# DEVELOPMENT OF CYANATE ESTER BASED CARBON/CARBON COMPOSITES

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**SUMMARY**: Presented a successful development of Primaset PT-30 cyanate ester based carbon/carbon composites. The PT-30 resin has comparable char yield of phenolics, very low volatiles, low viscosity at 120°C, and no by-products during cure. Hence PT-30 is an excellent choice for resin transfer molding (RTM) and C/C composites manufacturing. Starting with a RTMed PT-30 composite panel, complete carbonization and densification cycles were established. Densification was performed by conventional as well as RTM infiltration methods. The RTM method was found to be better because of no drying and disposal of solvents, and the panel can be cured in the RTM mold. Two types of 8-harness woven carbon fabrics were used, namely, T650 and T300-heatset made from 3K yarns. Density and mechanical properties were found to attain nearly optimum values after two densification cycles. Properties of T300 fabric C/C composites agree with the literature.

**KEYWORDS**: Carbon/Carbon Composites, Resin Transfer Molding, Cyanate Ester, Carbonization, Densification, Infiltration, Tensile Modulus, Interlaminar Tension Strength.

## **INTRODUCTION**

Carbon/carbon (C/C) composites are attractive candidates for high temperature applications because of their superior thermal stability, thermal shock resistance, and highest energy absorption rate of any known material. The mechanical properties at temperatures greater than 300°F, C/C composites including commercial graphite are better than those of conventional materials such as aluminum. The application of C/C composites include heat-shields for reentry vehicles, gas turbine engine in-lets and nozzles, low-cost rocket nozzles, high speed brakes, and internal combustion engine cylinders and pistons. But C/C composites are expensive, because they either use expensive processing set-up such as chemical vapor deposition and/or require a very long processing time. Hence the applications are limited to cost insensitive components.

There are three ways of processing C/C composites[1-2]: (1) chemical vapor deposition (CVD), (2) pyrolysis of thermoset composites, and (3) pyrolysis of thermoplastic compos-

ites. All these methods are described in reference 1. In the CVD process methane gas is blown into the fabric under controlled cracking conditions such that conversion of the methane to pure carbon is carefully controlled. This deposition eventually fills the voids in the fabric to create the finished structure. However, extreme care must be taken to make sure that the outside layers do not get filled before the center ones. This method has a tendency to create dry inner plies, and therefore the method is generally limited to thin structures. Although the CVD process is attractive, its initial setup cost is high and has infiltration problems for thick and complex parts. In the second and the third methods, the fabricated polymeric composite (thermosets or thermoplastics) is pyrolyzed in a furnace filled with an inert gas to get the carbon matrix. The pyrolysis procedure is less complicated, needs less expensive set-up, but requires long processing time (of the order of months). The thermoplastic composites is a high pressure process, needs high pressure chamber to infiltration, curing and charring matrix. Among the three processes, the thermoset based method is most simple and requires less expensive to set up. Most of the work on thermoset composites have been using phenolic prepreg, because of its excellent char yield (about 65%). Phenolc resin gives out water as a condensation by-product during curing and pyrolysis, hence controlled heating rates and evacuation of gasses are needed to avoid damaging (delaminate) composite. Phenolic resin is not suitable for resin transfer molding (RTM) because of condensation byproducts. Resin transfer molding is a method of manufacturing complex shaped components at low cost. The use of both RTM and carbonization processes is attractive to manufacture complex carbon/carbon composite parts.



The objective of this paper is to develop carbon/carbon composites from RTM processed cyanate ester composites. Then evaluate their mechanical properties. The resin selected was Lonza Corporation's Primaset PT-30 cyanate ester. This

matrix has 65% char yield, less than 0.5% volatiles, no decomposition by-products during curing, and low viscosity (80cP) at 120°C. The chemical structure of PT-30 resin is shown in Figure 1. Two types of fabrics were selected, namely, Toray's T-300 heat stabilized at 2650°C and Amaco's T-650/35 fabric processed at 2500°C. Both fabrics were 8 harness satin weave and the 3k yarn size.

#### **DEVELOPMENT OF C/C COMPOSITE**

Processing of C/C composites from thermoset composite part is described here. Details of RTM processing of cyanate ester PT-30 are given in references 3 - 5. Converting a polymeric composite part into C/C composite is accomplished by carbonization and densification cycles. Carbonization is a careful process of charring polymeric matrix into carbon matrix. During this process, polymer shrinks and releases gaseous by-product. Amount of char yield depends on the resin system. The PT-30 has about 65%. The remaining 35% of the volume of resin matrix will be filled by resin infiltration and re-carbonization. This cycle is called the densification. Repeated densification yields high density, low void content, and improved mechanical and thermal properties.

#### **Carbonization Process**

Carbonization process consists of 1) Carbonization cycle, 2) Carbonization furnace setup, and 3) Analysis of pyrolysis gases and filtration system.

### Carbonization cycle

The charring process results in a porous structure because of vaporization of volatile parts of the polymeric matrix. The gaseous products released during the carbonization of the polymer



matrix has to diffuse through the composite material before escaping out. The heat up rate in the carbonization cycle determines the rate of release of these gases. At higher heat up rates the composite part could crack and delami-Hence it was renate. quired to determine the maximum heat up rate that will not damage the com-This was estabposites. lished from TGA and DSC

data. Figure 2 shows the weight loss of PT-30 as a function of temperature. The weight loss starts at about  $350^{\circ}$ C, reaches very high at  $450^{\circ}$ C, and starts decreasing from  $520^{\circ}$ C and reaches nearly zero at  $650^{\circ}$ C. Based on this data a preliminary heating cycle was selected (see Fig. 3). Heating rates varied from  $3^{\circ}$ C/min to  $1^{\circ}$ C/min. This heat cycle was



found to be too high, and resulted in completely delaminated panels after carbonization. Subsequently, the heating rate was considerably reduced to about 0.1°C/min for the temperature range of 350°C to 650°C. Several trial studies were conducted, which resulted in interesting results. One such is, by increasing the hold time at  $600^{\circ}C$ vielded higher char.

Based on this data, a modified carbonization cycle was established and it is shown in Fig. 3 by the solid line. The panel temperature, measured by the thermocouple attached to the panel, is shown by broken line. The total duration of each carbonization cycle was about four full days.

## Carbonization furnace set-up

The setup used for the carbonization is shown in figure 4. Carbonization of the composite panel was done in a furnace capable of temperatures up to  $1200^{\circ}$ C. A continuous flow of nitrogen gas into the furnace was maintained during the carbonization cycle to create a non-oxidizing environment. A positive pressure (of about 51 mm of water) was maintained inside the furnace to avoid any air leak. Composite panels were embedded in coke granules to avoid exposure to any trace oxygen during the carbonization cycle. The gaseous products of the pyrolysis were filtered through a water bath and an activated carbon filter before exhausting to the atmosphere.



Fig. 4: Carbonization and pyrolysis gas filtration system

# Analysis PT-30 pyrolysis gas and filtering system

Primaset PT-30 matrix is a new material and no pyrolysis data was available in literature. Therefore, GC mass spectroscopy of PT-30 pyrolysis gasses was conducted. Pyrolysis gas samples were collected from 350 to 950°C at increments of 50°C. Constituent gasses and their concentrations were measured at these temperatures. The predominant gases were Acetonitrile, Benzene, and Toluene. A simple filtering system was designed using a water bath and an activated carbon filter (see Fig. 4). Pyrolysis gasses after passing through the filtration system were analyzed and found to be environmentally safe to be released to the outside atmosphere.

# **Densification Processes**

Several alternative polymers/solvent solutions and infiltration procedures could be used to fill the voids in the carbonized composite material. The final density and the mechanical properties depend on the efficiency of infiltration of these polymers and their carbon yield. Two different infiltration procedures were evaluated, namely, conventional vacuum/pressure using PT-30/MEK solution and RTM infiltration using neat PT-30. These two methods are described here.

#### Conventional Vacuum/Pressure infiltration

The densification of C/C composite panel involved two cycles of infiltration followed by carbonization. The carbonization cycle selected is same as that was presented in the previous section. Several infiltrants were experimented, among them PT-30/MEK solution was found to be a better choice. This method referred to as the conventional infiltration process and it is described here. The process consisted of vacuum infiltration followed by a pressure infiltration. Vacuum infiltration was performed by placing the C/C laminate in a desiccator and vacuum pressure was applied to remove as much air as possible from the interior of the sample. The setup used for the vacuum infiltration is shown in Figure 5(a). After maintaining the vacuum pressure on the carbonized sample for 15 minutes, 50/50 mixture of PT-30 and MEK solution was poured into the tray by opening the plug valve 1, so that sample is submerged in the solution. The sample and the infiltrants was brought to atmosphere pressure. Then they were re-heated to  $72^{\circ}$ C and subjected to a pressure of 0.62 MPa in a pressure chamber (see Fig. 5(b)) for a period of 90 minutes. To maintain the temperature of the infiltrating solution close to 72°C, steel blocks heated to 72°C were placed inside the pressure chamber along with the sample. After the pressurization cycle, the sample surfaces were cleaned and dried at  $72^{\circ}$ C for eight hours



Fig. 5: Conventional Infiltration process.

Following the infiltration cycles, the samples were cured at 149°C for four hours. To prevent resin run-off during the cure cycle, the samples were kept rotating about an horizontal axis at the rate of about 2 revolutions per minute, by a motorized arm.

## **RTM Infiltration Process**

Two main disadvantages of conventional infiltration processes were: drying solvents and disposing excess solvents. Both need laborious and time consuming procedures and has low efficiency in filling the voids because the presence of solvents, which eventually evaporate. An alternative procedure for infiltration is proposed. In this procedure the vacuum pressures and the resin pressures available in the RTM set-up was used. This set-up is same the RTM process used for manufacturing the composite part. The advantages of this procedure is the elimination of solvents, faster infiltration, attainment of higher temperature and pressure during densification, and curing the densified part in the mold.



Fig. 6: RTM infiltration set-Up

## Infiltration Mold Set-up

Carbonized quarters of the C/C composites were placed in the mold with fiberglass composite separators between them to keep them in position. These separators prevent the quarters from sliding into each other and crushing during the resin injection phase. The RTM setup is shown in Fig. 6. A Graco pump was loaded with degassed Primaset PT-30 cyanate ester matrix and preheated to 79 °C. The pump, mold and vacuum pump were connected together with vacuum tight copper plumbing and preheated with heat straps. The inlet side (between the pump and the mold) of the plumbing was heated to 79 °C. A vacuum of 690 mm (27 inches) of mercury was maintained for the length of time required to fill the mold with the PT-30 resin. The outlet (between the mold and the matrix trap) was heated to 93°C. The press platen was heated to  $177^{\circ}$ C and held with a 2.1 MPa (300 psi) clamping pressure.

# Infiltration Procedure

During the mold evacuation, the vacuum tightness of the mold and plumbing was checked periodically to make sure all connections and seals were vacuum tight. For this process to be effective, it was critical that a good mold vacuum was maintained. If the vacuum was lost during injection, the infiltration would not be successful. The vacuum line was turned off using the valve 2 and the hot resin was pumped into the evacuated mold containing the preform at about 15 cc/minute and at 0.55 MPa (80 psi) pressure. As the resin started to flow, the metering valve was adjusted to achieve the required flow rate. This process would take about 15 minutes. Again as the resin began to flow into the matrix trap, the matrix burp valve 2 was turned off. This allowed the liquid matrix pressure to reach 0.55 MPa. The line was burped several times to ascertain the last pockets of air in the mold is escaped. After the resin flowed freely without visible air bubbles or splatter, the burp valve was turned off and the matrix pressure of 0.55 MPa was attained. The pump pressure was then increased to 2.1 MPa at the end of the burping and the cure process continued for a total time of five hours. The plumbing lines between the mold and the resin trap and between the mold and

the metering valve may be cleaned and reused or discarded. The plumbing between the pump and the metering valve can be flushed with resin and reused without further cleaning. At this time the panel quarters are ready for the re-carbonization process, as explained in the carbonization section.

# **EVALUATION OF CARBON/CARBON COMPOSITES**

As cured composite panels were manufactured by RTM process. The panel dimensions were 305x305x2.6-mm. The panel was divided into four parts (see Figure 7). The first quarter was

As Cured	1st Carbonization
2nd Carbonization	3rd Carbonization
1st Infiltration	2nd Infiltration

used for determining the mechanical properties of the as cured laminate. The remaining three quarters were carbonized. The second quarter was carbonized and measured mechanical properties. The third quarter was carbonized + densified (infiltration+ carbonization) and then measured mechanical properties. The forth quarter was carbonized. twice densified and measured properties. Measured densities and mechanical properties of all three quarters are summarized in the next section. The mechanical properties include inplane modulus. strength and fracture stain, and interlaminar tension strength. Other tests are being planned and continued.

Each of the quarter was divided into specimens for tensile, and interlaminar tension (Button



specimen layout for the first quarter. Specimens for 2nd, 3rd, and 4th quarters were laid symmetrically to the first quarter. Specimen configurations for tensile and interlaminar inplane tension tests are shown in Fig 8 (b) and

(c), respectively.

## **Bulk Density**

The bulk density was measured from the overall volume and mass of the quarter panel. After the panel was made and the edges trimmed, length and width were measured at three points (two ends and one midsection) and the thickness was measured at eighth points (four corners and four midpoints on edges). The volume was calculated by multiplying the average length, the width, and the thickness. The mass of the panel was divided by the volume to obtain the density. Densities were measured at the end of each carbonization cycle.

Table 1. Densities of T650 and T300 fabric carbon/carbon composites						
		Density, gm/cc				
			Carbonization Cycle/Quarter			
Panel	Infiltration	As Cured	1/2	2/3	3/4	
T650/PT-30						
2NT	CON	1.54	1.24	1.34	1.4	
T11	RTM	1.54	1.35	1.44	1.47	
T12	RTM	1.52	1.32	1.49	1.52	
T300/PT-30						
T3	CON	1.56	1.42	1.53	1.54	
T13	RTM*	1.60	1.41	1.56	1.61	
* 7. 0						

rizes the densities of T650/PT-30 and T300/PT-30 C/C composite panels at various levels of densifications. The first quarter was used for as cured properties. Carbonized

Table 1 summa-

\* Preform was tackified with P-T60, 10% by fabric weight

Carbonized quarters are

designated by i/j, i represents the carbonization cycle and j represents the quarter number of the panel. The table includes results of conventional (CON) and RTM infiltration processes. The C/C Composite density increases with number of densifications. The conventional infiltration process yields less dense composite than RTM infiltration. The maximum density achieved by conventional infiltration was about 1.4 gm/cc for T650 fabric and 1.54 for the T300 fabric. Whereas RTM infiltration yields 1.5 and 1.6 gm/cc for T650 and T300 fabrics, respectively. The Theoretical limits for these two fabrics were 1.6 and 1.7 gm/cc. But the practical values reported by the industry for T300 fabric. The RTM infiltration process is found to be simple and efficient for flat panels and complex parts.

# Mechanical Properties of T650/PT-30 C/C Composites

Table 2 summarizes the inplane tensile modulus, strength, fracture strain and interlaminar tension strength of T650 fabric composites. Inplane properties were measured by tension coupon (see Fig 8(b)) using a displacement control test (0.51 mm/min). Tensile strength and fracture strains listed are at fracture load. The interlaminar tension strength was measured from 28.6-mm diameter circular disk specimen subjected transverse tension load. This test is referred to as the button test. The top and bottom surfaces of the specimen were bonded to aluminum cylinders, which are coaxial by an aluminum sleeve. The experiment was conducted by displacing the two cylinders apart at 0.05 mm/min. Fracture load was recorded. This is a delicate test. Any slight non-axiality of load due to slackness of the sleeve could induce bending and causing premature failure. Results in Table 2 includes both conventional and RTM infiltration processes. In both cases, the general trend is that the elastic strength, and fracture strain increase with number of carbonization cycles. In conventional infiltration

Table 2. Mechanical properties of T650/PT-30 carbon/carbon composite					
		Carbonization Cycle/Quarter			
Properties	Infiltration	1/2	2/3	3/4	
In-plane tensile test					
Modulus, GPa	CON	7.5 (0.5)	9.1 (1.0)	9.8 (0.1)	
	RTM*	8.4 (0.6)	9.6 (0.6	8.8 (1.6)	
Strength, MPa	CON	82.3 (0.7)	97.6 (1.6)	103.6 (0.2)	
	RTM	81.8 (0.6)	94.1 (0.7)	93.3 (0.8)	
Fracture strain, %	CON	0.16 (0.01)	0.31 (0.24)	0.15 (0.01)	
	RTM	0.17 (0.02)	0.14 (0.02)	0.11 (0.03)	
Interlaminar tancion test					
Internaminar tension test					
Strength, MPa	CON	-	-	1.31 (0.7)	
	RTM	-	1.30 (0.5)	0.97 (0.5)	
* 10% PT-60 tackifier was used					
** Standard deviation					

process, the increase from 1<sup>ST</sup> to 3<sup>rd</sup> carbonization was about 30% for elastic modulus and 25 for tensile % strength. However, for some reason. fracture strain decreased from  $2^{nd}$  to  $3^{rd}$ carbonization cycles. In RTM infiltration, all the properties decreased from 2<sup>nd</sup>

to 3<sup>rd</sup> cycles. The second cycle gave better properties than the third cycle. This maybe due to damage introduced by high-pressure infiltration in RTM process. The values within the parenthesis represent the standard deviation of the data from four samples. The interlaminar tension strength was about 1.31 MPa from conventional process and 1.30 MPa from RTM (2 cycles). Notice, that the interlaminar strength data has large standard deviation.

## Mechanical Properties of T300/PT-30 C/C Composites

Table 3 summarizes inplane tensile and interlaminar tension properties of T300/PT-30 C/C composites. All properties, in both infiltration processes, increased with number of carbonization cycles. The increase from  $1^{st}$  cycle to  $3^{rd}$  cycle was about 59% for elastic modulus and 88% for tensile strength in conventional infiltration. For some reason, the fracture strain

Table 3. Properties of T30				
		Carbonization Cycle/Quarter		
Properties	Infiltration	1/2	2/3	3/4
In-plane tensile test				
Modulus, GPa	CON	80.1 (0.7)**	126.9 (1.2)	127.0 (1.6)
	RTM <sup>*</sup>	-	104.8 (0.7)	118.3 (1.0)
Strength, MPa	CON	163.5 (2.1)	233.4 (0.9)	308.1 (0.7)
	RTM	-	251.2 (1.1)	308.1 (0.2)
Fracture strain, %	CON	0.43 (0.12)	0.20 (0.05)	0.28 (0.03)
	RTM	-	0.40 (0.10)	0.25 (0.03)
Interlaminar tension test				
Strength, MPa	CON	-	_	3.4 (1.0)
	RTM	0.40 (0.26)	-	2.0 (0.2)
* 10% PT-60 tackifier wa				
** Standard deviation				

first cycle data was not available for RTM process, but it showed general increases from cycle to cy-The final cle. properties achieved from the conventional infiltration after three carbonization cycles were: elastic modulus of 127.6 GPa , tensile strength of

decreased.

The

308.1 MPa, fracture strain of 2.9%, and interlaminar tension strength of 3.4 MPa. Using RTM process, the properties at the end of the 3<sup>rd</sup> cycle were, 118.3 GPa of elastic modulus,

308.1 MPa of tensile strength, 0.25% of fracture strain, and 2.0 MPa of interlaminar strength. These values are in the range of data reported by the industry.

## **CONCLUDING REMARKS**

This paper presents a successful development of Primaset PT-30 cyanate ester based carbon/carbon composites. The PT-30 has comparable char yield as that of phenolics (65%), very low volatiles, low viscosity at 120°C, and no by-products during cure. Hence PT-30 is an excellent choice for resin transfer molding (RTM) and C/C composites manufacturing. Starting with a RTMed PT-30 composite panel, complete carbonization and densification cycles were established. Duration of each carbonization cycle was about four days. Densification was performed by conventional as well as RTM infiltration methods. The RTM method was found to be better because of no drying and disposal of solvents, and the panel can be cured in the mold. Two types of 8-harness woven carbon fabrics were used, namely, T650 and T300-heatset made from 3K yarns. Density and mechanical properties were found to attain nearly optimum values after two densification cycles. Density attained was 1.54 gm/cc for T650 and 1.6 gm/cc for the T300 fabric. The T650 fabric C/C composites had tensile modulus of 9.8 GPa, strength of 103.6 MPa and fracture strain of 0.15%, and interlaminar tension strength of 1.31 MPa. The T300 fabric C/C composites had tensile modulus of 127.6 GPa, strength of 308.1 MPa and fracture strain of 0.28%, and interlaminar tension strength of 3.4 MPa. Properties of T300 fabric C/C composites agree with literature.

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