OPTIMAL COMPOSITE MATERIAL FOR LOW COST FABRICATION OF LARGE COMPOSITE AEROSPACE STRUCTURES USING NASA RESINS OR POSS NANOPARTICLE MODIFICATIONS

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SUMMARY

Thermoplastic laminates in situ consolidated via tape or tow placement require full mechanical properties. Realizing full properties requires resin crystallinity to be controlled - partial crystallinity leads to unacceptably low laminate compression properties. There are two approaches: utilize an amorphous matrix resin; or place material made from a semi-crystalline resin featuring kinetics faster than the process. In this paper, a matrix resin evaluation and trade study was completed with commercial and NASA amorphous polyimides on the one hand, and with PEKK mixed with POSS nanoparticles for accelerated crystallinity growth on the other. A new thermoplastic impregnated material, 6 mm wide (0.25-in) AS-4 carbon/LaRC™ 8515 dry polyimide tow, was fabricated. Since LaRC™ 8515 is fully amorphous, it attains full properties following in situ consolidation, with no post processing required to build crystallinity. The tow in situ processing was demonstrated via in situ thermoplastic filament winding it into rings.

INTRODUCTION TO THERMOPLASTIC PLACEMENT TIMING AND RESINS

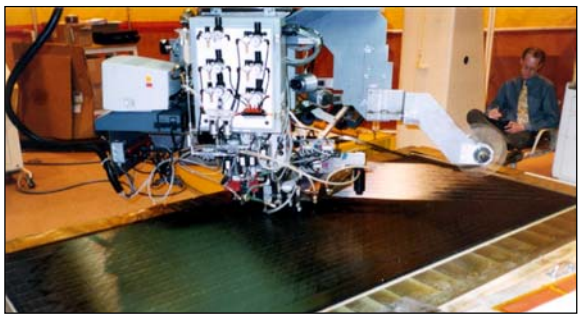

Figure 1 Thermoplastic automated tape placement is used to accurately consolidate deposit a 45° ply in place.

The thermoplastic automated tape placement head is mounted to a high-rail gantry motion mechanism. The coordinated gantry/head motion together with the on-head polymer process enables the fabrication of open-section flat laminates without requiring an autoclave. The deposition head preheats the thermoplastic tape and pre-laid laminate to the melting temperature, and then welds them together under heat and pressure until the composite material is healed and consolidated in place [1]. Figure 1 illustrates the heated head fabricating a 45° ply in a large [45/0/-45/90]ns laminate. Open Hole Compression (OHC) strength targets remain at 85% of properties obtained by testing autoclaved laminates [2]. Attention thus focused on matrix resin crystallinity [3]. Three examples were documented where the full polymer matrix crystallinity appears not to

have been achieved because the resin (polyetherketone or polyimide) crystalline kinetics were slower than the in situ process. Without full crystallinity, the full resin modulus is never attained, and compression properties of the composite laminate suffer.

Process options to accommodate the slow resin crystallinity were (1) to place more slowly, (2) increase the overall deposition head length, or (3) anneal the final part. The best material option is by controlling matrix resin crystallinity. The development of a carbon-fiber tow with the optimal thermoplastic resin became this program's goal.

DEFINE MATERIAL REQUIREMENTS

A "placement grade" thermoplastic tow and tape specification was defined. It specifies, among other attributes, a 75 mm (+0.00mm, –0.10mm) wide tape or 6.35mm ±0.127 mm tow, a thickness variation within 6% including the ends, 35 ± 1% resin weight fraction, a void content below 1%, and a goal fiber areal weight of 145 g/m^2.

Further, the resin must be either fully amorphous or semi-crystalline. If an amorphous material is used, it cannot crystallize out of the melt. If semi-crystalline, the resin must achieve full crystallinity within the placement time of the in situ process. Figure 2 shows the temperature-time history achieved by the automated tape deposition head placing at 3 mpm (10 fpm). The incoming laminate at 45°C is heated to 380°C, then chilled to near T_g over a 15 second time span. If the matrix resin is fully amorphous, this process timing is inconsequential; process conditions can be optimized to generate quality microstructure. With a semi-crystalline resin, the time to achieve full crystallinity must be considered. The optimal crystallinity growth rate is approximately 2/3rds the way from T_g to T_{melt}. Thus, to guarantee full crystallinity in the completed laminate, the crystalline kinetics must be quicker than 15 seconds. This requirement can be relaxed somewhat due to the heating effect from subsequent passes, but must be increased by the desire to place faster.

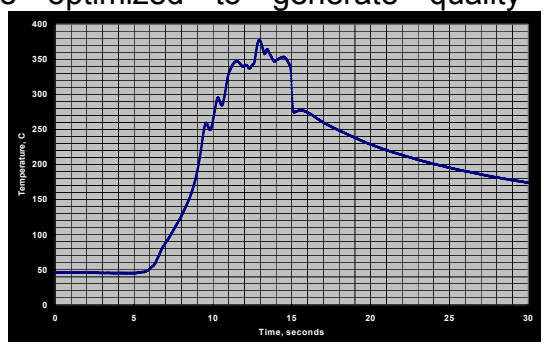

Figure 2 The heating/cooling cycle lasts 15 seconds.

SEMI-CRYSTALLINE RESINS

For semi-crystalline resins, the addition of POSS (Polyhedral oligomeric silsesquioxane) nanoparticles to increase the rate and amount of resin crystallinity was evaluated. Figure 3 shows PEEK is fast enough, but the two nanoparticles, Ph_8T_8 ("POSS 8") and $Ph_{12}T_{12}$ ("POSS 12") proved ineffective in speeding PEKK crystallinity at the nanoparticle ratios evaluated, likely due to inadequate particle blending. Advanced blending

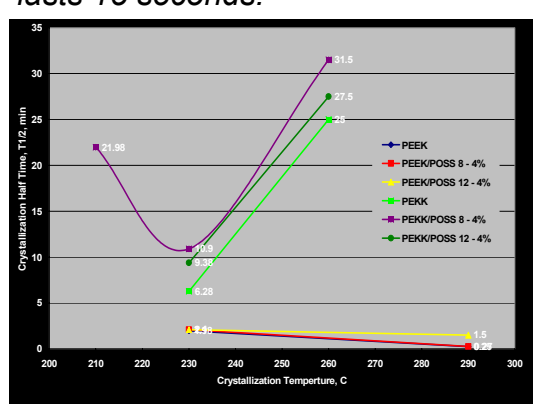

Figure 3 Nanoparticle additions fail to speed the rate of crystallinity

of the nanoparticles into the resin is expected to improve the crystallization rate, and is the focus of the next study.

AMORPHOUS RESINS CONSIDERED

Four sets of amorphous polymers were considered before NASA's LaRC™ amorphous polyimides were selected for development. The NASA resins included:

- NASA-LaRC™ - SI - (Soluble Imide) polyimide matrix resin
- NASA-LaRC™ - IA – a polyimide matrix resin based on oxydiphthalic anhydride and 3,4'-oxydianiline, and encapped with phthalic anhydride, with a melt processability at a low temperature (325-350°C)
- NASA-LaRC™ - IAX – a polyimide matrix resin based on ODPA dianhydrides with chains encapped with phthalic anhydride, a modification of LaRC™ - IA backbone by incorporating a mixture of 90 mole percent 3,4'-oxydianiline (3,4'-ODA) and 10 mole percent of a rigid diamine, p-phylene diamine p-PDA (10%)
- NASA-LaRC™ 8515 – aromatic polyimide is based on 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) and an 85:15 ratio of 3,4'-oxydianiline (3,4'-ODA) and 1-,3-bis(3-aminophenoxy)benzene (APB). The polyimide chains are endcapped with phthalic anhydride.

Stochiometric Offset	*Molecular Weight*
2%	22000
4%	11400
5%	9600
5.5%	9100

The LaRC™ polyimides can be formulated at 2% to 5.5% offsets (from stochiometry) to produce polymers with various MW and flow characteristics. Table 1 shows the effect of different offset chemistries resulting in different flow characteristics. Synthesizing LaRC™ 8515 with a 5.5% offset yielded a 9,100 MW polyimide but previous experience indicated the properties would suffer. At 2% and 4% offset, thermoplastic impregnation into a tow might suffer. A 5% offset yielding 9600 MW was likely acceptable for fabrication of a thermoplastic tow. Sample amounts of several of these polymers were obtained and DSC scans were run.

Figure 4 shows the T_g values from the second DSC cycle for five synthesized polyimides considered. Of the five, NASA LaRC™ 8515 features both the highest offset giving the lowest viscosity and the highest T_g. LaRC™ 8515 is thus clearly preferred over the other polyimides evaluated. In the actual DSC scans, there were no indications of crystallinity. NASA investigators found that heating the polymer to 380°C (715°F) eliminated the chance that the 8515 polymer would recrystallize from the melt.

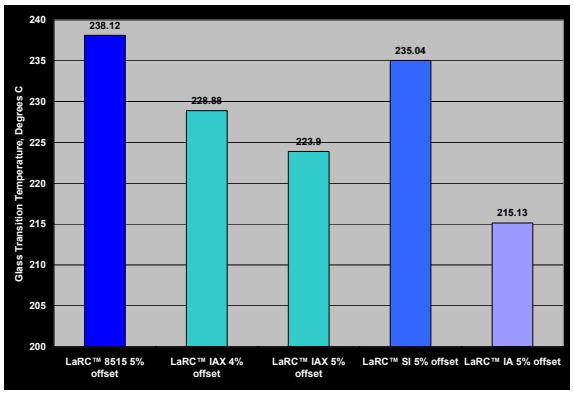

Figure 4 T_g values from the second cycle of the DSC scans.

Figure 5 compares the mechanical strengths for IM-7 carbon/NASA LaRC™ 8515 laminates made by Fiberite (now Cytec Engineered Materials) and by NASA with the

strength properties for IM-7 carbon/PETI-5 laminates made by NASA. Compared with PETI-5 composites, LaRC™ 8515 laminates have comparable OHC strengths, higher 0° flexure strengths, similar 90° flexure strengths, and higher interlaminar shear strengths, especially at room temperature conditions. Finally, LaRC™ 8515 laminates exhibit good solvent resistance.

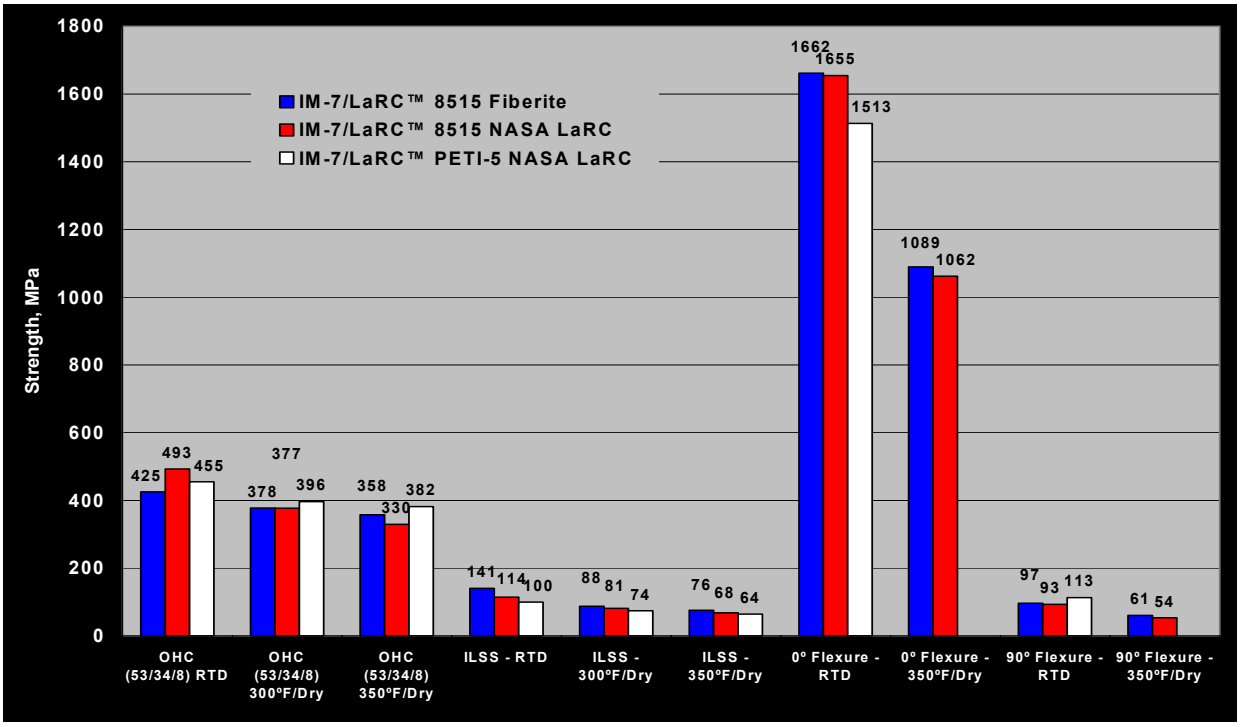

Figure 6 Strengths for IM-7/NASA LaRC™ 8515 compared with IM-7/PETI-5

The final polymer chosen for tow and part fabrication was NASA LaRC™ 8515, for its superior T_g, mechanical properties, good flow characteristics at melt, and no crystallinity after processing. The structure of LaRC™ 8515 is shown in Figure 7.

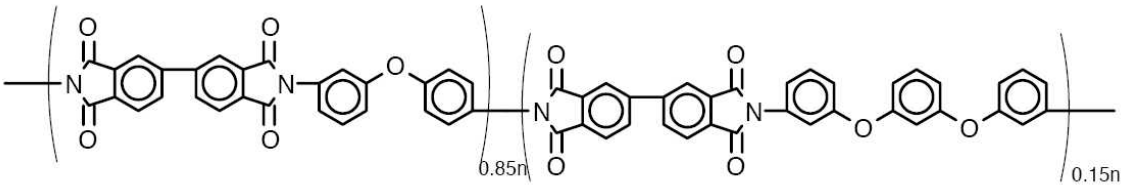

Figure 7 LaRC™ 8515

LaRC™-8515

RESIN SYNTHESIS AND TOW FABRICATION

Accudyne Systems cultivated a relationship with Imitech, a specialty synthesis chemistry firm with experience with NASA polyimides, to develop a route to make the LaRC™ 8515 dry powder. There were multiple goals in making the powder:

- Low volatiles, < 0.4%
- Uniform molecular weight distribution

- Small particle size in the polyimide powder
- Low melt viscosity – 5% offset should yield 9600 MW

Finally the polymer powder synthesis process had to be compatible with synthesizing larger quantities of powder for tow impregnation at large volumes and low cost.

Imitech informed us of the difficulty in synthesizing polymer with all four requirements met versus optimizing the synthesis for one characteristic. Imitech evaluated four powder synthesis processes, and settled on thermal imidization. This process made optimal powder with no crystallinity, low volatiles, and very fine, uniform particle size distribution.

Accudyne Systems used the Cytec Engineered Materials TIF line to fabricate AS-4 carbon/LaRC™ 8515 impregnated tow. The DSC scan for the impregnated tow showed a clear T_g at 237.17°C and no evidence of crystallinity via a cold crystallinity peak. Figure 8 shows four completed tow bobbins.

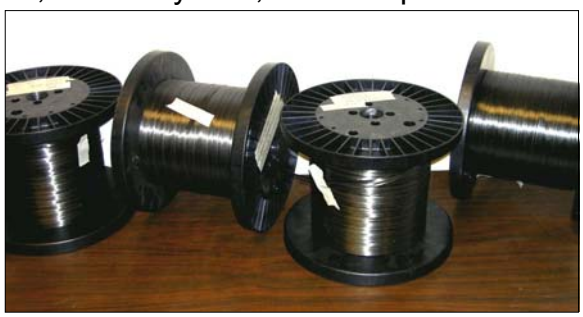

Figure 8 Four 8515 tow bobbins

Figure 9 shows the photomicrograph tow cross-section. The tow has reasonably good thickness uniformity, average fiber resin distribution, very good wet out, and some voids, thought to result from residual resin moisture. There is some room for improvement, but the tow is good enough quality for demonstration rings fabricated by filament winding.

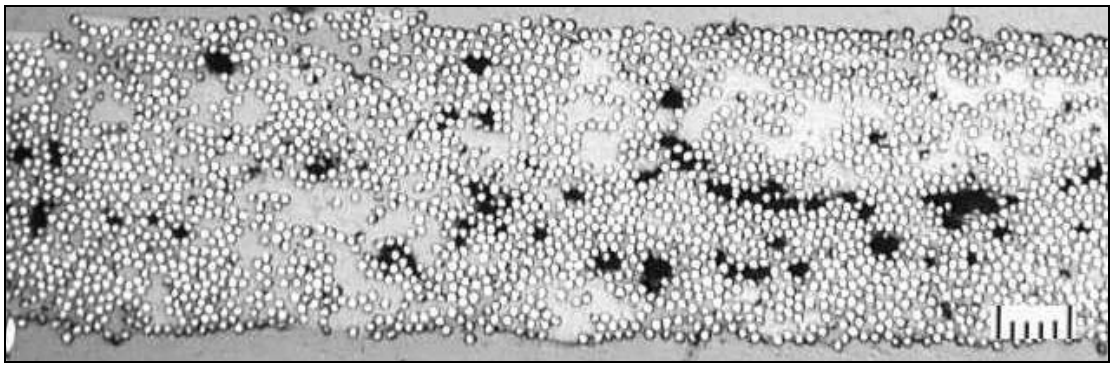

Figure 9 Sample photomicrograph at 100X of AS-4 carbon/NASA LaRC™ 8515 tow.

The tow was wound it into seven rings using thermoplastic filament winding and in situ consolidation. The ring's T_g is 235.8°C. Five of the seven rings are shown in Figure 10. Table 2 shows the filament winding process conditions.

Figure 10 The AS-4 carbon/NASA LaRC™ impregnated tow was filament wound into rings. This thermoplastic in situ consolidation process was completely out of the autoclave.

Table 2 The AS-4 carbon/NASA LaRC™ impregnated tow was filament wound into rings using the following out of the autoclave process conditions.

Thermoplastic Filament Winding Fabrication Data				
Part Number	**Tow Temp**	**Laydown Temp**	**Tow Tension**	**Comments**
	ºC	ºC	grams	
507141	390	390	3000	
507142	390	390	6000	
507143	360	360	3000	Tow was splitting
507144	360	360	3000	Repeat of 507143
507145	375	375	3000	
507146	400	400	6000	
507147	400	400	3000	

SUMMARY

A matrix resin evaluation and trade study was completed with commercial and NASA amorphous polyimides on the one hand, and with PEKK and PEEK mixed with POSS nanoparticles for accelerated crystallinity growth on the other. PEEK was found to crystallize sufficiently fast. PEKK crystallinity did not improve. A new thermoplastic impregnated material, 6 mm wide (0.25-in) AS-4 carbon/LaRC™ 8515 dry polyimide tow, was fabricated. Since LaRC™ 8515 is fully amorphous; it attains full properties following in situ consolidation, with no post processing required to build crystallinity. The tow in situ processing was demonstrated via in situ thermoplastic filament winding it into rings.

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