechanical properties of composites prepared from a poly(amide acid) precursor.

Three NASA Langley-developed polyimide matrix resins, LaRC™-IA, LaRC™-IAX, and LaRC™-8515, were produced via a "salt-like" process developed by Unitika Ltd. The "salt-like" solutions (sixty-five percent solids in NMP) were prepregged onto Hexcel IM7 carbon fiber using the NASA LaRC™ Multipurpose Tape Machine. Process parameters were determined and composite panels fabricated. Mechanical properties are presented for these three intermediate modulus carbon fiber/polyimide matrix composites and compared to existing data on the same polyimide resin systems and IM7 carbon fiber manufactured via poly(amide acid) solutions (thirty-five percent solids in NMP). This work studies the effects of varying the synthetic route on the processing and mechanical properties of polyimide composites.

KEY WORDS: Composites, Polyimides, Prepreg, and Processing

1. INTRODUCTION

Polyimides are attractive for aerospace applications because of their excellent thermooxidative stability and high mechanical properties. Controlled molecular weight, low melt viscosity polyimides are easily processed via thermoplastic forming techniques which makes them attractive matrix materials for advanced composite applications. Polyimides provide an excellent combination of high glass transition temperatures, excellent solvent resistance and high mechanical properties.[1-5]

NASA Langley Research Center has developed several polyimides that can be melt processed into various useful forms as coatings, adhesives, composite matrix resins and films.[1-10] These polyimides are prepared from various aromatic diamines and dianhydrides in several different solvents. The use of phthalic anhydride as an endcapping agent is to control the molecular weight of the polymer and, in turn, to make it easier to process in molten form.

Current technology for making prepreg and composites from polyimides utilizes solutions of the poly(amide) acids which are processed into prepreg with various reinforcing fibers.[11-12] In general, poly(amide acid) solutions are prepared at solid contents of 25 to 35% by weight with resulting Brookfield viscosities at ~20°C of 15,000 to 35,000 centipoise (cp). Therefore, processing these types of solutions requires overcoming significant problems such as solvent management and good fiber wet out from the high viscosity solutions. The resultant prepregs require residual solvent contents of 20 to 25 % by weight (of which ~2-3% is water from the imidization reaction) for adequate tack and drape. This residual solvent must then be removed during the composite cure cycle. Again, this poses a significant solvent removal and recovery problem, especially in large parts. Typically, solvent removal is accomplished by holding the material at an intermediate drying temperature, above the boiling temperature of the solvent, for extended periods of time (i.e. one to two hours) under full vacuum, 30” Hg. The material is then ramped to its final cure temperature at high pressure (~1.4 MPa) to ensure complete fiber wet-out and full consolidation.

In the present work, preimpregnated tape was fabricated from “salt-like” solutions of high temperature polyimides prepared by Unitika Ltd., Japan. These low viscosity (5,000 to 9,700 cp at 20°C), high solids content (65% by weight) solutions were solution coated onto reinforcing fiber to produce high quality prepreg with excellent tack and drape at 12-15% residual solvent (of which ~4-6% is water from the imidization reaction). Composites from this prepreg were of high quality, required significantly lower intermediate drying temperature utilizing only partial vacuum and a lower final pressure.

Mechanical properties are presented for the three intermediate modulus carbon fiber/polyimide matrix composites (IM7/ LaRC™-IA, IM7/ LaRC™-IAX, and IM7/ LaRC™-8515) and compared to existing data on the same polyimide resin systems with IM7 carbon fiber manufactured via poly(amide acid) solutions.

2. MATERIALS[2]

IM7 12K, unsized carbon fiber from Hexcel, Salt Lake City, UT was used exclusively in this work. Solutions of LaRC™-IA, -IAX, and -8515 were made by Unitika Ltd., Kyoto, Japan and prepared as described in Section 3.1. Prepreg was made at NASA LaRC™ on the Multipurpose Prepregger as described in Section 3.2. Composite panels were manufactured at NASA LaRC™ as described in Section 3.3. Test coupons were machined and tested as described in Section 3.4.

3. EXPERIMENTAL

3.1 "Salt-like" Solutions For example, LaRC™-IA polyimide "salt-like" solutions were formed from the reaction of oxydiphthalic anhydride (ODPA) dissolved in a mixture of NMP and MeOH at room temperature. This solution is treated at 60°C for 3 hours in order to convert the ODPA into ODP-dimethyl ester. The resulting solution, phthalic acid (PA) and 3,4'-oxydianiline is added to the ODP-dimethyl ester and stirred for 2 hours to yield a homogeneous polyimide "salt-like" resin. The chemical structure of the three polyimides utilized in this work are shown in Figure 1 while the properties of the three "salt-like" solutions are shown in Table 1.

3.2 Prepreg Fabrication Polyimide "salt-like" solutions were placed in the resin dip tank of the LaRC Multipurpose Prepreg Machine (Figures 2 and 3). The LaRC™-IA, -IAX and -8515 solutions had solids contents of 65% resin by weight in NMP with Brookfield viscosities ranging from 4955 to 9660 cp (Table 1). The hotplates were set at 149°C while the oven was set at 138°C. Nip stations 2, 3, and 4 utilized only contact pressure and were set at 93°C. The metering bar gap was set at ~0.4064 mm and the line speed was set between 0.55 and 0.76 m/min. The comb was adjusted to attain a fiber aerial weight of 145 g/m^2. Seventy ends of 12k unsized Hexcel IM7 carbon fiber were utilized. Prepreg tapes with FAW's of 148 to 150 g/m^2, ~35 wt. % dry resin content, and a wet volatiles content of 13 to 15 wt.% were produced. The 20.6 centimeter wide prepreg tape made from each material was of high quality with excellent wet out, tack and drape. A total of 107 linear meters of each material was produced. The properties of the each prepreg system are presented in Table 2.

3.3 Composite Panel Fabrication LaRC™-8515, -IA, and -IAX "salt-like" prepregs were processed into several different composite laminates by the process illustrated in Figure 4. As shown in Figure 5, one ply of Kapton™ film and one ply of 0.0635 mm Teflon™ bleeder /

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[2] The use of trademarks or names of manufacturers in this report is for accurate reporting and does not constitute an official endorsement, either expressed or implied, of such products or manufacturers by NASA.

breather cloth was placed on either side of several plies of unidirectional "salt-like" prepreg, which was placed in a closed mold and processed in a hydraulic vacuum press. The prepreg was heated to 121°C under isobaric conditions and held for one hour. During the one hour hold, the residual solvent within the material was removed. After 30 minutes at 121°C, 508 mm of Hg of vacuum was applied. Once the 121°C hold was completed, the material was heated to 225°C and full vacuum was applied. During the one and half hour hold at 225°C, the material becomes fully imidized. After the hold at 225°C, the polyimide was heated to the final cure temperature of 380°C, 0.6895 MPa was applied and the material was held at this temperature and pressure for 30 minutes. During this hold, the polyimides become amorphous and reach minimum viscosity which allows for proper consolidation. Once the hold has been completed, the material was cooled to ambient temperature under full vacuum and 0.6895 MPa pressure. At ambient temperature, the mold was removed from the hydraulic vacuum press and the laminate was released from the mold. Upon visual and ultrasonic examination, laminates were determined to be of excellent quality.

3.4 Composite Panel Mechanical Testing Specimens were machined for short beam shear (SBS) testing which is a flexural test used to qualitatively assess the interlaminar strength of a composite. This test is designed to force an interlaminar failure along the centerline of the composite beam. The SBS test utilizes a three point bending fixture and the span is determined from the distance between the two base points in the fixture. The test specimen of approximate length and width of 1.9 cm and 0.64 cm, respectively, were tested in accordance with ASTM D2344 at both room temperature (RT) and 177°C. The load is applied at a rate of 0.13 cm/min.

The transverse flexural test, ASTM D790, is very similar to the SBS test, except in this case a tension failure is forced to occur along one free face while the other is put in compression. The same fixture can be used, but the specimens differ in size in order to affect this tension failure. These test specimens were 7.0 cm long and 1.27 cm wide, while test temperatures were RT and 177°C. In this test there is an initial load of 0.34 MPa, and the load is again applied at the rate of 0.13 cm/min. until the initial failure occurs.

4. RESULTS AND DISCUSSION

4.1 Unidirectional Prepreg Tape Unidirectional prepreg was readily made with the "salt-like" solutions of LaRC™-IA, -IAX, and -8515. The low viscosity of these solutions resulted in excellent wet out of the fiber bundles and prepreg tape with excellent tack and drape with significantly less residual solvent than prepreg from poly(amide acid) solutions of polyimides (13-15 wt.% versus 20-25 wt.%).

4.2 Composite Panels Unidirectional panels fabricated according to the procedure describe earlier were determined to be of very good quality by both visual and ultrasonic inspection. Panels fabricated with poly(amide) acid solutions of the same resin systems required more pressure (1.4 MPa) to adequately consolidate the laminates. Therefore, "salt-like" solutions allow for the fabrication of quality panels at lower pressures than the same resins fabricated via poly(amide) acid solutions. The need for less residual solvent in the prepreg translate into less solvent removal during cure.

4.3 Mechanical Properties Short beam shear and 0° and 90° flexural strength and modulus were determined for each "salt-like" solution composite. Mechanical properties for composites fabricated from "salt-like" solutions are presented in Figures 6-9 and Tables 3-5. For comparison, data obtained from composites fabricated from poly(amide) acid solutions [13-15] are also presented in these figures. As shown in Figure 6, IM7/LaRC™-8515, IM7/LaRC™-IA, and IM7/LaRC™-IAX composites fabricated via the "salt-like" solution demonstrated superior or comparable 0° flexural properties at both RT and 177°C. Similar results were obtained for 0° flexural modulus properties as shown in Figure 7. IM7/ LaRC™-8515 composites also demonstrated improved or comparable 90° flexural strengths as shown in Figure 8. However, IM7/LaRC™-IA and IM7/LaRC™-IAX composites did not. SBS strengths were not as good as those determined for the poly(amide acid) solutions of all three materials at elevated temperature. Only IM7/ LaRC™-IA composites from "salt-like" solutions demonstrated improved SBS properties at RT. IM7/ LaRC™-8515 and IM7/ LaRC™-IAX composites resulted in lower RT SBS strengths compared to their equivalent poly(amide acid) composites.

In general, material properties are considered good if the 0° flexure moduli are between 110-131 GPa and RT short beam shear strengths are above 97 MPa [16]. Although the mechanical data for the "salt-like" solution materials were not all equivalent to the poly(amide acid) materials, determined test values are considered acceptable by the above criteria. The three "salt-like" solutions resulted in composites with 0° flexural moduli above 131 GPa at both RT and 177°C and RT SBS values above 103 MPa.

The poor SBS properties of the "salt-like" IM7/LaRC™-8515 composites may have been due to insufficient molecular weight build-up. The 8515 "salt-like" solution composites had a cured T_g of around 235°C as measured by DSC. This is significantly lower than the amide acid solution composite T_g of ~250-260°C. The lower T_g would indicate a lower molecular weight which would translate into poor SBS properties. These properties should improve with an increased dwell time at the final cure temperature which would allow for further molecular weight build-up to occur. Although, no apparent difference in T_g was observed between the "salt-like" and amide acid solution composites of IA and IAX (T_g ~235°C), a lack of molecular weight build-up may have resulted in the difference observed in the data. The lower 90° flexure, SBS, and elevated temperature 0° flexural of the IA and IAX "salt-like" solution composites may be improved by a longer dwell at 380°C allowing for more molecular weight growth.

5. CONCLUSIONS

"Salt-like" solutions of the NASA Langley-developed polyimide matrix resins, LaRC™-IA, LaRC™-IAX, and LaRC™-8515 were produced by Unitika, Ltd and solution prepregged onto Hexcel IM7 carbon fiber by NASA LaRC™. Using these unidirectional prepregs which contained ~12-15 percent N-methylpyrrolidinone solvent, processing parameters were developed to fabricate fully consolidated high quality flat panels. RT 0° flexural composite mechanical data for each "salt-like" polyimide prepreg was superior or comparable to the same material synthesized via the poly(amide) acid route. SBS and 90° flexural properties, however, were not equivalent. Overall, processing of polyimide composites from a "salt-like" precursor was readily achievable at lower pressures and with less residual solvent and resulted in composites of good quality with good mechanical properties.

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Table 1. "Salt-like" Solution Properties.

Resin System	Solids in NMP, wt. percent	Solution Brookfield viscosity, cp @ °C
LaRC™ IA	65	6780 @ 23
LaRC™ IAX	65	4955 @ 22
LaRC™ 8515	65	9660 @ 18

Table 2. Unidirectional IM7/ "Salt-like" Solution Prepreg Characteristics.

Resin	FAW, g/m2	Solvent Content , wt. %, wet	Solids Content, wt. %, dry
LaRC™ IA	150	13.2	34.0
LaRC™ IAX	150	13.8	37.5
LaRC™ 8515	148	15.0	35.7

Table 3. Mechanical Tests and Properties for LaRC™ 8515 / IM-7 "Salt-Like" Composites.

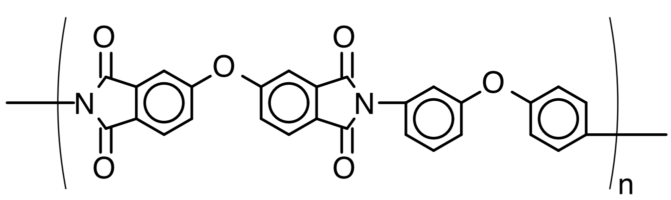
Mechanical Test	Test Temp., °C	No. spec. at each Temp.	Failure Load (kg)	Failure Stress (MPa)	Modulus (GPa)
SBS	RT, 177	10 10	352.7 ± 12.2 135.6 ± 9.9	117.8 ± 3.8 45.4 ± 3.0	N/A
0° Flexural	RT, 177	6 9	79.9 ± 4.4 57.4 ± 2.5	1725.1 ± 84.1 1299.0 ± 101.4	146.9 ± 3.4 137.2 ± 9.7
90° Flexural	RT, 177	5 5	26.4 ± 1.9 14.2 ± 3.3	117.9 ± 6.1 58.6 ± 13.1	4.62 ± 0.28 4.34 ± 0.28

Table 4. Mechanical Tests and Properties for LaRC™ IAX / IM-7 "Salt-Like" Composites.

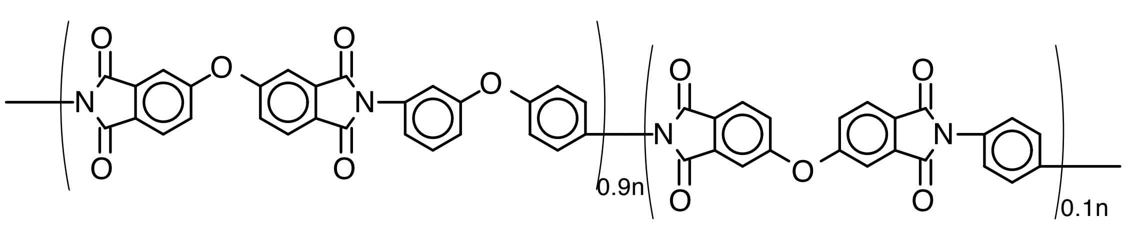
Mechanical Test	**Test Temp., °C**	**No. spec. at each Temp.**	**Failure Load (kg)**	**Failure Stress (MPa)**	**Modulus (GPa)**
SBS	RT, 177	10 12	313.9 ± 14.1 118.8 ± 3.6	103.3 ± 4.6 39.1 ± 1.2	N/A
0° Flexural	RT, 177	5 4	67.3 ± 2.9 45.8 ± 1.5	1525.1 ± 131.0 984.6 ± 91.7	145.5 ± 12.4 135.1 ± 9.7
90° Flexural	RT, 177	6 6	31.71 ± 2.54 16.83 ± 1.32	121.34 ± 11.72 66.88 ± 4.83	4.34 ± 0.28 3.03 ± 0.28

Table 5. Mechanical Tests and Properties for LaRC™ IA / IM-7 "Salt-Like" Composites.

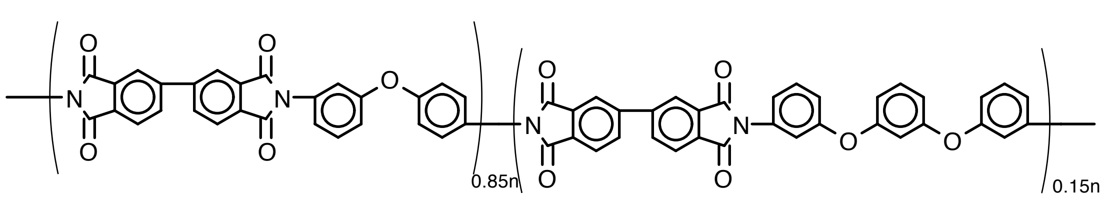
Mechanical Test	**Test Temp., °C**	**No. spec. at each Temp.**	**Failure Load (kg)**	**Failure Stress (MPa)**	**Modulus (GPa)**
SBS	RT, 177	10 12	380.2 ± 16.3 126.1 ± 3.2	125.1 ± 5.4 41.4 ± 1.0	N/A
0° Flexural	RT, 177	5 5	73.4 ± 3.4 47.1 ± 3.5	1589.9 ± 84.8 1065.9 ± 79.3	137.2 ± 9.7 131.0 ± 6.9
90° Flexural	RT, 177	5 5	35.74 ± 7.03 19.01 ± 1.59	133.1 ±17.2 73.1 ± 5.5	4.27 ± 0.34 3.44 ± 0.29



LaRC™-IA



LaRC™-IAX



LaRC™-8515

Figure 1. Molecular structure of LaRC™-IA, LaRC™-IAX, and LaRC™-8515.

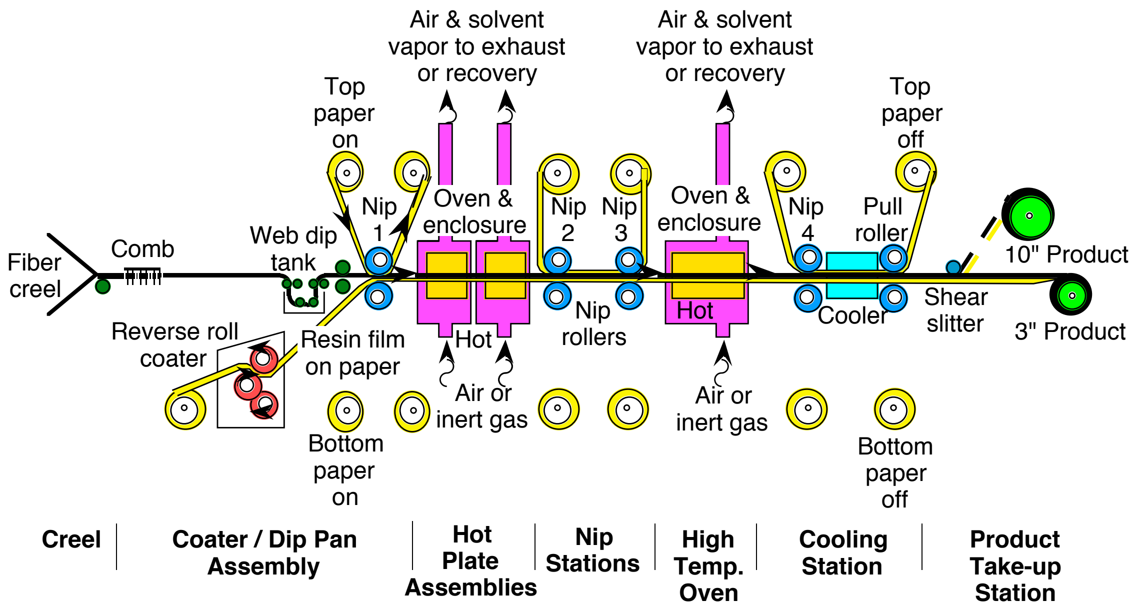


Figure 2. Schematic Diagram of the Tape Machine Modular Components.

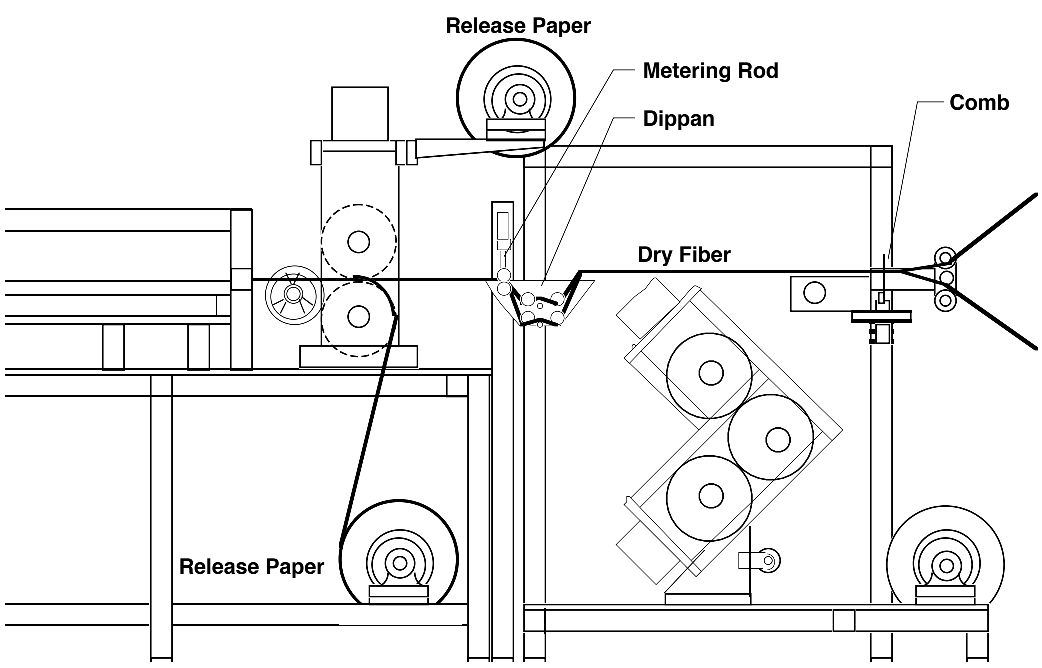


Figure 3. Solution Prepregging Using the Dip Tank Method.

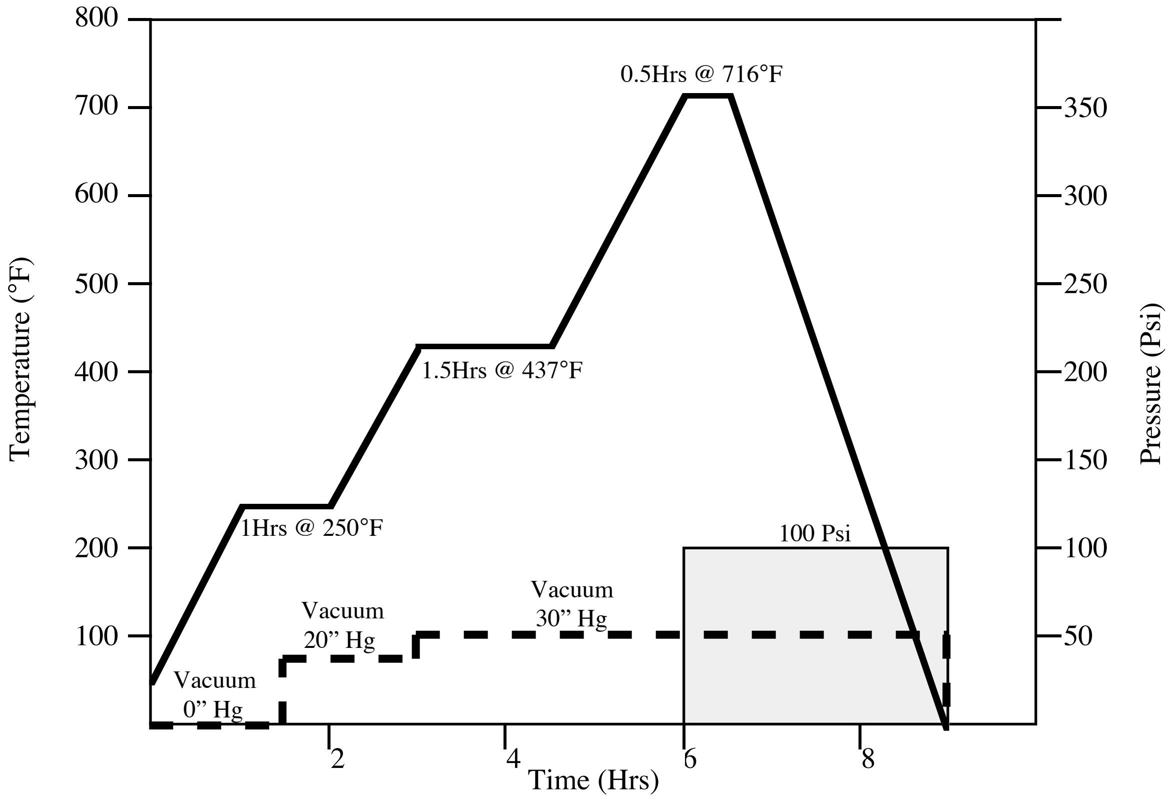


Figure 4. Cure Cycle for Polyimide Salt like Prepregs.

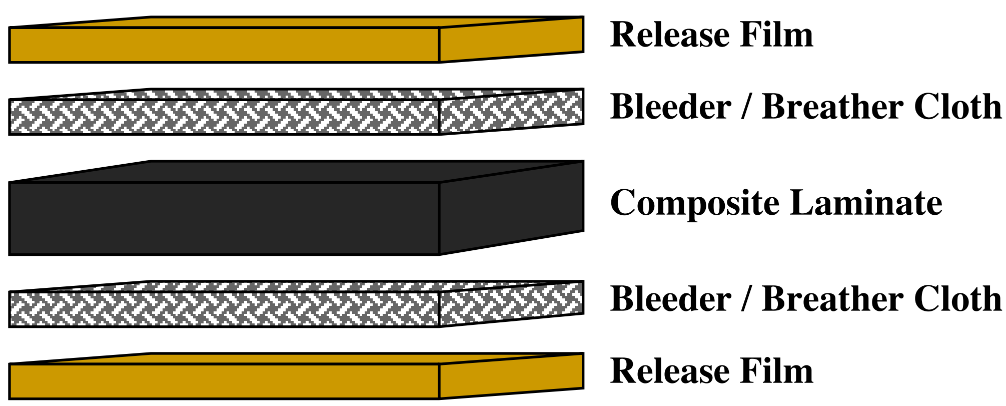


Figure 5. Composite laminate lay-up configuration.

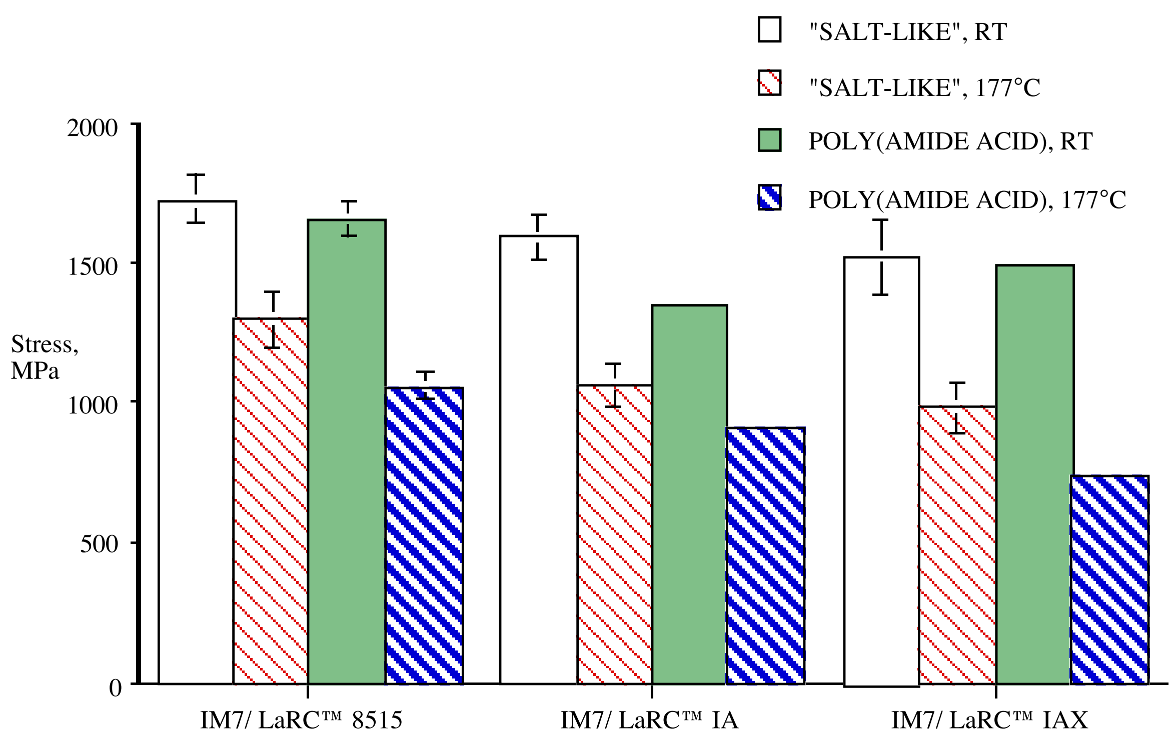


Figure 6. Zero degree flexural strength data.

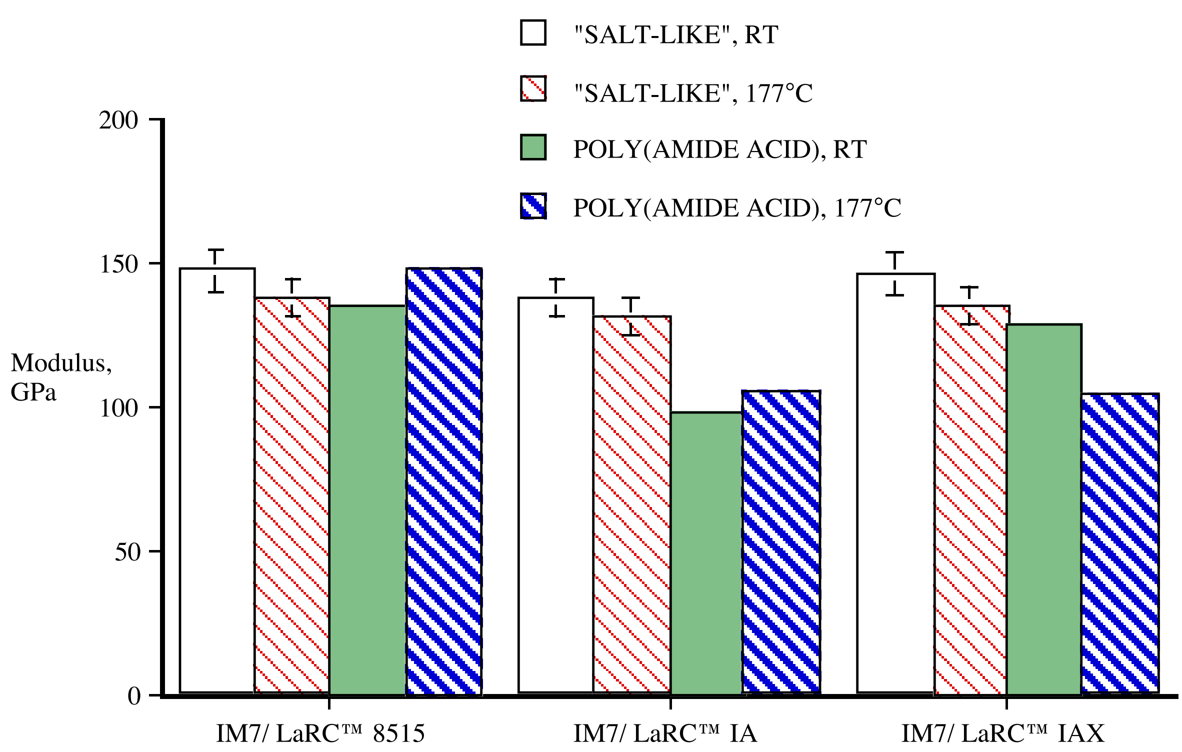


Figure 7. Zero degree flexural modulus data.

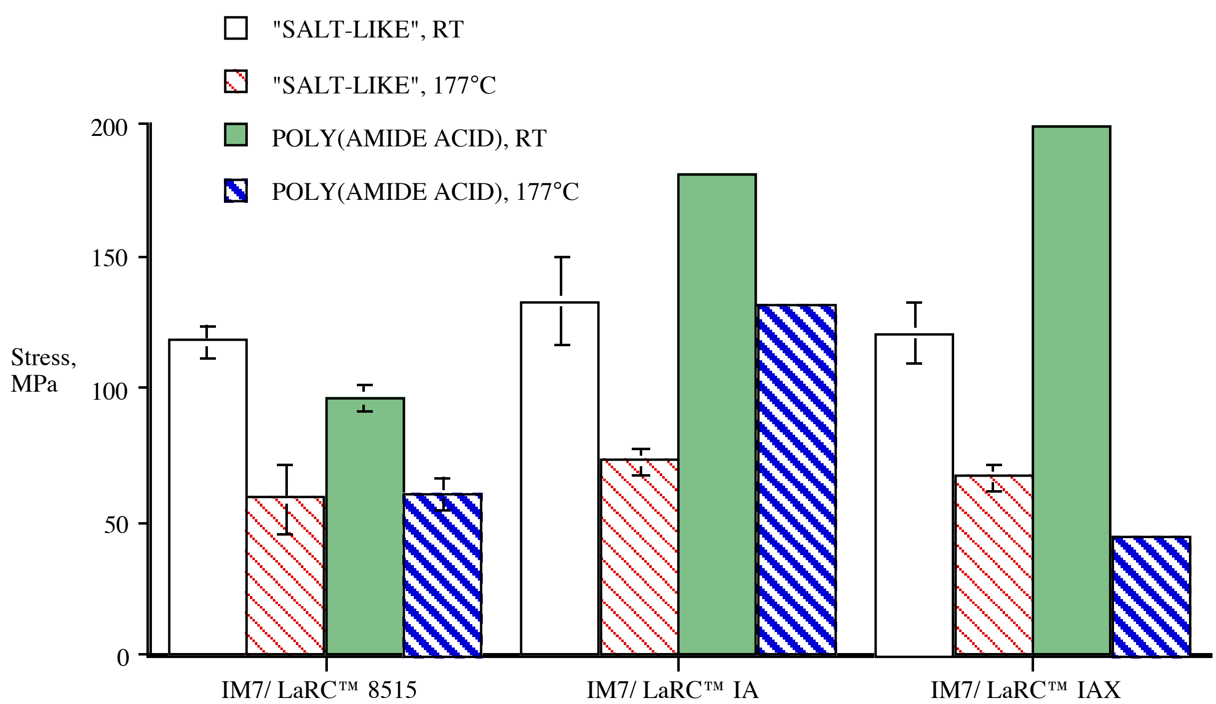


Figure 8. Ninety degree flexural strength data.

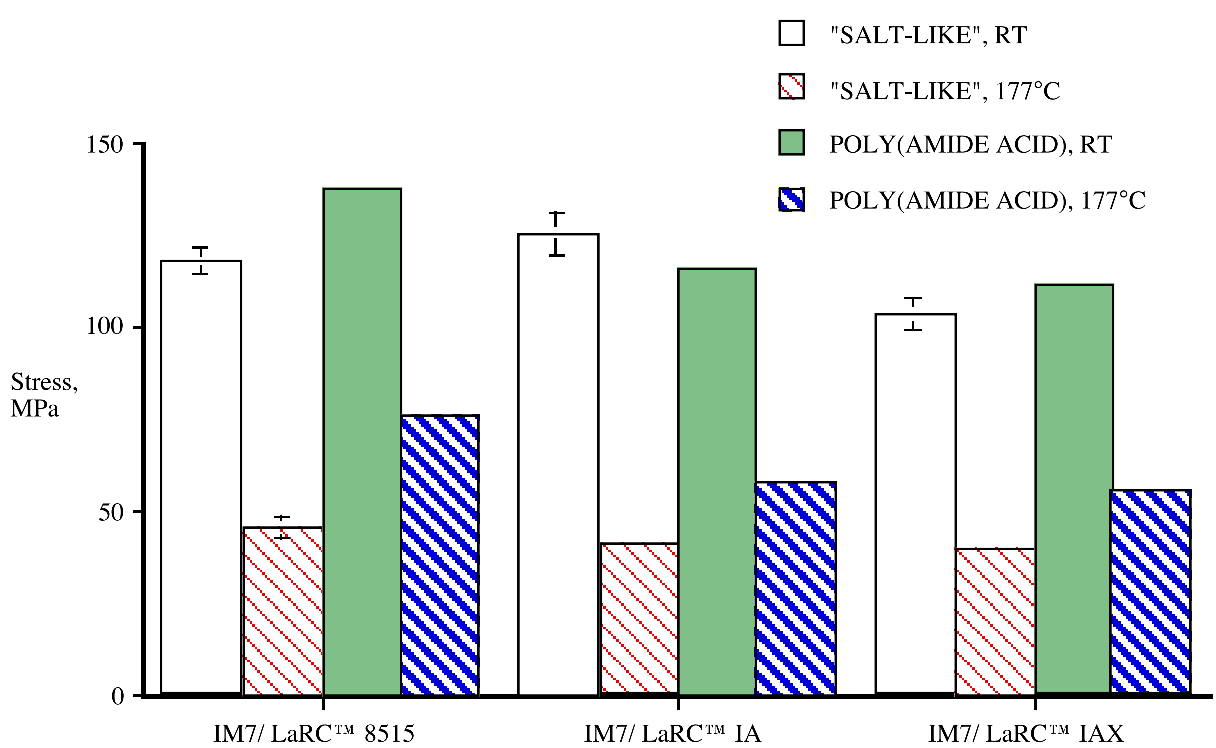


Figure 9. Short beam shear strength data.