

5. Processing of Advanced Thermoplastic Composites

5.1 Introduction

The lack of experience in processing high performance thermoplastic composites contributes to the inertia in utilizing these new materials. The techniques to process thermoplastic composites are not as well established as those developed for thermoset composite materials due to the novelty of this emerging class of materials. But there is a growing interest in the aerospace industry in demonstrating the feasibility to produce high quality thermoplastic composite parts for structural applications. A variety of innovative processes are currently being researched and developed to surmount the important obstacles to easy processing of thermoplastics (the high melt viscosity, high processing temperature, and the lack of drape and tack of prepreg). In this chapter, the processing of continuous fibre reinforced composites with high performance thermoplastic matrices reported in the open literature are reviewed. The benefits and disadvantages of processing thermoplastic composites compared to thermoset composites are discussed. The basic processing steps including fibre treatment, combination of fibres with thermoplastic matrix and processing techniques to produce laminates and form shaped parts are presented along with an overview of the lay-up procedure, residual stresses, processing models available, machining and reprocessability. Forming techniques for thermoplastic composites have been addressed in a more detailed way in a review by Okine [196]. Techniques to combine fibres and thermoplastic matrix polymer, to fabricate laminates and to form parts have been reviewed in References 1,55,195 and 197. The capability to produce APC-2 composite parts from a variety of processing strategies which are currently being researched have been demonstrated in References 102 and 233.

5.2 Advantages / Disadvantages

The major benefits in processing thermoplastic composites compared to thermoset composites are the unlimited shelf life, the short processing time, and their ability to be remelted and reprocessed. These advantages make them particularly attractive from an economic point of view. For most thermoplastic composites, the shelf life is unlimited and the processing time is in term of minutes rather than hours as it is for thermoset composites because polymerization has been completed before the combination of fibres with matrix [195]. No time is required for this chemical reaction to occur during processing as in the case of a thermoset. Thermoplastics have also the ability to be processed at various heating and cooling rates due to the absence of the exotherm experienced in the case of thermosets [1]. This may be an important issue in field repair considering the extremes encountered in processing conditions. However, as discussed in Chapter 3, the control of the cooling rate in the case of semi-crystalline thermoplastics is very important in determining the morphological structure and mechanical properties of the final composite.

The capability of thermoplastics to be remelted has led to the development of novel manufacturing technologies. Thermoplastic laminates showing voids or defects can be reconsolidated to eliminate these defects whereas a thermoset would be rejected. Excess or scrap material may be reused. Complex three-dimensional parts can be shaped or formed from a flat consolidated sheet. Composite parts can be thermally joined to form a composite assembly which eliminates the need for adhesive bonds and mechanical fasteners.

The main drawbacks with processing advanced thermoplastics compared to processing thermosets are their high melt viscosity and high processing temperatures needed to melt them. The high T_g desired for advanced thermoplastic composites leads to high melt viscosity and high processing temperatures, often close to the decomposition temperatures. At such high temperatures, depending on the thermal stability of the polymer which may vary significantly from one polymer to another, thermal and oxidative degradation and hydrolysis may occur [195]. In general, most organic linkages in high-performance thermoplastic polymers become thermally unstable about 450° C [75]. For this reason, minimizing the hold time at peak processing temperature and provision of an oxygen free environment are highly recommended. The high melt viscosity of thermoplastic renders the full impregnation of fibres by the polymer rather difficult. To demonstrate the importance of this problem, Cattanaach, Guff and Cogswell [55] presented this example: "to make 10 cc of a totally wetted fibrous composite containing 50% by volume of fine (10 µm) fibres it is necessary to spread 5cc of resin over 2 m² of surface area". In the case of thermosets, it can be considered equivalent to spreading a sticky liquor over the surface of a table but in the case of thermoplastics, the sticky liquor is replaced by a material equivalent to two pieces of chewing gum that has to be spread over the same area. The difficulty is increased by the constraint of not physically damaging the fragile fibres. The lack of tack and drape of most thermoplastic prepreps is another drawback. It is difficult to lay-up prepreg plies against a contoured shape. To overcome the problems of high melt viscosity and the lack of tack and drape of prepreps, some innovative processes of combining fibres and thermoplastic polymers and producing high quality laminates have been developed recently; they are presented in this chapter.

5.3 Treatment of fibres

For improved composite properties and water and chemical resistance, a good fibre-resin interfacial adhesion is very important. In the case of thermoplastic composites, it is a major concern that the interfacial adhesion to carbon fibres exhibited by the thermoplastic matrices such as polyphenylene sulfides, polyetherimides and polysulfones is less than that observed for epoxies [1]. This might be an important factor contributing to the low compression and shear properties of thermoplastic composites. But it is not well understood why the resin interfacial adhesion to carbon fibres is lower with thermoplastic matrices and how it can be improved. According to Muzzy [195], the fact that most thermoplastics have been

polymerized before having been combined with fibres and that they are relatively inert renders the achievement of a good adhesion between the matrix and the fibres generally difficult. In contrast, Leeson and Banister [77] affirm that most thermoplastics show an affinity to carbon resulting in good fibre-matrix interfaces without the addition of a coupling agent. However, for weaving operations, sizing is required for protecting the fibres during the process; usually a small amount of a matrix polymer is applied to the fibre prior to weaving. These authors [77] also affirm that with glass fibres, a coupling agent is needed since most thermoplastics do not adhere well to glass due to the inert nature of the glass surface.

Fibre treatment is a means to promote and enhance adhesion. The extensive work reported in the literature dealing with fibre treatment is almost exclusively on thermosets. In addition, most fibre treatment processes for thermoplastic composites are proprietary [195]. The choice of the proper fibre treatment is complex. It depends both on the type of fibre and on the nature of the thermoplastic involved [1]. It may include cleaning, etching and oxidizing of the fibres to provide reactive sites for adequate bonding to the sizing and the application of the sizing itself [195]. These operations are often accomplished at the same time as the fibre or prepreg formation in order to reduce the handling of the fibres. If a sizing has to be applied, it must be non-volatile, easy to apply, compatible with the matrix and thermally stable. A fibre treatment tailored for thermoset composites may not be suitable or optimized for thermoplastic composites [1]. The possible degradation of the sizing at the high processing temperature of high performance reinforced thermoplastics is also an important issue. At temperatures close to 400° C, none of the epoxy sizings will resist degradation.

Turner and Cogswell [169] have evaluated the mechanical properties of PEEK based composites with a variety of fibres and have explored the varying interfacial properties that result from the differing fibre types. The fibres included E, R and S glass fibres, aramid fibres (Kevlar), high strength (HS), high modulus (HM), intermediate modulus (IM) and ultra high modulus (UHM) carbon fibres. Mechanical properties with the R glass and aramid fibres were particularly low. It is believed that in the case of R glass fibre, the manufacturer's size may have degraded while in the case of aramid fibres, degradation of the fibres may have occurred due to the high processing temperature which is close to the decomposition temperature of Kevlar.

5.4 Combination of Fibres with Matrix

There are several techniques reported in the literature for combining fibres with thermoplastic matrix [1, 8, 55, 71, 77, 98, 195, 197 - 204]. They include hot melt coating, solution processing, in-situ polymerization of monomers or pre-polymers, film stacking, powder coating and fibre hybridization. Some of these are well established since they are employed with thermosets while others have been recently developed especially to overcome the difficulty of fibre impregnation due to the high melt viscosity of the matrix. Depending on

the combining process, impregnation may be accomplished during this step of combining fibres and matrix, or later during "in-situ" fabrication of laminates and parts. Based on APC-2 samples fabricated from pre-impregnated products and from products relying on a post impregnation taking place during laminate consolidation, Cogswell [197] showed that pre-impregnated strategies available today lead to better mechanical performance (see Table 29). He attributed this difference to the "fibre attrition during the post moulding impregnation stage where the forces necessary to squeeze the resin into spaces between the fibres also force the fibres together; by contrast in preimpregnated products each fibre is lubricated with a protective coating of viscous polymer". Techniques for combining fibres and matrix are described below.

5.4.1 Hot Melt Coating

Hot melt coating [1, 55, 195, 198] is probably the process that is the most commonly employed to combine fibres and matrix. Figure 41 shows a melt extrusion process used by Chung [16] but there are many possible variations in this process [198]. Initially, fibre tows are unwound from a spool or a creel of spools without twisting and they may go through a comb to achieve a better collimation. Fibres are then spread by a roller or air jet to expose as many fibres as possible to the polymer and reduce the gaps in the prepreg material. The fibres are fed into a die where the molten polymer is either added or furnished as a resin coating on release paper which is later removed. At this stage, pressure is applied on the melt in order to coat the individual fibres and not only the fibre bundles. Considerable pressure may be needed to achieve a total impregnation of the fibres [195]. At the die exit, the hot tape is cooled and rolled up.

No solvents are needed in this process. In the case of semi-crystalline polymers such as PEEK and PPS for which there are no known solvents in which to prepreg, hot melt coating is currently the impregnation method of choice [1,8]. The wet out is generally excellent with a low void content but the prepreg obtained is stiff, boardy and tackless. The hot melt coating method is not appropriate for thermoplastic polymers possessing a very high melt viscosity. There is some danger of thermally degrading the polymer when heating it to lower its viscosity.

5.4.2 Solution Processing

Solution processing [1,55,77,195] is very well established for the thermoset polymers. The technique consists of dissolving the resin in a suitable solvent and wetting the fibres with the solution. As it reduces the viscosity of the thermoplastic polymers, full impregnation of fibres becomes much easier. The complete devolatilization of the prepreg will result in a tackless and boardy thermoplastic tape or fabric. If some of the solvent is left, a certain degree of tack and drape can be obtained. The drawbacks associated with this technique are two fold [8,55,77]. First, if the prepreg is not devolatilized, the prepreg must be handled by conventional

TABLE 29. Properties of APC-2 as a Function of Impregnation Route [197]

	Axial flexural strength MN/m ²	Short beam shear strength MN/m ²	Impact energy 2 mm sheet J
Preimpregnated Products			
Cross Plyed Uniaxial	907	76	23
Woven Single Tow	929	68	23
Impregnated Woven Fabric	1052	80	29
Impregnation After Shaping			
Cowoven Fibres	782	60	13
Film Stacked	680	67	9
Powder Coated Fabric	545	54	

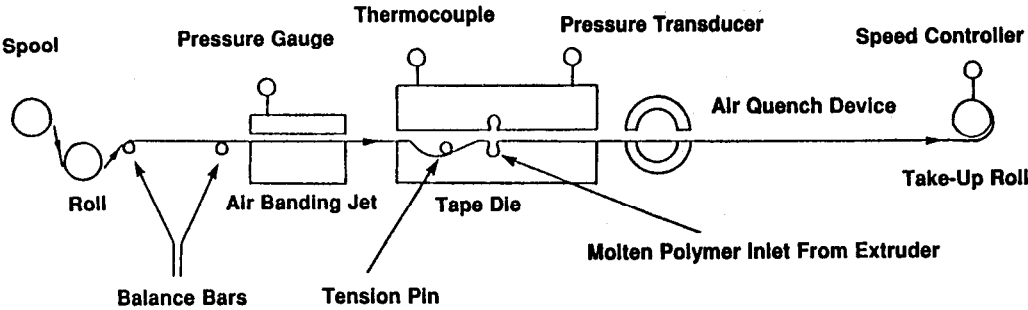


FIGURE 41. Hot Melt Coating Process [195]

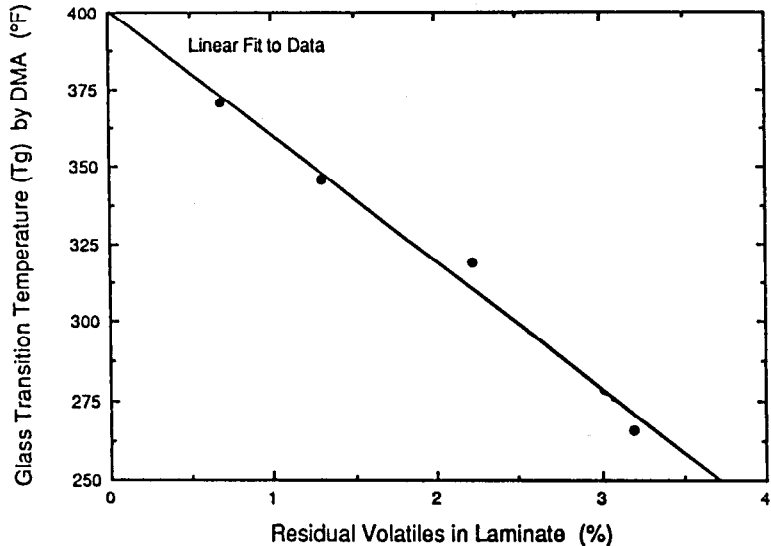


FIGURE 42. T_g as a Function of Residual Volatiles in Laminate [77]

thermoset technology where the solvent is removed later on during the curing process. There may be difficulty in removing all of the solvent from the thermoplastic product. The incomplete removal of solvent may be detrimental to the composite part. Figure 42 shows that an increase of the residual volatiles in the laminate may result in a decrease of the T_g [77]. In addition, volatiles released at high temperature increase the risk of void and blisters formation in the composites. Secondly, the thermoplastic has to possess sufficient solubility in organic solvents, hence this method is often used with amorphous polymers [1,8]. Prepregs made of Torlon polyamideimide, Ultem polyetherimide and Udel polysulfone are produced by this technique. Usually thermoplastic polymers exhibit limited solubility at high concentration and most high performance thermoplastics cannot be dissolved in low boiling point solvents at room temperature [71,195]. However, if the thermoplastic polymer is readily soluble in those solvents, it might be attacked by some solvents later as a composite part in service applications.

5.4.3 In-Situ Polymerization of Monomers or Prepolymers

This technique consists of the impregnation of the fibres with monomers or prepolymers in solution followed by in-situ polymerisation [1,8,55,195]. The solvent left in the prepreg confers good tack and drape on the material. During storage, the solvent may evaporate and transform the tacky prepreg into a tackless and boardy material. But solvents may be sprayed over a boardy prepreg to give back its handleability quality. In-situ polymerization is suitable for a limited range of polymers. Certain polyimides called thermosetting thermoplastic or pseudothermoplastic (described in Chapter 2) can be processed by this approach. They are produced essentially like a thermoset, they undergo some chemical reaction during the processing cycle, but they possess thermoplastic properties. Dupont's Avimid K and Avimid N polyimides are examples of materials produced by this method [1,195]. The reaction of monomers in solution proceeds with the production of water and must be removed with the solvent during autoclave processing. Pressures and heat-up rates are essentially the same as those employed with epoxy, but the processing temperatures are much higher (343° C for Avimid K versus 177° C for epoxy). Care must be taken so that the evolution of volatiles will not contribute to formation of voids [159]. A major disadvantage of this technique is that curing and post-curing is long, even when compared to crosslinkable thermosets. Consequently the advantage of the fast processing of a thermoplastic is lost.

5.4.4 Film Stacking

Film stacking consists of interleaving layers of reinforcement fibres in the form of tape or fabric with layers of thermoplastic polymer films or powder [1,55,197]. Wetting of the fibres is achieved during the consolidation process. To obtain a high quality laminate (low void and good impregnation of the fibres), the stack has to be consolidated under severe conditions (high pressure and temperature, and /or a protracted molding cycle).

5.4.5 Powder Coating

Powder coating is an attractive continuous process that overcomes the difficulty of working with thermoplastics with high melt viscosities and poor solubility [1, 8, 55, 71, 195, 199]. Figure 43 illustrates the powder coating process being developed at Georgia Institute of Technology [71, 195, 199]. Polymer in the form of fine powder (generally 2 to 50 μm in diameter [1], but even 90, 110 and 240 μm [199]) is charged and fluidized. The powder is electrostatically deposited on the fibres passing through a fluidized bed. The fibres are ground to promote powder pick-up. Liquid suspension is a variant of air fluidization [55]. The coated fibres exiting from the fluidized bed can be rolled-up immediately [205] or they can be fed into an oven where the polymer melts on the fibres [71, 195, 199] before it is cooled and rolled up. The resulting towpreg possesses good drape and sometimes good tack if a tackifier is used. If the coated fibres do not go through the heating and melting process, less severe stresses are imposed on the fibres but care has to be taken not to remove powder from the fibres during further handling. To prevent powder removal, water may be sprayed over the prepreg prior to handling or laying-up [205].

One of the main concerns with powder technology is to obtain a uniform distribution of powder around the fibres [8] but, in general a very high degree of impregnation can be achieved [55, 195, 199]. The powder coating process has demonstrated the capability to produce high quality fibre reinforced prepreg from a wide variety of thermoplastic powders with no evolution of solvent or by-products [8, 199]. AS4 carbon fibres combined by this process with PEEK have led to laminates with mechanical properties equivalent to laminates made from commercial APC-2 prepreg tapes [199]. Powder coating can be used with a wide variety of polymers; they need to have the capability to be ground into fine powder [55] and most can be but not all [205]. The cost associated with the preparation of a very fine powder from a tough thermoplastic is high [1] but an economic analysis has shown that the powder coating process is economically attractive [199]. Major developments are expected to emerge in this new area of powder coating which would increase the choice of matrix materials. Weaving, pultrusion and filament winding are fabrication techniques being considered with powder coated fibres.

5.4.6 Fibre Hybridization

Another approach to combine fibres with thermoplastic matrix material which is undergoing considerable development is fibre hybridization [1, 98, 125, 127, 200 - 204]. As with the powder coating process, the hybrid technology is particularly attractive when using polymers having high melt viscosity and poor solubility. The process consists of combining a yarn of fibre reinforcement with yarn spun from a thermoplastic material. The combination can be done by commingling, serving or co-weaving (Figure 44) [200, 201]. In commingling, the reinforcing fibres and thermoplastic fibres are intimately mixed at the individual fibre level.

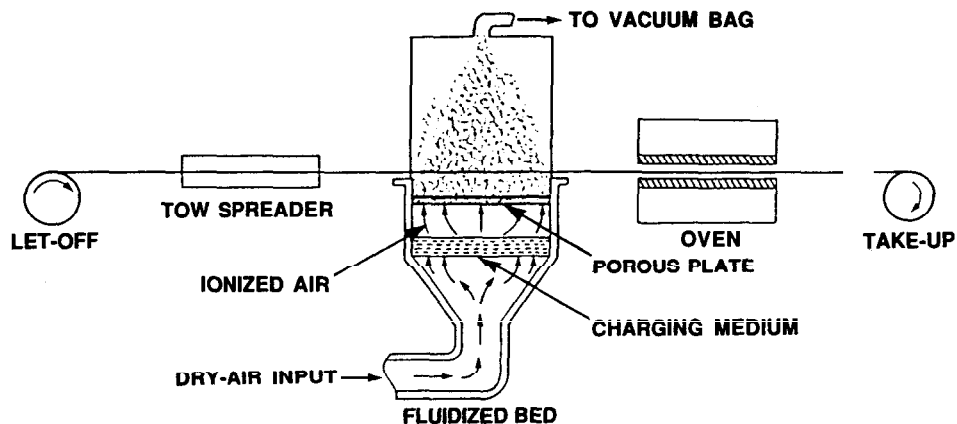


FIGURE 43. Electrostatic Fluidized Bed Powder Coating Process [199]

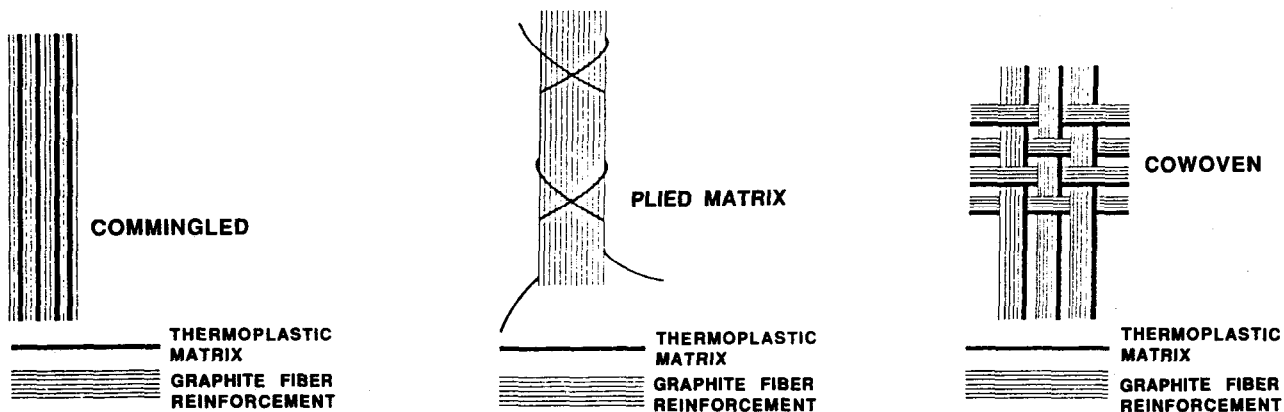


FIGURE 44. Hybrid Yarn Forms [201]

Serving refers to the wrapping of the reinforcement fibres with the thermoplastic fibres. Weaving of bundles of continuous thermoplastic filaments and reinforcement filaments existing as separate yarns result in a "co-woven fabric" whereas weaving commingled hybrid yarns refers to a "commingled woven fabric". In an experimental study, Silverman and Jones [98] found that commingled woven fabric composites of carbon/PEEK generally exhibited higher physical and mechanical properties than co-woven fabric carbon/PEEK composites due to a better fibre/matrix distribution and adhesion. An improved blending of the carbon fibres with the matrix is achieved in the case of commingled woven fabric composites.

Hybrid yarns can be woven into a wide variety of highly conformable and drapeable fabrics. Three-dimensional fabrics have been recently fabricated with commingled yarns, either by stitching layers of fabrics or as a fully integrated structure [125, 127, 200, 204]. Figure 45 shows a three dimensional fibre architecture which is a fully integrated structure. Preliminary experimental results have shown that 3-D woven fabrics lead to composites possessing better damage tolerance and delamination resistance than composites fabricated from 2D woven fabrics or from prepreg tape [200, 204]. Figure 46 presents the compression strength after impact obtained by Hua and Ko [204] for APC-2 laminated composites and PEEK/carbon commingled 3D-braid. 150 G PEEK/carbon commingled 3-D braid exhibited higher compression strength than APC-2 laminates for the three impact energy levels. However, the results obtained in Reference 207 and presented in Tables 30a and 30b show that 3-D fabrics exhibit lower $\pm 45^\circ$ tensile strength, compressive strength and fracture strain than 2-D fabric and prepreg tape.

Woven structures can be designed to conform to very complex contours without preheating and without yarn separation during consolidation [201]. Wetting of the fibres is deferred until the consolidation process. Under heat and pressure, the thermoplastic yarn melts, wetting the reinforcing fibres. To ensure a good wetting of the dense fibre network, longer processing time and/or higher temperature and pressure are required for commingled woven fabrics compared to unidirectional thermoplastic preregs.

Presently, commingled yarns of carbon with either PEEK, PEK, PPS [203] and PEI [163] are produced commercially. In general, the mechanical properties obtained from thermoplastic laminates manufactured from both co-woven and commingled woven fabrics are lower than those obtained with thermoplastic laminates fabricated from prepreg tapes [98, 207]. This characteristic is corroborated by the data in References 98 and 207 generated during studies on carbon/PEEK laminates made from unidirectional prepreg tape and fabric and are shown in Tables 30 and 31. The reduction in mechanical properties is attributed to fibre breakage during the weaving process, poor fibre/matrix distribution and in some cases poor fibre/matrix adhesion. In addition, the greater freedom of the fabric fibres to move results in fibre kinks, bends and misalignment before and during consolidation. Considerable development of this novel technology is anticipated such as improvements in mechanical

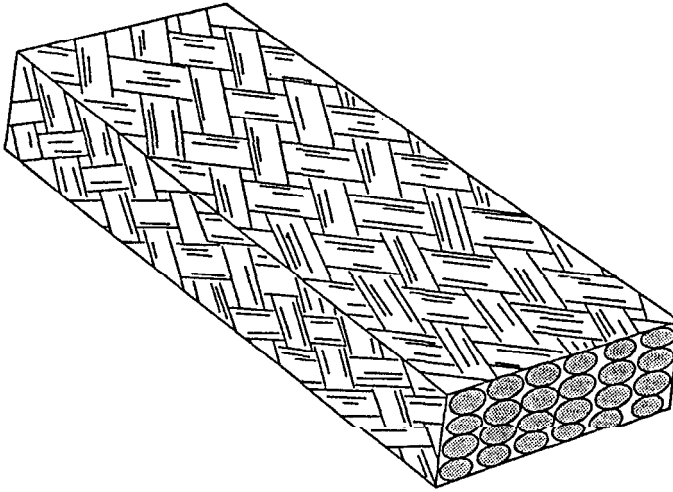


FIGURE 45. 3D Braid Fabric [204]

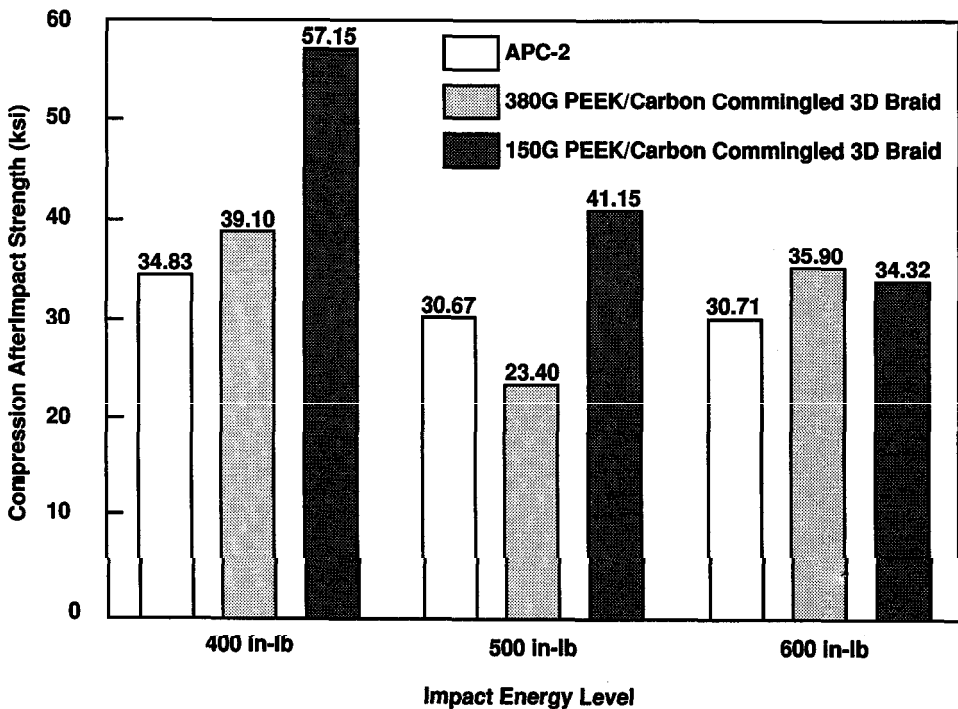


FIGURE 46. CAI Strength Comparison of APC-2, 380G PEEK/Carbon Commingled 3D Braid and 150G PEEK/Carbon Commingled 3D Braid [204]

**TABLE 30a. Comparative Transverse
Tensile Properties of PEEK Composites
Made from Unidirectional Prepreg
Tapes and Fabrics [207]**

Transverse (± 45) Tensile Properties of PEEK Composites

Material	Strength(MPa)	Modulus(GPa)	Fracture Strain * (%)
Prepreg	309	7.72	26.
2-D Fabric	255	8.00	14.
3-D Fabric	155	8.34	7.0

* Measured by crosshead travel.

**TABLE 30b. Comparative Compression
Properties of PEEK Composites
Made from Unidirectional
Prepreg Tapes and Fabrics [207]**

Material	Strength(MPa)	Modulus(GPa)	Fracture Strain (%)
0/90 prepreg	396	16.2	2.5
0/90 2-D fabric	391	12.0	2.6
0/90 3-D fabric	194	14.6	1.2

TABLE 31. Comparative Room Temperature Properties of Composite Laminates Made from Unidirectional Prepreg Tapes and Fabrics [98]

	Prepreg Tape	Comingled Woven	Comingled Woven	Co-Woven
		Plain Weave	No Crimp Structure	Plain Weave
Plies	10	16	8	12
Panel Thickness Per Ply (mils)	5	7.9	10	7.5
Specific Gravity	1.56	1.55	1.53	1.53
Fiber Content (vol %)	60.0	56.1	57.7	61.8
Void Content (vol %)	1.9	2.1	3.2	4.4
Flexural Properties Strength, ksi (MPa)	244.7 (1687.1)	219.6 (1514.1)	177.2 (1221.7)	166.8 (1150.0)
Modulus, Msi (GPa)	15.7 (108.2)	14.2 (97.9)	15.4 (106.2)	9.4 (64.8)
Transverse Tensile Strength, ksi (Mpa)	13.2 (91.0)	9.3 (64.1)	3.7 (25.5)	(Not Tested)
H ₂ O Absorption (wt %)	0.15	0.22	0.17	2.0

properties of hybrid yarns, optimization of fibre/matrix bonding, new textile processes, weaving of powder coated fibres [201] and the pultrusion and filament winding of hybrid yarns [203].

5.5 Lay-up

Most thermoplastic prepregs (prepregs include the matrix and fibres combined by one of the above combination techniques) are in a finished state as they have undergone the chemical reaction of polymerization. Therefore, the prepregs possess their full rigidity and are boardy. They do not possess enough drape to be easily laid-up against a contoured shape. Instead they have to be laid-up as a flat panel which is subsequently thermoformed into the desired 3-D shape. The other alternative for producing complex shapes is to use woven fabrics. In addition to the poor drapability, most prepregs are tackless rendering the lay-up process difficult. Lay-up requires that each ply must be tacked to the previous one such that it will be held in place. Normally tacking is done by spot welding with ultrasonic guns or soldering irons.

5.6 Processing Techniques for Thermoplastic Composites

To produce a fibre reinforced thermoplastic composite, prepregs have to go through melting, consolidation and solidification [195, 208]. These steps described below are illustrated in Figure 47 where a typical time-temperature-pressure profile for the consolidation of plies into a flat laminate is shown.

5.6.1 Melting

Thermoplastic prepregs are heated until the matrix melts. During heating, low pressure can be applied. If no reaction of polymerization occurs and there is no evolution of volatiles, rapid heating is possible. In crystalline structures, the peak processing temperature is preferred to be higher than the melting temperature in order to erase all spherulite nuclei and then produce a new more uniform crystalline morphology [102]. In the case of forming composite parts, melting of the laminate is generally done in an external heating oven. Then, the laminate is transferred to the forming system that has its temperature set at the forming temperature which is generally lower than the melting temperature in order to cool and solidify the formed part.

5.6.2 Consolidation

Once the matrix is molten, a consolidation pressure is applied to bring the plies into intimate contact, to remove voids, to cause matrix flow and to allow bond formation at the ply interface for good interlaminar adhesion. The mechanisms of matrix flow, deformation

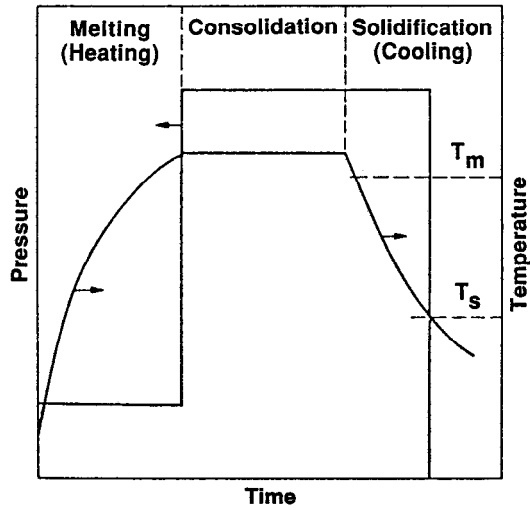


FIGURE 47. Pressure-Temperature-Time Profile for Consolidation [208]

processes and adhesion of plies are discussed in References 55, 195, 197, 208, and 209. Pressure consolidates while deconsolidation occurs when a consolidated thermoplastic composite is heated to melt temperature without pressure. Because of the high melt viscosities and short processing times for thermoplastics, resin flow out and void formation are not a major concern as is the case with thermoset composite processing. Most thermoplastic composites included in this report require a consolidation pressure of about 1.4 MPa, but some necessitate higher pressure in the range of 7 - 9 MPa. There is presently considerable development aimed at minimizing this processing parameter as well as the processing temperature and time. Any reduction in these parameters will decrease production cost and increase production rate.

In contrast to thermoset processing, the vacuum operation used to avoid degradation and void formation from oxygen, water and volatiles within the composite is rarely applied to thermoplastics [195]. This is due to the fact that water absorption is not a major concern with thermoplastics, that solvent is not used for most thermoplastics and it is easier to process without vacuum; i.e. no vacuum bagging or vacuum equipment are needed. The consolidation pressure applied to the part is often sufficient to eliminate trapped gases. However, even though vacuum is not absolutely necessary and rarely applied in most thermoplastic composites, it is recommended.

5.6.3 Solidification

After consolidation, the composite part is cooled. In general, the consolidation pressure is maintained during solidification to prevent delamination and to compensate for void formation due to thermal and crystallization shrinkage [195]. Pressure is released when the temperature of the composite is below T_g . As discussed in Chapter 3, for semi-crystalline polymers, the cooling rate is an important issue on the development of the crystalline structure which will affect subsequently the mechanical properties.

5.6.4 Residual Stresses

The large mismatch between thermal expansion properties of typical matrices and fibres, especially with carbon or Kevlar 49 aramid fibres, can lead to substantial residual thermal stresses during processing. These stresses can cause voids or matrix cracking. Because of the high processing temperatures of thermoplastic composites, residual stresses are an important issue [1, 195, 210 - 214]. They are generally higher than in their thermoset counterparts. But, according to Reference 195, residual stresses can be partially relieved during processing when the thermoplastic temperature is close to or above its T_g .

The mechanism of stress build-up depends on the type of matrix [211 - 214]. The analysis for epoxies or amorphous thermoplastic matrices is quite simple. During the processing of epoxies, the stresses build up during cooling from the cure temperature [213].

When processing amorphous thermoplastics, the stresses build up as the material temperature drops below T_g and then are not expected to vary significantly with processing conditions [212 - 214]. In the case of semi-crystalline thermoplastics, the mechanism of stress build-up begins during crystallization and depends on processing conditions [213, 214]. Nairn and Zoller [213] state, "If the semicrystalline matrix assumes enough solid-like character early in the crystallization region, the constrained shrinkage will be large resulting in large residual stresses or cracking. If stress does not build up until after the crystallization is nearly complete, the stresses will be smaller but dimensional changes may be significant". The differential shrinkage is generally highest for semi-crystalline thermoplastics than for amorphous thermoplastics [211 - 213].

In addition to the magnitude of the residual thermal stresses, it is important to know the effects of these stresses on the matrix and composite properties. Some thermoplastic composites may not support high residual stresses without cracking. In their study on the build-up of residual thermal stresses in semi-crystalline thermoplastic composites (carbon reinforced PEEK, J-Polymer, PET and Nylon-66), Nairn and Zoller [211] found that the level of residual stresses in these matrices were ranked as follows: PEEK > J-Polymer > PET > Nylon-66. In reinforced PEEK, the composite with the highest residual stress, no cracking was exhibited while occasional evidence of cracking was observed in J-Polymer composite and a lot of cracking was seen in PET indicating that some matrices cannot tolerate a very high level of residual stress when constrained by fibres in a composite.

5.6.5 Models

General models are being developed to simulate the different steps which take place during the processing of thermoplastic matrix composites [195, 208, 215, 216], starting with the very first step of pre-impregnation [216], going through the different mechanisms involved during consolidation such as fibre wetting, matrix flow, interply adhesion and autohesion (diffusion of the polymer across the interface) [195, 208, 216], and ending with solidification where relations have been established between cooling rate and the crystalline morphology of the composite and its mechanical properties [107, 108, 216]. Many of these models have been supported by experimental measurements.

5.7 Processing of Flat Thermoplastic Laminates

The different techniques to convert a lay-up of plies of fibres combined with matrix to a flat consolidated laminate are presented below. They include compression molding, autoclave technology and automated lamination and consolidation.

5.7.1 Compression Molding

Compression molding [1, 55, 102, 196] is a simple processing technique consisting of placing the thermoplastic prepreg plies inside a heated mold located between two platens of a hydraulic press. Pressure is applied as the material melts. Once the polymer is molten, it takes only seconds to fuse under heat and pressure. Processing time, mostly due to the heat up and cool-down requirements, is short. The process can be accelerated with the use of two presses, side by side, one hot and the other cold.

It is widely used because of its convenience; very often suitable presses are already installed. The dies, usually made of metal, are precisely machined to provide a uniform consolidation pressure. The very tight tolerance of the gap between the two half dies incurs high costs. If a mismatch in thickness between the composite part and the die should exist, then non-uniformity in pressure and heat transfer will occur resulting in a non-uniform consolidation. Pressure uniformity can be improved by incorporating a compliant layer between the platens of the press and the stack of plies [102].

5.7.2 Autoclave Technology

Conventional autoclave technology can be used to consolidate flat sheets [1, 55]. It is an interesting method if there is an autoclave installed for thermoset processing that can work at the temperatures and pressures required to consolidate thermoplastics. Large surfaces can be produced with a lower tooling cost than compression molding because prepregs are consolidated against a single surface rather than two. However, a short processing time, one of the primary advantages when using thermoplastics, is mostly lost. Even if the hold time is reduced for most thermoplastics compared to thermosets, the time required to heat up and cool down a large autoclave is long.

5.7.3 Automated Lamination and Consolidation

Automated techniques for the lay-up and consolidation of flat thermoplastic laminates have been recently developed [217 - 221]. In this continuous process which is well established for thermoset composites, the prepreg tape is automatically unwound from roll and fed to a lay-up machine allowing any ply orientation to be laid. Lay-up may be accomplished by heating the tape to the melt temperature and laying it on previously consolidated heated plies with applied pressure [217, 219]. Another version of automated lamination consists in flattening the tape layer and tacking it by spot welding to the layers directly underneath [218]. The whole completed stack is subsequently heated to melt temperature and pressure is applied.

Automated lamination technique possesses many advantages over currently extensive manual labor. High processing speeds can be attained and large panels that would be difficult

to laminate manually can be produced. Laminates of 1.2 by 3.0 m and 96 plies thick have been produced with PEEK and PPS [217]. Also, the positioning of the individual ply in the desired orientation is very accurate providing high reproducibility. Some limitations exist [217, 218] e.g. angle cuts cannot be as complex as hand cuts. Short lengths will be difficult to feed and lay on the surface. For small parts where times for acceleration/deceleration and head turn-around become important, processing speeds can be low. To reduce the number of roll changes and hence reduce waste, manufacturers should provide longer rolls of prepregs. According to Reference 217, the automated production of contoured laminates is expected to be a difficult challenge. Presently, McDonnell Aircraft Co. is performing research into design and construction of fully automatic manufacturing equipment capable of producing thermoplastic composite structures [188].

5.8 Forming Techniques

Forming refers to the transformation of a 2D laminate into a 3D composite part. Forming techniques are not very well established for advanced thermoplastic composites. Even though the literature on the subject is recent and is not extensive, a growing interest and effort to develop adequate forming processes for thermoplastic composites is now underway.

Typically, a thermoforming process consists of heating a preform in an external oven to the forming temperature [196]. Heating can be accomplished through infrared radiation, conduction between two heated platens or a convection oven. Then the preform is transferred into a forming system where the laminate is shaped to the geometry imposed by the die. After forming, the composite part is cooled under pressure to below its T_g before being removed from the forming system. The composite part may be trimmed to its final shape depending on the preform used. The preform may be either a lay-up of thermoplastic prepreg plies or a preconsolidated laminate that may be flat and rectangular or cut in a particular shape. More plies can be placed in some areas of the workpiece where thinning is expected to be very pronounced. The preform may be constituted either of a fabric or a unidirectional tape depending on the final geometry and desired mechanical properties. Woven laminates have lower mechanical properties than laminates made of unidirectional plies [98, 207] but they are much easier to handle. Fabrics tend to restrict gross fibre motion [196]. This helps in restricting lateral fibre displacements and in obtaining uniformity in fibre orientation and distribution. But at the same time, the motion restriction may impede interply slippage resulting in possible fibre buckling and wrinkling.

Depending on the part geometry, the constitutive behavior of the material and the forming process employed, changing a 2D part into a 3D curved surface may involve large deformations [139, 195, 196]. Discussions, theories and models related to deformation mechanisms are emerging [55, 196, 197, 209, 222 - 224]. Excessive bending may cause fibre buckling and wrinkling. To circumvent fibre buckling which is due to compressive stresses,

low tensile stresses (0.3 to 0.7 MPa) can be applied to the composite during forming [222, 223]. High tensile loading may break fibres. Interply slip as shown in Figure 48 is often beneficial in countering buckling and wrinkling but it can lead to fibre misalignment. Thin spots and lateral fibre displacement may also occur. These forming difficulties are mainly due to the lack of extensibility of the continuous fibres which causes stress build-up in the laminates. Matrix alone or chopped fibre reinforced resin is much easier to form.

The cost to produce a thermoplastic composite part and the quality of the part depend on the forming process used. Successful parts of a particular geometry produced by a forming process might not be as well produced by another forming process. Presently, a variety of techniques to form parts from thermoplastic composite materials are available. They include matched-die press forming, rubber pad press forming, diaphragm forming, hydroforming, autoclave/vacuum forming and rubber pad press forming. They are briefly described below and are followed by the description of pultrusion, filament winding and roll forming processes for thermoplastic composites, as well as machining and reprocessability of thermoplastic composites.

5.8.1 Matched Die Press Forming

Matched die press forming shown in Figure 49 has been described previously as a compression molding process in subsection 5.7.1. It is presently the most widely used forming technique because presses are often available [196]. As already mentioned, the molds have to be machined to a high degree of precision to obtain uniform pressure and heat transfer during consolidation. Matched metal tooling has proved to be unsuccessful in forming parts because of the very rapid cooling of the composite when brought into contact with cold tooling [1]. The material does not flow sufficiently throughout the laminate, and delamination and fabric distortion may occur. It is also difficult to control fibre displacement due to the non-deformability of the metal dies. Usually, rigid metallic material, such as aluminum, is used for the female tooling and an elastomeric material, such as silicone rubber, within a rigid base is substituted for the male metal tooling [1, 139, 196]. The elastomeric tool is matched to the metal tool half. When under pressure, the pliable tool applies a more uniform consolidation pressure than an all-metal die set (at a reasonable cost). The cost and the complexity of precisely matched metal tools are reduced. But the elastomeric material has to survive at the forming temperature; current silicone rubber material may be limited to 232-288° C in air.

5.8.2 Rubber Pad Press Forming

In this case, the rubber is not matched to the metal tool half [196]. A rubber pad, generally much larger than the tool, that may be profiled to the tool geometry is attached permanently to the press platen replacing one tool half (Figure 50). Under pressure, the rubber pad conforms to the solid tool half. High forming pressures can be achieved but they are not

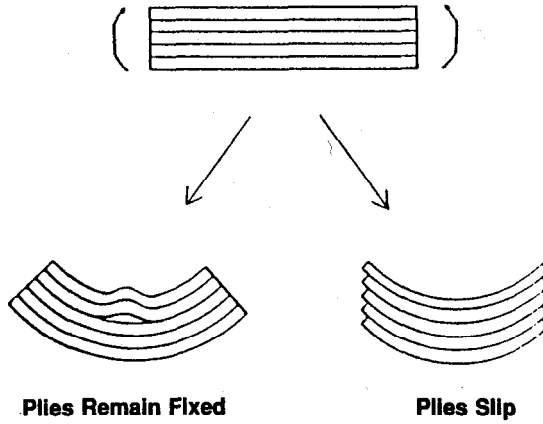


FIGURE 48. Laminate Response to an Applied Bending Moment. If the Plies are Allowed to Slip Relative to Each Other, the Compressive Stresses are Relieved and No Buckling Occurs. [223]

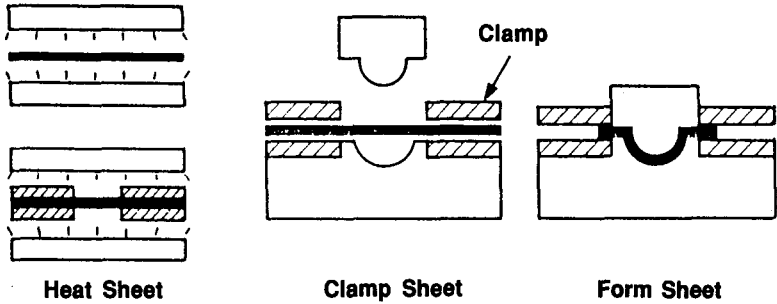


FIGURE 49. Schematic of Typical Matched-Die Press Forming [196]

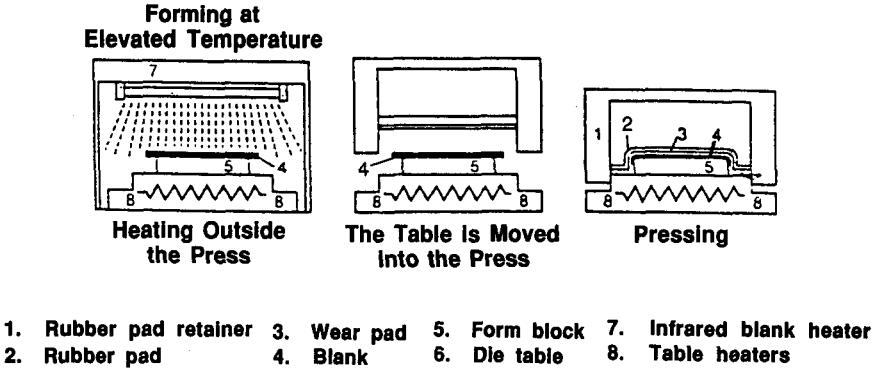


FIGURE 50. Schematic of the Rubber Pad Forming [196]

always uniform over the workpiece as they depend on the local extension of the rubber. Pressure on parts with smooth details can approach uniformity. Again, the rubber material has to survive the high forming temperatures.

5.8.3 Diaphragm Forming

In diaphragm forming, the unconsolidated sheet is placed between two thin disposable plastically deformable diaphragms [102, 196, 225 - 228] (Figure 51). These diaphragms are clamped around the edges such that a biaxial tension is maintained on the laminate during deformation. This tension helps to prevent laminate wrinkling, splitting and thin spots. The workpiece as well as the diaphragms are heated up to the processing temperature in a process chamber which might be an autoclave. Then under pneumatic pressure, they are forced to conform over a forming metal mold to produce the desired geometry. The workpiece is usually under vacuum to allow the extraction of gases. Depending on the size of the pressure chamber, cycle times may be long because of the heating/cooling time. Materials used for the diaphragms have to be extensible in the range of temperature where the workpiece will be deformable. The most commonly used materials are superplastic aluminum and polyimide films such as Kapton (by Dupont) and Upilex-R (by UBE Industries, Japan). Diaphragm forming seems to produce the best fibre alignment amongst the forming processes [195, 196]. Parts have been successfully formed from APC-2 by this method [102, 226, 228]. The effects of diaphragm forming temperatures on the final material structure of APC-2 have been investigated by O'Bradaigh and Mallon [227].

5.8.4 Hydroforming

Hydroforming is a technology that is widely used in sheet-metal forming [1, 102, 196]. The process is illustrated in Figure 52. It consists of a flexible diaphragm (thick rubber), usually much larger than the workpiece, that is attached to the upper platen. Behind the diaphragm is a fluid medium, usually a hydraulic fluid. Under pressure, the preheated workpiece is deformed against a male or female tool. High pressures (69 MPa for massive systems) and low cycle times can be achieved. Because the whole system is pressurized, peripheral equipment such as thermocouples, cooling and heating lines cannot be connected to the tool itself [196].

5.8.5 Autoclave/Vacuum Forming

Autoclave/vacuum forming is essentially similar to diaphragm forming [1, 196] (Figure 53). Vacuum pressure is drawn in the cavity between the workpiece and the tool forcing the workpiece covered by two flexible diaphragms to conform to the tool. To consolidate and form a thermoplastic part, vacuum alone is not sufficient, higher pressures are needed. The forming

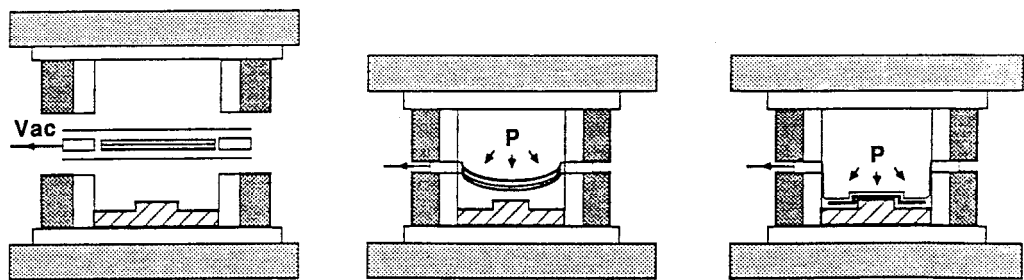


FIGURE 51. Schematic of the Diaphragm Forming Process [225]

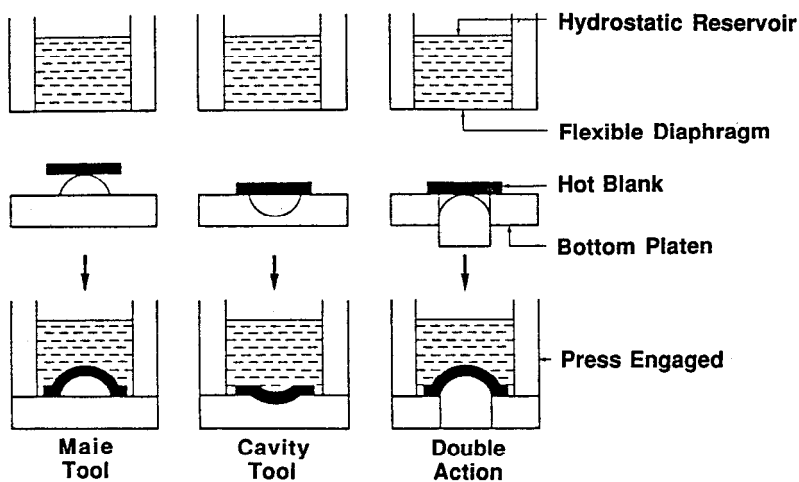


FIGURE 52. Schematic of the Hydroforming Process [102]

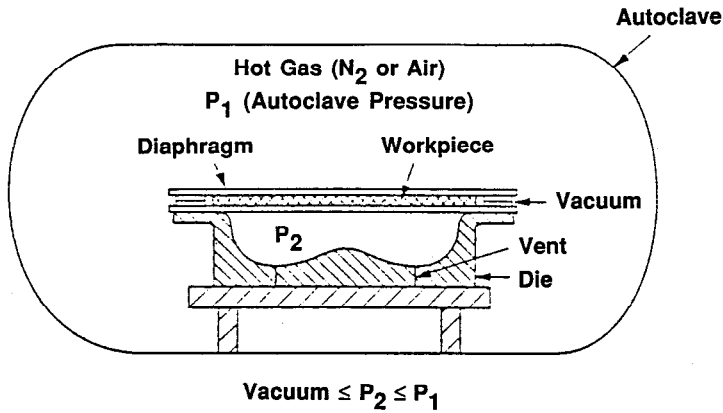


FIGURE 53. Schematic of the Autoclave/Vacuum Forming [196]

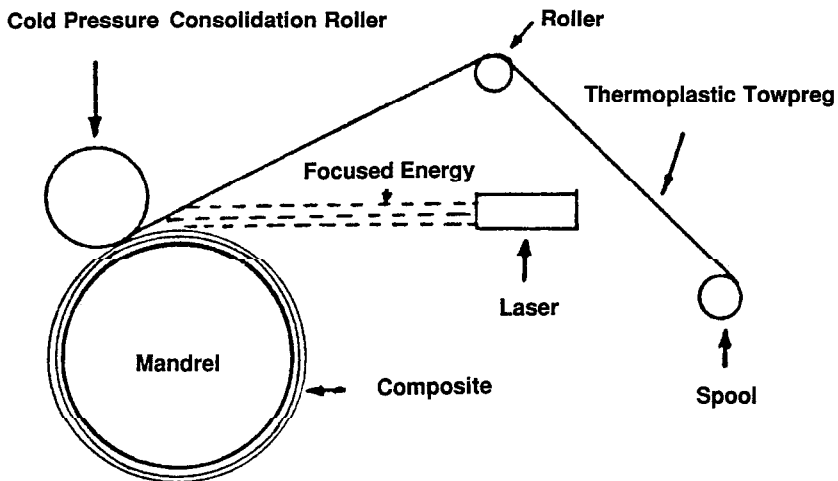


FIGURE 54. Schematic of Filament Winding of Thermoplastic Composites [195]

cavity is then pressurized with air. Again, cycle times may be long if the autoclave is large. However it is an attractive process if an autoclave is available and the need for only one tool half also lowers the tooling costs.

5.8.6 Filament Winding

Filament winding of thermoset composites is a well established process consisting of winding unreacted polymer coated fibres on a mandrel followed by curing. Thermoplastic composite wound structures do not have to go through the long and costly curing operation. They can be filament wound using the same equipment but slightly modified. A heat source is needed to heat the incoming tape to the melting temperature as it is applied on the already consolidated layers (Figure 54) [102, 219, 229, 230]. Consolidation takes place under heat and pressure applied from a roller. The possible localized heat source may be hot gas, flame, microwaves, induction, infra-red lamps or laser. When heat is removed from the melt region, solidification of the material occurs. Cooling rate which affects the microstructure of the composite depends mostly on the tape speed and the thermal boundary conditions (number of consolidated layers, material of the mandrel...) [229]. A model to study heat transfer during continuous filament winding using laser assisted tape consolidation has been presented by Beyeler and Güçeri [229]. Filament wound parts have been produced with PEEK/carbon [219, 230] and with PPS [131, 219].

5.8.7 Pultrusion

Pultrusion is another process well established for thermoset composites but it is at an early stage of development for thermoplastic composites [1, 26]. Existing pultrusion equipment for thermosets or slightly modified equipment can be used with thermoplastics provided that they have the high temperature and pressure capability required. Simple pultruded shapes such as rods, bars, half circles and tubes containing unidirectional glass or carbon fibres in PPS as well as complex shapes which incorporate off-axis reinforcement such as woven fabric have been produced by Phillips Petroleum [26]. Good consolidation, good surface appearance and good mechanical properties have been obtained. Reshaping or post forming was easily done on those PPS pultrusions. Strong and Hauwiler [231] have studied the failure mechanisms for straight pultruded rods and for pultruded rods post-formed (bent) to 90° and 135° angles when subjected to cantilever loading. Rods were made of PPS matrix reinforced with either unidirectional glass or carbon fibres. The investigators concluded that post-formed rods are about 50% weaker than straight rods under cantilever loading and that they experience different failure mechanisms. Fibre waviness was detected on the inside surface of the bends. However, Strong and Hauwiler added that the bending operation can be improved to give better mechanical properties.

5.8.8 Roll Forming

Roll forming technology borrowed from metal working technology might be promising for producing straight and curved structural thermoplastic composites [1, 55, 102, 232]. It is an automated, continuous process where continuous lengths of preconsolidated thermoplastic composites are pre-heated to the molding temperature and are formed progressively through a series of matched roller dies (Figure 55). Roller surface speeds up to 0.25m/s can be achieved [1].

5.9 Machining of Thermoplastic Composites

Thermoplastic composites can be machined with conventional metal machining tools, however, tools need to be very sharp (usually diamond tipped), cutting speeds need to be high, using slow feed rates [233] and because of the nature of the thermoplastic, cooling fluids have to be provided during machining [102]. If cooling fluid is not provided, the thermoplastic matrix may melt on the tool. Water jet cutting has been successfully used on APC-2 sheet [233]. Satisfactory back surface support has to be provided to prevent fibre pick out on the rear face. Holes can be successfully drilled and threads cut in APC-2 without damaging the laminate [102, 233].

5.10 Reprocessability

Scrap or excess material from thermoplastic composite moldings can be ground up, diluted with additional resin and reused for injection molding [102]. Due to the longer fibres present in the compound based on APC-2 scrap material, better mechanical properties can be obtained with these moldings compared to moldings from commercial compounds designed for that purpose. However, it would be too expensive to use virgin consolidated thermoplastic composite as a feedstock for injection molding, but the thermoplastic composite scrap from trimmings (from different processing techniques) can be considered as a high value feedstock for injection molding rendering fabrication processes more economic.

In addition, poor quality thermoplastic laminates can be remolded to eliminate defects and produce high quality products. In the processing study of Avimid K composites of Wedgewood and Grant [235], the ability to repair defects caused by manufacturing was investigated. Open hole compression samples with good and poor quality holes were prepared. The poor quality holes produced a 10% reduction of the compression strength. Poor quality samples were remolded and full recovery of the compression strength was achieved (Figure 56). When remolded at a temperature higher than the one used for the original laminates (360 vs 343° C), compression strength was increased to a higher value. High void content laminates (5 - 8% volume voids) based on Avimid K have also been successfully reprocessed and have yielded low void (< 0.5% void volume) high quality laminates [158].

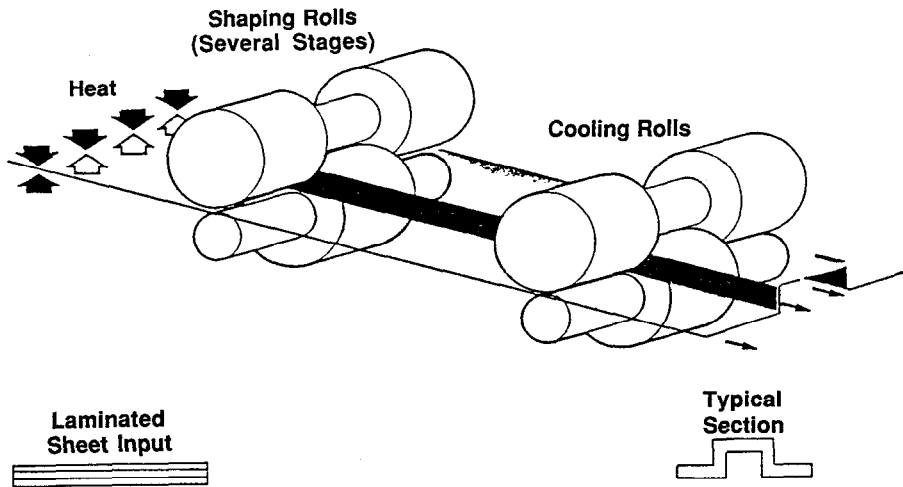


FIGURE 55. Schematic of the Roll Forming [102]

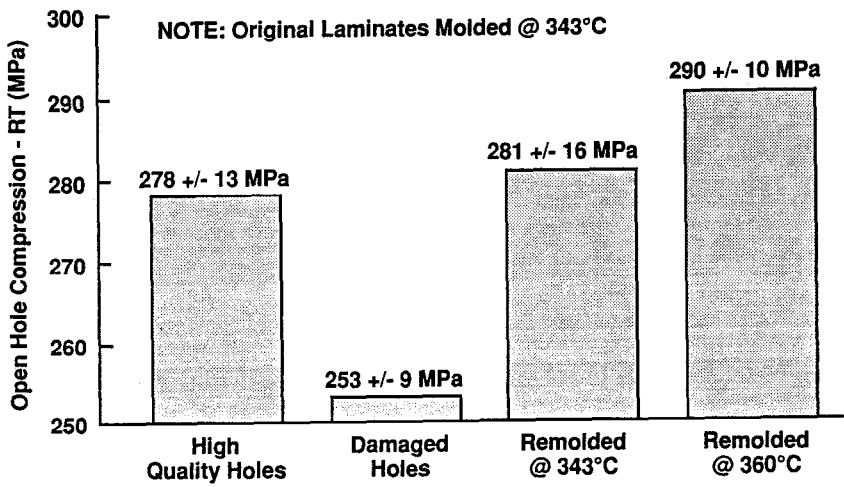


FIGURE 56. Open Hole Compression Strength of Original and Remolded Poor Quality Samples [235]

Theoretically, thermoplastics can be reprocessed many times. However, some thermoplastics exhibit a thermoplastic thermoset character limiting their processing cycle [129, 130]. For example, upon heating in air, PPS [129, 130, 137, 234] and PEEK [129, 130, 172, 234] (but to a lesser extent), can undergo slight oxidative cross-linking, chain extension or chain scission reaction. These processes are greatly slowed down when the oxygen atmosphere is substituted by nitrogen. The level of cross-linking is low and the thermoplastic can be reprocessed, but the highest degree of crystallinity achievable will not be as high as it would have been with the original material and it will decrease with the number of processing cycles. This in turn may affect the chemical and mechanical properties.

This cross-linking phenomena occurring in certain thermoplastics should be investigated, especially to determine how the degree of polymerization changes with the number of times a thermoplastic has been reprocessed and how it affects the mechanical and chemical properties.

5.11 Summary

In this chapter, a variety of processing routes to produce high quality thermoplastic composite parts for aerospace applications has been reviewed. They are summarized in the following text along with some recommendations.

The major benefits in processing thermoplastic composites compared to thermoset composites are the unlimited shelf life, the short processing time and their ability to be remelted and reprocessed while the main drawbacks are the high melt viscosity, high processing temperature and the lack of tack and drape of most prepregs.

The interfacial adhesion between fibres and matrix is generally lower than that observed for epoxies. Means to improve the interfacial adhesion (such as fibre treatment) and their effects in controlling mechanical properties should be investigated.

Several techniques for combining fibres with thermoplastic matrix are available; they include hot melt coating, solution processing, in-situ polymerization of monomers or prepolymers, film stacking, powder coating and fibre hybridization. Some of them are well established since they are employed with thermosets while others have been recently developed. Hot melt coating is a process where no solvent is needed, wet out is generally good with a low void content but the resultant prepreg is boardy and tackless. It is not a technique appropriate for thermoplastic polymers with very high melt viscosity. In the case of solution processing, thermoplastics have to exhibit solubility which may be not a desirable characteristic for particular service applications and this technique has the drawback that devolatilization must be carried out. Depending on the content of residual solvent, prepregs are more or less boardy and tacky. In-situ polymerization of monomers or prepolymers is

similar to thermoset processing; i.e. processing cycles are long and elaborate with the evolution of solvents. The prepregs made from this technique possess generally good tack and drape. Film stacking is quite straightforward but high pressure and temperature are needed for the obtention of a high quality laminate. Powder coating and fibre hybridization are two attractive processes recently developed that overcome the difficulty of working with thermoplastics that have a high melt viscosity and poor solubility. In the case of powder coating, wet out is generally good and the prepregs possess good drape. However, thermoplastics must have the ability to be ground into fine powder and this is a costly operation. Fibre hybridization leads to tackless prepregs but with high drapability and conformability. They are easy to handle but in general, composites made from fibre hybridization, either in co-woven fabric form or commingled woven fabric form, have lower mechanical properties than those laminates fabricated from prepreg tapes.

Lay-up of prepreg plies is generally more difficult than with epoxy as most prepregs are boardy and tackless.

Residual stresses are an important issue when processing high performance thermoplastic composites since they are likely to be higher than those found in thermoset composites due to the higher processing temperatures. Care should then be taken regarding voids and matrix cracking due to residual stresses during processing.

Techniques to produce flat laminates or to form shaped parts are generally derived from metal forming or from thermoset composite processing. Some processing techniques have the advantages that existing equipment can be used as is, such as presses and autoclaves (provided they can go to high enough temperatures) and other processing equipment may need minor modifications such as filament winding. Among the processing techniques used to produce flat laminates, the automated lamination and consolidation is the most attractive since it offers high reproducibility, accurate positioning of the prepreg plies, high processing speeds and lower processing cost. Matched die press forming, rubber pad press forming, diaphragm forming, hydroforming and autoclave/vacuum forming can be used to form a 3-D composite part. Filament winding and pultrusion are two processing techniques well established for thermoset composites that can be adapted for thermoplastic composites. Filament winding is particularly attractive as thermoplastic composite wound structures do not have to go through the long and costly curing operation. Roll forming, a technology borrowed from metal working technology might be promising for producing straight and curved structural thermoplastic composites as it is a continuous and automated process.

Thermoplastic composites can be machined by conventional means. Parts with defects can be reprocessed and scrap material can be reused. However, the effect of processing history (number of processing cycles) on morphological structure and mechanical and chemical properties should be more thoroughly investigated.