THE FABRICATION OF CARBON-FIBER COMPOSITES BY AQUEOUS SUSPENSION PREPREGGING WITH LARC-TPI AND PEEK.

by

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1. INTRODUCTION

1.1 General Introduction on Composite Materials.

Trends in the automotive, marine, air- and spacecraft industries have created demands for new materials combining low weight and high strength. These requirements can often be met best by composite materials consisting of combinations of reinforcing agents and matrix materials (see Table 1). While the term "composite material" usually refers to relatively new materials developed within the last three decades, it can also be used for wood, which is a natural composite material, as well as reinforced concrete and asphalt. At the end of the nineteenth century, composites were made of paper and cotton. In 1867, manilla paper and glue were used to fabricate boats for the U.S. Naval Academy. Later, during the Second World War, bearings and switchgear were made of asbestos and cotton-reinforced phenolics [1]. In the last forty years, much materials science research has focused on developing, understanding and designing composite materials and broadening their applications. While some aspects of composite technology are understood reasonably well, there are still numerous unsolved problems and unanswered questions.

The mechanical and chemical properties of a composite are a complex

Table 1 : Comparison of mechanical properties of composites and metals. *[8].*

Material	Density ($g\ cm^{-3}$)	Tensile strength σ (GNm^{-2})	Young's modulus E (GNm^{-2})	σ/ρ	E/ρ
Composite*					
E glass	2.1	1.1	45	0.5	20
HS carbon	2.0	1.5	140	1.0	90
HM carbon	1.5	1.1	220	0.7	130
Aramid	1.4	1.4	75	1.0	50
Metal					
Steel	7.8	1.3	200	0.2	26
Aluminium	2.8	0.3	73	0.1	26
Titanium	4.0	0.4	100	0.1	25

*60% vol unidirectional reinforcement

combination of the properties of : (i) the reinforcement, (ii) the matrix, and (iii) the interface. The critical importance of the latter is now well accepted [2,3,4]. D.V. Rosato says that "it is the behavior and properties of the interface that generally control the properties of the composite" [1]. Although it is relatively easy to obtain mechanical and chemical data on the reinforcement and the matrix separately, it is not a simple matter to characterize the interface.

1.1.1 Reinforcing Agent.

One of the components of a composite is the reinforcing agent which can consist of fibers (short, long, or continuous) or discrete filler particles. Fibers can be made out of organic material such as cellulose, aramid, polymers, or inorganic materials such as graphite, boron, and glass. "Filler" is a generic term denoting particles of various shapes and materials such as alumina powder, glass flakes, beads or spheres, mica, sand ...[1].

The load distribution in a composite varies with the type of reinforcing agent. If it is a filler, the load is born by the matrix (filler particle smaller than 0.1 micron) or shared by both matrix and reinforcement (filler particle larger than 1 micron). In the case of fibers, the load is born essentially by the fibers [5].

The modulus of the composite is strongly dependent on the direction of the fibers with respect to the direction of the applied stress. Consequently the longitudinal modulus is typically much higher than the transverse modulus for

composites made with continuous fibers. In composites made with chopped fibers, the fiber orientation is typically random. These composites are often manufactured by injection molding. While this process is considerably simpler than fabrication processes for composites made with continuous fibers, there are several problems : (i) composites made with chopped fibers generally do not have mechanical properties that approach those made with continuous fibers and (ii) chopped ceramic and carbon fibers are highly abrasive and thus quickly wear out extruder dies. Thus, continuous fibers are most commonly used for high performance composites [6]. The fibers are usually made of boron, silicon carbide, aramid, glass, and graphite. Because of their high mechanical strength, high modulus and low specific gravity, continuous graphite fibers are well suited for high performance composites. They are often surface- treated to enhance their binding properties. A sizing is applied sometimes to the surface to protect the fibers and to facilitate the handling. Continuous fibers are sold in bundles but can also be found as fiber cloth or braided in a three dimensional network.

1.1.2 Matrix.

A matrix acts as an adhesive between the reinforcement and gives solidity to the composite material while protecting the reinforcing agent from environmental attacks such as moisture and corrosive atmospheres. Four categories of matrices are used : (i) polymer, (ii) metal, (iii) ceramic and (iv) carbon. When the

temperature does not exceed 100 C to 200 C, the matrix is often a polymer. The composite is then called a Fiber-Reinforced-Plastic or FRP. For higher temperatures, metals and ceramics (up to 1000 C) or carbon (up to 2500 C) are used as matrix materials [6]. Of all these, polymer matrices are the most common. They can be subdivided in two fundamentally different categories : (i) thermosets and (ii) thermoplastics.

Thermosets :

A thermoset is cross-linked polymer typically formed during a several hour long curing stage in an autoclave. Common thermosets are epoxies and polyesters. Bismaleimides (BMI) and some polyimides (PI) also belong to this category [7]. Thermoset prepregs consist of fibers impregnated with monomers or partially cured oligomers. These prepregs typically require refrigerated storage and are characterized by good drapability and good tackiness. However, disadvantages of thermoset composites include brittleness, finite shelf-life and low resistance to high temperatures [8]. Epoxy composites can be used continually at temperatures below 160 C to 180 C. BMI and PI can be used up to 260 C and 315 C respectively, but the curing step is then performed at higher temperatures for longer times and the matrices tend to be more brittle. Blends with thermoplastics and use of additives can toughen the resin [5,7]. Despite these disadvantages, epoxide composites formed 80 % of the FRP produced in 1984. They are cost

ompetitive and find numerous applications in the automotive industry (ventilating systems, hoods, and bumpers), in the sport industry (skies, golf clubs, and tennis racquets), and in the aerospace industry (aircraft wings, tails, and fuselage components) [1].

Thermoplastics :

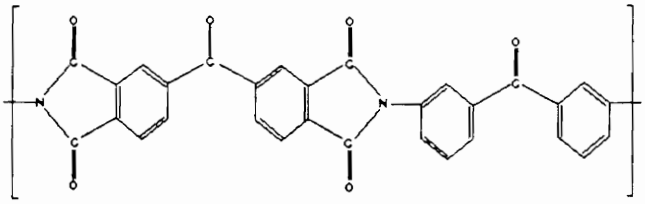
Thermoplastic polymers do not form a three-dimensional cross-linked network upon heating. They retain their ability to flow and can be reformed or consolidated several times. Some thermoplastics are amorphous, such as polycarbonate, and are characterized by a glass transition temperature (T_g). Some are semi-crystalline, such as Poly(ether ether ketone), and are characterized by a glass transition temperature (T_g) and a melt transition temperature (T_m). Semi-crystalline thermoplastics are solid below T_g, semi-fluid between T_g and T_m, and form a viscous melt above T_m. Crystallinity imparts solvent resistance and some brittleness. Thermoplastics have stiffness and strength similar to those of thermosets but have greater toughness and better fracture resistance. Advantages of thermoplastic prepregs include an indefinite shelf-life and shorter processing time [9,10]. However their processing temperatures are usually higher than for thermosets.

Thermoplastics suffer from some disadvantages in composite processing. Thermoplastic prepregs are stiff and not tacky in contrast to thermosets. This

makes them relatively difficult to lay-up and handle [8]. While uncured thermosets form relatively low viscosity melts or solutions, thermoplastics have relatively high hot melt viscosities, typically on the order of 10,000 to 100,000 Poise [11]. Thus, it is often difficult to impregnate a fiber bundle and achieve good wetting at the fiber surface with many thermoplastics. This is a major problem which has hindered their use in the composite industry. The traditional impregnation methods used with thermosets are not suited for thermoplastics. Hence, new processing procedures need to be developed [9].

Polycarbonate, poly(ether sulfone) and polyacrylic find applications in the space industry. Advantages of these systems include excellent fiber-matrix wetting, and good strength and stiffness [1]. Poly(ether ether ketone) has exceptional resistance to solvent attack. APC-2™ is a PEEK-carbon fiber prepreg developed and commercialized by ICI [7]. Aromatic linear polyimides have the advantages of good thermal stability, high glass transition temperatures and excellent solvent resistance [9]. For this work, two thermoplastic matrices were used : PEEK, synthesized in Virginia Tech Chemistry Department, and LaRC-TPI produced commercially by Mitsui Toatsu Chemicals,Inc. (see Figure 1) [12,13,14].

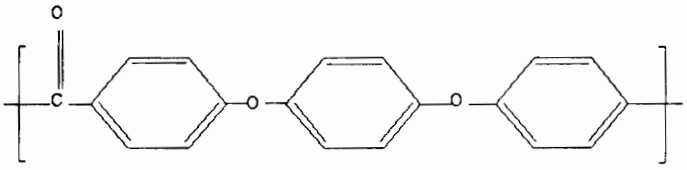
As mentioned above, the fabrication of thermoplastic composites is still a bit of an art. Much research remains to be done to find new methods of manufacturing, particularly for composite made with novel thermoplastics with very high T_g's [9,15,16]. It is the objective of this project to explore suspension



LaRC-TPI , obtained from Mitsui Toatsu Chemicals, Inc.

Tg = 260 C, Tm = 305 C .

Figure 1-a.



PEEK , from Virginia Tech Chemistry Department.

Tg = 147 C, Tm = 339 C .

Figure 1-b.

Figure 1 : LaRC-TPI and PEEK molecular structures.

prepregging as a new method of impregnation. We will first explain the general principles of fabrication which apply to thermosets as well as thermoplastics.

1.2 Continuous Fiber Composite Fabrication.

The fabrication of continuous-fiber-reinforced plastic composites consists of a three-stage process : (i) combination of fibers and resin, (ii) orientation of the prepreg and (iii)consolidation of the composite [17]. Sometimes, the steps can be done simultaneously while, in other processes, each step is done separately.

During the first step, fibers and matrix are combined to form a prepreg, an impregnated bundle or cloth. The prepreg can be wound onto a cylindrical mandrel (filament winding), onto a drum or can be woven or braided. The method depends largely on the polymer matrix : (i) solubility, (i) T_g, (iii) T_m (if there is one), and (iv) melt viscosity.

Orientation refers to the position of the fibers relative to each other and to the general shape of the final composite. In the case of filament winding, it is done immediately after the combination step. Cloth can be shaped in a mold. It is also possible to form crossplies of unidirectional prepreg to make a multidirectional panel. The choice is dictated by the desired composite application.

Finally, the panel is consolidated using a prescribed time-temperature-pressure cycle. This is called the "cure cycle" in the case of thermosets. A cycle

is designed specifically for each type of resin.

The final product requirements are dictated by intended application. These requirements, which are the critical issues for a composite manufacturer, are [17]:

(1) desired fiber/matrix content.

(2) minimum void content.

(3) maximal adhesion between fiber and matrix.

(4) mechanical properties such as flexural strength and fracture toughness in desired ranges.

(5) minimal processing time.

In this work we were particularly concerned with items 1 to 4 for composites made with thermoplastics by suspension impregnation. This and other impregnation techniques are discussed next.

1.2.1 Prepregging Techniques.

The first step towards controlled fiber/polymer content is to achieve controlled impregnation of the fibers by the matrix. Since this project focused on thermoplastic composites, the impregnation methods specifically used with thermoplastic polymers will be discussed next.

(1) Hot melt impregnation - The carbon fiber bundle is impregnated by passing through a resin pot containing molten polymer (see Figure 2). A die, located in the lower part of the resin pot, controls the amount of polymer which goes onto the fibers. Polymers that have been processed by melt impregnation include poly(etheretherketone) and poly(ethersulfone).

This method can be difficult to use with thermoplastics because of their high hot melt viscosity [18]. Moreover, high performance thermoplastics with high glass transition temperature may require processing temperature close to their degradation temperature, resulting in undesirable matrix degradation.

(2) Solution impregnation - The fiber bundle goes through a resin pot containing the polymer dissolved in an organic solvent (see Figure 2). As in the hot melt method, a die can be adjusted to vary the amount of polymer which impregnates the fibers [19,20]. This procedure has been widely used, even though the solvents are hazardous and expensive. They are often high-boiling point solvents such as 1-Methyl-2-Pyrrolidinone. Solvent removal has to be effected before the consolidation step and constitutes a major problem. Residual solvent is very undesirable since it is (i) difficult to control and (ii) affects the properties of the composite, especially at the interface [18,21,22]. Since a polymer must be soluble in some solvent for solution prepregging, this technique is limited to certain polymer-solvent combinations. Because of these drawbacks, it is unlikely that

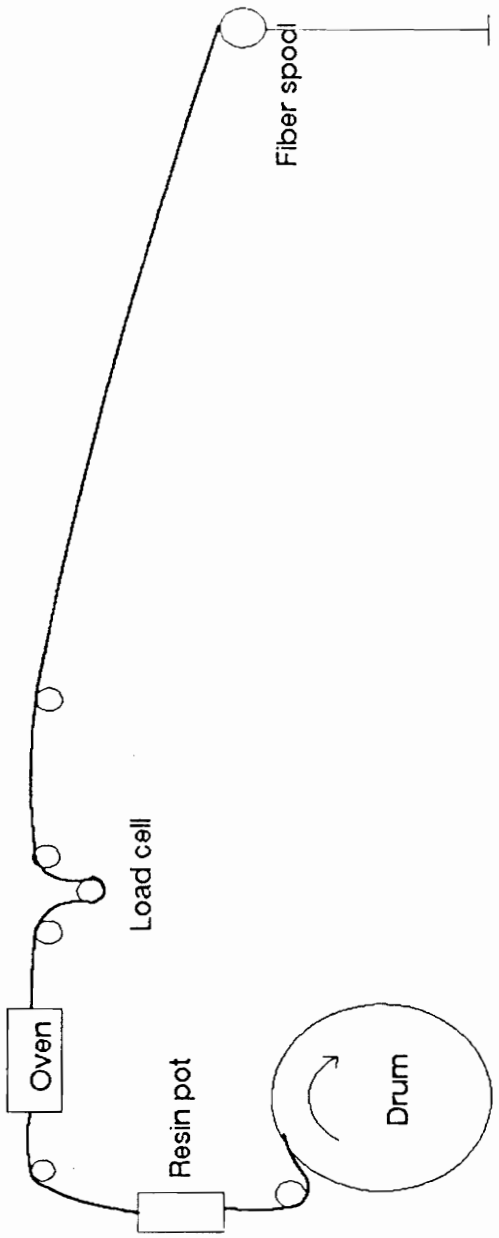


Figure 2 : Prepregger for hot melt and solution impregnation.

solution prepregging will be a viable method for prepregging in the future. unless relatively nontoxic, water-soluble, high-performance polymers can be developed.

(3) Commingled yarns - Emerging techniques consist in manufacturing commingled yarns or fabrics where the polymer has been spun into a filament. Due to the proprietary nature of this technology, little information is still available on this method [10,23].

(4) Dry powder impregnation - This is the most common method used to overcome the problems associated with hot melt and solution prepregging. The polymer is deposited onto the fibers as a dry powder. The bundle, spread up to a few centimeters, goes through a chamber containing dry, powdered polymer often suspended in a gas stream (see Figure 3)[11,18]. Since there is no solvent, there is no problem of interaction between the solvent and the matrix and the fibers. However, particle binding has been a recurrent problem with this technique [24,25]. Another critical issue is the control of the polymer particle size. The particles need to be small, typically 1 to 40 microns, to allow good impregnation [11,24]. It is also desirable to have narrow and reproducible particle size distribution to control the amount of polymer deposited. This requirement is particularly difficult to meet with commercially available polymers. Extensive research remains to be done in this area [22,26,27].

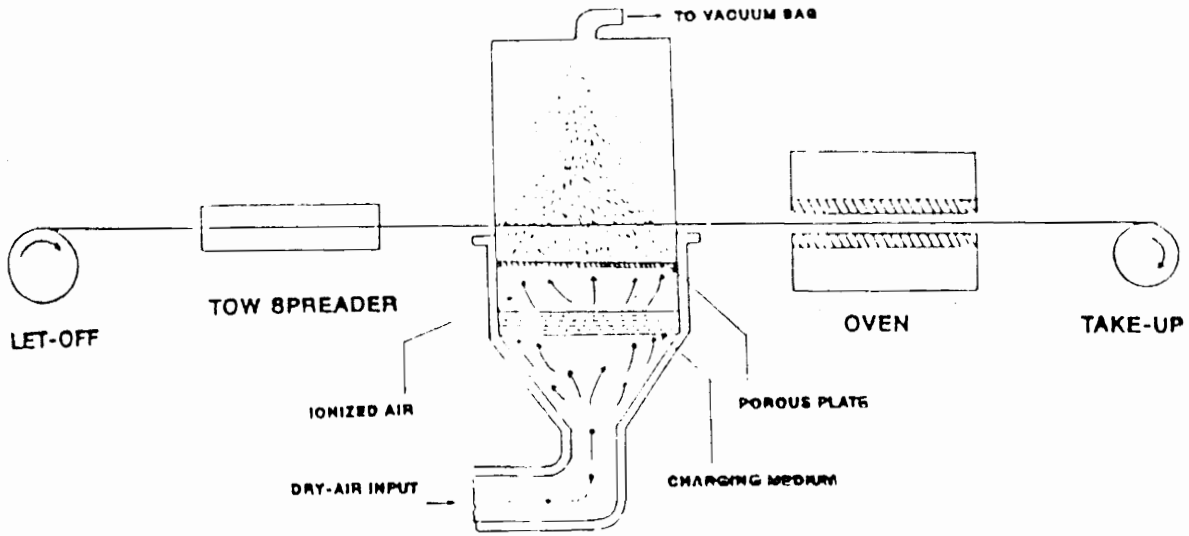


Figure 3 : Dry powder impregnation technique. *[27].*

(5) Slurry impregnation - This has been proposed as an alternative to dry powder impregnation. The fiber bundle goes through a resin pot containing a suspension of polymer particles in an aqueous medium (see Figure 4). The water is removed before consolidation by drying [28,29,30]. Dr. T. Towell and Dr. D. Hirt, at NASA-Langley Research Center, have developed a suspension prepregging technique with LaRC-TPI powder and found that a high performance polymeric binder was needed to bind the polymer particles to the carbon fiber and to disperse the colloidal polymer particles to achieve sufficiently small sizes. They measured the short beam shear and flexural properties of the resulting composites, under dry and wet conditions, at room and high temperatures. The fracture toughness values G_{Ic} of the composites were higher than that of the laminates made with a melt/pultrusion method.

The advantages of this method include : (i) there is no polymer solubility limitation, (ii) there is no melted polymer involved, and hence thermal degradation is avoided in the impregnation step, (iii) suspension prepregging with aqueous suspensions is much safer than solution prepregging with NMP solutions, (iv) aqueous suspensions have low viscosities, typically less than 100 mPa.s, which facilitates impregnation, (v) the wet prepreg shows good drape properties, (vi) a variety of polymeric binders/stabilizers, both commercial as well as those developed at Virginia Tech, can be employed, permitting great flexibility in controlling the chemistry of the matrix-fiber interphase, (vii) it would be applicable

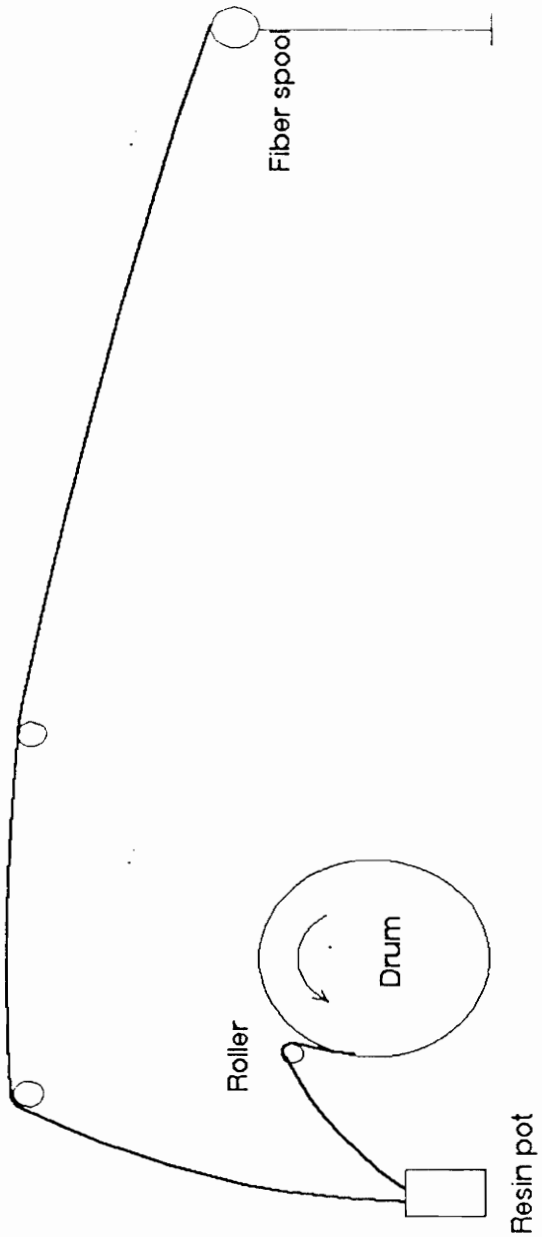


Figure 4 : Prepregger for suspension impregnation.

to any kind of polymers that can be made in a powder form at room temperature. Finally, (viii) new polymer synthesis techniques and new polymeric stabilizers can be used to formulate aqueous suspensions with particles in the submicron range. This last advantage would be essential to impregnate carbon fiber cloth which cannot be spread like unidirectional fiber tow to allow large particles, e.g. larger than 50 microns, to penetrate the bundle.

For these reasons, aqueous suspension prepregging offers an attractive alternative to the other prepregging methods discussed. The key aspects of this method will be reviewed next.

1.2.2 Suspension Prepregging.

As the bundle goes through the suspension, some of the suspended particles penetrate into the bundle. The amount of particles impregnating the fibers depends on : (i) the polymer concentration, (ii) the polymer particle size, (iii) the number of fibers in the bundle, (iv) the wetting of the fibers by suspension's liquid phase, (v) the degree of fiber spreading, and (vi) fiber tension and speed.

Parameters such as polymer concentration, fiber bundle size, bundle spreading, and fiber tension and speed are easily controlled in principle. The wetting of the fibers by the liquid phase is affected by added surfactant. This will be discussed in Chapter 4. The key aspect of prepregging in this research was controlling the size of the polymer particles and their subsequent binding onto the

fibers. It is believed that small particle size, typically less than 40 microns, should promote impregnation of the fiber bundle.

Small thermoplastic particle size can be achieved through different ways : (i) grinding of a solid, (ii) spray drying of a polymer solution, (iii) polymerization to form colloidal particles in suspension, and (iv) precipitation from a polymer solution.

Grinding of polymers results in small particles in some cases but is generally not a practical method for large-scale processing of thermoplastics, particularly for those with relatively low T_g's. In addition, grinding is limited to making particles mostly larger than about ten microns.

Spray drying, as done by Mitsui Toatsu in making fully imidized LaRC-TPI, can be done on a commercial scale for those polymers that are soluble in some solvent.

At present, there is no known method for forming colloidal particles of high performance polymers by direct polymerization. Perhaps the most promising technique for making colloidal thermoplastic particles in the desired range is by precipitation from a polymer solution. This was recently demonstrated for PEEK for the first time by Dr. James McGrath's group at Virginia Tech [31]. This PEEK was used to make composites and thus was a major focus of the present research. The synthesis and precipitation of PEEK will be discussed in more detail in Chapter 2.

Once particles in the sub- to micron range form by any one of these methods, they must be stabilized in aqueous suspensions to prevent agglomeration that forms aggregates of 100 microns size or larger. Stabilizing agents such as surfactants and polymeric dispersants, and sonication are common techniques used to inhibit particle aggregation which almost invariably results when submicron particle are suspended in a fluid. This was a main focus point in this research. In the case of composites, low molecular weight surfactants should be avoided since, as was the case with residual solvent, their presence at the matrix-fiber interface can adversely affect the mechanical properties. Therefore it is preferable to use a high performance polymeric dispersant which adsorbs onto the matrix particles in suspension, resulting in steric stabilization [32] (see Figure 5). Molecular structure, molecular weight, electrical charges, concentration, temperature are all contributing factors to the steric effect and will determine the magnitude of stabilization. This is discussed in detail in Chapter 3.

An ideal polymeric dispersant for suspension prepregging would have the following features:

(1) is water soluble.

(2) has the capability to stabilize polymer particles smaller than one micron in water.

(3) works at very low concentrations, preferably less than 0.1 w% based on matrix content.

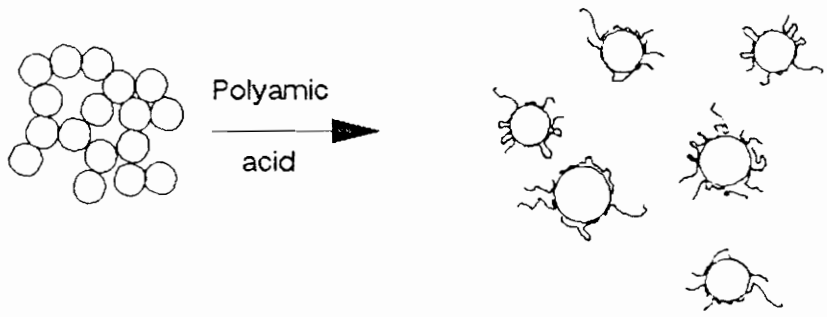


Figure 5 : Steric stabilization.

(4) does not release by-products during consolidation.

(5) is miscible with the matrix after consolidation so that it improves or, at least does not hurt, binding between fibers and matrix if it does not burn out.

(6) leaves harmless residues behind if it burns out.

It may take some time before dispersants are synthesized which meet all of these requirements. Of these, (1), (2), and (5) are the most important.

Dispersants used in this project included various polyamic acid obtained from Mitsui Toatsu Chemicals and from the Virginia Tech Chemistry Department. Unfortunately, polyamic acids release water during the consolidation stage. Work in underway at Virginia Tech to develop copolymer dispersants which do not release volatile species during consolidation.

1.2.3 Prepreg Orientation and Consolidation.

Following the impregnation step, it is necessary to combine several layers of prepreg in the consolidation step of the laminate. Since suspension prepregging is a novel technique, it is reasonable to start with unidirectional panels,i.e., panels where the fibers are oriented in the same direction. This allows a ready comparison of the mechanical results with most published data.

Consolidation of the prepreg is effected in two steps : (i) removal of the

water from the wet prepreg and (ii) use of a hot press to consolidate the panel. This portion of the work focused essentially on the time-temperature-pressure cycle during which the polymer particles melt and coat the fibers. An optimum cycle should result in composites with (i) a good fiber distribution through the thickness of the panel, (ii) minimal void content, and (iii) good adhesion between fibers and matrix.

The fiber distribution and the void content depend on the wetting on the fibers by the melt and on the melt rheology. This rheological aspect of consolidation is extremely complex and no convenient technique is available to obtain in-situ information. A trial and error approach was adopted to optimize the consolidation cycles. A study of the polymer melt rheology will be part of the future work recommendations.

The adhesion between fibers and matrix is affected by several factors including : (i) fiber surface chemistry, i.e., smoothness of the fiber surface, composition of the fiber and presence of sizing or other surface treatment [4], (ii) surface tension of the melt on the fiber, and (iii) specific fiber/matrix interactions,e.g, grafting of polymer onto the fiber surface or crystallization of ia onto the fiber.

For semi-crystalline matrices, such as PEEK, it is important to control the crystallinity with the time-temperature-pressure consolidation cycle since the morphology of these polymers affects their physical and chemical properties. The

rate of cooling and the pressure under cooling are particularly critical. The rate of cooling affects especially the degree of crystallinity and the spherulite size. Increase in crystallinity and larger spherulites result in higher tensile strength and solvent resistance but lower the fracture toughness of the composite. High degree of crystallinity could also result in slower physical aging. Optimized composite properties require close control of the time-temperature-pressure cycle and thorough characterization of the crystalline phase of the matrix. This would allow the manufacturer to tailor the matrix morphology corresponding to the application requirements [7,15,33,34,35].

1.3 Goals of this Work.

The objectives of this project were to :

(1) explore the feasibility of composite fabrication by suspension prepregging, using commercial and novel polymer matrix and binder systems.

(2) probe the nature of stabilizer-particle interactions and assess their importance in suspension prepregging.

(3) develop suitable consolidation procedures for composite materials made with selected thermoplastic polymers, i.e., LaRC-TPI (amorphous) and PEEK (semi-crystalline).

(4) conduct tests to evaluate the laminate properties :

o compare the mechanical properties with commercial composites and other research groups's results.

o characterize adhesion at the fiber-matrix interface.

o evaluate the fiber distribution and the void content.

This report is organized as follow : Chapter 2 describes the materials used. Chapter 3 discusses the experimental procedures dealing with the particles-stabilizer interactions and Chapter 4 those related to the fiber-stabilizer interactions. The prepregging procedure is described in Chapter 5. Test procedures are presented in Chapter 6. Results for composites made with LaRC-TPI and PEEK composites are discussed in Chapters 7 and 8, respectively. Finally, conclusions and recommendations for future work are presented in Chapter 9.

2. MATERIALS

2.1 Polymer Matrices.

Two thermoplastic polymers were used as matrices in this project. The first stage was conducted with amorphous LaRC-TPI. In the second stage, composites were made with novel semi-crystalline PEEK in the form of an aqueous colloidal dispersion stabilized by various polyamic acids.

2.1.1 LaRC-TPI.

LaRC TPI, which stands for Langley Research Center Thermoplastic Polylmide), was developed at NASA, Langley Research Center in the late 1970's. It is a high performance linear thermoplastic polyimide (see Figure 6). It is available both as a fully imidized dry powder and in the form of its polyamic acid precursor dissolved in diglyme. Annealing at temperatures above 330 C [36], 350 C [37], results in an amorphous material whose T_g is 255-260 C, with no crystalline phase present.

LaRC-TPI's unique properties, including excellent thermal and thermo-oxidative stability [38,39], high chemical resistance [40], resistance to water exposure [14] and good adhesive properties [14,39], justify its use for high

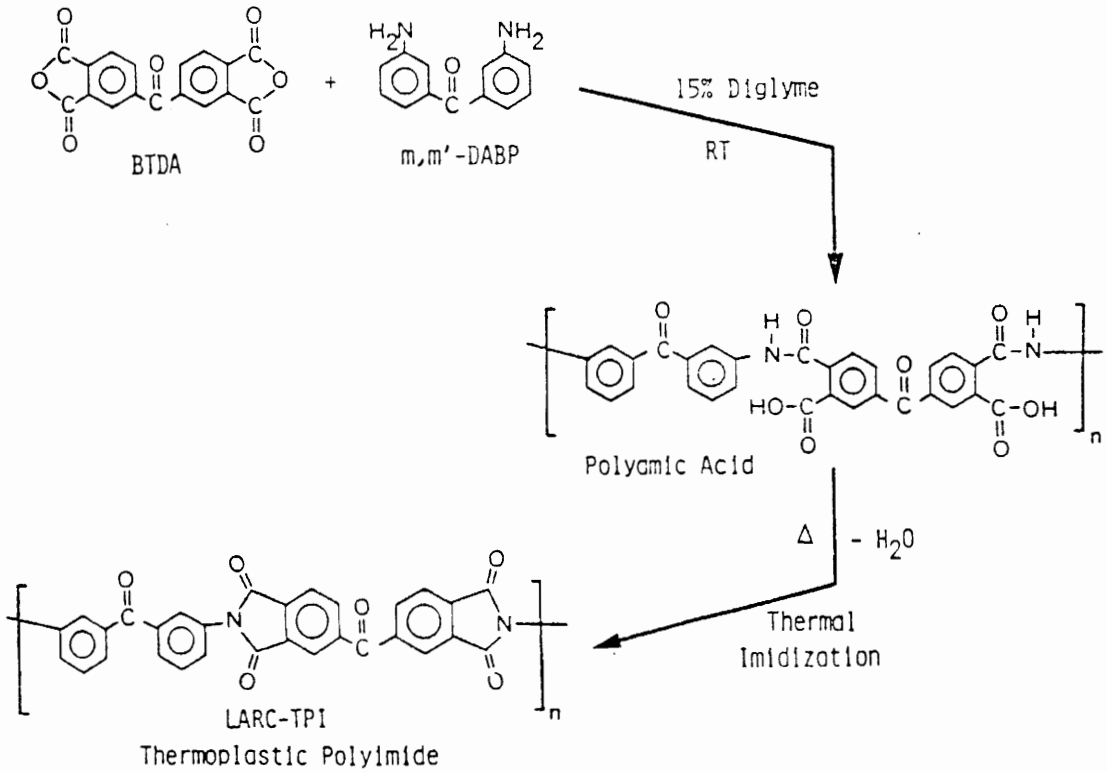


Figure 6 : Synthesis of LaRC-TPI. *[38]*.

performance applications [38]. Variations of LaRC-TPI, for example LaRC-IA and LaRC-I-TPI, since one of LaRC-TPI monomers, i.e. 3-3'-DABP, is no longer commercially available in the United-States [39,41], have currently been developed

.

Three lots of LaRC-TPI 1500 High Flow Grade were obtained from Mitsui Toatsu Chemicals, Inc.. Two lots were used for the preliminary experiments : # 2941 and # 9003. Lot # 24-703 was used in making all the composites reported in this work.

2.1.2 PEEK.

The use of PEEK in the composite experiments was motivated by several factors :

(i) excellent mechanical and thermal properties.

(ii) solvent resistance due to crystallinity.

(iii) availability as colloidal particles made by a novel synthesis procedure recently developed by Mr. Keith Lyon in Professor McGrath's group at Virginia Tech [31,42].

The formation of PEEK colloidal particles involves the synthesis of a linear amorphous polymer precursor, a ketimine, which is then transformed into semi-crystalline poly(etheretherketone) in a separate reaction/precipitation step. This method results in high molecular weight polymer. The procedure is as follows (see

Figure 7):

(1) reaction of 4,4'difluorobenzophenone and aniline to produce bis(4-fluorophenyl)ketimine.

(2) synthesis of the amorphous poly(arylene ether)ketimine by reacting bis(4-fluorophenyl)ketimine and hydroquinone.

(3) synthesis of semi-crystalline poly(etheretherketone) by cleaving poly(arylene ether)ketimine with hydrochloric acid.

(4) extraction and filtration of the PEEK in water.

Since particle aggregation is undesirable, the final PEEK particles were provided by Professor McGrath's group as a semi-solid, wet cake. The wet PEEK had the consistency of bread dough, even though the water concentration was as high as 80 to 85 w%. The PEEK particles were flocculated, trapping the water in the floc structures shown in Figure 8. The highly flocculated particles required the use of a polymeric dispersant to disperse the aggregates, thus releasing the bound water, to obtain reasonable viscosity.

Three batches of PEEK, of 80 g, 120 g and 225 g of powder, were provided by Professor McGrath's group.

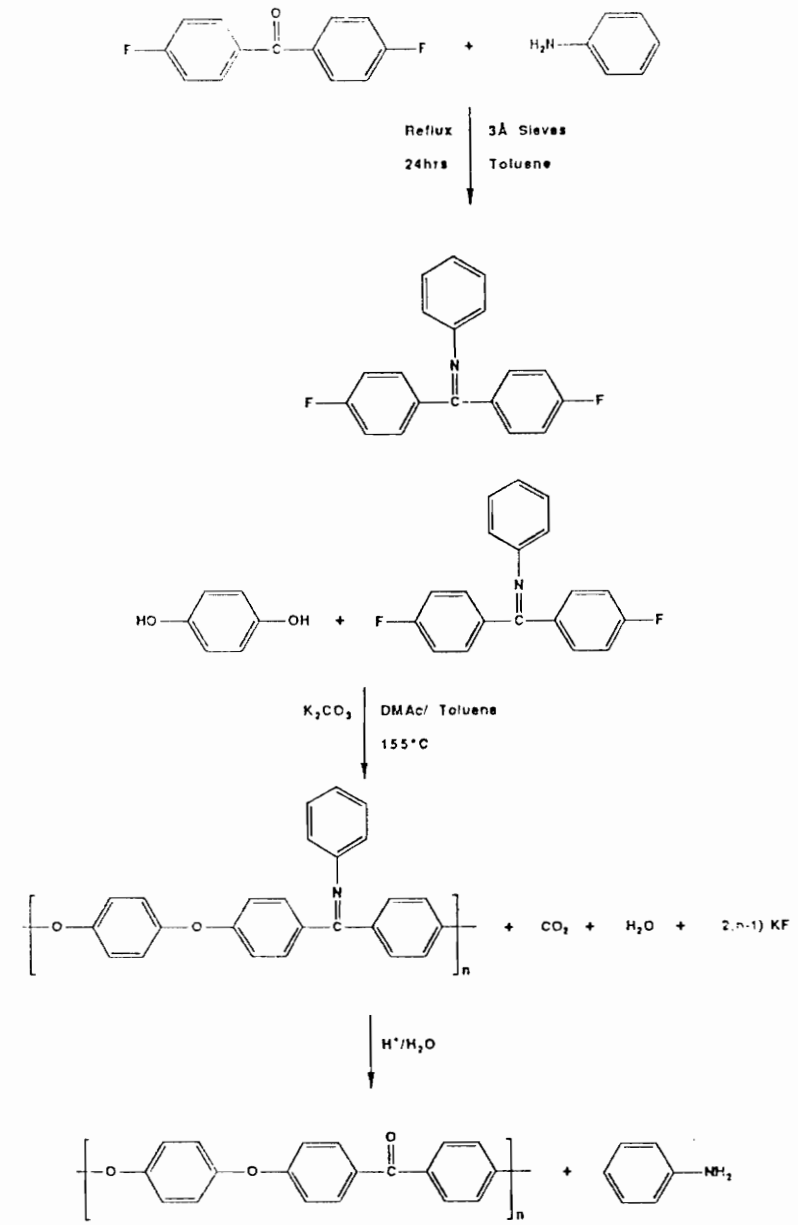


Figure 7 : Synthesis of PEEK [31].

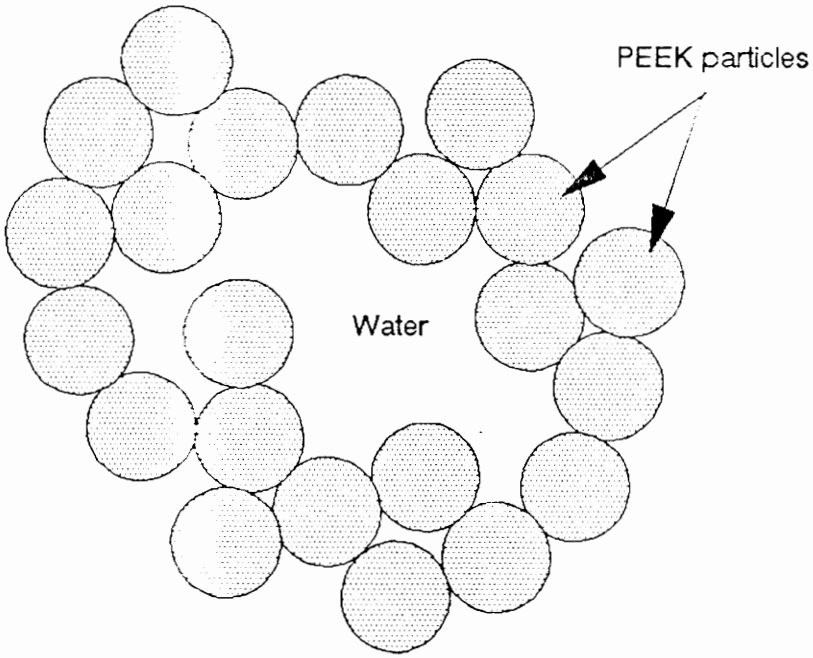


Figure 8 : Structure of PEEK clusters.

2.2 Polymeric Dispersants.

Two polymeric dispersants were used : LaRC-TPI polyamic acid and BisP-BTDA polyamic acid. They are described below.

2.2.1 LaRC-TPI Polyamic Acid.

LaRC-TPI polyamic acid is available either dissolved in an organic solvent, which is not suitable for suspension prepregging, or as a dry water soluble polymer powder, which was the form used in this work. Water soluble LaRC-TPI polyamic acid powder was obtained from Mitsui Toatsu Chemicals, Inc. as Lot # 58-703. During the consolidation step, it imidizes to form what is believed to be a cross-linked form of LaRC-TPI. The resulting polyimide is miscible with LaRC-TPI.

Recent work at NASA, Langley Research Center showed that LaRC-TPI polyamic acid was a binder [29]. The present research demonstrated that LaRC-TPI polyamic acid is able to disperse LaRC-TPI aggregates to some extent. It also has a surfactant-like action since it decreases the contact angle between the aqueous phase and the fibers. Even more interesting is the ability of LaRC-TPI polyamic acid to improve the binding between the LaRC-TPI matrix and the fibers. These aspects of LaRC-TPI polyamic acid action will be discussed in chapter 4.

While LaRC-TPI polyamic acid is a dispersing and binding agent for the PEEK particles studied in this work, the resulting polyimide was not miscible with PEEK as shown in Figure 9. Immiscibility leads to phase separation between PEEK

and the imidized LaRC-TPI polyamic acid that results in the formation of an heterogeneous matrix. The interfaces between PEEK-rich regions and polyimide-rich regions are expected to affect the adhesion fiber-matrix and the cohesion of the matrix itself and result in poorer composites.

2.2.2 BiSP-BTDA Polyamic acid.

Due to the immiscibility of LaRC-TPI and PEEK, other polyamic acids were studied that convert during the consolidation step to polyimides that are miscible with PEEK. Dr. Attila Gungor, in Dr. McGrath's group, synthesized BisP-BTDA polyamic acid which is water soluble, is a PEEK stabilizer and whose polyimide is miscible with PEEK. Two molecular weights, 10,000 and 20,000 were used in the composite experiments (see Figure 10).

2.3 Carbon Fibers.

Continuous carbon fibers constituted the reinforcement of the composites. Unsized, treated, 12K, AS4 fiber tow was purchased from Hercules. Carbon fibers's unique properties stem from crystalline carbon's high anisotropy which results in very high tensile strength and modulus in the plane parallel to the crystal base. Carbon fiber precursors are mostly rayon, pitch and Poly(AcryloNitrile) or PAN. Hercules AS-4 fibers are derived from PAN.

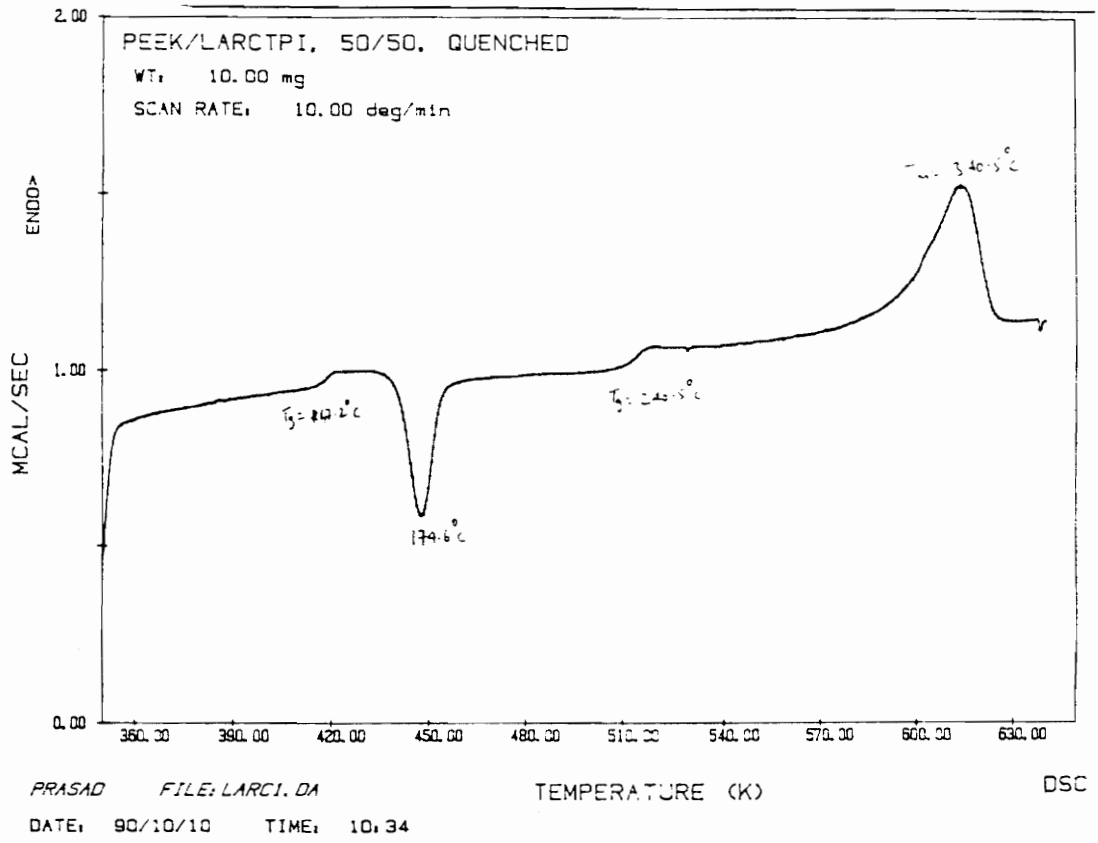


Figure 9 : DSC of PEEK-imidized LaRC-TPI polyamic acid. 50/50 blend. *Courtesy to Dr. Marand, Virginia Tech Chemistry Department.*

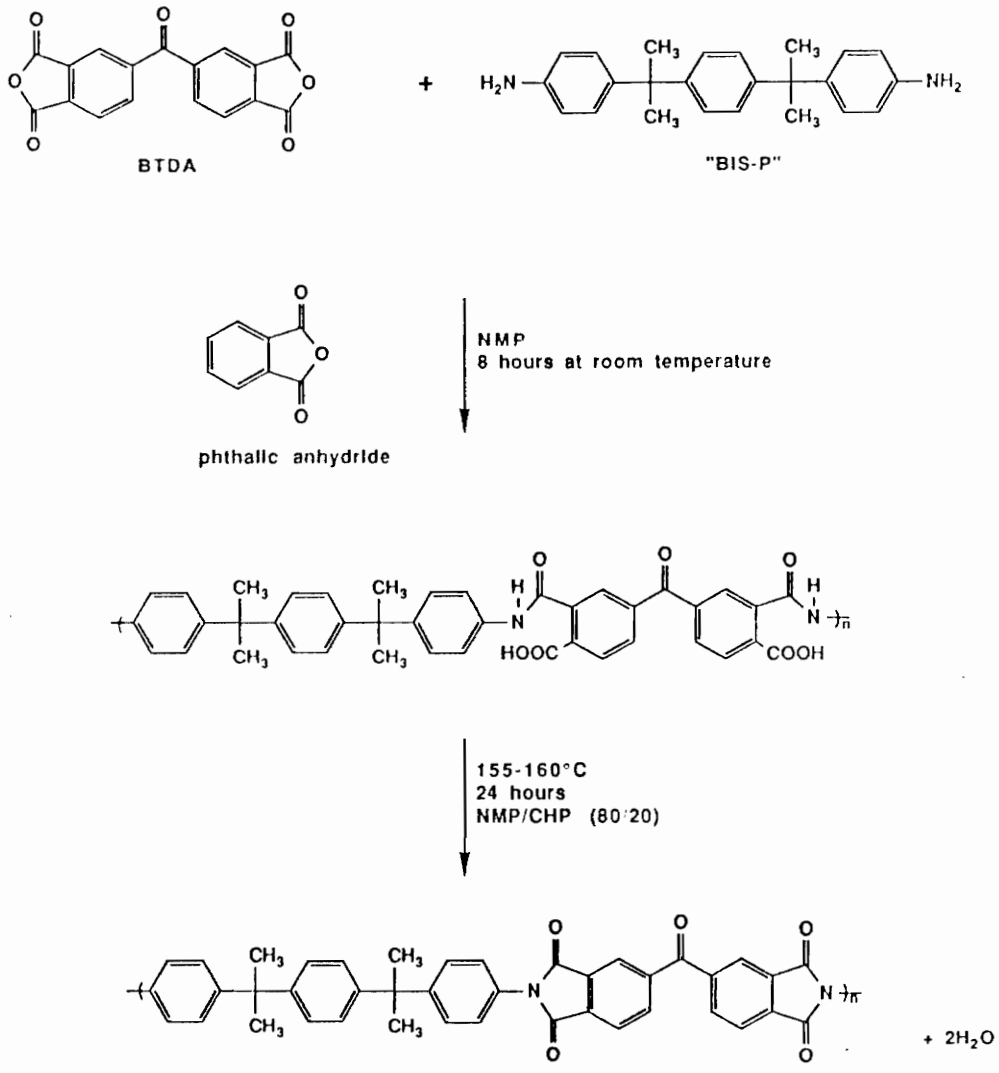


Figure 10 : Synthesis of BisP-BTDA polyamic acid and resulting polyimide. *Courtesy to Mrs. K. Stickney.*

PAN fibers are generally made by a wet-spinning process : the polymer in solution is spun in a bath containing a coagulating agent. The fibers are then washed, stretched and dried. Stretching improves the mechanical properties by inducing a preferred orientation of the fibrils parallel to the fiber axis. The fibers are then thermally stabilized by an oxidation process at 200-220 C. The last step consists in the carbonization of the fibers at temperature ranging from 1000 C to 1500 C for carbon fibers, around 1700 C for graphite fibers.

Post-treatment,i.e. surface treatment and/or sizing, is commonly applied to the fiber surface. Surface treatments include wet and dry oxidation. Hercules uses a wet oxidative technique by electrolysis in NH_4OH which results in improved adhesion to the matrix. Sizing refers to the coating of the fiber by an agent such as polyvinyl alcohol, epoxy, polyimide or water. It improves the handleability, the abrasion resistance and the adhesion to the matrix.

2.4 Miscellaneous.

Water used in these experiments was deionized in a NanoPure II™ unit equipped with a 0.2 micron filter at the exit tap and had a resistivity typically of 15 Megaohm-cm.

Ammonium hydroxide used in these experiments was analytical reagent grade and had a molarity of 0.015 M.

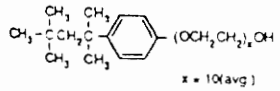
Various surfactants were used (see Figure 11) :

- Triton X-100, from Aldrich, is a nonionic surfactant.

- F-38 and F-108, from BASF, are nonionic surfactants.

- 2A-1, from Dow Chemical, is an anionic surfactant.

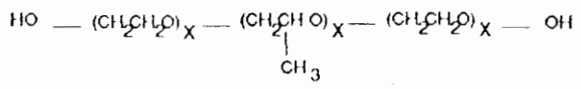
- Hydroxypropylcellulose (HPC) was obtained from Hercules.



x = 10(avg.)

Triton X-100 : nonionic

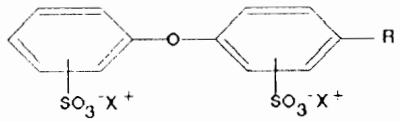
M_w = 646



F-38 and F-108 : nonionic

F-38 : M_w = 4,700

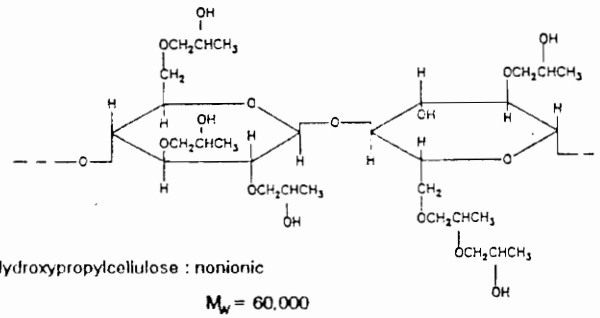
F-108 : M_w = 14,600



2A-1 : R = tetrapropylene

anionic surfactant

M_w = 576



Hydroxypropylcellulose : nonionic

M_w = 60,000

Figure 11 : Molecular structures of Triton X-100, F-38, F-108, 2A-1 and HPC.

3. PARTICLES - STABILIZER INTERACTIONS.

Due to the colloidal nature of the LaRC-TPI and PEEK particles used in this work, i.e. particle sizes in the 0.1 to 10 micron size range, it was necessary to examine the effect of colloidal stability on suspension prepregging. Specifically, the interactions of polyamic acids with LaRC-TPI and PEEK particles are discussed in this chapter with emphases on (i) polyamic acid adsorption onto LaRC-TPI, (ii) LaRC-TPI sedimentation tests, and (iii) effective size of thermoplastic particles in suspension. Before discussing these topics, the theory of colloid stabilization via polymer adsorption will be reviewed briefly.

3.1 Theory of Colloid Stability.

Particle-particle interactions in colloidal suspensions can be described by the modified Deryagain-Landau-Verwey-Overbeek (DLVO) theory which characterizes interactions in terms of a total potential energy function $V_T(H)$ given by [43] :

$$V_T(H) = V_A(H) + V_R(H) + V_S(H) \qquad (1)$$

where : H = *surface-surface separation*

$V_A(H)$ = *Van der Waals force*

$V_R(H)$ = *electrostatic force*

$V_S(H)$ = *steric force*

The original DLVO theory, developed in the 1940's, only considers the Van der Waals and the electrostatic forces. In the presence of dissolved macromolecules in the continuous phase, it is necessary to add to these forces the effect of the steric force. Van der Waals forces are almost always attractive and have a relatively short range of 1 to 10 nm in colloidal suspensions while electrostatic forces have a variable range (roughly 1 to 50 nm) and are repulsive if all particles have a net charge with the same sign. The range of the electrostatic forces depends on the thickness of the electrostatic double-layer at the particle surfaces and particle surface charge density. The double layer thickness K^{-1} is given by [44] :

$$K^{-1} = \left[\frac{\varepsilon\ k\ T}{2\ e^2\ I}\right]^{1/2} \qquad (2)$$

where ε = *solution dielectric constant,*

k = *Boltzmann's constant,*

T = *temperature,*

e = *electronic charge.*

and the ionic strength I is given by :

$$I = \frac{1}{2} \sum n_i (z_i)^2, \qquad (3)$$

where n_i = *molarity of ionic species in solution,*

z_i = *valence of ionic species in solution,*

and the summation is over all low molecular weight ionic species in solution.

For 1-1 salts used in these experiments, I is the molarity of the salts. At 25 C for 1-1 salts, equation (2) simplifies to :

$$K^{-1} = \frac{0.304}{I^{\frac{1}{2}}} \quad \textit{where } K^{-1} \textit{ has units of nm.} \qquad (4)$$

A major problem in electrostatic stabilization stems from the sensitivity of the double-layer thickness to the ionic strength of the liquid medium. In the absence of adsorbed polymer, i.e. $V_s = 0$, and at low ionic strength, the electrostatic repulsive forces dominate the attractive Van der Waals forces, resulting in

electrostatic stabilization. However, high ionic strengths result in compression of the double-layer and reduce greatly the range of electrostatic forces (1nm at 0.1 M).

Steric stabilization is a common technique used to enhance stability of dispersed systems (see Figure 12). It involves attachment of macromolecules to the particle surfaces, by chemical or physical adsorption, forming a steric layer at the surface [32]. The critical point in steric stabilization is the configuration of the macromolecules at the particle surface : when two particles get close, their steric layers interact by (i) interpenetration (short-range effect) and (ii) denting (long-range effect). Interpenetration of the steric layers leads to attractive or repulsive forces, depending on the solubility of the macromolecules in the liquid medium while denting causes compression of the steric layers without interpenetration. The resulting steric forces are a balance between the mixing (interpenetration) and the elastic (denting) components. The size of the particles, the molecular weight of the stabilizing moieties, the solubility of the macromolecule in the liquid medium will affect the range of the steric forces.

Advantages of steric stabilization over electrostatic stabilization include : (i) low sensitivity to ionic strength, (ii) effectivity at high solid contents, and (iii) reversibility of the process by addition or dilution of non-solvent.

Copolymers (block or graft) are generally more effective stabilizers than

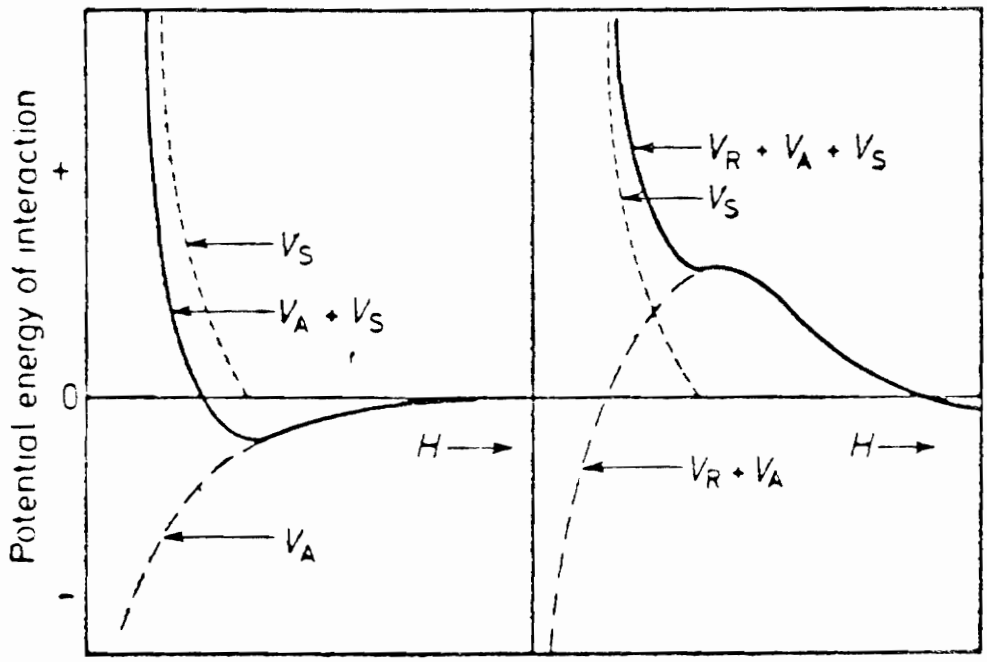


Figure 12 : Schematic interaction energy diagrams for sterically stabilized particles with and without electrostatic repulsion [45].

homopolymers. They consist of an anchor, which is insoluble in the solvent, and a stabilizing tail, which is soluble. Due to the lack of availability of suitable copolymers, this work focuses on the stabilization of LaRC-TPI and PEEK with polyamic acid homopolymers. The different polyamic acids were suspected to stabilize the LaRC-TPI or PEEK polymer particles by forming a steric layer at the particle surfaces. The suspension preparation method and the various techniques used to demonstrate the existence of such stabilization will be discussed next, followed by the results and discussion for LaRC-TPI and PEEK.

3.2 Experimental Procedures.

3.2.1 Solution Preparation.

Due to the insolubility of the different polyamic acids in water, it was necessary to dissolve them in aqueous solutions of ammonium hydroxide, NH_4OH, to form a solution of the neutralized ammonium salt of the acid.

Due to the LaRC-TPI polyamic acid particle size and particle size distribution, it was difficult to dissolve in ammonium hydroxide at room temperature. Coarse particles, larger than roughly 100 microns, did not dissolve and instead formed a gel which was not suitable for suspension prepregging. BisP-BTDA polyamic acid also did not readily dissolve in water or ammonium hydroxide at room temperature.

Two dissolution procedures were used : the first applies to small LaRC-TPI polyamic acid particles, the other was used for larger LaRC-TPI polyamic acid particles and for the BisP-BTDA polyamic acids.

Polyamic acid dissolution (first method)

This procedure was developed at the NASA-Langley Research Center for LaRC-TPI polyamic acid. Ammonium hydroxide was added to neutralize the acid. Since a slight excess of ammonium hydroxide facilitates the dissolution of the polyamic acid, NH_4OH was added to deionized water :

$$x_{paa} = \frac{m_{paa}}{m_{paa} + m_{NH_4OH} + m_w} \tag{5}$$

where x_{paa} = *mass fraction of polyamic acid in solution,*

m_{paa} = *mass of polyamic added in solution,*

m_{NH_4OH} = *mass of ammonium hydroxide,*

m_w = *mass of water*

$$\text{where } m_{NH_4OH} = \frac{2.25\ M_{NH_3^+}\ m_{pa}}{0.293} \tag{6}$$

$M_{NH_3^+}$ = *molecular weight of ammonia,*

2.25 = 2.25 *moles of* NH_3^+ *per mole of polyamic acid,*

0.293 = *mass fraction of* NH_3^+ *in ammonium hydroxide*

$$Thus,\quad x_{paa} = \frac{1}{1.245 + \frac{m_w}{m_{paa}}} \tag{7}$$

$$or,\quad m_{paa} = \frac{m_w}{\frac{1}{x_{paa}} - 1.245} \tag{8}$$

$$Therefore,\quad m_{NH_4OH} = \frac{0.245\ m_w}{\frac{1}{x_{paa}} - 1.245} \tag{9}$$

$$that\ is:\ m_{NH_4OH} = \frac{0.245\ m_w}{a} \tag{10}$$

$$v_{NH_4OH} = \frac{0.272\ m_w}{a} \tag{11}$$

$$with\ a = \frac{1}{x_{paa}} - 1.245 \tag{12}$$

While stirring the solution with an overhead stirrer, the LaRC-TPI polyamic acid powder was added, over a period of time ranging from thirty minutes to an hour, according to :

$$m_{paa} = \frac{m_w}{a} \tag{13}$$

It is important to do this very slowly to help the dissolution and to prevent polyamic acid from forming a viscous gel.

After an hour of stirring, the solution was transparent. The solution was mixed overnight and filtered with a Buchner funnel and two filters (glass and paper) to remove dust and undissolved particles. The solution was stored at 4 C to prevent degradation and should be used within a couple of days. Polyamic acid is believed to hydrolyze at room temperature. Unfortunately no systematic study has been done to confirm and quantify this phenomenon.

Polyamic acid dissolution (second method)

Due to the difficulty of grinding dry polyamic acid powder to the small size (less than 50 microns) needed for rapid dissolution at room temperature, a second dissolution procedure was developed at Virginia Tech. The same amounts of water, ammonium hydroxide and polyamic acid as in the first dissolution method (see equations (5) to (13)) were mixed in a corked flask on a magnetic stirring plate, while heating to about 50 C for ten to fifteen minutes. Polyamic acid dissolved rapidly in this water-ammonium hydroxide solution to form a perfectly clear solution.

The question of a possible degradation of polyamic acid upon heating was raised. Since the heating temperature does not go above 60 C and the solution is heated for not more than a fifteen minutes, we considered that this was not likely

to occur to such a extent as to affect greatly its properties. However, some experiments are underway to study the evolution of the molecular weight of LaRC-TPI polyamic acid with time after dissolution with this second method. No data are available at this time.

3.2.2 Suspension Mixing.

LaRC-TPI polymer

LaRC-TPI is a yellow dry powder that was added as received to the polyamic acid solution, according to :

$$x_{TPI} = \frac{m_{TPI} + m_{PI}}{m_{TPI} + m_{PI} + m_{wreleased} + m_{w} + m_{NH_4OH}} \qquad (14)$$

where x_{TPI} = *mass fraction of LaRC-TPI in suspension*

m_{TPI} = *mass of LaRC-TPI*

m_{PI} = *mass of imidized LaRC-TPI polyamic acid*

$$= \frac{m_{paa}}{M_{paa}} M_{TPI}$$

M_{paa} = *molecular weight of LaRC-TPI polyamic acid*

M_{TPI} = *molecular weight of LaRC-TPI*

$m_{wreleased}$ = *mass of water released during imidization*

$$= 2 \frac{m_{paa}}{M_{paa}} M_w$$

M_w = *molecular weight of water*

Therefore :

$$x_{TPI} = \frac{m_{TPI} + \frac{m_{paa}}{M_{paa}} M_{TPI}}{m_{TPI} + \frac{m_{paa}}{M_{paa}}(M_{TPI} + 2\ M_w) + m_w + m_{NH_4OH}} \qquad (15)$$

$$m_{TPI} = \frac{m_w}{a\ (1 - x_{TPI})} (-\ b + x_{TPI}\ (a + b + 2c + 0.245)) \qquad (16)$$

where $a = \frac{1}{x_{paa}} - 1.245$

$$b = \frac{M_{TPI}}{M_{paa}} = 0.9326$$

$$c = \frac{M_w}{M_{paa}} = 0.0337$$

The suspension was mixed for two to three hours with an overhead stirrer and was stored at 4 C and used within two days.

Poly(etheretherketone), PEEK.

The polyamic acid solution and the PEEK cake were combined in a blender for several minutes to promote intimate contact between the PEEK clusters and the polymeric dispersant so as to achieve efficient breakup of PEEK flocs. An overhead stirrer did not provide enough mixing energy to disperse the PEEK particles. The amount of added polyamic acid solution was determined by the weight ratio (polyamic acid)/(PEEK particles) which was kept between 5.5 and 6 w%. Water was sometimes added to this mixture to reach the desired final PEEK particle concentrations which ranged from 9 w% to 13 w%.

3.2.3 Adsorption Isotherm.

Since colloidal stabilization as discussed in section 3.1 depends upon the adsorption of polyamic acid onto either LaRC-TPI or PEEK, polyamic acid adsorption isotherm experiments on LaRC-TPI were performed to characterize the adsorption process. An adsorption isotherm represents the adsorbance Γ (mass of stabilizer adsorbed per gram of polymer particles) versus the concentration of stabilizer in the liquid phase.

Suspensions of various LaRC-TPI polyamic acid concentrations but identical LaRC-TPI concentration (20 w%) were mixed overnight in corked conic flasks with a wrist-action shaker. After sedimentation of the LaRC-TPI particles in graduated cylinders for fifteen days, samples of the liquid phases were taken and filtered.

The adsorbance experiments were carried out with a UV-spectrophotometer (Varian Techtron Model 635). Since LaRC-TPI polyamic acid adsorbs strongly at wavelengths between 240 and 265 nm, all measurements for this polymer were done at a 255 nm wavelength.

The procedure is as follows : the zero-optical density point is set by filling both cells with deionized water. The testing cell was then filled with the actual solution and the optical density is read.

A calibration curve relating the optical density to the concentration is drawn by testing solutions of known LaRC-TPI polyamic acid concentrations. The optical density was plotted versus the concentration to get a linear correlation described by :

$$OD = A * x_{paa} + B \qquad (17)$$

where OD : optical density

A and B : constants

x_{paa} : *LaRC-TPI polyamic acid concentration* (*w%*)

The constants A and B for LaRC-TPI polyamic acid were determined by a least-squares linear regression to have values : A = 733.64 and b = 0.000123. To be within the range of the apparatus, the calibrating concentrations were below

0.0015 %. The real samples, of unknown concentration, were diluted in order to be within the range of the apparatus. The read optical density was used with the reference curve described by equation (17) to yield the polyamic acid concentration after dilution. The original concentration is calculated according to :

$$c_f = c_{after\ dilution} \frac{V_{initial} + V_{added\ water}}{V_{initial}} \qquad (18)$$

where c_f = polyamic acid concentration of solution in equilibrium with LaRC-TPI particles

The adsorption isotherm was obtained by plotting the adsorbance Γ versus the initial concentration of LaRC-TPI polyamic acid c_i, as determined by :

$$\Gamma = \frac{M_{il}\,(c_i - c_f)}{M_{is}\,(1 - c_i)} \quad in \frac{g\ of\ adsorbed\ LaRC\text{-}TPI\ polyamic\ acid}{g\ of\ particles} \qquad (19)$$

where : M_{il} = initial mass of liquid phase

M_{is} = initial mass of solid phase

c_i = initial concentration of LaRC-TPI polyamic acid

c_f = final concentration of LaRC-TPI polyamic acid.

3.2.4 Particle Size Analysis.

Since particle aggregate size in dilute suspensions is a sensitive measure of colloidal stability, the size of LaRC-TPI and PEEK particles were measured as a function of various mixing procedures.

The apparatus used to determine the polymer particles size was a Centrifugal Particle Size Analyzer (Shimadzu Model SA-CP3, with cells part No.321-38622.10) whose principle is based on the sedimentation method.

Three experimental modes are available : gravity, centrifuge and multi. The choice of the most appropriate mode depends on the particle size range. If the size is around 100 microns, the gravity mode is recommended. If it is below 20 microns, the centrifuge is preferable. For intermediate values, the multi mode -a combination of gravity and centrifuge- is adequate.

For the centrifuge and multi modes, the centrifuge acceleration rate (120, 240 or 480 rpm/mn) needs to be selected. The higher the acceleration rate, the shorter the experimental time. This is particularly important for extremely small particles (less than 0.1 microns) when a run can last up to several hours. Most of our experiments were done at 240 rpm/mn so that runs typically required thirty minutes for LaRC-TPI and PEEK particles.

The maximum and minimum sizes detectable with this apparatus range from 0.02 to 150 microns and are functions of the liquid density, the liquid viscosity, the particle density, and the sedimentation mode selected.

The particle size analyzer cannot operate with either very turbid or very clear samples. One needs to work within a certain range of turbidity, 70 to 140 on the arbitrary optical density scale of the instrument. Thus, it is usually necessary to dilute the sample before running a particle size analysis. Ideally, the diluting liquid should be identical to the liquid phase of the suspension.

The zero turbidity point is given by filling the cell with deionized water. The water is then removed and replaced by the sample to be tested, after dilution if necessary. The apparatus defines a 100 % turbidity point from the initial turbidity of the sample. As the experiment goes on, the particles settle and the turbidity of the sample decreases. Two situations can lead to the end of the experiment :

(1) the percentage turbidity goes below the set end point turbidity (usually between 1 and 5 %).

(2) the time at which the smallest detectable particles have settled has been reached.

In both cases, the experiment stops and a summary sheet is printed out. Assuming spherical particles, a median diameter is given as well as 5 % and 95 % diameters (5 % of the particles have a diameter less than x microns, 95 % of the particles have a diameter less than y microns) and particle size distribution histograms. The 5 % and 95 % diameters are particularly useful when the particle size is polydisperse. The cumulative histogram represents the variation in turbidity with time while the differential histogram displays the particle size distribution.

3.2.5 Sonication.

Sonication is another method, other than grinding or stabilizing, which is used to break particle aggregates. It can be particularly efficient in presence of a dispersing agent. A Tekmar sonic disruptor (Model TM 300) was used to sonicate the suspensions. It is more or less successful depending on the particle concentration in the suspension. At high solid contents, sonication may increase the number of contacts between suspended particles that will promote aggregation and result in more flocculated systems.

Selected LaRC-TPI and PEEK samples were sonicated at a power level of 75 Watts for three minutes using sonicator horn with a microtip and used for particle size analysis within a few minutes.

3.3 LaRC-TPI - Stabilizer Interactions.

3.3.1 Adsorption Experiments.

Suspensions of various LaRC-TPI polyamic acid concentrations ranging from 0 w% to 3 w% were mixed and shaken with a wrist-action shaker for 24 hours. The LaRC-TPI concentrations were equal to 20 w% in all samples. The concentration range of LaRC-TPI polyamic acid and LaRC-TPI were suggested by previous work at NASA [29]. The suspensions were kept in 30 ml glass graduated cylinders for fifteen days during which sedimentation occurred. At the end of the sedimentation

experiment, the liquid phase polyamic acid concentration was measured according to the procedure in section 3.2.1 and the adsorbed amount Γ was calculated from equation (19). For LaRC-TPI polyamic acid, at a 255nm wavelength, the reference curve relating the optical density OD to LaRC-TPI polyamic acid concentration c_f (w%) was determined by least-squares linear regression (see Figure 13).

Adsorbance measurements with the solution containing no LaRC-TPI polyamic acid showed that the presence of LaRC TPI particles in the suspensions had had some effect on the liquid phase. A new zero-adsorbance point was defined with the liquid phase from the suspension containing no LaRC-TPI polyamic acid.

Figure 14 shows the adsorbance Γ versus the initial concentration of polyamic acid. For LaRC-TPI polyamic acid concentrations between 0 and 3 %, Γ generally increased. It is not clear from the trend whether full coverage of LaRC-TPI particle surface was reached.

It would be important in future work to measure the adsorption isotherms more precisely and to determine whether there is a plateau or not. For the present, the existence of a LaRC-TPI polyamic acid adsorption on the LaRC-TPI particles has been demonstrated.

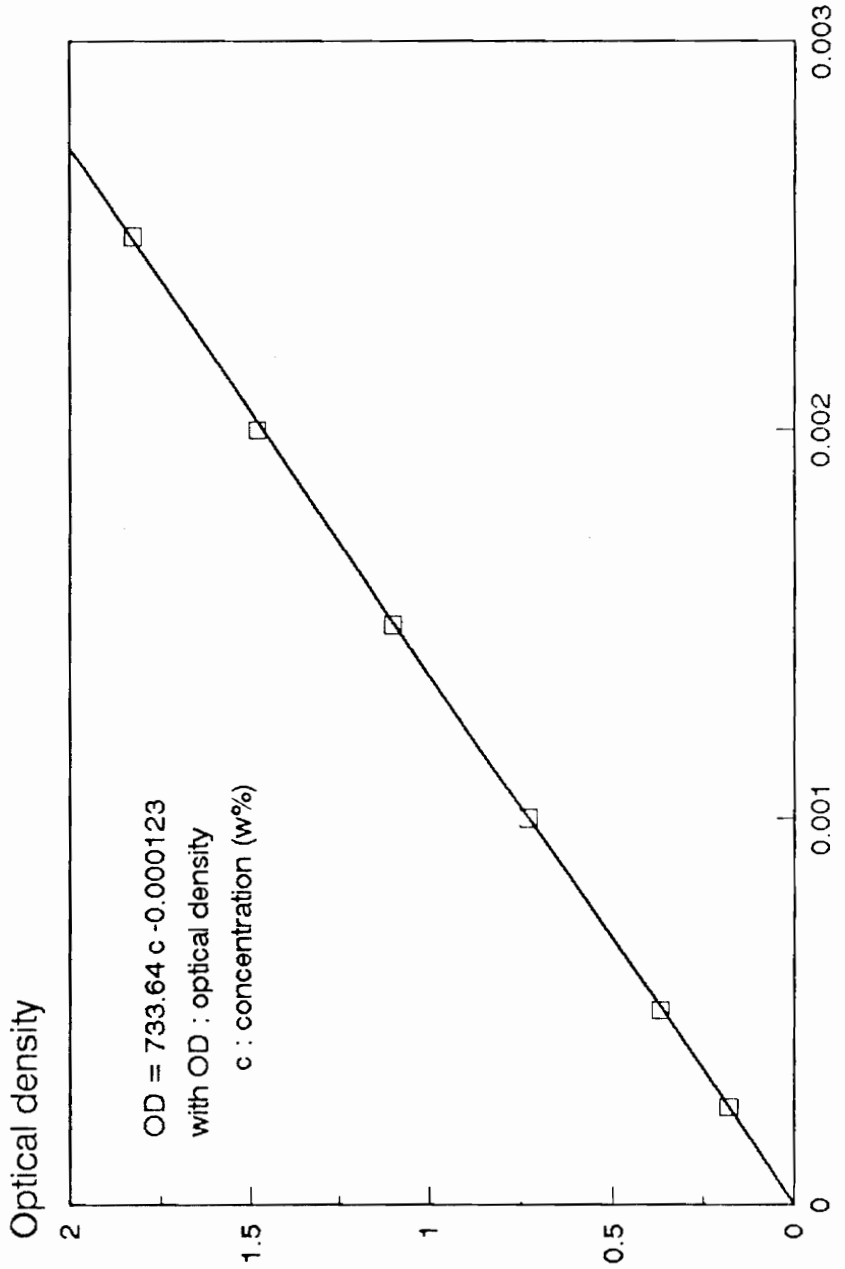


Figure 13 : Optical density reference curve for LaRC-TPI PAA at 255 nm.

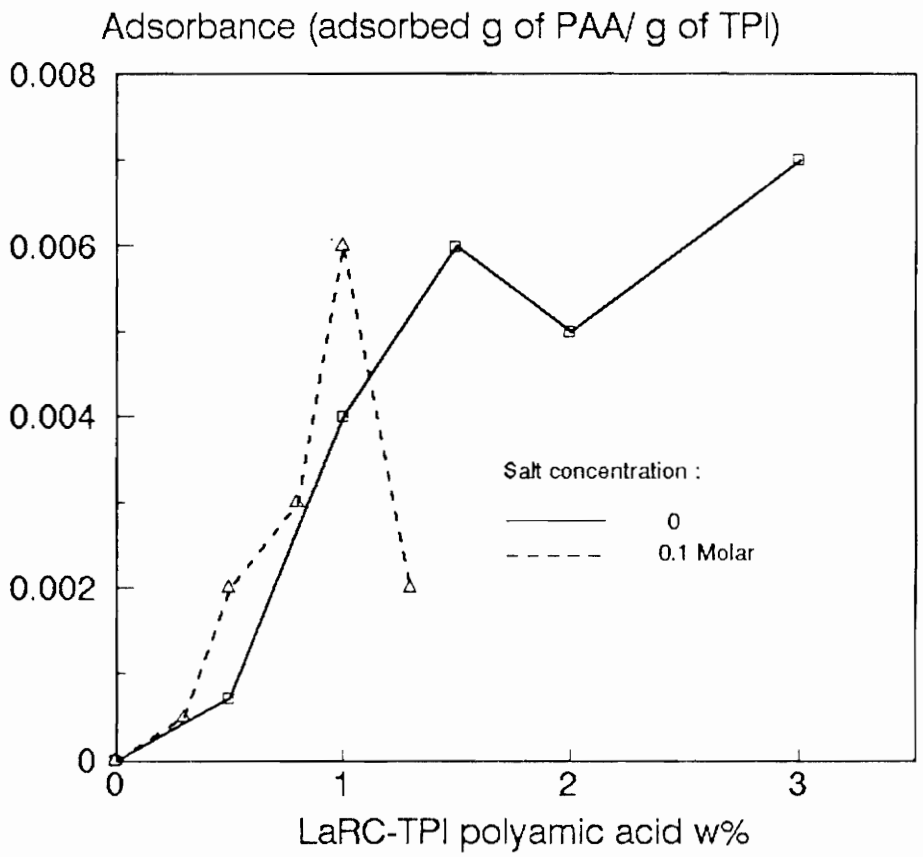


Figure 14 : Adsorption isotherm of LaRC-TPI PAA on LaRC-TPI particles at low and high ionic strength.

3.3.2 Sedimentation.

Since LaRC-TPI polyamic acid adsorbs at the surface of LaRC-TPI particles, the effect of LaRC-TPI polyamic acid on the state of aggregation of LaRC-TPI particles in suspension was investigated next.

Sedimentation tests have long been used to characterize the relative degree of aggregation of colloid ceramic particles [46]. Flocculated suspensions form loosely packed sediments with relatively high volumes compared to stabilized particles which form dense, tightly packed sediments with low volume. Thus, sediment tests can be used to characterize the effect of LaRC-TPI on the stability of LaRC-TPI particles.

The suspensions used were those prepared for the adsorption experiments where the LaRC-TPI concentration was held fixed at 20 w%. The LaRC-TPI polyamic acid concentrations in the solutions were :

Sample 1 : $x_{paa} = 0$ %

Sample 2 : $x_{paa} = 0.5$ %

Sample 3 : $x_{paa} = 1.0$ %

Sample 4 : $x_{paa} = 1.5$ %

Sample 5 : $x_{paa} = 2.0$ %

Sample 6 : $x_{paa} = 3.0$ %

During the experiment, suspensions 1 and 2 were very turbid and the turbidity did not decrease before about two days. Solutions 3, 4, 5 and 6 lost their

turbidity rapidly.

The sedimentation results can be represented by the relative sediment volume, RSV, defined by [46] :

$$RSV = \left(\frac{sediment\ volume}{total\ volume} \right)_{sample\ i} \tag{20}$$

or by the sediment density ρ_s, defined by :

$$x_{TPI} = \frac{\rho_s V_s}{(\rho_s V_s + \rho_l V_l)} \tag{21}$$

$$that\ is : \rho_s = \frac{x_{TPI}\ \rho_l V_l}{V_s (1 - x_{TPI})} \tag{22}$$

where : x_{TPI} = *LaRC-TPI mass fraction in suspension*

ρ_s = *density of the sediment*

V_s = *volume of sediment*

ρ_l = *density of the liquid phase*

V_l = *volume of liquid phase*

Figure 15 shows the relative sediment volume normalized by the RSV of the sample containing no LaRC-TPI polyamic acid (sample 1) versus the initial LaRC-TPI polyamic acid concentration as a function of ionic strength. Figure 16 shows

the sediment density for various LaRC-TPI polyamic acid concentrations at low and high ionic strengths.

The relative sediment volume and the sediment density do not show any clear dependence on the LaRC-TPI polyamic acid concentration. However, there were striking differences between the sediment densities. After removing the liquid phase from the graduated cylinders, a spatula was dipped into the sediment. The solid phase from suspension 1 offered very little resistance and it was easy to reach the bottom. Solid phases from suspensions 2, 3 and 4 were more dense and it was more difficult to reach the bottom of the cylinder. Finally, solid phases 5 and 6 offered so much resistance that it was impossible to dip the spatula very far into the sediment. It is suggested that, at concentrations below 3 w%, LaRC-TPI polyamic acid induces aggregation of LaRC-TPI particles by bridging flocculation. This phenomenon has been observed when suspended particles are not fully covered by a polymeric stabilizer, i.e. LaRC-TPI polyamic acid. At low concentration, a molecule of LaRC-TPI polyamic acid can possibly adsorb on two LaRC-TPI particles and form a "bridge" between these particles [44]. Bridging flocculation results in loosely packed aggregates with higher relative sediment volume and lower sediment density.

The effect of the ionic strength of the liquid medium on the sediment volume was also tested at I = 0.1 molar sodium chloride solutions. The samples had a 20 w% LaRC-TPI concentration. Concentrations of LaRC-TPI polyamic acid ranged

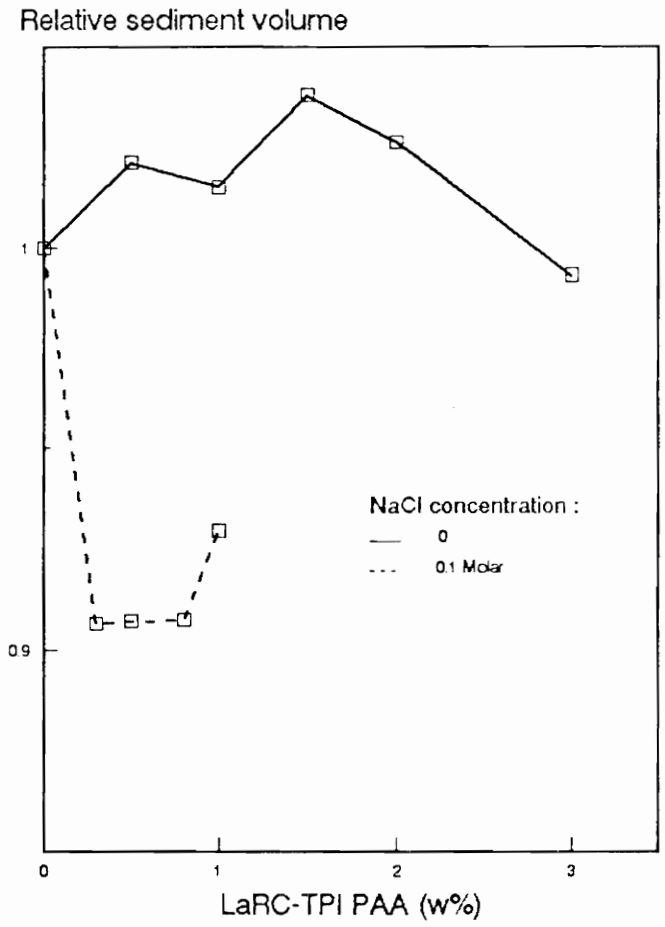


Figure 15 : Relative sediment volume of LaRC-TPI particles at low and high ionic strengths.

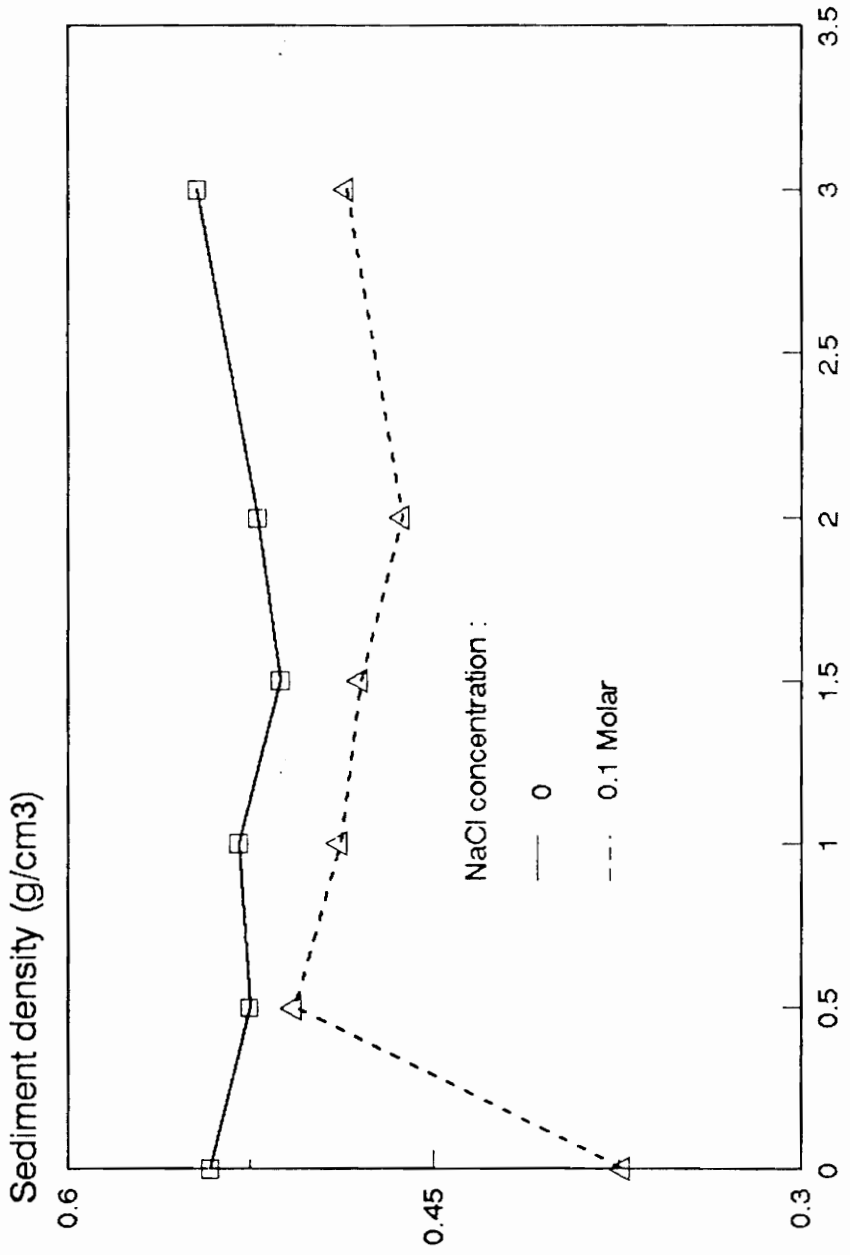


Figure 16 : Sediment density versus LaRC-TPI PAA concentration at low and high ionic strength.

from 0 to 1 w%.

Sample 1 : $x_{paa} = 0$ %

Sample 2 : $x_{paa} = 0.3$ %

Sample 3 : $x_{paa} = 0.5$ %

Sample 4 : $x_{paa} = 0.8$ %

Sample 5 : $x_{paa} = 1$ %

In this experiment, sample 1 lost its turbidity rapidly while samples 2, 3, 4 and 5 were turbid for about two days. The results, in Figure 15, show that the relative sediment volume decreases sharply with increasing LaRC-TPI polyamic acid concentration. This suggests that LaRC-TPI polyamic acid acts as colloidal stabilizer at 0.1 M sodium chloride. This is corroborated by qualitative observations of sediment density. A spatula was dipped into the solid phase of each sample. Sample 1 offered no resistance while samples 2 to 5 displayed a higher density.

Increase in ionic strength decreases the range of the electrostatic forces V_R but also changes the conformation of LaRC-TPI polyamic acid molecules on the particle surface. It is suggested that, at low ionic strength, the polyamic acid chains are lying at the particle surface. At higher ionic strength, however, the chains may have a loops-tails-trains conformation which would increase the steric layer and the range of the steric force V_s.

3.3.3 Particle Size Analysis (PSA).

The objective of this experiment was to determine if the adsorption of LaRC-TPI polyamic acid on the LaRC-TPI particles had an effect on LaRC-TPI aggregate size. Particle sizes were measured with the Shimadzu Particle Size Analyzer as a function of : (i) concentration of LaRC-TPI polyamic acid, (ii) concentration of nonionic surfactant and (iii) with or without sonication. The surfactant Triton X-100 was used to make the comparison between a low molecular weight surfactant and a polymeric stabilizer. Triton X-100 is often used to disperse colloidal particles for size analysis, especially when used in conjunction with sonication. Figure 17 shows the average diameter (in μm) for the different experimental conditions. The results suggest that :

(1) Without LaRC-TPI polyamic acid or surfactant, the LaRC-TPI aggregate size varies between 30 and 50 μm.

(2) In absence of sonication, neither Triton X-100 nor LaRC-TPI polyamic acid have any significant effect on LaRC TPI particle size : adsorption of either of them on the solid surface did not prevent particles from aggregating.

(3) Sonication alone does not prevent particle aggregation.

(4) Smaller clusters with a median size of 9 microns can be achieved with a combination of surfactant and sonication.

(5) Further size reduction can be achieved by replacing the surfactant by LaRC-TPI polyamic acid, followed by sonication. Under these conditions, the

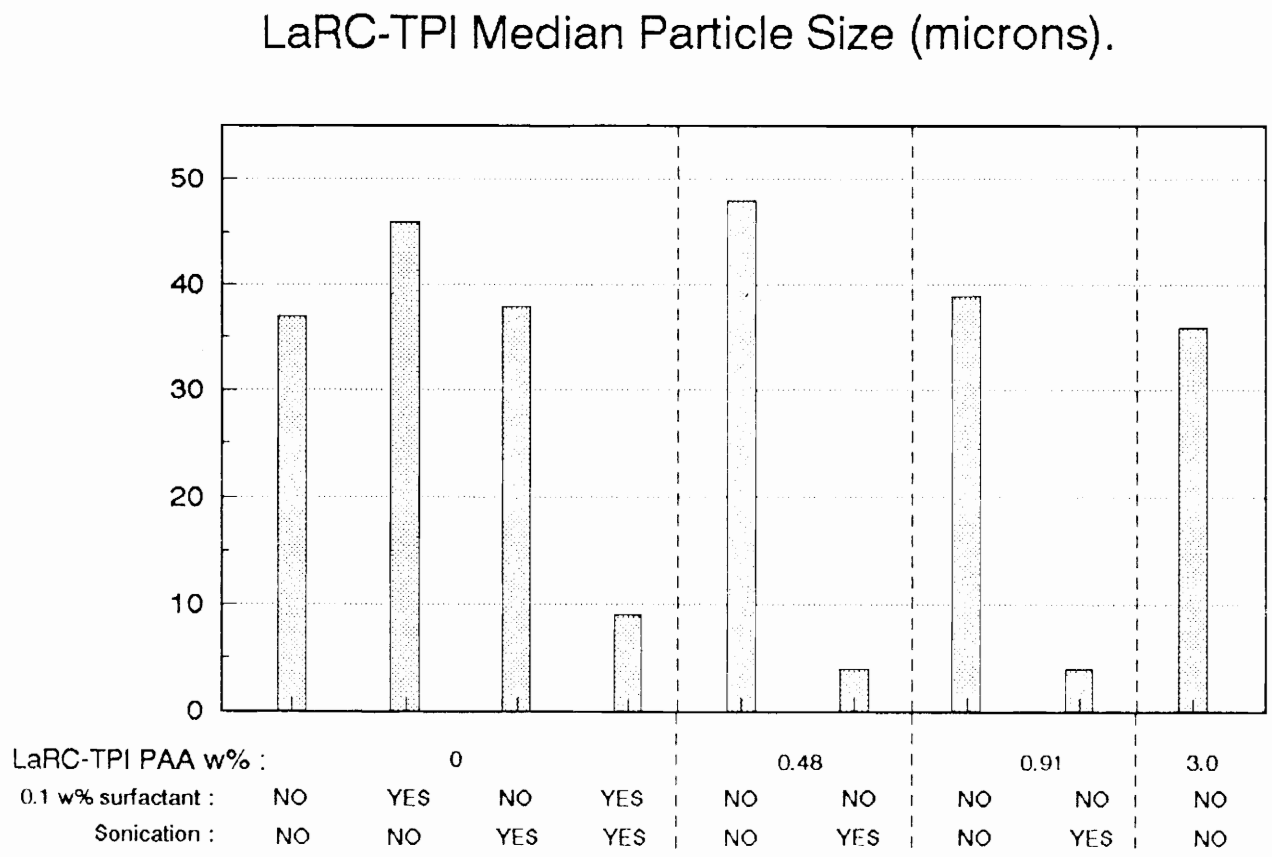


Figure 17 : LaRC-TPI median particle size in presence of LaRC-TPI PAA or Triton X-100, with or without sonication.

particle size was around 4 μm. This is likely to be the primary size of LaRC TPI particles.

This experiment showed that it was possible to reduce the LaRC-TPI median particle size by an order of magnitude by sonicating the suspension in LaRC-TPI polyamic acid solution. The addition of LaRC-TPI polyamic acid to LaRC-TPI suspensions results in adsorption of the polyamic acid molecules onto the LaRC-TPI surface. This promotes dispersion of LaRC-TPI particles in the liquid phase.

3.4 PEEK - Stabilizer Interactions.

In the case of PEEK, the dough-like consistency of the 20 w% polymer makes it an absolute necessity to add a stabilizing agent to obtain a suspension with sufficiently low viscosity to perform suspension prepregging.

Experiments were conducted to define a stabilizer for PEEK and to determine its effect on the PEEK particle size.

3.4.1 Stabilizing Agent Scouting Experiments.

Various surfactants and polymers in aqueous solution were tested for their stabilization effects by adding a few drops to a small amount of PEEK paste from batch 1 until a significant decrease in viscosity was observed. The materials were :

* pure water (control)

Low molecular weight surfactants :

* 2 A1 (anionic, M_w = 576)

* Triton X-100

* F-38 (nonionic, M_w = 4700)

* F-108 (nonionic, M_w = 14600)

Polymers :

* HydroxyPropylCellulose (HPC)

* LaRC-TPI polyamic acid

* BisP-BTDA polyamic acid.

The viscosities resulting after addition of the surfactants were still too high to permit suspension prepregging. Only HPC, LaRC-TPI polyamic acid and BisP-BTDA polyamic acid dispersed the PEEK aggregates sufficiently to obtain low viscosity suspensions. The minimum (dispersant/PEEK) ratio was lower with these polymeric dispersants (5 to 6 w%) than with HPC (17 w%). Since it is important to maximize the fiber-matrix interface strength, only LaRC-TPI polyamic acid and BisP-BTDA polyamic acid were used in prepregging experiments due to the high temperature performance of polyimides. By comparison, HPC decomposes in the range 250-300 C [47].

Batch 1 and batch 2 of PEEK were stabilized with LaRC-TPI polyamic acid only. Batch 3 was stabilized with LaRC-TPI polyamic acid, BisP-BTDA polyamic acid 10K and BisP-BTDA polyamic acid 20K.

3.3.2 Particle Size Analysis.

Particle sizes for the different batches of PEEK under various conditions (nature of the dispersant, normal or high concentration of NH_4OH, sonication) are listed in Figure 18 and Figure 19 .

The results suggest that :

(1) Excess NH_4OH is necessary to minimize PEEK median size.

(2) Sonication without excess NH_4OH reduced average particle size somewhat for PEEK batches 1 and 2. A significant reduction in median particle size upon sonication was observed for PEEK batch 3 dispersed with BisP-BTDA 10 K. However, sonication of batch 3 stabilized with BisP-BTDA 20 K resulted in a general slight increase in average particle size. This may be due to bridging flocculation of batch 3 by the higher molecular weight polyamic acid (20 K) induced by sonication. Flocculation of colloid suspensions by sonication has been observed in previous work.

(3) Sonication of all PEEK batches in the presence of excess NH_4OH results in a significant reduction in all particle average sizes. For batch 1, the median size decreased from 17 to 1 microns; for batch 2, the median size decreased from 14 to 9 microns; for batch 3, the median size decreased from 17 to 3.7 microns for particles stabilized with BisP-BTDA 10 K and decreased from 14 to 5.2 microns for particles stabilized with BisP-BTDA 20 K.

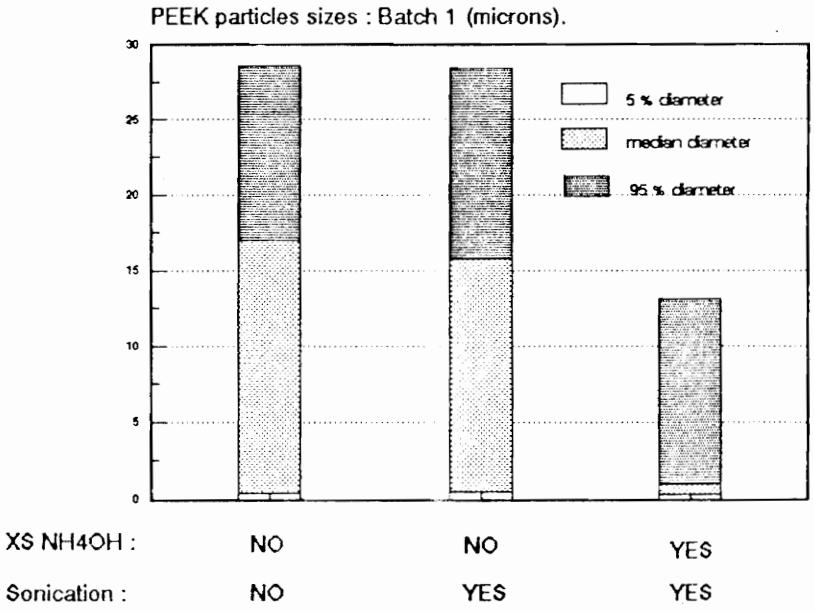


Figure 18-a.

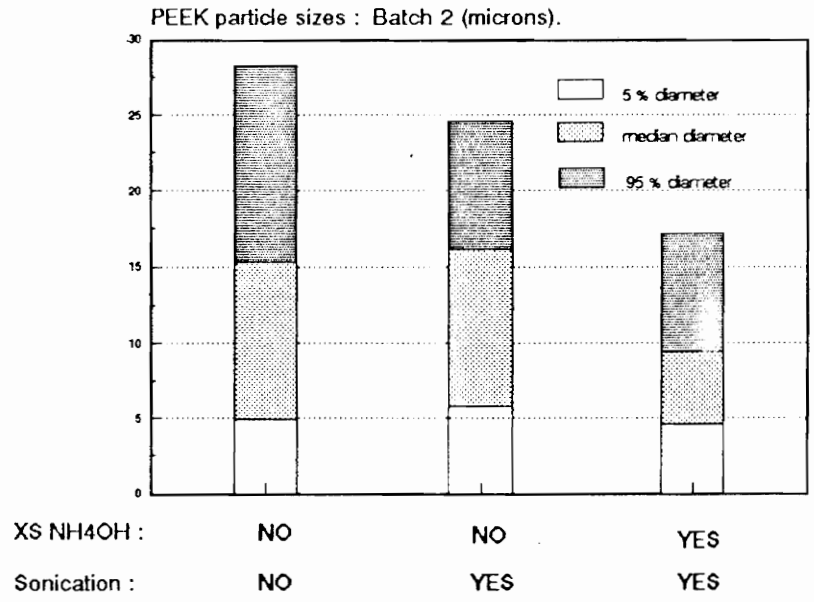


Figure 18-b.

Figure 18 : PEEK particle size for batches 1 and 2.

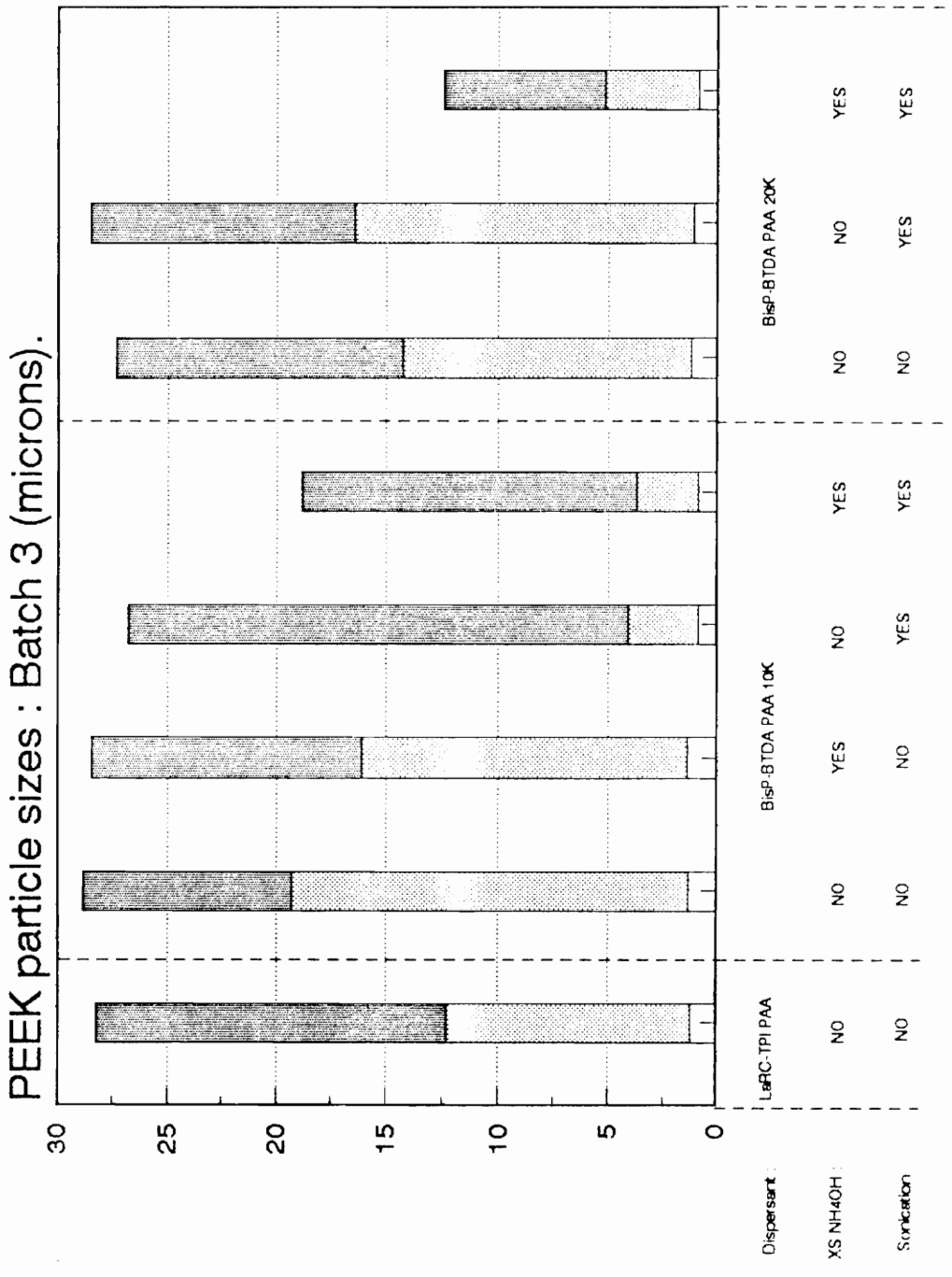


Figure 19 : PEEK batch3 particle size.

4. FIBER - STABILIZER INTERACTIONS.

The various polyamic acids used in this project were chosen with regard to their solubility in water and their ability to disperse LaRC-TPI and PEEK aggregates. Dispersion involves the interactions of LaRC-TPI polyamic acid with the suspended polymer particles. Another important interaction is that between LaRC-TPI polyamic acid and carbon fibers which affects the contact angle of the liquid medium on the fiber and thus the wetting of the liquid phase on the fibers. Still another effect of LaRC-TPI polyamic acid is to bind LaRC-TPI and PEEK particle to carbon fibers.

The surface tensions and contact angle measurements were measured for different LaRC-TPI polyamic acid concentrations. The binding of LaRC-TPI and PEEK was also evaluated as a function of LaRC-TPI polyamic acid concentration. Before these results are discussed, the experimental procedures willbe described.

4.1 Experimental Procedures.

4.1.1 Surface Tension and Contact Angle.

An electric Cahn micro-balance (DCA-322 system with Data Acquisition and

Control Station) was used to measure surface tensions and contact angles. The micro-balance was monitored by the DCA Version 2.0D Software. This instrument belonged to Professor James P. Wightman of the Department of Chemistry who kindly allowed its use in these experiments.

The procedure is as follows :

For surface tension measurements : clean very carefully a glass slide using acetone. Dry it with air. Hold the slide with an alligator clamp and pass the glass slide over a flame to burn off the impurities at the surface of the glass. Hang the clamp with the glass slide carefully on the stirrup on the microbalance.

For contact angle measurements : glue a single fiber on a thin copper wire. Bend the copper wire and hang it to the stirrup so that the fiber will enter the fluid at an angle of 90 C.

Once the slide or the fiber is in place, the beaker containing the liquid is placed on the platform. The liquid surface should be very close to the rim of the slide or to the end of the fiber. The beaker is raised at 20 μm/s. When three millimeters of the glass slide or of the fiber are in the liquid, the beaker is lowered to its home place. The force applied to the slide or fiber is recorded at the rate of one point per second and treated with a least-squares regression algorithm.

The equation used in the DCA Version 2.0D software is :

$$F = \frac{\gamma * p * \cos\theta}{9.81} \qquad (23)$$

where F = *force (g)*

γ = *surface tension (dyne/cm)*

P = *perimeter of slide or fiber (cm)*

θ = *contact angle with liquid*

The operator can choose the portion of the curve to be analyzed. Advancing and receding values are calculated (see Figure 20).

Contact angle measurements include a lot of noise, especially during the advancing phase when the fiber is entering the fluid. In our case, the reproducibility being better than expected, the experiment was repeated only four times for each solution instead of the normal five times. The fiber was changed each time.

4.1.2 Binding Fiber-Matrix.

The ability of the polyamic acids to bind LaRC-TPI and PEEK particles to Hercules AS-4 fibers prior to consolidation was checked by soaking a carbon fiber bundle in LaRC-TPI or PEEK suspensions and drying in air for 48 hours at room temperature.

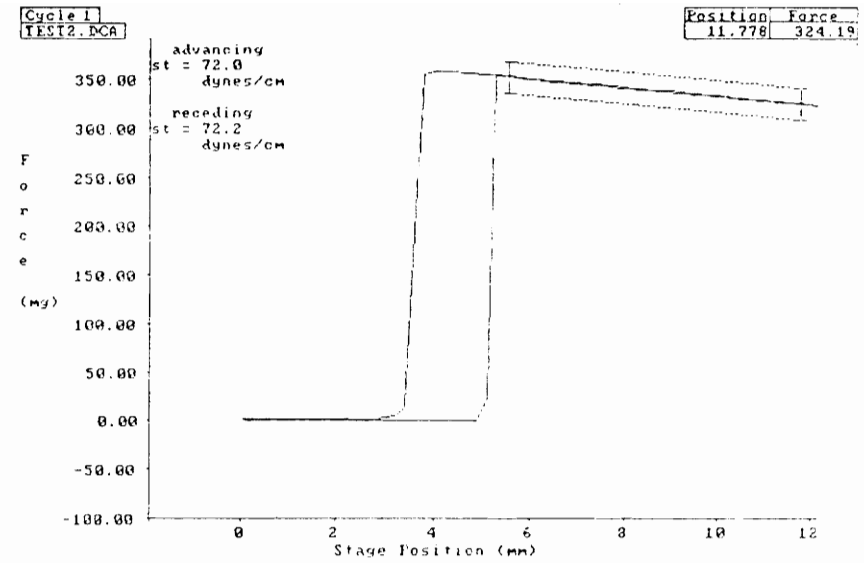


Figure 20-a.

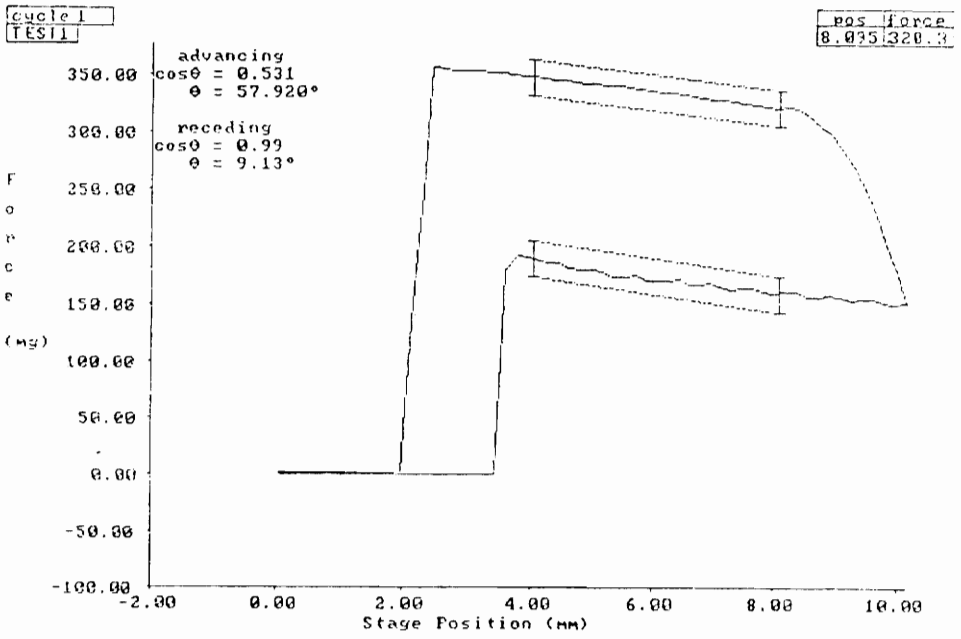


Figure 20-b.

Figure 20 : Cahn balance graphic output for (a) surface tension and (b) contact angle [48].

4.2 Fiber-LaRC-TPI Polyamic Acid Interactions.

4.2.1 Surface Tension Measurements.

Solutions of various LaRC-TPI polyamic acid ranging from 0 to 3 w% and Triton X-100 surfactant at concentrations of 0.05 to 0.3 w% were mixed with the dissolution method 1. Figure 21 shows the average of the advancing and receding surface tensions for each solution versus the LaRC-TPI polyamic acid concentration. The surface tension of the polyamic acid solutions decreased by about 10 %, indicating that LaRC-TPI polyamic acid exhibits relatively little surface activity at the air-water interface. However, when some surfactant Triton X-100 was added, the surface tension decreased dramatically by over 50 % for concentrations ranging 0.05 and 0.3 w%. The critical micelle concentration for Triton X-100 at 3 w% LaRC-TPI polyamic acid is probably less than of equal to 0.05% since the surface tension at this concentration is the same as that at 0.3 w%. It is clear from this experiment that LaRC-TPI polyamic acid alone does not lower the surface tension.

4.2.2 Contact Angle Measurements.

Contact angles on carbon fibers of solutions with various LaRC-TPI polyamic acid and surfactant (Triton X-100) concentrations were evaluated as an indicator of fiber wetting by the aqueous phase.

Figure 22 shows the average advancing and receding contact angles (in

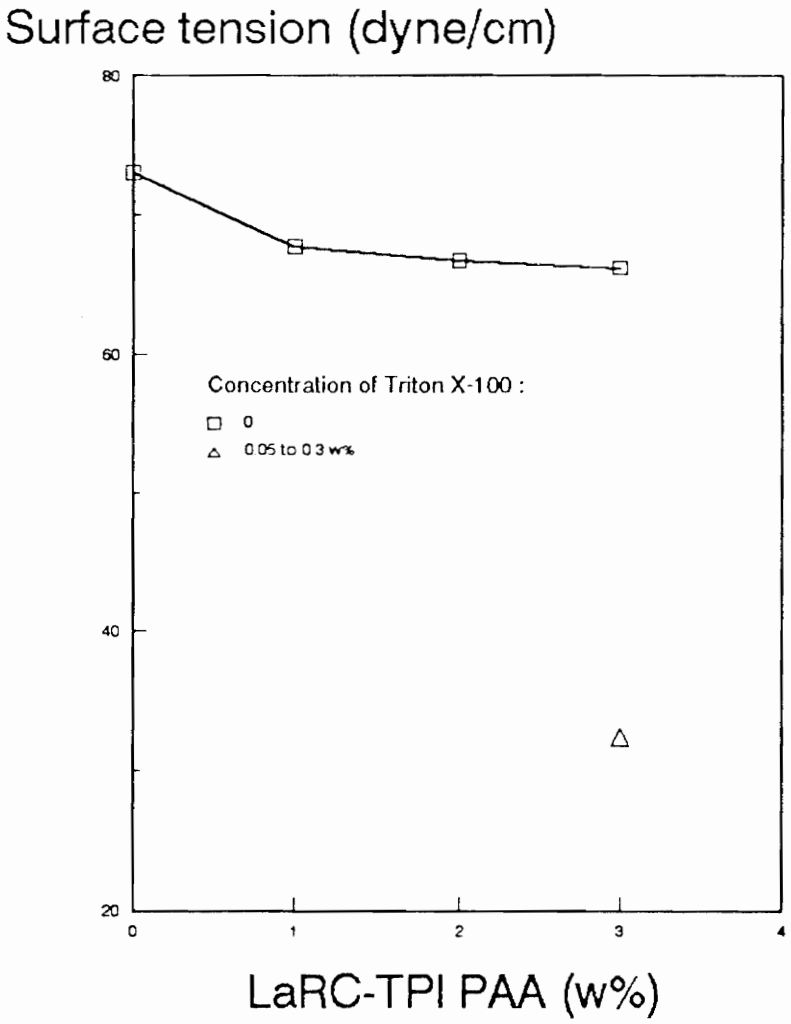


Figure 21 : Surface tension of LaRC-TPI PAA solutions.

degree) for each solution versus the surfactant concentration. The main results are : (1) In all cases, some hysteresis was observed. This can be explained by the adsorption phenomenon occurring at the surface of the fiber : water, polyamic acid and/or surfactant adsorbs at the surface of the fiber and, as the fiber is in contact with the solution for longer times, more polyamic acid adsorbs onto the fibers, thus lowering the contact angle and increasing the wettability of the fiber.

(2) The contact angle of pure deionized water on the fibers, whether the advancing or the receding contact angle, was less than, but close to 90. Thus, deionized water does not wet AS-4 carbon fiber to a significant extent.

(3) In the presence of surfactant, the advancing and receding contact angles decreased significantly. The advancing and receding contact angles do not vary significantly with the surfactant concentration within the range which was tested.

(4) The liquid phase containing Triton X-100 equilibrates very rapidly with the fiber surface since there is little difference between advancing and receding contact angles. This is consistent with the shorter times that are expected for low molecular weight surfactant adsorption on a surface compared to polymer adsorption.

4.3 Binding with LaRC-TPI Polyamic Acid.

Previous work on aqueous suspension prepregging suggested that LaRC-

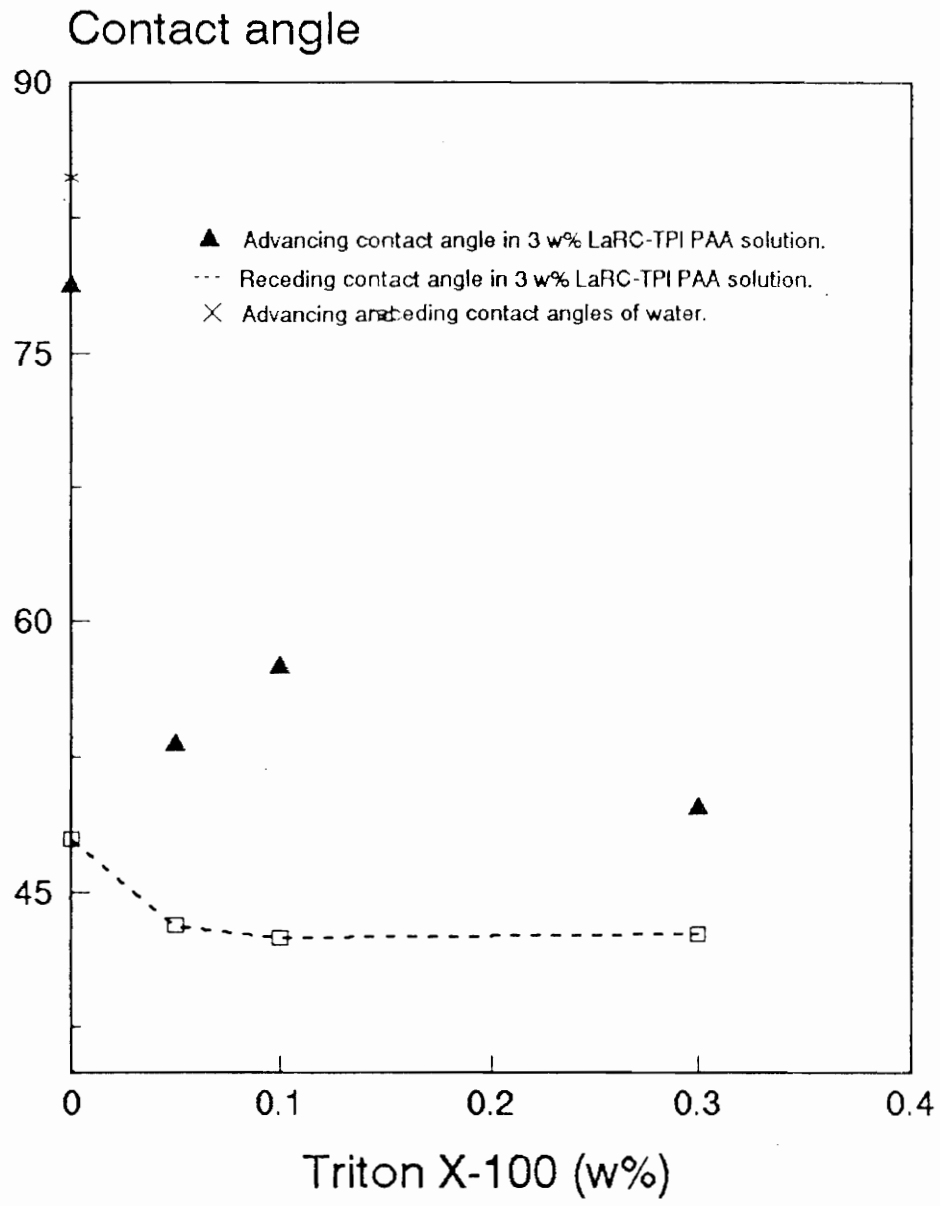


Figure 22: Contact angles of LaRC-TPI PAA solutions on AS-4 fibers.

TPI polyamic acid was necessary to bind LaRC-TPI particles onto carbon fibers both before and after consolidation. Thus, a set of experiments was conducted to determine the qualitative effect of LaRC-TPI polyamic acid as a binder for LaRC-TPI and PEEK particles.

LaRC-TPI matrix : Two suspensions were mixed : one was a suspension of LaRC TPI in a LaRC-TPI polyamic acid solution. The other was a suspension of LaRC TPI in water as a control. Both had a LaRC-TPI concentration of 20 w%. The first suspension was divided in two parts : to the first half, nothing was done. The liquid phase of the second half was replaced by deionized water. The resulting suspensions were :

1. LaRC TPI in water,
2. LaRC TPI in 3 w% polyamic acid solution,
3. "Adsorbed" LaRC-TPI polyamic acid on LaRC TPI particles in water.

The results were :

Suspension 1 :

Wetting was not very good and the impregnation more difficult to achieve. The prepreg was completely different from those made from suspensions 2 and 3 : the fibers did not stick together. The matrix looked like a yellow powder and did not stick to the fiber.

Suspensions 2 and 3 :

After curing at room temperature for 48 hours, the exteriors of the bundles were stiff but the cores seemed to be flexible. The prepreg made with suspension 3 had a more uniform surface than the prepreg made with suspension 2 : less yellow stains due to LaRC-TPI aggregates were present but some small particles were still visible.

These results suggest the necessity of a binding agent in the form of a water-soluble polymer which, upon drying, forms a filmcoating particles and fibers, thus binding these two components together. Previous work with aqueous suspension prepregging of LaRC-TPI at NASA-Langley Research Center showed that the water soluble polymer hydroxypropyl cellulose served as an effective binder for LaRC-TPI on carbon fibers before consolidation. However, after consolidation at temperatures above the decomposition temperature of HPC (250 to 300 C), the LaRC-TPI matrix showed very poor adhesion to the carbon fibers [49]. These results and the present work suggest that a variety of water-soluble polymers may act as effective particle-fiber binders before consolidation but that a high performance polymer such as polyimide is needed to efficiently bind LaRC-TPI particles to carbon fibers after consolidation.

PEEK Matrix ;

Suspensions of PEEK particles in water and in LaRC-TPI polyamic acid solutions were mixed and used to impregnate a carbon fiber bundle.

After drying at room temperature for 48 hours, the resulting impregnated bundles were different. The suspension in pure water led to very poor binding of the powder to the matrix. By contrast, the suspension in LaRC-TPI polyamic acid solution resulted in some adhesion between fibers and matrix.

The addition of a binder, in this case LaRC-TPI polyamic acid, is necessary to bind the PEEK particles to the carbon fiber. It is likely that LaRC-TPI polyamic acid may not be the best binder for this polymer. Future work should include development of alternative binders.

5. PREPREGGING AND CONSOLIDATION.

5.1 Prepregger.

All prepregging experiments were done with a Research Tool Corporation Model-30 prepregger designed originally for solution and hot melt prepregging. Modifications, described below, were made to allow prepregging with suspensions with low viscosities.

Referring to figure 4 which shows the prepregger, the take-off roll is equipped with brakes which control the tension of the fiber bundle. The fibers can pass through an oven to burn off impurities at the surface of the carbon fibers. However, the oven was not used in the present experiments. The rotation rate and the axial carriage movement of the drum can be varied independently to control the degree of overlap.

Polymer solutions used in prepregging have viscosities on the order of 2000 to 4000 cp [19]. Solution prepregging with this drumwinder has been done with the solutions contained in a resin pot equipped with a die slit on the bottom where the impregnated fiber bundle exited. This worked reasonably well with viscous solutions of poly(ethersulfone), PES, in NMP. However, the viscosity of aqueous suspensions used in suspension prepregging are typically two orders of magnitude

lower. Thus, it was necessary to design a new resin pot (see Figure 23).

The first and third rollers guide the carbon fiber bundle in and out of the resin pot. These are free to rotate. The second roller is fixed. Its function is to spread the bundle to improve impregnation. More rollers were included in the resin pot at the beginning but were found to be unnecessary and to cause some fiber breakage. The pump, located at the bottom of the container, stirs the suspension and prevents the polymer particles in the suspension from settling. The resin pot requires a minimum volume of 150 ml for acceptable operation. In addition to being suitable for prepregging with fluids with very low viscosity, fiber breakage is dramatically reduced by the absence of an exit die.

Prepregging procedure :

The general prepregging procedure is described below. Details that are specific to prepregging with either LaRC-TPI or PEEK are given in Chapters 7 and 8 respectively.

(1) The drumwinder is turned on. From the control board, it is possible to control :

(i) the carriage movement speed (left or right),

(ii) the drum rotation (forward or backward) speed

(iii) the tension on the spool is adjustable and the actual value is displayed

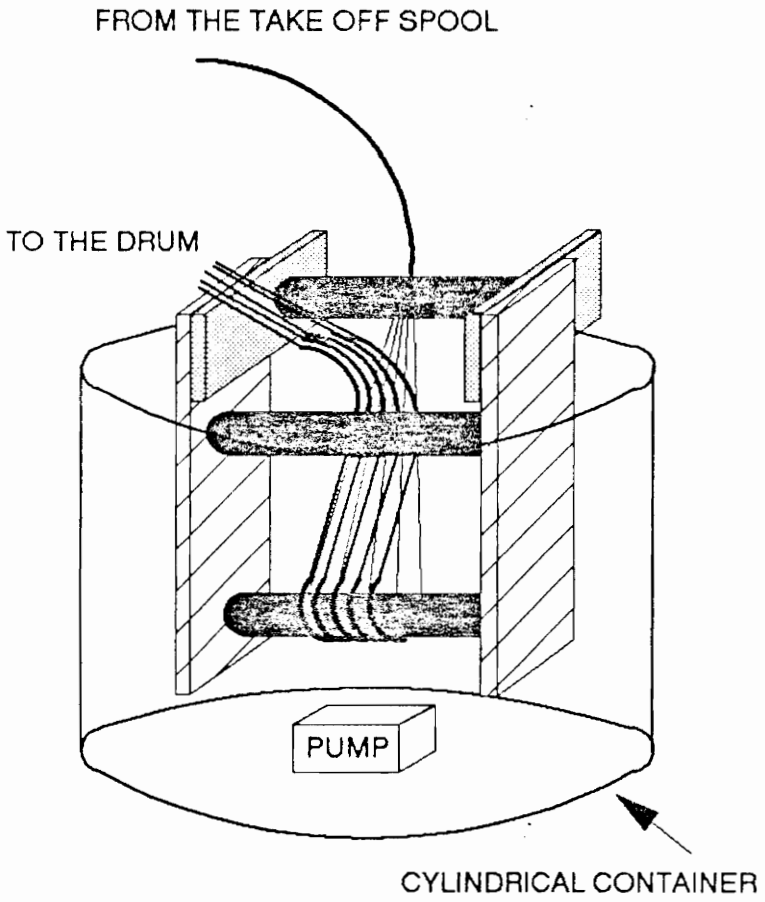


Figure 23 : Resin pot for suspension impregnation.

on a screen. It usually fluctuates a lot.

(2) A 13-inch wide Mylar sheet is cut and taped on the drum with some double sticky tape. It is important that there be no air bubbles and no dust between the drum and the Mylar sheet.

(3) The resin pot is set in front of the drum and is aligned with the drumwinder so that the carbon fiber bundle spreads adequately in the resin pot for good impregnation.

(4) The fiber take-off roll is about six meters away from the drumwinder. The carbon fiber spool is put on the upper take-off roll. It should not be too tight. When removing the plastic sheet around the spool, it is very important not to twist the bundle. There is usually a piece of tape holding the fibers of the bundle together which is useful to avoid turning the bundle upside down. The bundle goes around the load cell, through the oven, is guided by a couple of bars before going into the resin pot and then to the drum.

(5) The bundle is taped on the side of the drumwinder. Alignment is checked by rotating the drum once or twice with the dry fibers before getting started.

(6) The suspension of polymer is poured into the resin pot, the tension is applied and carriage and rotational speeds are selected. The resin pot should be regularly filled in during the drumwinding experiment to keep the residence time constant.

It is possible to make multi-layer prepreg by reversing the carriage movement direction.

5.2 First Drying Step. Cutting.

At the end of the drumwinding experiment, carriage movement and drum rotation rate should be set to zero. The carbon fiber bundle is cut just before the drum. Once the carbon fiber bundle and the resin pot are removed, infra-red lamps can be put under the drum which is then set to rotate again to speed up the drying process. After thirty minutes to an hour, the prepreg is less damp and easier to handle. It is cut along the notch on the drum and laid flat on a table.

A polyethylene sheet is laid on the top of the prepreg and then the prepreg is flattened with a heavy roller. With the top of a mold of suitable size, 7.62 cm x 7.62 cm, 7.62 cm x 12.7 cm or 15.24 cm x 15.24 cm rectangles are cut with a sharp knife and then stacked to make an 8 or a 16-ply unidirectional panel.

Wet panels are kept in porous teflon bags and stored in plastic bags for future use and analysis.

5.3 Second Drying Step.

The Blue M convection oven in the Composite Fabrication Laboratory is

heated up to a temperature depending on the polymer matrix. The panels, still in the porous teflon bags, are removed from the plastic bags and are put in the oven on a heavy aluminum platen. The prepreg is dried for three hours after which the laminate is said to be "B-staged". Ideally, the B-staged prepreg, now in the panel form, should not contain any water. This willbe discussed further in Chapters 7 and 8.

5.4 Consolidation.

The dry panels were consolidated in a Tetrahedron Pneumapress P-400 pneumatic hot press. Different consolidation cycles were used for each polymer matrix and are discussed in detail in Chapters 7 and 8 for LaRC-TPI and PEEK respectively. Independently of the time-temperature-pressure cycle, consolidation can be done with or without a vacuum bag. Consolidation of a prepreg in a vacuum bag can result in lower void content and greater removal of volatile gases These procedures willbe treated next.

5.4.1 Without Vacuum Bag.

After the drying in the convection oven, a thermocouple is plugged in the dry panel. Two Kapton films are cut and sprayed with release agent. One of these films is put on the bottom part of the mold (sprayed side up), then the laminate,

then the other Kapton film (sprayed side down) and finally the top part of the mold. Only the sides of the mold parallel to the fibers should be kept (see Figure 24).

The mold is positioned at the very center of the bottom platen of the hot press, ready to be subjected to a consolidation cycle. The platen heaters are turned on and then pressure is applied once a certain temperature is exceeded. Full details of the time-temperature-pressure cycle are given in Chapters 7 and 8. At the end of the consolidation cycle, the platen heaters are turned off and the press is cooled.

Since no cooling system is available, one or two fans are used to cool the mold and the laminate down. When the temperature of the platen is right below T_g, the pressure is released and mold taken out of the hot press.

While Pneumapress has precisely aligned platens and can make high quality laminates, it is difficult to control the pressure and the cooling rate precisely. 10 F/min is about the fastest cooling rate achieved. It would be very desirable to be able to control both the temperature and pressure cycles more precisely.

5.4.2 With Vacuum Bag.

The purpose of the vacuum bag is to decrease the void content by removing the air and the released gaseous by-products from the laminate. The mold is prepared exactly the same way as in the previous method. It is then put

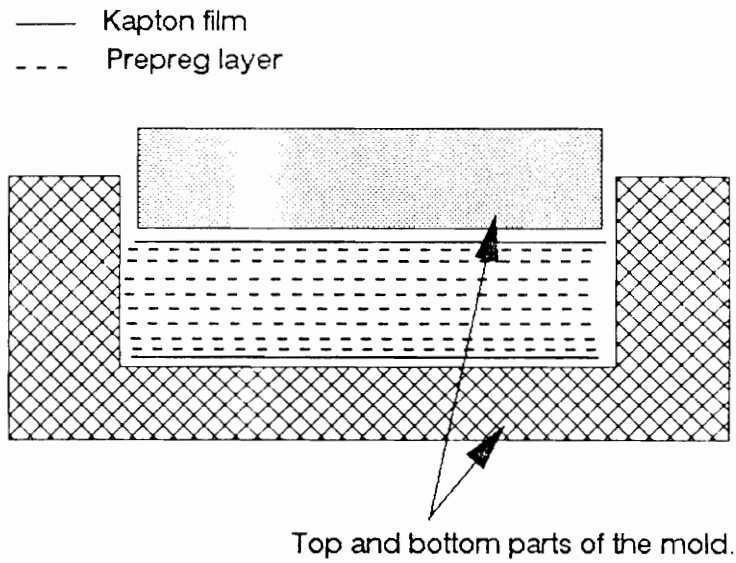


Figure 24 : Dry panel in the mold.

in a folded aluminum foil, sealed with low temperature sealant (see Figure 25). High vacuum (a thousandth of an atmosphere) is provided by a vacuum oven before putting the aluminum foil between the hot press platens.

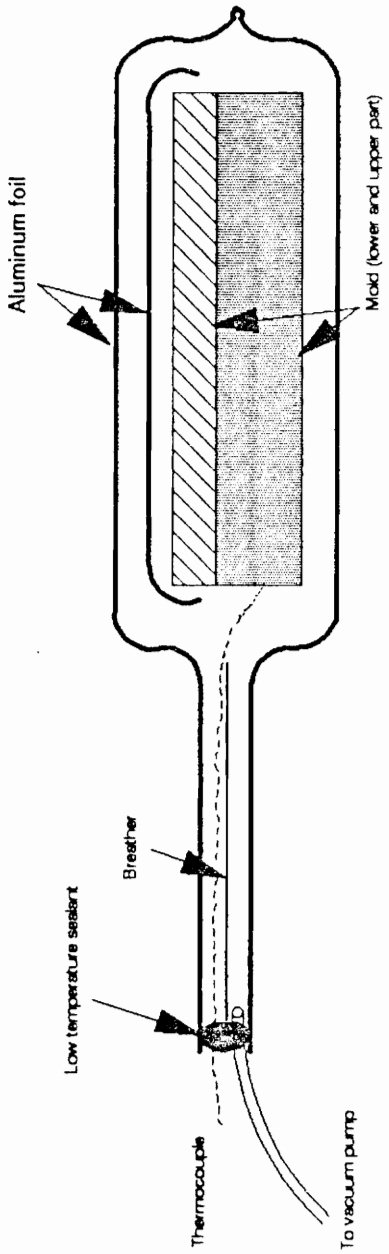


Figure 25 : Mold in a vacuum bag.

6. COMPOSITE CHARACTERIZATION

Once the laminate is consolidated, it has to be characterized to determine its mechanical properties. A variety of characterization techniques are used to check the reproducibility of the prepregging and consolidation processes, to evaluate novel impregnation and/or consolidation procedures, especially with regard to industrial processes, and to determine the effect of parameters such as polymer and fiber chemistry, polymer concentration, cooling rate, applied pressure, to name some of the most important factors.

Characterization tries to determine what the features of the composite are and whether they are acceptable or not. The interpretation is not easy, especially in a rapidly-growing field like composite materials. Even though numerous tests are performed, there is still a lack of agreement on which tests furnish exploitable information and on the subsequent interpretation. A composite is such a complex material that its complete understanding and its numerical modelling will still require years of study.

Polymer content calculations and ultrasonic C-scan testing were carried out systematically after consolidation. Mechanical tests were performed, including flexure test, short beam shear and transverse tensile tests. Normalization of the mechanical properties to certain fiber volume fraction using micromechanics

equations was investigated. Matrix wetting and adhesion to carbon fibers were characterized with Scanning Electron Micrographs. Finally, optical micrographs were taken to evaluate the fiber distribution and the void content.

6.1 Polymer Content.

In suspension prepregging, the polymer content of the final composite is controlled by varying the solid content in the suspension. One needs to be able to measure the polymer content in the final composite to calibrate the resin pot. Also, this is an important piece of information to perform valid comparison of different laminates since the mechanical properties are strongly dependent on the polymer content.

Two methods for measuring polymer content are available. The first consists of measuring the polymer content in the prepreg by washing the impregnated polymer off the carbon fibers. The second method is by acid digestion of the matrix from the laminate.

6.1.1 Prepreg Washing.

5 to 10 grams of prepreg is dried completely in a vacuum oven. The sample is dried at 70 C for seven hours. The dry weight of the sample, W_1, is then recorded. Washing is effected by plunging the sample in several 1.5 liter beakers

filled with water. The number of washing steps depends on how easy it is to remove the polymer so that little polymer remains visible on the fibers. It is often impossible to remove all the powder.

The washed fibers are then dried in a vacuum oven at 120 C for seven hours. The dried fibers are weighed, W_2.

The polymer content is :

$$\textit{Weight fraction: } P_w = 1 - \frac{W_2}{W_1} \tag{24}$$

$$\textit{Volume fraction: } P_v = \frac{1}{1 + \frac{\rho_p}{\rho_f}\frac{W_2}{W_1 - W_1}} \tag{25}$$

The fiber content is :

$$\textit{weight fraction : } F_w = \frac{W_2}{W_1} \tag{26}$$

$$\textit{volume fraction : } F_v = \frac{1}{1 + \frac{\rho_f}{\rho_p}\frac{W_1 - W_2}{W_2}} \tag{27}$$

6.1.2 Acid Digestion.

After consolidation is complete and the laminate removed from the hot press mold, it was sometimes observed, especially when vacuum bags were used to consolidate the laminate, that some of the matrix had been squeezed out of the laminate while the matrix was molten. Also, as the polyamic acid imidized to form

polyimide, water was released from the polyamic acid backbone. This results in a net reduction in the matrix content which makes it very desirable to measure the polymer content of the consolidated laminate. Acid digestion provides the best method to do this and should be used if the squeeze-out phenomenon during the consolidation step occurs to any significant extend. Moreover, acid digestion clean the fibers completely of polymer particles while this is impossible to achieve with prepreg washing.

The procedure ASTM D 3171-76 (reapproved 1982) describes the different steps to follow. The objective is to use certain acid or combination of acids, which depend on the resin, to dissolve the matrix of the laminate. After digestion, the fibers are washed in water a few times to remove any traces of acid and are then dried. Procedure B of ASTM D-3171-76, for polyimide and phenolic matrices, was used was used for both LaRC-TPI and PEEK matrices. The weight of the laminate (W_1) and of the dried fibers (W_2) were used to calculate the polymer and fiber contents (see equations 24 to 27).

6.2 C-scan.

Ultrasonic scanning is a widely used non-destructive evaluation technique. Applied to composite materials, its primary function is to detect subsurface flaws such as voids.

A high-frequency sound wave traveling through the thickness of a laminate is subjected to energy loss and reflection. Energy loss is principally due to conversion of mechanical energy into heat. Reflection takes place at the boundary of two mediums with different acoustic properties. The amount of reflection depends on the acoustic impedances of the media on either side of the interface : if the impedances are similar, very little reflection occurs. If the difference is large, however, the reflection is almost complete. Since the impedance of air (4 E-11 $g/cm^2.s$) is much smaller than that of many materials (typically between 0.1 E-6 and 5 E-5 $g/cm^2.s$), voids can be easily detected.

Analysis of the deflected waves leads to the location (x,y,z) of the flaws. Transmission and pulse-echo are two principal methods used to do ultrasonic scanning. Pulse-echo is mostly used since it records both time and signal while only the signal is recorded with the transmission method. Pulse-echo inspection can result into three types of displays : A-scan (analysis of a single point), B-scan (analysis of a line) and C-scan (analysis of an area) [50].

Ultrasonic C-scanning was performed on all laminates with an S-80 C-scan unit. A graphic printer is connected to the C-scan equipment and provided an image of the panel with the voids superimposed according to their (x,y) location (see Figure 26). The black areas represent void-free zones and the white areas represent void-rich zones. It is important to emphasize the qualitative aspect of this method and it should be kept in mind that "black" and "white" are meaningless

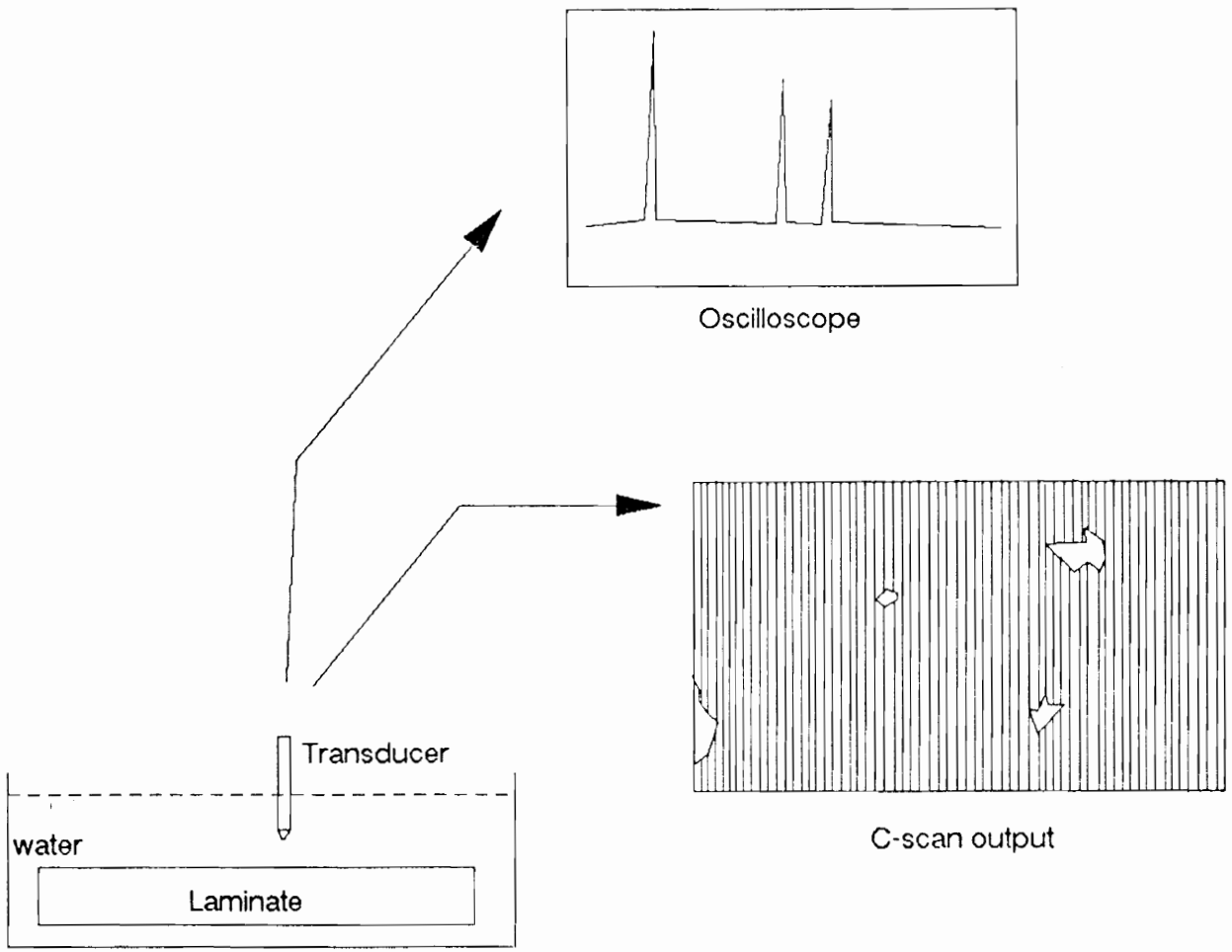


Figure 26 : C-scan unit and C-scan output.

without a sample reference output done at least before each experiment and sometimes even after. It is impossible to compare any C-scan without this reference.

6.3 Mechanical Tests.

Once test panels are made, it is essential to test them for their mechanical properties. C-scan is usually the first test done. It gives a qualitative evaluation of the panel. Mechanical tests, such as flexure test, short beam shear test, tensile test, double cantilever beam, provide quantitative data which one can use to compare the laminate with data from the literature.

Most samples in this project were small (15.24 cm x 15.24 cm maximum, often only 7.62 cm x 7.62 cm). Thus, the only tests that could be used were those requiring relatively small samples. After consultation with Dr. Doug Hirt (then at NASA- Langley Research Center) [49], three mechanical tests were chosen : flexure test, short beam shear test, and transverse tensile test. Before explaining the test procedures, the sample preparation willbe described.

6.3.1 Sample Preparation.

Mechanical tests have to be done on precisely cut samples : the length (l) and width (w) should conform to those required by the ASTM methods and the

sides of the sample need to be parallel or perpendicular to the fibers. Even though it is not always an easy task, it is important to observe these requirements to obtain mechanical properties which are reproducible and representative of the panel quality.

The easiest way to cut a carbon fiber reinforced composite is by using a diamond saw. A Fleker cut-off Machine (Model 41-AR) located in the Engineering and Science Mechanics department was used for this purpose. The procedure is the following :

(1) The tank is filled up with two water buckets.

(2) The table is wiped off to remove the protecting oil.

(3) The position of the blocking device is adjusted with scraps of panels. The length cut should be accurate to a thousandth of an inch. To hold the composite laminate in place, thick double sticky tape has been proved to work well.

(4) Once the length is adjusted, the real panel is stuck on the tape, the motor turned on. A continuous flow of water comes from two hoses down to the diamond coated blade. It should be checked that this water flow is not hindered or stopped during the cutting process.

(5) With the hands on both sides of the table, one slides the table slowly towards the blade. After the cut, the table is slid back.

(6) The motor is turned off. The sample and the scrap are removed and

dried.

(7) The edges of the sample are slightly polished with fine sand paper.

It is highly recommended to wear labcoat and glasses during this operation. A paper mask should also be worn to prevent carbon powder from being inhaled.

6.3.2 Flexure Test.

The ASTM D-790-86 procedure was used to perform this test. The size of the sample depends on the span-to-depth ratio. For a ratio of 32:1, ASTM recommends : for thickness, t = 1.59 mm, w = 2.54 cm and 1 = 7.62 cm.
After consultation with Dr. D. Hirt (then at NASA-Langley Research Center) [49], the sample size used by NASA was chosen : for a thickness comprised between 1.52 and 2.03 mm, w = 1.27 cm and 1 = (t x 32 + 1.27) cm.
The crosshead speed was of 0.127 cm/min. A 5.08-cm span feature was used (see Figure 27).

The tests were conducted on an Instron testing machine (Model 4204) located in the Engineering and Science Mechanics department, connected to a graphic table.

The flexure strength F_s (N/m^2) and the flexure modulus F_m (N/m^2) are calculated :

It is best to carry out this test on at least five samples from the same panel

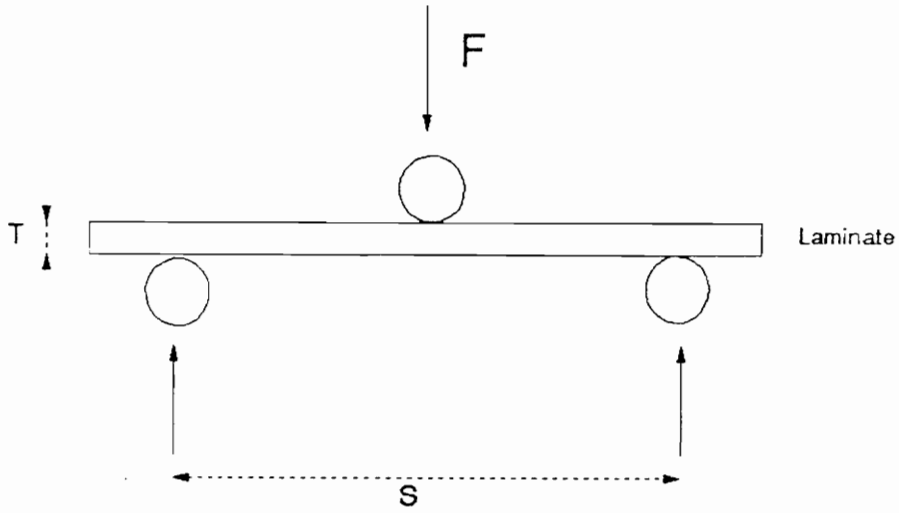


Figure 27 : Flexure and short beam shear features.

$$F_s = \frac{3\,P\,s}{2\,w\,t^2} \tag{15}$$

$$F_m = \frac{s^3 m}{4\,w\,t^3} \tag{16}$$

with P : *maximum load* (N)
s : *span* (m)
w : *width* (m)
t : *thickness* (m)
m : *slope* (N/m)

to obtain statistically meaningful average values and a standard deviation σ for flexure strength and flexure modulus. The experimental probable error, which is defined as the width of the error bar at a 50 % confidence interval, is calculated according to :

$$E = \pm\frac{2}{3}\sigma \tag{30}$$

with σ : *standard deviation*

6.3.3 Short Beam Shear Test.

The ASTM D-2344-84 procedure was used to do this test. For a span-to-depth ratio of 4:1, the sample size recommended by ASTM is : l/t = 6 and s/t = 4.

As with the flexure test, the procedure used by Dr. D. Hirt at NASA was used in the short beam shear test [49]. For a thickness of 3.17 mm, the size was

w = 0.63 cm, l = 1.9 cm and s/t = 4:1.

The crosshead speed was 0.127 cm/min. The tests were effected on the same Instron machine as for the flexure test.

The shear strength S_s can be calculated from this equation:

$$S_s = \frac{3P}{4wt} \tag{31}$$

with : P: maximum load (N)

w : width (m)

t : thickness (m).

The error can be calculated the same way as for the flexure test (see equation 30).

6.3.4 Transverse Tensile Test.

The ASTM D-3039 procedure was followed to do transverse tensile test. The samples were half an inch wide, four inches long and no endtabs were used. The tests were performed on the same Instron machine as for flexure and short beam shear tests, at a 0.127 cm/min crosshead speed (see Figure 28). An extensiometer was used to determine the strain-to-failure of the test pieces.

The transverse tensile strength TT_s is equal to :

$$TT_s = \frac{P}{wt} \tag{32}$$

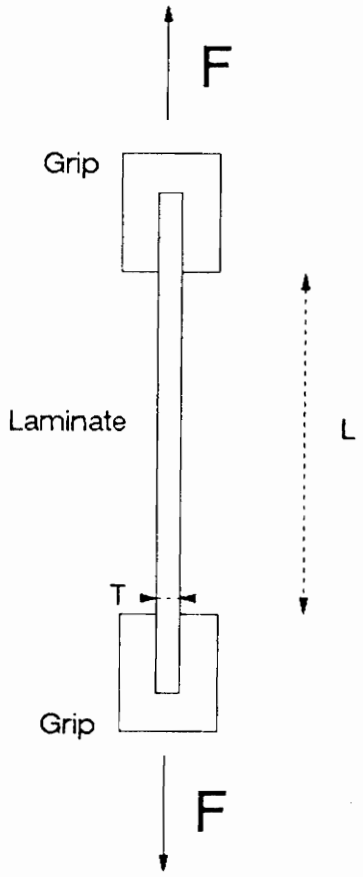


Figure 28 : Transverse tensile test feature.

With : P : maximum load (N)

w : width (m)

t : thickness (m).

6.4 Prediction and Extrapolation.

As was explained in Chapter 5, the resin pot had to be calibrated for each polymer used to deliver the desired amount of polymer to the carbon fiber. Since the PEEK supply was limited, no resin pot calibration was performed for this polymer. As a result, some test panels were made with polymer content higher than the target value. This raises some difficulties when comparisons are made between mechanical data from these panels and data from the literature for test panels made with different matrix content.

The "Engineers'guide to composite materials" [51], provides simplified equations to predict common mechanical properties such as in-plane uniaxial strength, fracture toughness, impact resistance, knowing the polymer content, the void content and the fiber and matrix properties. It assumes perfect interface binding. The purpose of these mathematical relations is to estimate the mechanical properties of composite materials. It is understood that no precise values could be obtained with these simplified micromechanical equations. However, consultation with Dr. A. Loos and advice from Dr. J. Morton, professors in the Engineering and

Science Mechanics Department, raised questions about the interpretation of data calculated with these expressions. Since the derivations and the mathematical assumptions leading to the simplified equations are not provided, it is difficult to evaluate how appropriate the micromechanical model is for our particular system. Therefore, it was decided not to use any extrapolating equations for lack of accepted valid micromechanical equations.

6.5 Scanning Electron Microscopy Test.

Scanning electron Microscopy, SEM, is an effective tool to evaluate the adhesion between matrix and fiber in a composite material. Fracture surfaces were examined at magnitudes ranging from 300x to 1500x.

Samples used in mechanical tests are too big to be used for SEM and thus need to be cut to a reasonable size with the diamond saw. The sample is stuck on a sample holder with some thin double sticky tape. The sides of the composite specimen as well as the surface of the sample holder are coated with silver paint. When dry, the sample is gold coated in a sputter coater for 120 seconds at a voltage between 0.62 V and 0.75 V. The last step is drying in a vacuum oven for seven to eight hours at room temperature.

SEM experiments were performed by Mr. D. Rodriguez and Miss J.

Muellerleile, PhD students with Dr. G. Wilkes and Mr. S. Wilkinson, a PhD student with Dr. T. Ward.

6.6 Optical Microscopy.

Optical microscopy is complementary to scanning electron microscopy in that it provides information about the fiber distribution and the existence of microscopic voids while SEM characterizes the state of the fiber-matrix interface. The sample preparation is long and tedious but is necessary to obtain good results.

Small samples (about 1.27 cm x 0.64 cm) are cut with the diamond saw. The surface to be micrographed must be polished thoroughly. Micrographs are usually taken of surfaces perpendicular to the fiber orientation. This provides the best details on fiber distribution.

Before polishing, the specimen is first mounted in a mold with an epoxy resin (epoxide resin and epoxide hardener from Buehler). It is dried overnight at room temperature before being removed from the mold. A clip can be used to hold the sample in place.

Polishing is done first with a roller grinder and then with a polisher. One starts with the coarsest sand paper by holding the sample parallel to the grinding surface. Once all the previous scratches are eliminated, one uses the next finer

paper to remove those just made. The scratches willbe finer and finer from one grinding paper to the next. The polisher should remove them completely, using polishing paste with particle sizes from 5 μm to 0.05 μm. The final surface should be sufficiently smooth so that scratches are not visible at 200x magnification.

The sample preparation and the optical micrographs were done by Steve Wilkinson, a doctoral student working with Professor Ward in the Department of Chemistry at VPI & SU.

7. LaRC-TPI COMPOSITES

LaRC-TPI composite processing constituted the first stage of this research. Beside making and testing LaRC-TPI laminates, our goal was to become familiar with the suspension prepregging procedure and the testing equipment, to evaluate our methods with respect to the procedures developed at NASA, and to define suitable processing conditions with the equipment available at Virginia Tech.

Dr. D. Hirt and Dr. T. St Clair from NASA-Langley Research Center kindly provided us with their latest procedures and results [29]. Their research had led to the conclusion that a binder, in this case LaRC-TPI polyamic acid, was necessary to obtain adequate adhesion between the matrix and the fibers. Although their resin pot was somewhat different from that used in the present work, their methods, including suspension preparation and consolidation cycle were still directly applicable.

The prepregging and consolidation conditions used in this work are discussed next, followed by the laminate characterization. Finally, the results on LaRC-TPI composites are discussed.

7.1 Prepregging Procedure.

Most of our prepregging experiments were performed with 20 w% LaRC-TPI suspended in 3 w% LaRC-TPI polyamic acid solution, the concentrations used in the earlier NASA work. However, due to the difference in resin pot design, polymer concentrations in the panels higher than the target of 32 w% were achieved. The resin pot was calibrated by impregnating fiber with suspensions of known LaRC-TPI content and then washing the prepreg to determine the amount of polymer deposited on the fibers (see Figure 29). The calibration curve relates the polymer weight fraction in the suspension to that in the laminate.

The prepregging conditions are characterized by :

(1) the carriage movement (27 to 50 %).

(2) the rotational speed (2 to 3 rpm).

(3) the tension on the bundle (0.2 to 5.7 lb).

The degree of overlap was typically of 25 to 30 %.

Table 2 summarizes the prepregging conditions for the different panels.

Before consolidation, the panels were dried in a convection oven at 399 F (204 C) for three hours.

7.2 Consolidation Conditions.

Two consolidation procedures were tried (see Figure 30) .

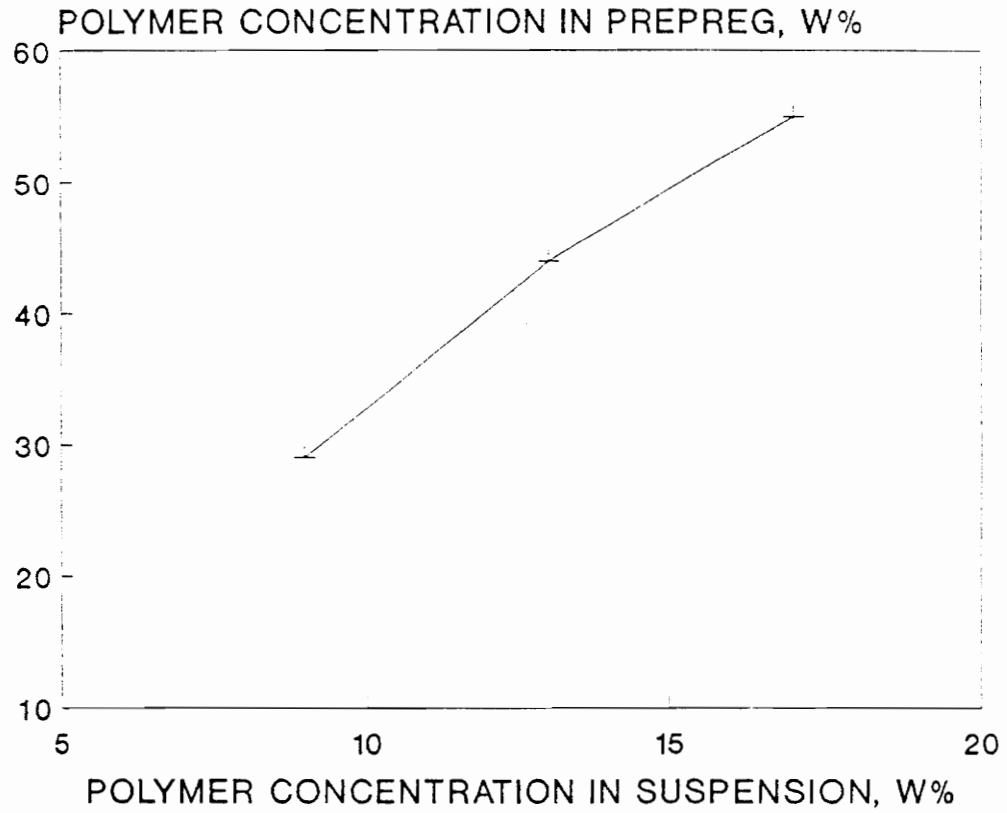


Figure 29 : Resin pot calibration for suspension prepregging with LaRC-TPI powder.

Table 2 : LaRC-TPI prepregging conditions.

	Panel 1	Panel 2	Panel 3	Panel 4
Particle size (μm)	18.87	18.87	14.3	14.3
LaRC-TPI PAA w%	3.0	3.0	3.0	3.0
LaRC-TPI w%	20.0	20.0	20.0	20.0
Roller size (inch)	0.44	0.44	0.44	0.44
Rotational speed (rpm)	2.0	2.0	3.0	3.0
Carriage mvt. (%)	27.0	27.0	40.0	40.0
Tension (lb)	0.2 to 2	0.2 to 2	2.5 to 5.7	2.5 to 5.7
Prepreg layers	1	1	2	1
Panel layers	8	8	8	16
LaRC-TPI w%	N/A	N/A	54.3	61.7

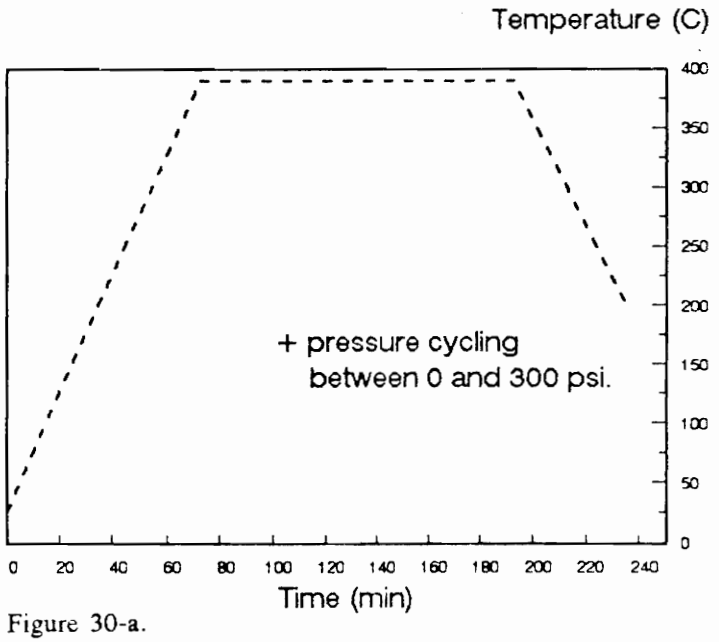


Figure 30-a.

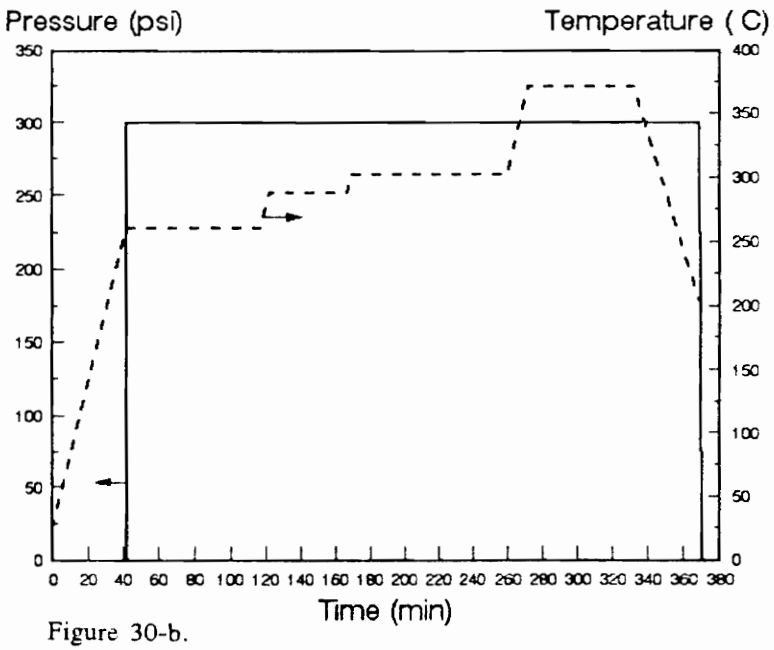


Figure 30-b.

Figure 30 : LaRC-TPI consolidation cycles (a) experimental cycle and (b) cycle developed at NASA.

Procedure a is a simple "ramp and hold" cycle for the temperature, while the pressure is cycled between contact pressure and 300 psi. This kind of pressure cycling is called "degas method". It was used with panels 1 and 2.

Procedure b was developed at NASA-Langley Research Center. It involves a series of temperature ramps and holds and gives better consolidated laminates. It was used with panels 3 and 4.

7.3 Composite Characterization.

Some modifications of the resin pot and of the prepregging procedure were effected between the prepregging of panel 1 and that of panel 2. Thus, the prepreg of panel 2 was more uniform than the prepreg of panel 1. This explains why the C-scans of panel 2 (see Figure 31-b) is better than that of panel 1 (see Figure 31-a). However, it is not as good as the consolidation of panels 3 and 4 (see Figure 32-a and Figure 32-b). Even in panels 3 and 4, some void-rich regions can be observed. Samples for mechanical tests were cut from regions that were as free of voids as possible.

Panels 1 and 2 were subjected to flexure testing. Table 3-a shows the flexure strength and modulus obtained, compared with results from NASA.

Short beam shear tests were performed on panels 3 and 4 and their shear

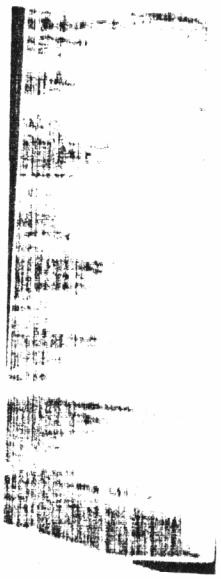
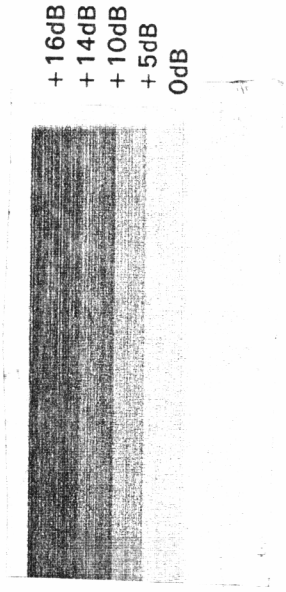


Figure 31-a.



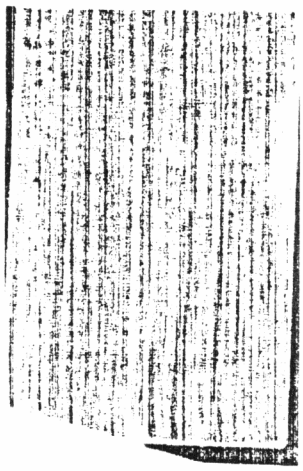


Figure 31-b.

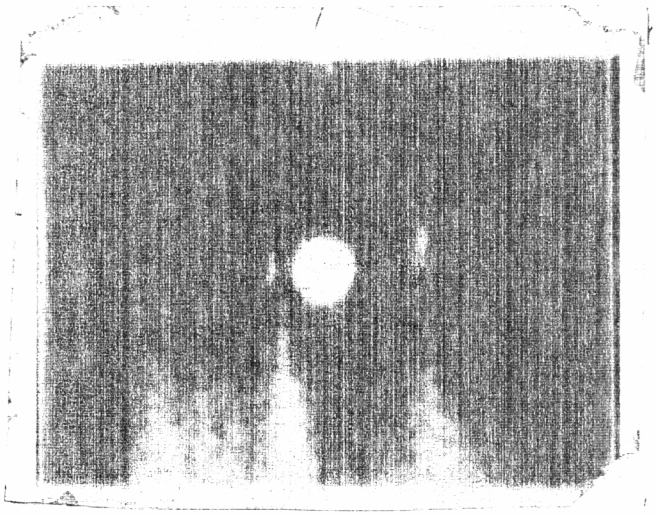
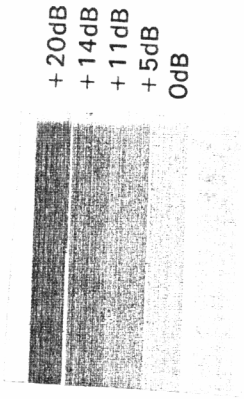


Figure 32-a.



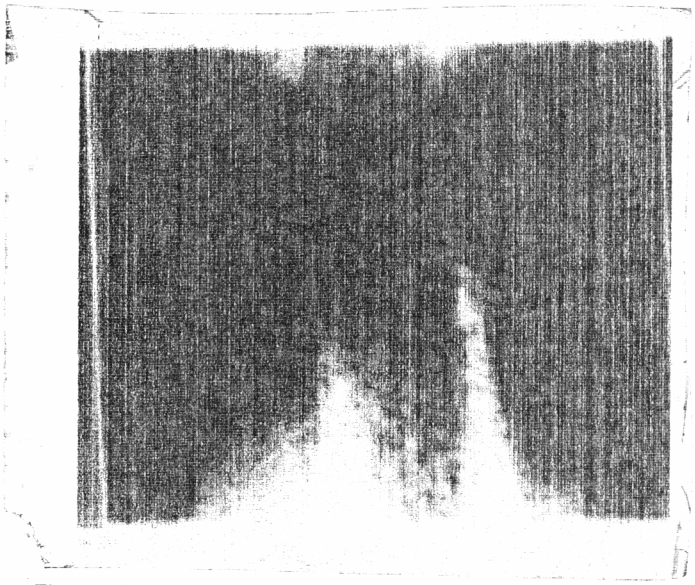


Figure 32-b.

Figure 32 : C-scans of LaRC-TPI composites : (a) panel 3 and (b) panel 4.

Table 3 : LaRC-TPI composites (a) flexural and (b) short beam shear properties.

	Fiber v/v	Flexure strength (MPa)	Flexure modulus (GPa)
Panel 1	≃ 31	1092 ± 40	63 ± 1.7
Panel 2	≃ 31	1433 ± 38	78 ± 0.7
NASA	59	1573 ± 60	78 ± 4.0

Table 3-a.

	Fiber v/v	Shear strength (MPa)
Panel 3	38	110 ± 2.9
Panel 4	31	100 ± 2.1
NASA	55	94 ± 4.0

Table 3-b.

strengths are displayed in table 3-b.

SEM was done on a fracture surface after short beam shear testing on panel 3. The micrographs, shown in Figure 33, suggest good wetting of the fibers and fairly good adhesion between fibers and matrix since no really bare fiber can be seen.

7.4 Discussion.

Suspension prepregging with LaRC-TPI suspensions results in well-impregnated carbon fiber prepreg. With the present resin pot, a concentration of less than 20 w% LaRC-TPI particles in suspension is needed to achieve 32 w% final polymer concentration in the laminate. The absence of a slit die in the resin pot reduces the fiber breakage to a negligible amount, thus improving the laminate properties.

Consolidation with procedure b, developed at NASA, leads to better consolidated panels in that their C-scans show lower void content and their mechanical properties are similar to those obtained by researchers at NASA.

Adhesion between fibers and matrix is reasonably good as determined by SEM. Optical microscopy remains to be done to evaluate the fiber distribution and the void content.

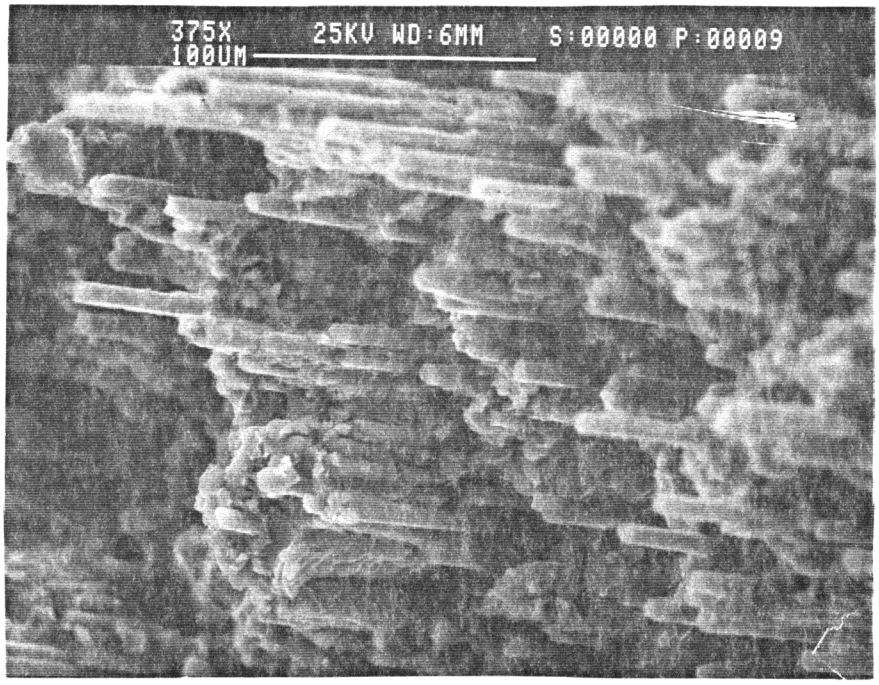


Figure 33-a.

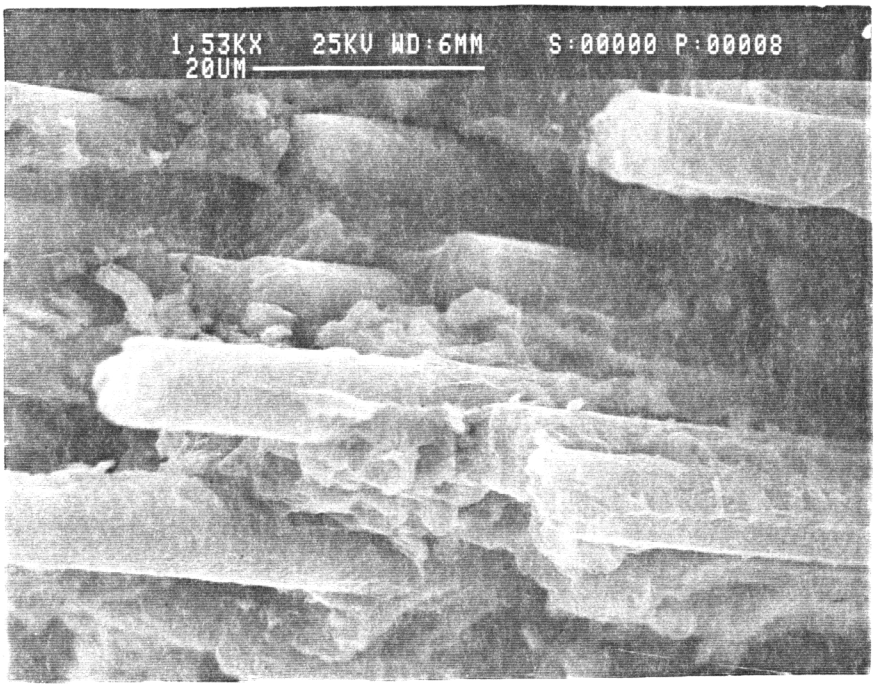


Figure 33-b.

Figure 33 : SEM on panel 3 fracture surface after short beam shear test.

8. PEEK COMPOSITES

Suspension prepregging with LaRC-TPI was the first stage of this project. The goals of this first phase were to identify the important process variables and to compare the results with earlier work conducted at NASA-Langley Research Center. The second phase of this work concerned the fabrication of novel PEEK composites using new colloidal PEEK particles synthesized only recently at Virginia Tech by members of Dr. James McGrath's group in the Department of Chemistry. In the second phase, the effects of several variables were studied. These included :

(1) PEEK matrix molecular weight,

(2) Polyamic acid type,

(3) Polyamic acid molecular weight,

(4) the time-temperature-pressure consolidation cycle.

It must be emphasized that PEEK composites made with these colloidal particles and by suspension prepregging are completely new. Consequently, there is no published literature on what the best processing and consolidation methods are. Common sense, advice from technicians, related literature and, above all, trial and error are currently the best tools available.

8.1 Prepregging Procedure.

Since small amounts of polymer were available, the resin pot was not calibrated for PEEK suspensions. The PEEK concentration was 13 w% for batches 1 and 2, which resulted in composites with a polymer content of typically 55 w%. Thus, for PEEK batch #3, the PEEK concentration in the resin pot was reduced to 9 w% which lowered the PEEK content in the final laminates to values close to the target of 32 w% quoted for ICI's APC-2 PEEK prepreg.

The polyamic acid concentration in the liquid phase of the suspension was 1 w% for batch 1, 0.83 w% for batch 2 and 0.5 w% for batch 3 to keep the ratio (polyamic acid)/PEEK between 5.5 and 6 w% because this ratio was found to disperse the PEEK particles adequately.

The carriage movement sometimes had to be adjusted when the alignment of the fiber spool, of the prepregger and the resin pot was not perfect. Very low tension was applied in all cases, typically one to two lbs force.

Table 4 summarizes the conditions under which eight panels were made.

Prior to consolidation, the panels were dried at 220 F (104 C) for an hour and at 350 F (177 C) for two hours.

8.2 Consolidation Conditions.

Two panels made with PEEK batch 1 were consolidated. The first panel was

Table 4 : PEEK prepregging conditions.

Panel number :	1	2	3	4	5	6	7	8
Particle size (μm)	17.0	17.0	15.3	15.3	15.3	12.2	19.3	14.2
PAA : LaRC, BB10, BB20	LaRC	LaRC	LaRC	LaRC	LaRC	LaRC	BB10	BB20
PAA / PEEK (w%)	6	6	5.5	5.5	5.5	5.5	5.5	5.5
PEEK concentration (w%)	13	13	13	13	13	9	9	9
PEEK batch number :	1	1	2	2	2	3	3	3
Roller size	0.44	0.44	0.44	0.44	0.44	0.44	0.44	0.44
Rotational speed (rpm)	3	3	2.5	2.5	2.5	3	3	3
Carriage movement (%)			35	35	35	50	varied	45
Tension (lb)	low	low	low	low	low	low	low	low
Prepreg layers	1	1	1	1	1	1	1	1
Panel layers	8	8	8	8	8	8	8	8
Polymer content (w%)	--	--	56	57	56	49	29	32
Consolidation cycle	--	--	a	b	c	d	d	d

processed twice (see Figure 34-a) since the laminate was very poorly consolidated after undergoing the first consolidation cycle. The second panel was processed only once (see Figure 34-b).

With batch 2, three methods of consolidation were tried (see Figure 35 a, b and c). The parameters (number of cycles, temperature set point, pressure) were arbitrarily set up.

With batch 3, a fourth method was used (see Figure 35-d).

With the Pneumapress, the cooling rate was close to 10 F/min (5.5 C/min). With the present equipment it is very difficult to control it. This lack of cooling rate control was not critical for LaRC-TPI since the matrix was amorphous, but this is undesirable with semi-crystalline matrices, such as PEEK, since the degree of crystallinity depends upon the cooling rate. For future work, it is imperative that a hot press be used with much better temperature control.

8.3 Composite Characterization.

The various prepregging and consolidation conditions of PEEK composites were designed so as to vary one parameter at a time. These parameters were :

1. PEEK chemistry.

2. Polyamic acid chemistry.

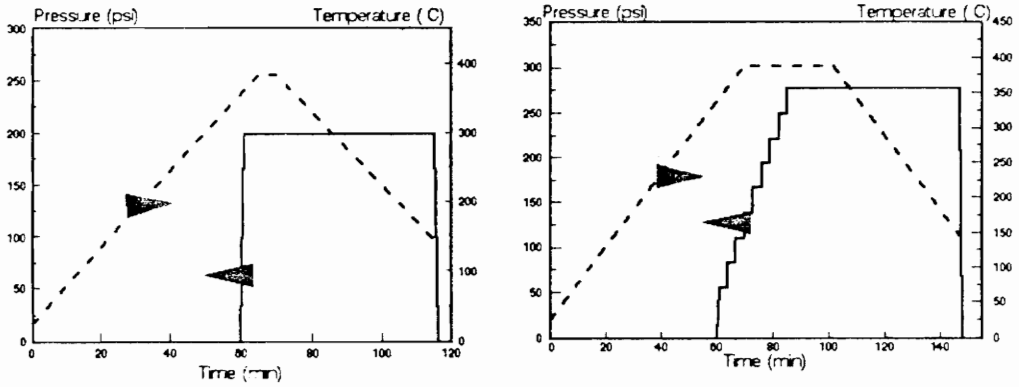


Figure 34-a.

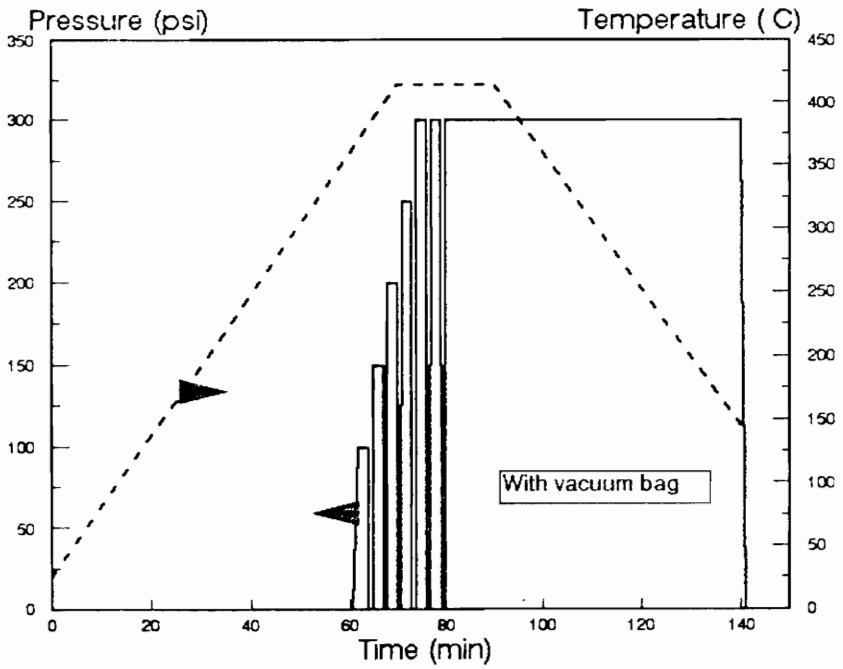


Figure 34-b.

Figure 34 : Consolidation cycles of PEEK composites : (a) panel 1 and (b) panel 2.

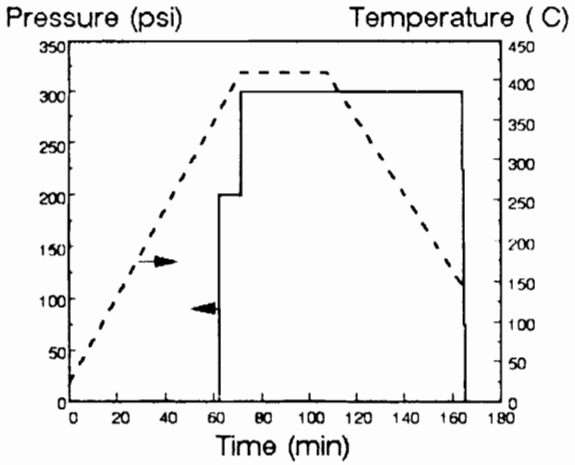


Figure 35-a.

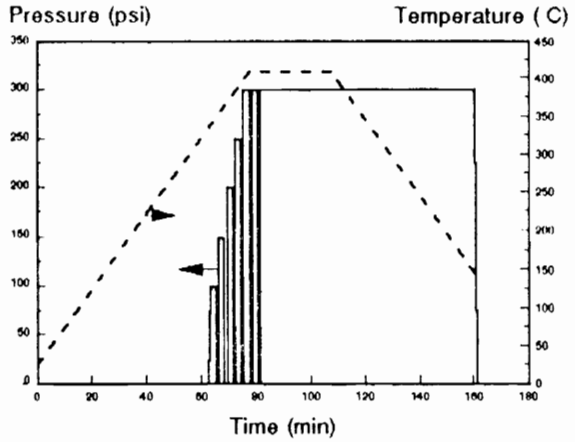


Figure 35-b.

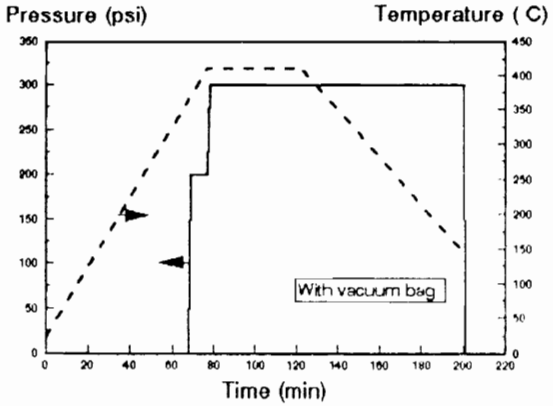


Figure 35-c.

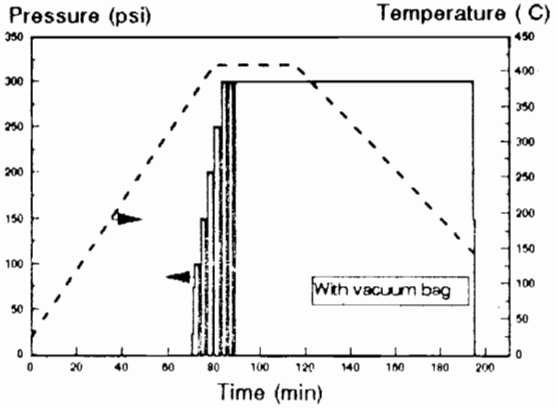


Figure 35-d.

Figure 35 : Consolidation cycles of PEEK composites : (a) procedure a, (b) procedure b, (c) procedure c and (d) procedure d.

3. Pressure cycle.

4. Temperature cycle.

5. Volatile release method.

With each batch of PEEK, two or three panels were made with one or two varying parameters. This allowed us to compare the laminates with each other and to draw conclusions to define the current best processing conditions.

PEEK chemistry : the laminates made with PEEK batch 1 (panels 1 and 2) were both very badly consolidated. There were cracks parallel to the fibers and the panel was easy to break. Fracture surfaces revealed a striking lack of adhesion between fibers and matrix. Since the consolidation was so poor, no mechanical tests were performed on these laminates .

Since parameters 2 to 5 for panel 2 were identical to those for panel 7, whose consolidation was good, it suggests that the PEEK chemistry needed improvement. The suspected low molecular weight of batch 1 PEEK (around 16,000) probably explains the poor consolidation that resulted. The combination of low cooling rate and low molecular weight probably led to a high degree of crystallinity, resulting in a very brittle matrix. Even though no numerical data are available at this time, it is known that batches 2 and 3 had higher molecular weight and, indeed, panels 3 to 8 showed good consolidation.

Consolidation cycle : The procedures used with panels 3 to 5 held

parameters 1 and 2 constant and varied the consolidation processes (parameters 3 to 5). Ultrasonic scanning and flexure test were performed on the panels. As mentioned above, the higher molecular weight of PEEK led to crack free laminates. However, the C-scans showed an overall poor consolidation, resulting in laminates with high void content (see Figure 36 and Figure 37-a). The flexure strengths and moduli are shown in Table 5, compared to ICI literature. The strengths of panels 4 and 5 are slightly better than that of panel 3.

This suggests that consolidations b and c were slightly better than cycle a. Thus, a procedure d was developed by combining cycles b and c. As was expected, the mechanical properties of composites consolidated with procedure d (panels 6, 7 and 8), were closer to the ICI standards than those of panels 3 to 5 (see Table 6). Their C-scans reinforced this opinion that cycle d provides relatively good consolidation (see Figure 37-b and Figure 38). Nevertheless, it is almost certain that procedure d can still be optimized.

Beside PEEK chemistry and consolidation cycle, the miscibility of the imidized polyamic acids and PEEK was another issue addressed in this study. This was investigated with PEEK batch 3.

Miscibility: the effect of PEEK chemistry (principally molecular weight) and the consolidation cycles were studied with PEEK batches 1 and 2. The processing conditions of panels 6, 7 and 8 differ only by the type of polyamic acid used

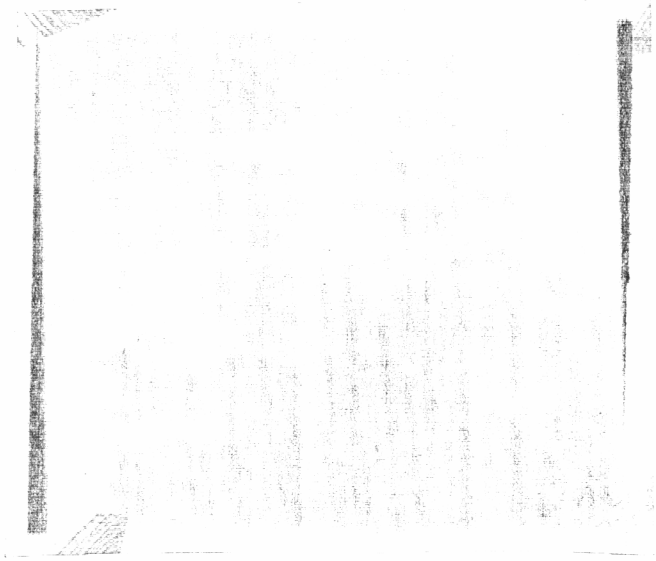


Figure 36-a.

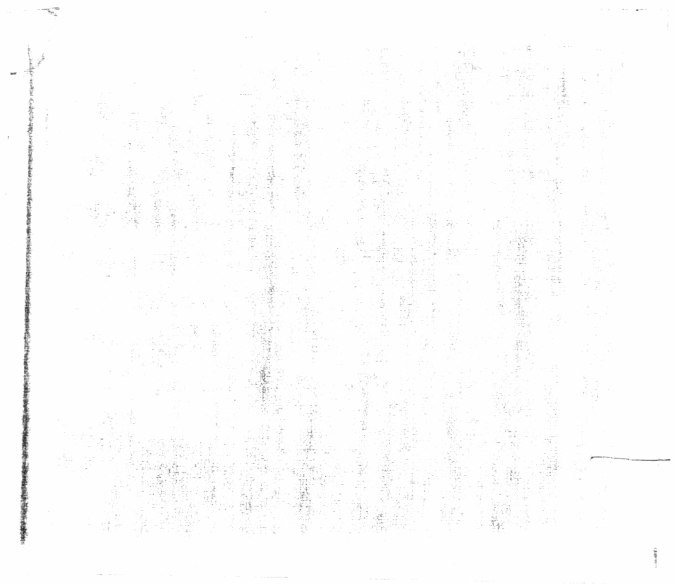


Figure 36-b.

Figure 36 : C-scans of PEEK composites : (a) panel 3 and (b) panel 4.

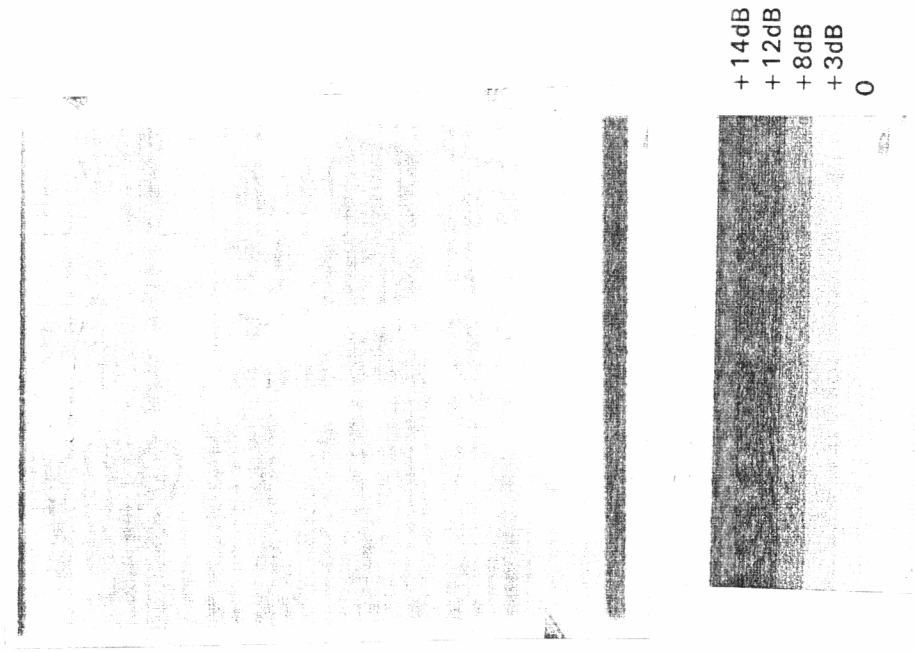


Figure 37-a.

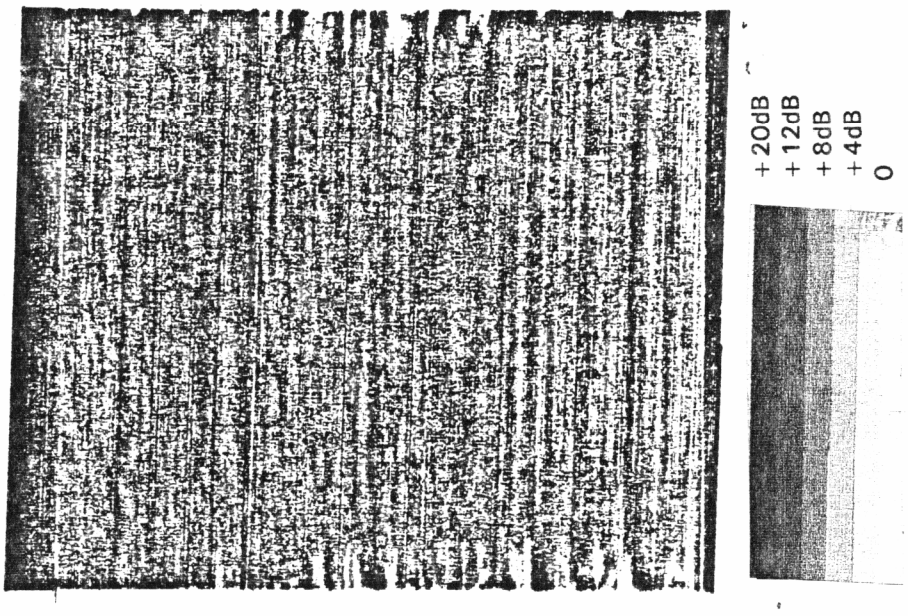


Figure 37-b.

Figure 37 : C-scans of PEEK composites : (a) panel 5 and (b) panel 6.

Table 5 : PEEK composites flexural properties.

Panel #	Fiber (v/v)	F_s(MPa)	F_m (GPa)
3	36	813 ± 63	59 ± 1.7
4	35	869 ± 13	62 ± 1.2
5	36	883 ± 50	63 ± 1.7
ICI	68	**1883**	**121**

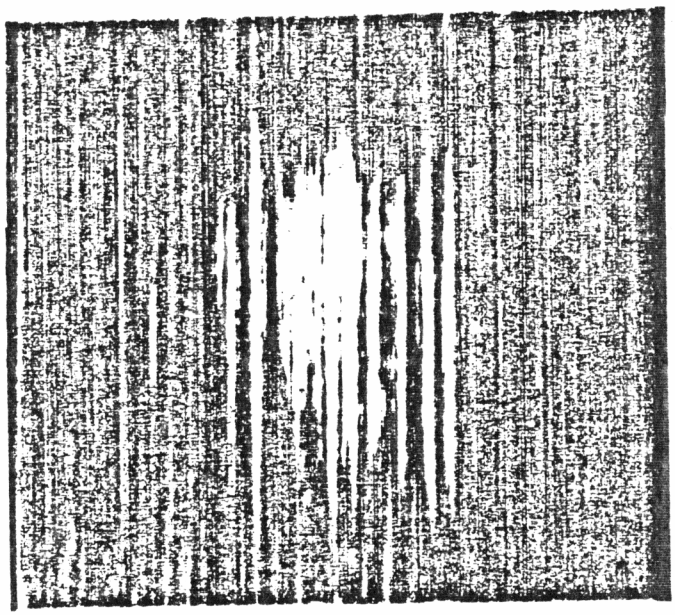


Figure 38-a.

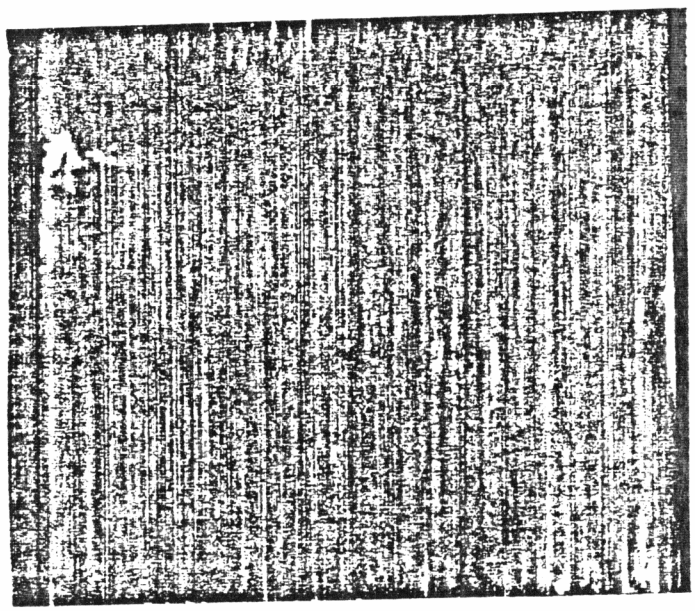


Figure 38-b.

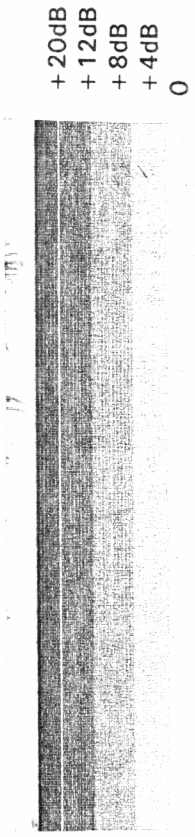


Figure 38 : C-scans of PEEK composites : (a) panel 7 and (b) panel 8.

(parameter 2). The polyamic acids - LaRC-TPI polyamic acid, BisP-BTDA polyamic acid 10 K and BisP-BTDA 20 K differ in two important respects : miscibility of the imidized form with PEEK and molecular weight. From Chapter 2, it can be seen that LaRC-TPI, the imidized form of LaRC-TPI polyamic acid, is not miscible with PEEK whereas the imidized forms of both BisP-BTDA's are miscible. The molecular weight of LaRC-TPI polyamic acid was not measured but the molecular weights of BisP-BTDA 10K and 20K were controlled at 10,000 and 20,000, respectively.

Panels 6, 7 and 8 were ultrasonically tested (see Figure 37-b and Figure 38) and subjected to a transverse tensile test. This mechanical test was also performed on a consolidated APC-2 panel. The C-scans show good consolidated panels. A few void-rich regions are still present. The transverse tensile test results are given in table 6 with the ICI literature data. Panels 6 and 8 have strengths similar to the published ICI value. Panel 7 has a low transverse tensile strength that probably results from the alignment problem encountered during the impregnation step. The transverse tensile moduli have not been calculated yet.

SEM was done on fracture surfaces after transverse tensile testing with panels 6, 7, 8 and the in-house-tested APC-2 (see Figure 39 and Figure 40). In all cases, wetting of the fibers is good and the failure was of cohesive nature. Panels 7 and 8 show very good adhesion that compares well with the APC-2 sample. The fracture mode of panel 6 seems to be different from that of panels 7, 8 and APC-2. Alignment problem during the prepregging of panel 7 explains the poor properties

Table 6 : PEEK composites transverse tensile strength.

Panel #	Fiber (v/v)	TTS (MPa)
6	43	73.4 ± 1.4
7	64	58.8 *
8	61	73.1 ± 1.7
APC-2	61	94.7 ± 2.0
ICI	61	**80.0**

* single value.
APC-2 : sample tested at Virginia Tech.
ICI : literature value.

Figure 39-a.

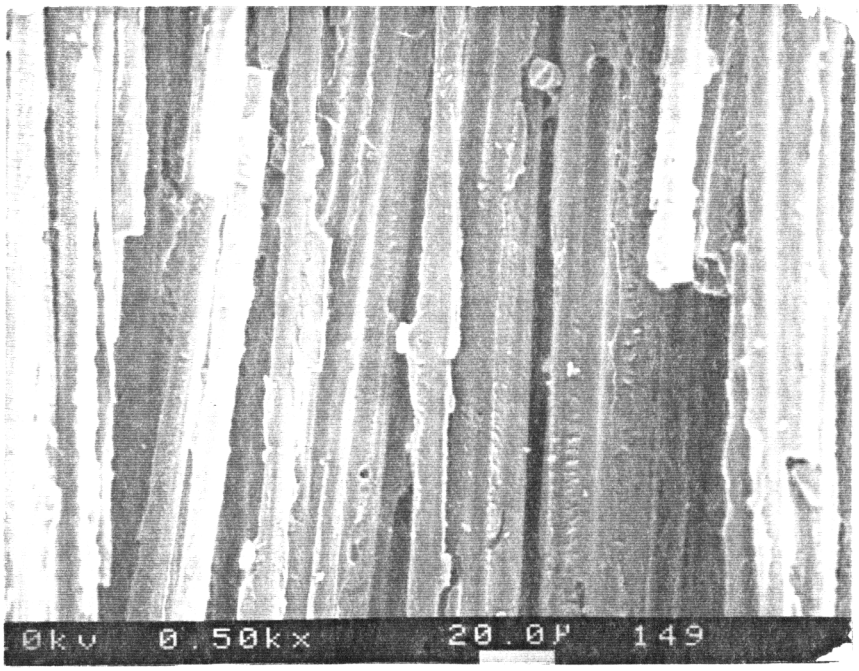


Figure 39-b.

Figure 39 : SEM on PEEK composites after transverse tensile test : (a) panel 6 and (b) panel 7.

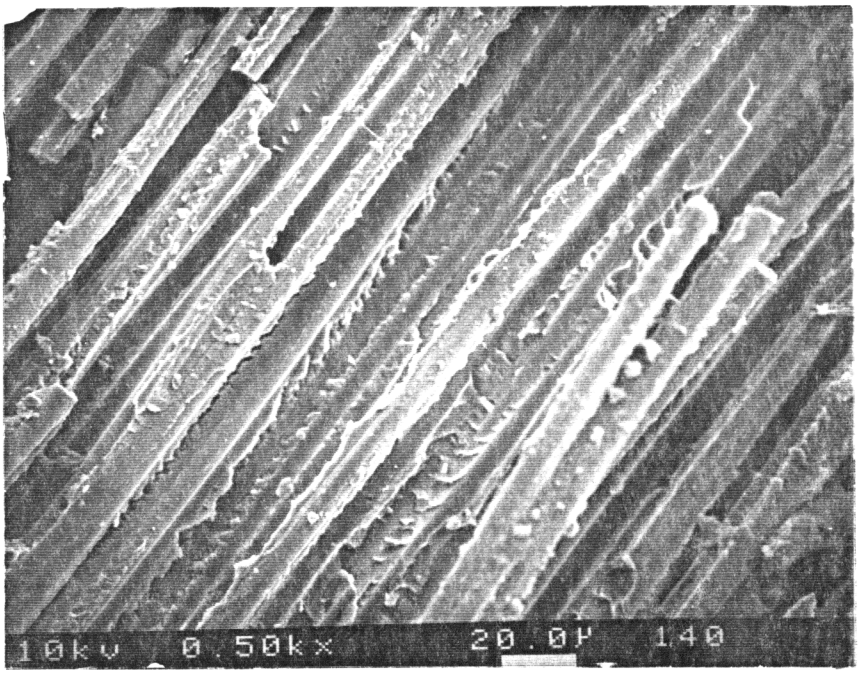


Figure 40-a.

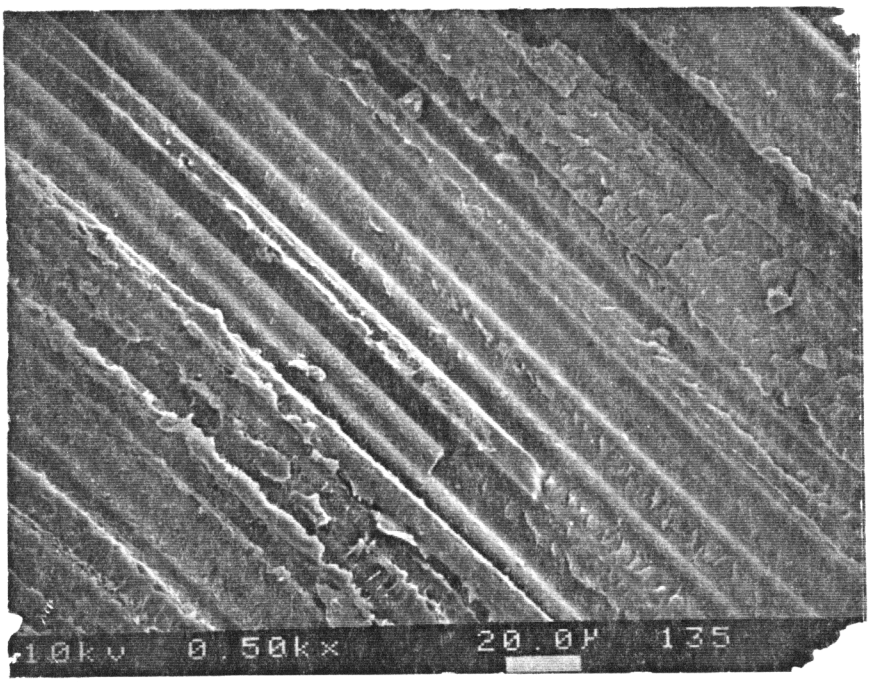


Figure 40-b.

Figure 40 : SEM on PEEK composites after transverse tensile test : (a) panel 8 and (b) APC-2.

of this laminate. It is believed that better composites can be made with BisP-BTDA polyamic acid 10K, but in absence of evidence, our conclusions will concern panels 6 and 8 only.

Mechanical properties very close to those published by ICI demonstrate that cycle d results in good consolidation, even with the immiscible imidized LaRC-TPI polyamic acid.

SEM showed good wetting of the fibers, both for panels 6 and 8, and brought out the importance of miscibility : the fracture surface of panel 6, with the immiscible imidized LaRC-TPI polyamic acid, is very chunky, suggesting a rather brittle failure which suggests that failure occurred at the boundaries between immiscible LaRC-TPI-rich and PEEK-rich phases. However, the fracture surface of panel 8, with the miscible imidized BisP-BTDA polyamic acid, is very smooth, suggesting a ductile failure, and resembles that of commercial APC-2. This suggests that improved fiber-matrix adhesion can be achieved by using a binder that is miscible with the matrix and that comes into intimate contact with the fiber as a water-soluble polymer during the prepregging stage.

The optical micrographs reveal the presence of voids in panels 6, 7 and 8 (see Figure 41 and Figure 42). This is likely to be the effect of released water during the imidization of polyamic acid. The fibers are better distributed in panel 6 than in panels 7 or 8.

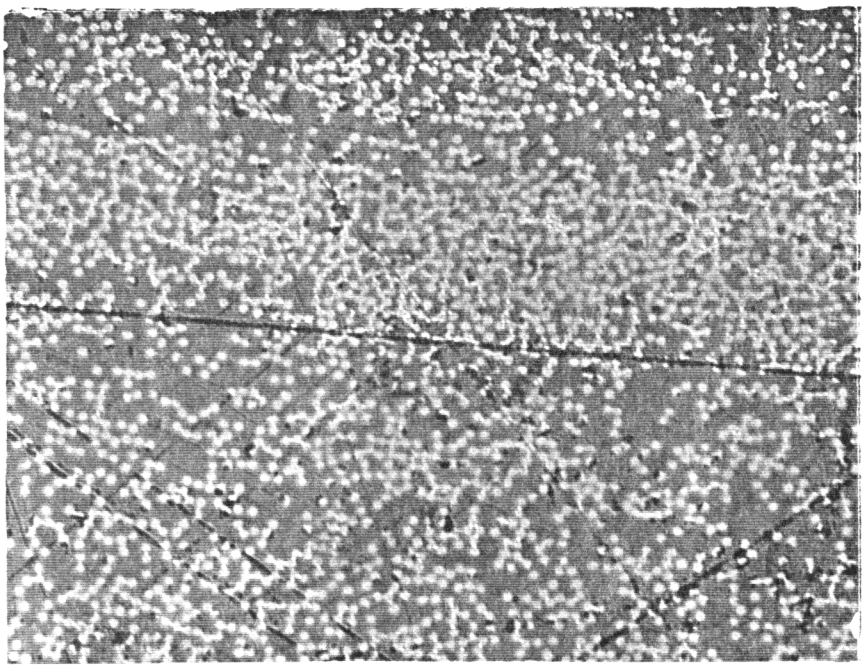


Figure 41-a.

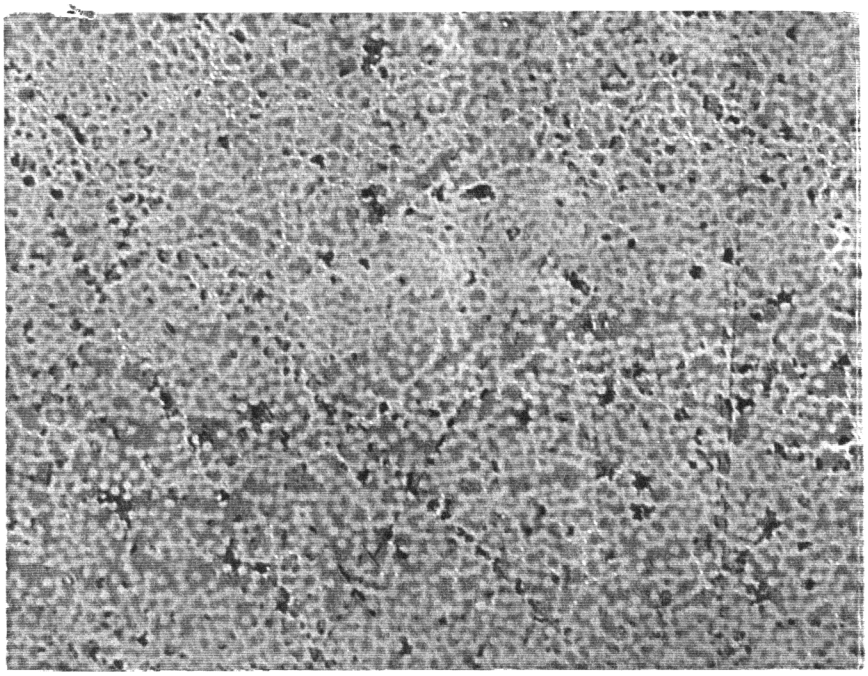


Figure 41-b.

Figure 41 : Optical micrographs at 200x of (a) panel 6 and (b) panel 7.

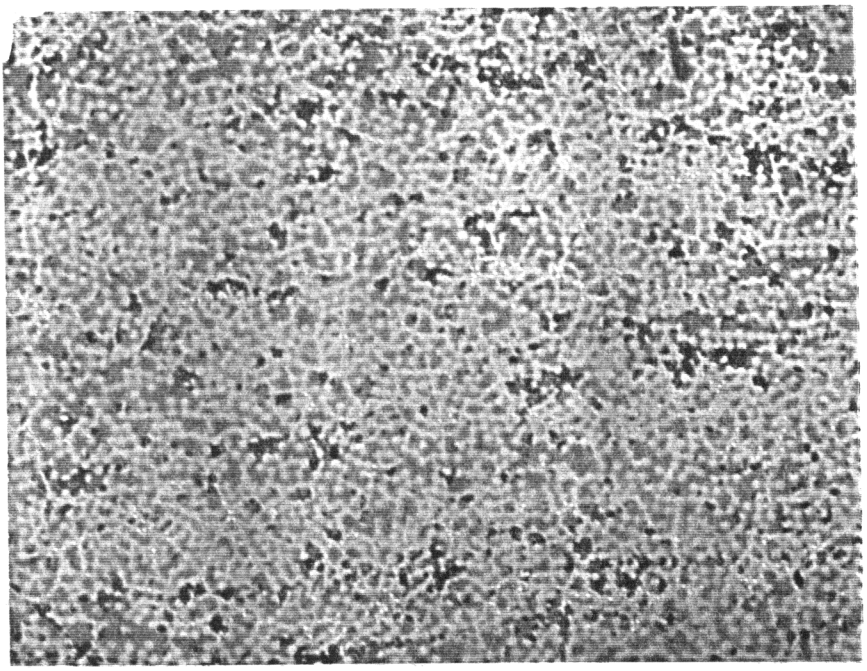


Figure 42 : Optical micrograph at 200x of panel 8.

The approach taken in the development of the PEEK composites processing conditions enabled us to separate the effects of different parameters and to assess the importance of the PEEK and polyamic acids chemistry, the miscibility aspect, and the consolidation cycle (time, temperature, pressure, vacuum). A high molecular weight polymer and a miscible water soluble polymeric dispersant are necessary to achieve well consolidated panel with an homogeneous matrix. The combination of pressure cycling and vacuum bagging seems to be the best way at present to process the PEEK prepreg after suspension impregnation.

CONCLUSION AND FUTURE WORK

This study demonstrated that suspension prepregging is a feasible technique to make carbon fiber prepreg with thermoplastic polymer powder. The composite matrices used in this work were an amorphous (LaRC-TPI) and a semi-crystalline, poly(etheretherketone), thermoplastics.

A variety of experiments, namely adsorption, sedimentation and particle size analysis, assessed the importance of the interactions between the powder particles and different polyamic acids. A dispersant must be used with wet PEEK polymer powder to decrease the PEEK suspension viscosity. Also, a miscible binder was found to be necessary with PEEK powder to obtain good adhesion between fibers and matrix. These dispersing and binding functions were both performed by addition of either LaRC-TPI polyamic acid or BisP-BTDA polyamic acid. The dispersion mechanism involves steric stabilization of the particles by adsorption of LaRC-TPI polyamic acid on the particle surface. BisP-BTDA polyamic acid seems to operate in a similar way. Sonication after adsorption of a polyamic acid dispersant on the polymer particle surface can then lead to smaller particle sizes (typically 4 microns for LaRC-TPI, 1 to 9 microns for PEEK).

Prepregs were made by impregnation of an AS-4 carbon fiber bundle with aqueous polymer suspension. A new resin pot was designed to use low viscosity

suspension. This resin pot provided sufficient spreading of the carbon fiber bundle, allowed good impregnation and minimized fiber breakage.

The LaRC-TPI consolidation procedure developed by NASA produced well-consolidated panels. Various PEEK consolidation cycles were investigated. A combination of pressure cycling and vacuum bagging appears to give the best consolidation (procedure d) (Figure 40-d).

Laminate evaluation (C-scan, SEM, optical microscopy) and mechanical tests (flexure, short beam shear and transverse tensile tests) were performed. C-scans of LaRC-TPI panels consolidated using the NASA procedure showed good consolidation. This was also observed with PEEK panels consolidated with consolidation procedure (d). SEM micrographs showed fibers that were well wetted and fair fiber-matrix adhesion. When the imidized form of the added polyamic acid dispersant was miscible with PEEK , adhesion of PEEK to the fibers was improved. The optical micrographs showed a few microvoids and good fiber distribution. These microvoids are probably due to the release of water during the imidization of polyamic acid during the consolidation step. The mechanical properties calculated from the different mechanical tests were compared to published literature. The properties of LaRC-TPI composites were consistent with NASA results. Mechanical properties of PEEK panels stabilized with BisP-BTDA 20K and consolidated with procedure (d) agree well with the ICI data.

The future work recommendations include :

(1) Matrix-miscible high performance dispersing and binding agents that do not release volatile by-products such as water need to be developed. These should yield composites with good fiber-matrix adhesion and lower void content.

(2) New techniques need to be developed to produce colloidal suspensions of amorphous matrix polymers such as new polyimides as well as crystalline polymers. These new matrix polymers could be combined with novel binders-dispersants to create advanced composites with improved mechanical properties.

(3) A rheology study of molten LaRC-TPI and PEEK polymers, in the absence and presence of a dispersing and binding agent, would provide extremely useful information on the melt behavior during the consolidation step. This information would help to optimize the PEEK time-temperature-pressure consolidation cycle.

(4) A programmable vacuum hot press would provide better control over the consolidation cycles and permit better reproducibility.

(5) A consolidation model including the effects of heat transfer, melt rheology, consolidation pressure, and time-dependent changes in binder chemistry, if any, should be developed.

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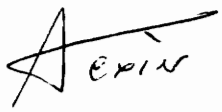

The Fabrication of Carbon-Fiber Composites by Aqueous Suspension Prepregging with LaRC-TPI and PEEK.

by
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ABSTRACT

A novel method of impregnation was used to make thermoplastic prepregs with aqueous suspension of polymer powder and AS-4 carbon fibers. The prepregging, consolidation and laminate evaluation procedures are described in this report. The need and importance of a dispersing and binding agent and its interactions with the composite matrix are assessed. A time-temperature-pressure consolidation cycle was designed for PEEK prepreg.

Two thermoplastic polymers were studied : LaRC-TPI, provided by Mitsui Toatsu Chemicals, and Poly(etheretherketone), synthesized in Virginia Tech Chemistry Department.

Comparison of LaRC-TPI composites to those made at NASA-Langley Research Center demonstrated good reproducibility of the techniques used in this study. The last PEEK composites fabricated compared well to the ICI standards.