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A New NASA LaRC Multi-purpose Prepregging Unit

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ABSTRACT

A multi-purpose prepregging machine has been designed and built for NASA Langley Research Center. The machine has numerous advantages over existing units due to its various modular components. Each of these can be used individually or simultaneously depending on the required prepregging method.

A reverse roll coater provides the ability to prepare thin films from typical hot-melt thermoset formulations. Also, if necessary, the design allows direct fiber impregnation within the reverse roll coater gap. Included in the impregnation module is a solution dip tank allowing the fabrication of thermoplastic prepregs from solution. The proceeding modules within the unit consist of four nip stations, two hot-plates, a hot-sled option and a high temperature oven. This paper describes the advantages of such a modular construction and discusses the various processing combinations available to the prepregger.

A variety of high performance prepreg material systems were produced on IM7 (Hercules) carbon fiber. These included LaRC™ RP46, a PMR-type resin processed from methanol and two polyamide acids, LaRC™ IA and LaRC™ ITPI, prepregged from N-methyl pyrrolidinone (NMP). Parameters involved in the production of these prepreg materials are presented as are the mechanical properties of the resulting good quality laminates. A brief introduction into the existing prepregging science is presented. Topics relating to solution prepregging are identified with a focus on the current research effort and its future development.

Key Words: Prepregs, Equipment and Machinery

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1.0 INTRODUCTION

As part of a polymer composite materials research program, a multi-purpose prepregging machine has been designed and built for NASA Langley Research Center (LaRC). The machine is capable of impregnating continuous fibers with high performance polymeric resins and has a number of advantages over existing units due to its various modular components. Each of the modules can be used individually or simultaneously depending on the required prepregging method.

This paper describes the advantages of such a modular construction and discusses the various processing combinations available to the prepregger. An analysis of the design and operating features of the prepreg tape machine was conducted to provide insight into the full utilization of the machine (1).

2.0 NASA LaRC Multipurpose Prepregger

The prepregger consists of various modules and is shown schematically in Figure 1. These modules are combined in different configurations depending on the method of impregnation.

2.1 Modules Spools of fiber tow are placed on the creel and each tow is threaded into the machine. The creel is split into two sides, each side consisting of five rows of ten fiber spools. Located in front of the fiber creels are a series of horizontal bars. When each tow from its corresponding row has been threaded over each bar on either side of the creel, the comb is threaded in a systematic manner (1) to prevent tow crossing and fiber damage.

The reverse roll coater module is traditionally used to prepare films onto release paper from hot-melt resin systems (Figure 2). The resulting films are brought into contact with the dry fiber web at the first nip roller station where the resin is released from the paper and impregnated into the web (Figure 3). The filming process is controlled by the gap dimensions at the coater (1). Resin is sheared onto the paper surfaces as the paper passes between the applicator and metering roll as illustrated in Figure 2. The rollers may be heated to control resin viscosity; also, if desired the dry fiber web can be passed through the roller gap and impregnation can be performed at this position.

Two dip tanks are available for running a solution impregnation operation. One tank is 38.1cm (15 inches) long and is used for prepreg tape 30.5cm (12 inches) wide. The tank has a maximum capacity of 3.3 liters and minimum capacity of 0.86 liters. The second is 12.7cm (5 inches) wide and was specifically designed for prepreg tape up to 7.62cm (3 inches) wide utilizing polymer solutions in research quantities. The maximum and minimum quantities for this second tank are 1.5 and 0.32 liters respectively. The dip tank assembly consists of three subassemblies. The first is the tank carriage and guides. The dip tank raises up to the fiber path which is pre-threaded for impregnation. The second subassembly consists of the dip pans and submerged impregnation bars hung from two steel rods over which the dry fiber web is passed. The impregnation bars are split in two and provide the prepregger with the option of passing the fiber web over two tiers, or kept as one unit and passed over the bottom tier. A heating unit is located underneath the dip tanks to provide viscosity control. By increasing the temperature, the viscosity may be lowered while maintaining a constant weight-percent loading of solids in the solution. The third subassembly is the metering rod assembly. The gap at the metering rods controls the prepreg resin content and is the most important part of the solution coating process. Resin content may be controlled by adjusting both the metering bar gap and/or the pressure. The gap is adjusted using wedge blocks that move inward to close the bars together. An adjustment screw is turned clockwise to adjust the metering gap and feeler gages are used for monitoring the gap dimensions.

The first nip station is used in conventional prepregging but it is not used in solution coating since the wet web is not amenable to nipping until initial drying has taken place in the first hot-plate. This first nip station is used for the resin film transfer process to impregnate fibers with hot-melt materials that have already been pre-filmed (Figure 3). The rollers have the option of being heated, if desired; this gives control over resin viscosity of hot-melt systems.

All nip rollers in the machine provide gap dimensions that remain constant along the roller length. A tuning bar is located in front of each roller and allows each wedge block, at either side of the roller, to be individually moved while maintaining the other stationary. Moving a particular wedge forwards or backwards provides the operator with the ability to raise and lower each side of the roller. Feeler gages are used to monitor the consistency of the gap dimensions. Two locks provide access to each wedge block movement and are situated on this bar and can be individually released.

Initial solvent devolatilization is achieved with hot-plates, Figure 1. The bottom paper remains on the underside of the prepreg to protect the plates from resin build-up. At the beginning of a run, ovens and hot-plates are raised to operating temperature prior to start-up. During operation, heat from the hot-plates is taken away by solvent evaporation and convection to air and by heating the web and paper as they pass over the plate. Since the prepreg web is very thin, its capacity to carry heat is small relative to the heat required for solvent evaporation.

To achieve a desired fiber aerial weight while maintaining fiber uniformity across the width (requiring tow-tow adhesion and no splits or gaps within the web), is an important aspect of product quality. Nip stations 2 and 3 are essential in the elimination of splits and gaps formed in the prepreg web during the devolatilization process. At this primary control point, the following parameters may be adjusted to eliminate splits:

- Gap width between rollers, creating resin squeeze out and lateral movement of the fibers
- Roller temperature (effects the flow properties of the prepreg)
- Back pressure to the nip rollers (effective when the rollers ride entirely on the web surface and are not forced apart by the wedge blocks)

Other parameters that are controlled/adjusted to contribute to the elimination of gaps and splits are:

- Web speed (this effects the pressure exerted on the web and the residence time in the devolatilization units)
- Web solution concentration (a function of the hot plate temperatures and original solution concentration since the polymer concentration in the web changes the web elasticity)

The above parameters help establish the range of operating conditions under which gap free prepreg can be produced. These conditions essentially define the operating protocol for this machine. As discussed later, this protocol will also include the use of the Prepreg Flow Number, (PFN), (2-4) that provides a temperature-pressure-velocity superposition relationship for the prepregging process.

A critical unit within the prepregger is the oven since it provides control over the solvent content in the final product. Operating variables which can be changed to remove solvent are oven temperature, air flow and web speed. Hence, residence time and temperature become important parameters in the equations for heat and mass transfer that describe the solvent vapor removal in the ovens (1).

The oven is heated by hot air. Air flows counter to the direction of travel of the prepreg web. This has the effect of both heating the solution within the web to vaporize the solvent and to sweep away solvent from the prepreg surface. Solvent evaporation has a cooling effect and should be a concern during the heat transfer analysis. The mass transfer process of devolatilization consists of solvent evaporation and diffusion through the prepreg thickness to the surface and convection into the air.

Nip station 4 provides the last opportunity to nip the prepreg web and to remove the remaining gaps and splits. The roller gap width and the roller pressure exerted on the web are the major parameters that can be changed to attain such goals. The solvent content within the prepreg must be monitored and controlled prior to this nip. Hence, resin content, distribution, and fiber aerial weight may be affected depending on the resin's prior history through the other modules.

The chill plate is located between nip station 4 and pull-roll station and cools the web prior to take-up and storage. It is capable of maintaining temperatures between 5-15°C. The chill plate is raised 0.95cm (3/8 inch) above the web line to ensure that the web remains in contact with the plate. The chill plate tends to "freeze" the resin and reduce flow. therefore, any effects on resin impregnation at the pull rollers are minimal. In turn, the lack of flow which freezing imparts on the prepreg web prevents resin loss through excessive squeeze-out and adhesion to the take-up paper. The chill plate may, therefore, have some effect on the final product quality in terms of reducing damage on wrapping as the release paper is removed.

The hot-sled module is designed to provide pressure needed to achieve impregnation during processing of high viscosity polymer solutions or melts (1). The hot-sled has several functions.

- It provides through-the-thickness penetration and wetting.
- It provides sufficient pressure to the fibers to create lateral movement and fiber nesting which helps eliminate splits and gaps.
- It increases contact pressure time. This improves fiber matrix adhesion of pre-impregnated material. Such material would include polymeric powders that coalesce together more efficiently under longer contact pressure times.
- It provides an alternate approach when nip stations 2 and 3 alone are inadequate to produce good quality product.

2.2 Safety Features Emergency stop buttons are located at several positions along the machine. The pneumatic circuitry is interfaced with the electrical circuitry and can be activated by pushing an emergency stop button when hazardous conditions such as loss of air flow in the ovens, excess solvent concentration, a high temperature alarm or interruption of the light screen occur. In the event of an emergency stop condition, the following steps automatically take place.

- All nip rolls open.
- The drive roll opens.
- Backing and metering rolls open.
- Heat to hot-plates and ovens is shut off and reset to a 260°C maximum.
- Electrical power to motors shuts off.
- Motor clutches disengage.
- Rewind clutches disengage.
- All sensors and instruments remain operable and continue to monitor the situation.

The emergency stop condition remains until the emergency condition has been cleared and the reset buttons on both the control cabinet and the control console have been pressed.

Since this machine can prepreg from solution, solvent vapor concentration must be detected to ensure a safe atmosphere and to prevent the possibility of explosion. Therefore, a real-time gas detection system has been designed into the system. Samples are drawn from the three hot-plate and oven assemblies using a Venturi vacuum pump. The sample gas is detected by a combustible sensor and a signal is sent to the system module where the concentration is displayed. If the concentration of any of the channels exceeds 25% of the lower explosion limit (LEL) of the solvent being tested (when calibrated correctly), the system will shut off all the heater and motor power to the machine.

The gas detection system is a back-up for the air flow control system in the oven or hot-plate hoods. An air flow sensor is located in the duct connecting all three hoods. If the blower is not on, or fails, all heating elements turn off until the problem is corrected. As a general rule, about 283,000 liters (10,000 cubic feet) per minute of air is mixed with every 3.785 liters (1 gallon) of evaporated solvent. If the air flow through the ovens is adequate, the system is safe without the gas detection system.

The required amount of air flow is based on line speed, percent solvent in solution and resin content and needs to be calculated (1) prior to every run. The air flow in each oven is adjusted accordingly with a damper. Make-up air in the hot-plates comes from the surrounding room; oven make-up air is supplied by an inlet blower.

All sprockets and chains are open in the back of the machine to facilitate maintenance of the bearings, chain, brakes and clutches. A light curtain which operates the entire length of the machine is used to prevent contact with moving parts. If the light screen is interrupted by an object, the motors stop and will not restart until the restart button is pushed. Indicator lights located on the body of the curtain are lit when the screens are operating correctly with no obstacles breaking the beam.

The chains are protected from the front operating side by chain guards which prevent the operator from inadvertently reaching the chain. All guards can be easily removed if required.

2.3 Operating Procedures The NASA machine is capable of fabricating pre-impregnated tape from a variety of material forms by the following methods:

- Solution prepregging with a dip tank
- Solution and hot-melt prepregging at the reverse roll coater
- Prepregging pre-cast films made on- or off-line at the reverse roll coater
- Collation and fusing of pre-impregnated tows.

These methods can be combined depending on the resin properties and solvent systems. Design equations describe the necessary procedures to estimate the required gap setting (1).

2.3.1 Reverse Roll Coating The off-line film coating process is most commonly employed to doctor onto release paper a film using hot-melt thermosets. The unit, illustrated in Figure 2, uses three rollers. Resin is applied to the preset gap between the backing and metering rolls, carried through the metering gap and pressed against the release paper surface which travels on a third roller in a counter direction. A thin resin film adheres to the paper surface after the resin profile has been sheared by the opposing motion of paper and resin. This shear splitting effect must be taken into account in calculating the metering gap dimensions. Prepreg resin content is primarily controlled by the film's resin aerial weight (1).

2.3.2 Direct Impregnation An alternative to the off-line paper coating process described above involves on-line coating which is similar to hot-melt prepregging. The fiber is impregnated on-line within the gap between the metering and applicator rolls, as illustrated in Figure 4. This process is typically performed with resin solutions that possess high viscosity's and can not be impregnated by the solution dip tank process. A standing puddle of resin is maintained at the gap with dams at either end of the rollers. Top and bottom release papers are brought into the metering bar gap along with the fiber web and resin system. Impregnation takes place at this junction.

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* Use of trade names or manufacturers does not constitute an official endorsement, either expressed or implied, by the National Aeronautics and Space Administration.

2.3.3 Solution Dip-Tank The solution dip-tank and metering rods are shown in Figure 5. The gap between the metering rods is adjusted to control the amount of solution added to the fiber web. Impregnation pressure is a combination of mechanical and capillary pressures. A detailed description of how the impregnation bar geometry inside the dip tank effects these parameters is discussed elsewhere (1).

3.0 Results and Discussion

3.1 Resin Systems Processed The polymer matrix systems that have been prepregged with this machine are presented in Table I. Both hot-melt and solution techniques have been employed. For the latter, both N-methyl-pyrrolidinone (NMP) and methanol were the solvents of choice. Other high performance resins such as the LaRC™ RP46 system were studied. In this case methanol was the solvent.

3.2 Operating Conditions The prepregger processing parameters set forth in Table II need to be established for each individual prepregging run. The number of variables and conditions that need to be considered illustrate the complexity of the prepregging operation.

3.3 Properties A comparison of mechanical properties was made between laminates fabricated using prepreg made on the tape machine and prepreg prepared with a drum winder. A 30% solids solution of the LaRC™ IA amide acid in NMP was utilized in both prepregging operations. The results are given in Table III where 0° flexural strength and moduli show substantial improvements when a laminate was prepared using tape machine prepreg compared to laminates manufactured with drum-wound prepreg. The results are normalized for 60% fiber volume fraction.

3.4 Prepregging Science and Technology The most critical process during prepregging is the impregnation of the dry fiber web by the resin. Depending on how the impregnation takes place, i.e., through filming techniques or via the solution impregnation method, the lateral resin impregnating flow into the fibers must be addressed in terms of (a) the mechanical pressure being applied and (b) the capillary pressure found within the web pores. Capillary pressure is created by the fiber packing geometry and the solution-fiber wetting characteristics.

Flow modeling equations (2-5) are available for analysis of the prepregging process. Darcy's law is used to describe the impregnation rate, v, in the thickness, Y, direction. It is a function of the resin viscosity, μ, fiber bed permeability, kf, and the applied pressure, P.

$$v = \frac{k_f}{\mu\ (T)}\left(\frac{dP}{dY}\right) \tag{1.}$$

This equation for resin flow through the web is the starting point for most prepregging analysis. Equations are needed to describe both impregnation through permeation and the resistance of this impregnation due to the resin's viscous flow. Seferis (2-4) has discussed fiber impregnation by introducing the term PFN (prepreg flow number) which describes the interrelationship between temperature, pressure and production rate. It is dependent on the operating conditions of the prepregger and the geometry of a fibrous preform.

$$\mathrm{PFN} = \frac{K P_{eff}}{\mu V Y_f} \tag{2.}$$

K = Permeability
P_{eff} = Effective pressure
μ = Viscosity
V = Production rate
Y_f = Thickness of a collimated fiber tow

Seferis utilized Darcy's law with the mass and momentum conservation relationships to develop the PFN concept and discusses how it describes the interrelationship between temperature, production rate and impregnation pressure(2-4). The PFN number is the ratio of the impregnating forces to the resistance for impregnation. A PFN greater than one implies that resin is easily impregnated into the fiber web and a PFN less than one indicates that the resistance to viscous flow is high and the prepreg may be poorly wet-out. An excessively high PFN number could be detrimental to the hot-melt prepregging process. Too much flow may create resin starved prepregs due to excessive squeeze flow of the resin. The PFN approach was used to analyze the impregnation of fiber webs with hot-melt thermoset films. The PFN approach could be extended when impregnation occurs through a solution dip tank (1), although further parameters may need to be considered. Such parameters may include the change in the viscoelastic nature of the impregnated web as solvent is removed during the drying process and also the effect of entrained air which is brought into the dip tank by dry fiber tows.

In a solvent impregnated web, which is rich in solvent as well as polymer and fiber, the web becomes more elastic as solvent is removed during the drying process. The reduction in its viscous behavior and a concomitant increase in its elastic behavior provides a prepreg web that is more difficult to process. A major problem occurs when the increase in the web's elasticity causes web splitting and creates gaps during the drying oven process. This is an area for future analytical development.

3.5 Design Correlation's Operating experience has shown that the equations based on geometry and density used to calculate the metering bar gap dimensions are insufficient (1). Often, to achieve the desired **prepreg resin content**, the calculated metering bar gap setting had to be significantly increased.

Two experiments were performed to study this problem. Two 30% solids solutions of LaRC™ ITPI in NMP and Amoco's Udel Polysulfone in NMP were employed. These solutions were prepregged with Hercules IM7 carbon fiber. The metering bar gap was opened at 0.001 inch increments and prepreg samples taken. Each sample was B-staged at 250°C for 2 hours. Acid digestion studies were performed to determine the resin solids content. In Figure 6 the solids content on the prepreg is plotted versus the actual metering bar gap size. A curve representing the calculated theoretical prepreg solids content at various metering bar gap dimensions is also presented. A clear discrepancy can be observed between the calculated and actual percent solids on the prepreg. One possible explanation, which deserves further study, is that the prepreg web is not fully impregnated. The large amount of air bubbles observed within the dip tank suggests that entrapped air within the impregnation zone changes the solution density, thus the geometry and density equations may not be followed. A possible starting point for further study could utilize the calculation of the Prepreg Flow Number (PFN) (2-4) for each solution prepregged within the dip tank impregnation zone.

Devolatilization of solvent is a difficult process. The temperatures required to remove high boiling point solvents may chemically advance the resin beyond an acceptable level where processability is diminished. In certain instances where polyamide acids were being used, the excessive heating may cause the imidization reaction to proceed. This may reduce the processability of the resulting polymer.

The **removal of splits** is a vital process in the production of quality prepreg. It has been noted that the formation of gap-free prepreg at nip stations 2 and 3 is extremely important in producing good quality product. When gap-free prepreg enters the oven, the removal of more solvent may lead to the formation of more gaps. However, gap formation could be reduced by increasing fiber aerial weight at the dip tank. This ensures that the collimated fiber tows are kept together at the hot-plate and are less likely to split when the prepreg web is dried further in the high temperature oven.

In the two experiments discussed above, volatiles can be removed quite readily by increasing the oven temperature. For example, an increase in oven temperature from 188°C (370 °F) to 221°C (430 °F) decreased the percent volatiles by approximately 6%. However, the quality of the resulting prepreg was found to deteriorate as the temperature increased and the gap formation became more pronounced.

In an attempt to remove these gaps, the width of the dry web was decreased at the point of entry into the dip tank. It was thought that the desired width could still be obtained by controlling the gap size at the second nip station. In practice, this was found difficult to achieve. A decrease in the gap width tended to squeeze out excess resin rather than increase the width of the tow. That is, resin flows in the transverse direction more readily than carbon fibers move.

It was noted that the best quality prepreg was obtained when the prepreg web exiting from the #3 nip was completely gap-free. In these cases, further solvent removal tended to contract the web and few gaps were observed.

3.6 Future Work As discussed above, further development studies are required to establish design and operating information from which good quality prepreg can be produced. Theoretical and experimental studies relating to prepreg resin content, solvent devolatiliztion and the elimination of splits and gaps in the product are needed.

4.0 REFERENCES

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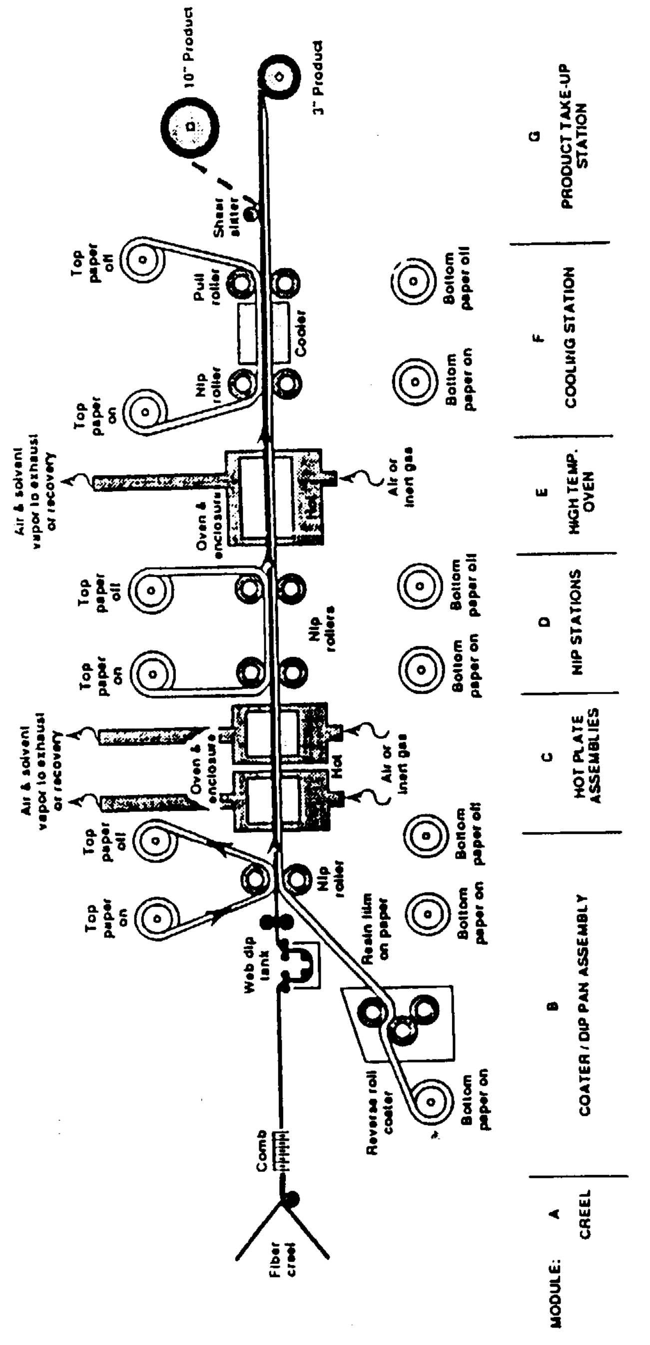

Figure 1. Schematic Diagram of the Tape Machine Modular Components.

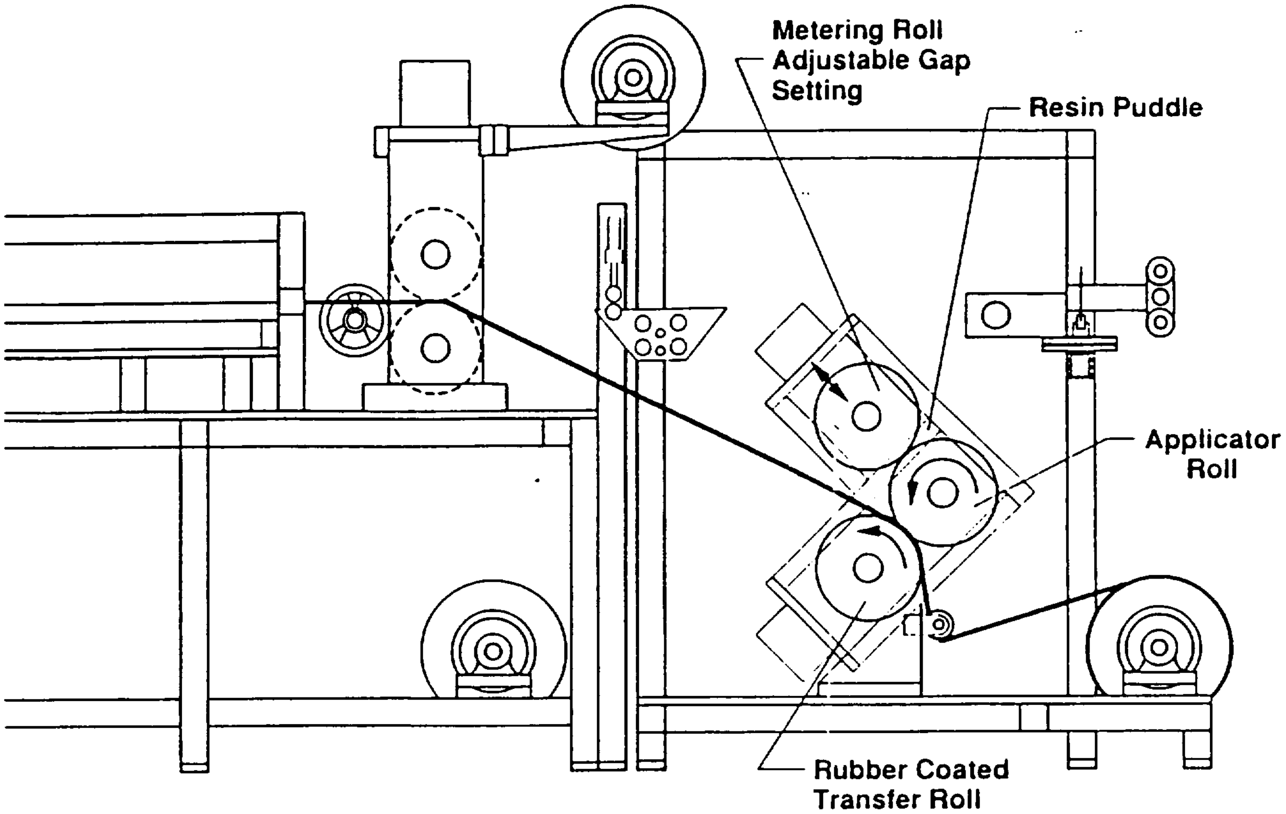

Figure 2. The Film Coating Process Using the Reverse Roll Coater.

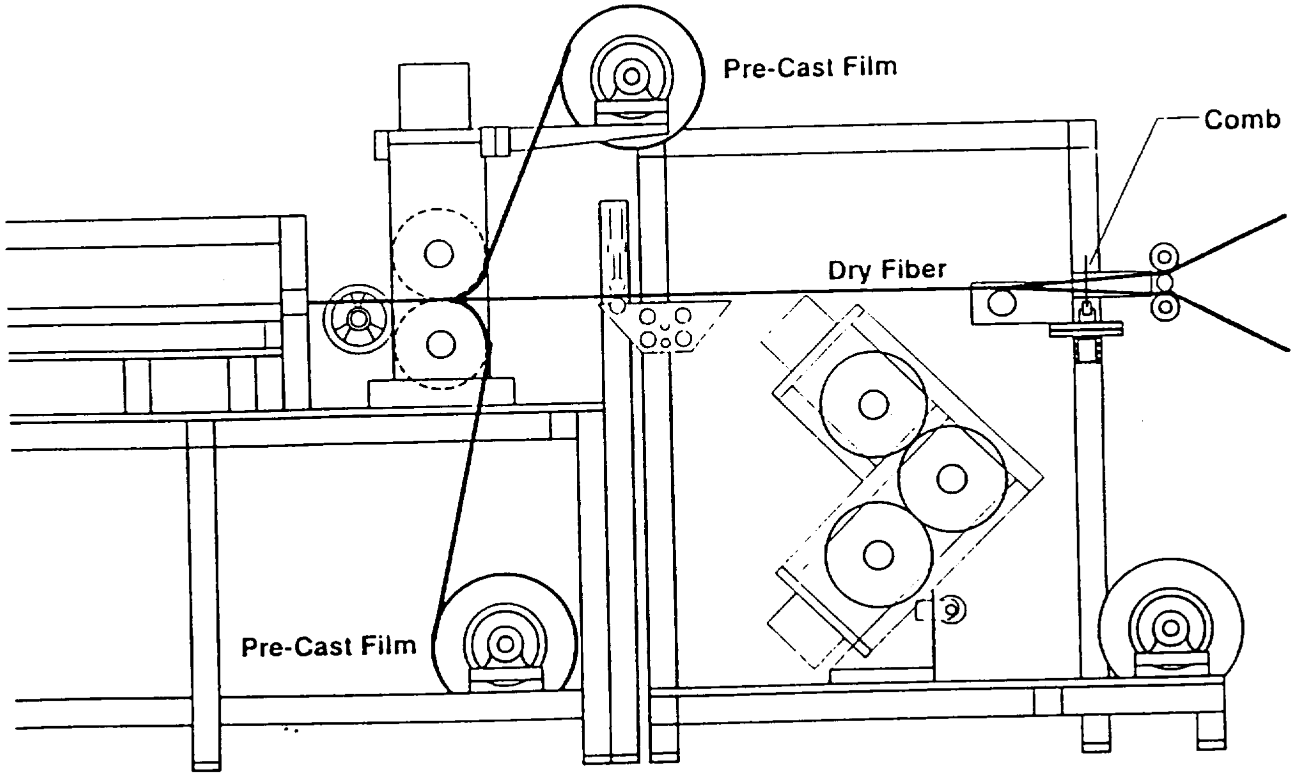

Figure 3. Common Fiber Impregnation Process Using Pre-Cast Films.

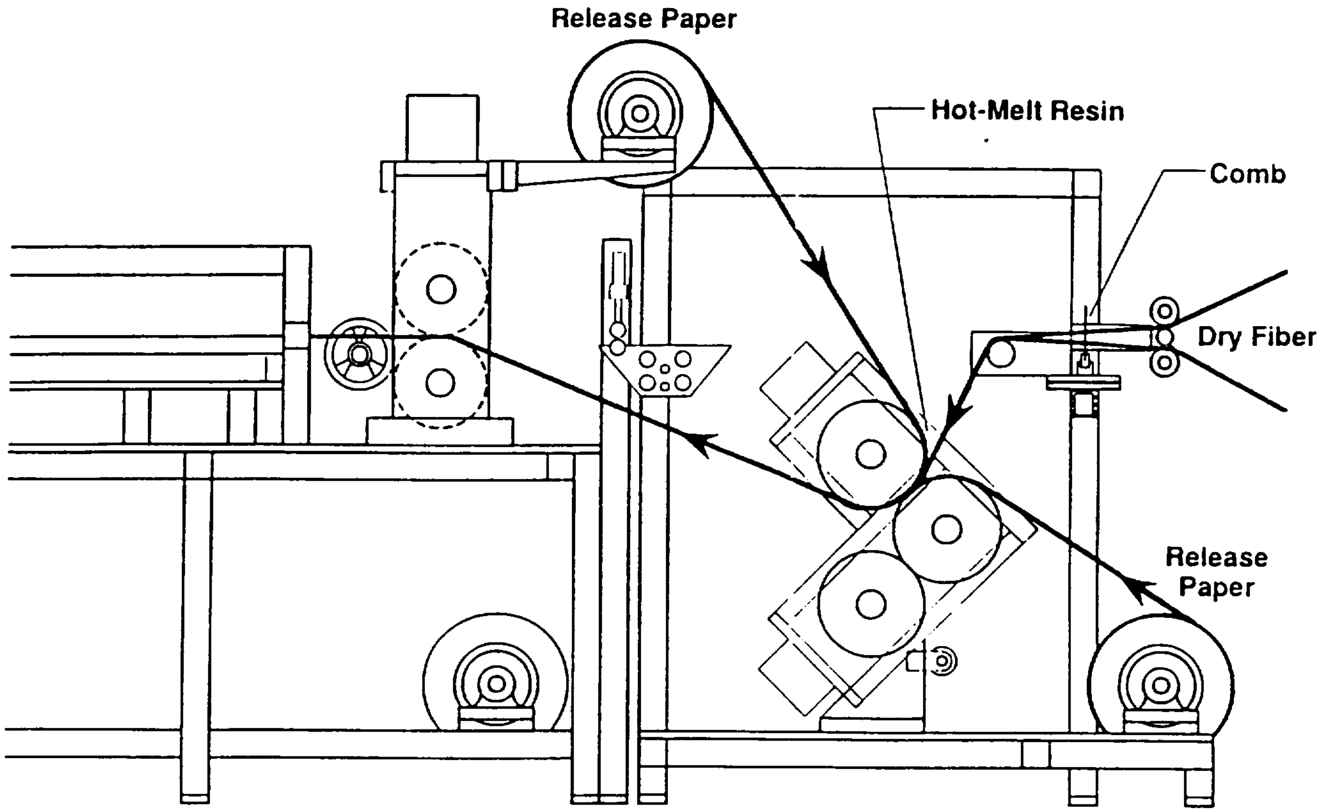

Figure 4. Direct Impregnation at the Reverse Roll Coater.

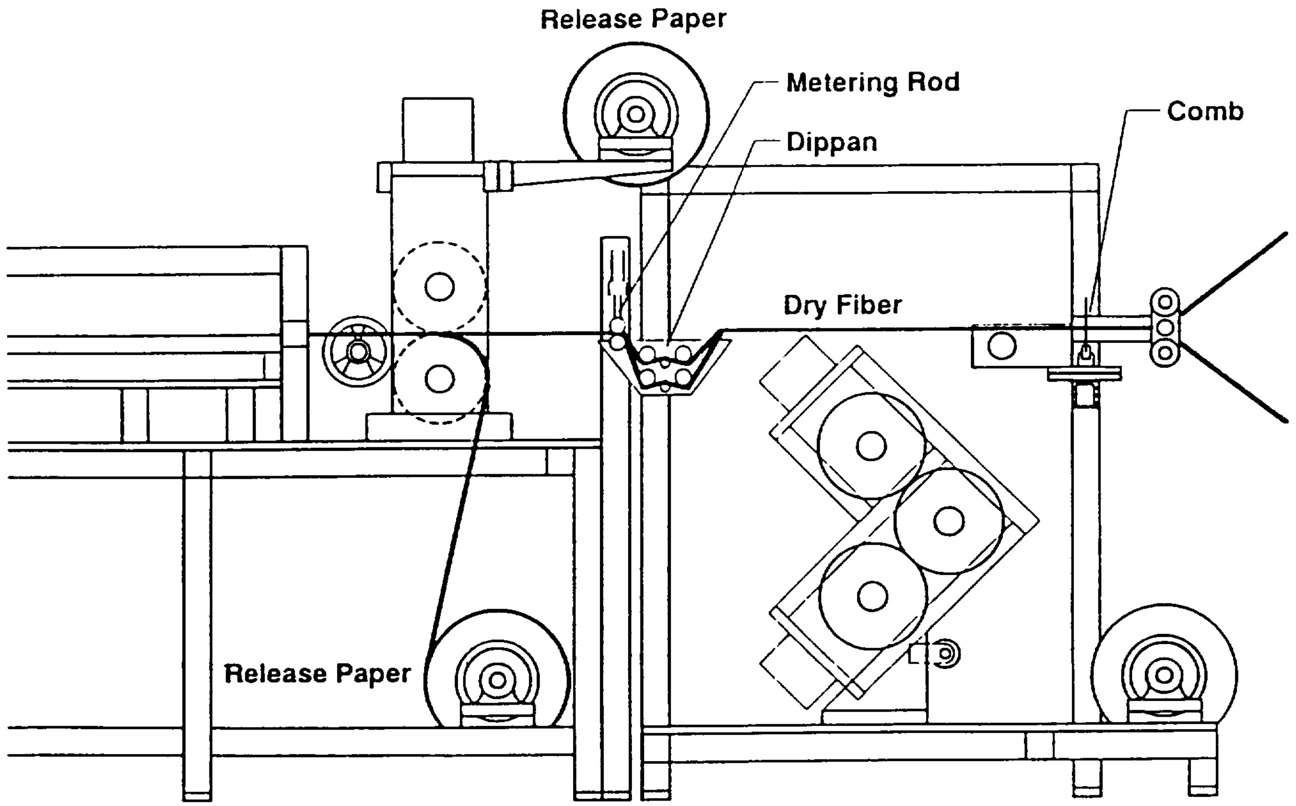

Figure 5. Solution Prepregging Using the Dip Tank Method.

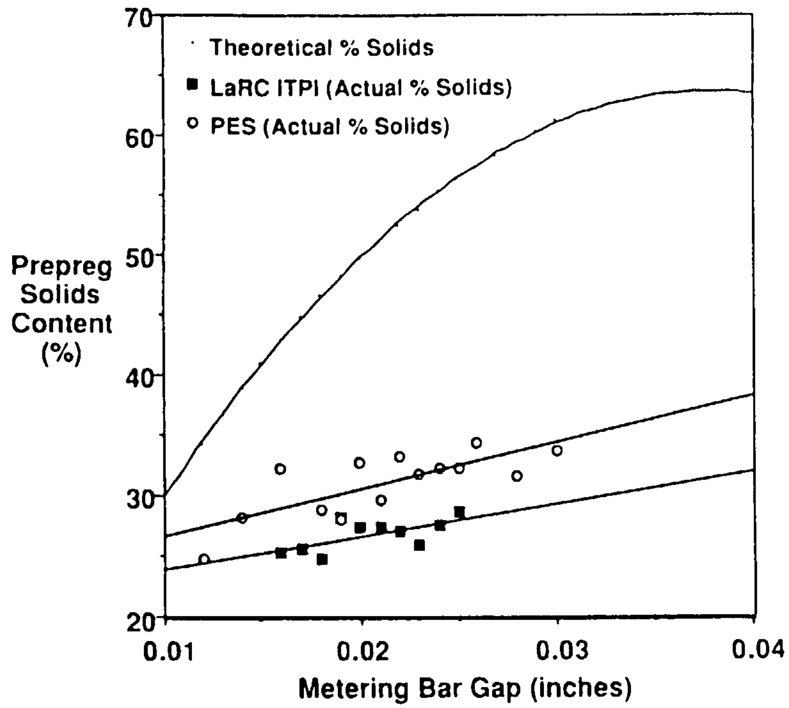

Figure 6 Actual Percent Solids of IM7/LaRC™ ITPI and IM7/Polysulfone Prepregs as a Function of Metering Bar Gap Dimensions

Table I
Material Systems Prepregged On The Tape Machine

Resin System	Solvent	% Solids in Solution
LaRC™ IA amid acid	NMP	30
LaRC™ ITPI amid acid	NMP	30
Polysulfone	NMP	30
High Mw Polyamide acid	NMP	30
LaRC™ ITPI isoimide/amide acid blend	NMP	23
LaRC™ RP46	Methanol	70

Table II
Machine Operating Parameters

Prepreg Batch Number ____________
Coating Method ____________
Fiber ____________
Matrix ____________
% Solids ____________
FAW ____________
Width (cm) ____________
Fiber Yield (g/m^2) ____________
Dry Resin Content ____________
Number of Tows ____________
Comb #/Angle ____________
Prepreg Thickness (cm) ____________
Line Speed (M/sec) ____________
Dip Tank Metering Gap ____________
Nip Roll Data (Temp/Pressure/Gap/Speed Ratio)
Hot Plate Temperatures (°C) ____________
Oven Temperatures (°C) ____________
Unwind Tension Settings ____________
Rewind Pressures ____________
Product Pressures ____________

Table III
0° Flexural Properties for LaRC™ IA/IM7 Composites

	Tape Machine Prepreg	Drum Wound Prepreg
0° Flex Strength (MPa)		
25°C	1611±63	1474±8
177°C	1163±50	956±52
0°Flex Modulus (GPa)		
25°C	137±6	93±8
177°C	132±6	98±1

All results are normailzed for 60% fiber volume fraction.