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5.1 Introduction

This chapter describes manufacturing processes for textile composites based on thermoset resin systems. A wide range of processes are available here, summarised in Table 5.1 in terms of their ability to be used with different reinforcement or textile forms. In the present chapter processing issues and material considerations associated with two families of processing routes will be addressed: pre-impregnated composites and liquid moulding.

Table 5.1 Comparison of processing routes for textile-based thermoset composites, illustrating capability with respect to different reinforcement forms

	Open mould (wet lay-up)	Prepreg	Liquid moulding
True unidirectional	No	Yes	No
Weaving	Yes	Yes	Yes
Weft knitting	Yes	Unlikely	Yes
Warp knitting	Yes	Yes	Yes
Braiding	Yes	Unlikely	Yes
Non-wovens	Yes	Unlikely	Yes

5.2 Pre-impregnated composites

In many composites processing methods, the matrix is added to the fibres at the time of manufacture. Resin transfer moulding and conventional hand lay-up are examples of this. An alternative approach is for the material supplier to bring the resin and fibre together, so that the user has only to lay the material onto a tool and then process it. These materials are called pre-impregnates, almost universally referred to as prepregs.

Like any other thermosetting composite material, the curing process requires heat and pressure. The trick with prepregs is to allow them a reasonable shelf-life while ensuring that they process at an acceptable temperature. To

achieve this the prepreg will typically be stored in a freezer and then cured at an elevated temperature. A further complication is that the prepreg must have a useful 'out-life', which is the maximum time during which the prepreg can be uprocessed without curing. The earliest prepreps produced in the 1960s necessitated quite high cure temperatures and had very short out-lives. Now it is possible for them to be stored in a freezer, have an out-life of possibly several months and a cure temperature of between 50 and 200 °C. Not surprisingly, the higher temperature cure materials have the longer out-lives.

Prepreps tend to be epoxy resins reinforced with carbon, glass or aramid fibres. Other matrix materials are occasionally used, in for example, high-temperature polymer composites.

5.2.1 Material systems

The earliest prepreps were developed for the aerospace industry. They were based on carbon fibre reinforcements and required very high pressures and temperatures to cure them. This drove the users to either autoclaving or hot pressing to achieve the necessary conditions (possibly 3 bar and 200 °C). The cost of these processes became very high. Not only was the equipment, such as the autoclave, expensive, but so also were the materials and the tooling and consumables needed to withstand the aggressive processing conditions.

For around two decades, prepreps were limited to niche applications in large aerospace structures, generally in non-critical parts. For many and complex reasons, the anticipated move of large civil aircraft aerospace to carbon prepreps in primary structures never really happened, and the materials remained inaccessible to industry, generally because of their high costs and difficult processing. Military aircraft did adopt prepreg materials, to the point that now most of the structure is carbon fibre. Light aviation also adopted composites with enthusiasm. Aircraft such as the Slingsby Firefly were essentially entirely composites. However, these have only recently started to move towards prepreps.

In the early 1980s, two factors led to important developments in prepreg technology. The first was that some areas of motorsport, particularly Formula 1, adopted prepreg composites. While this did not significantly change the technology, it did raise the profile. The other was the widespread adoption of carbon fibre composites for racing yachts, particularly in the America's Cup. Along with other applications, the yachts introduced a requirement for prepreg materials on parts that could not be autoclaved. It also meant that the curing temperatures had to be lower as the new customers, often with very large parts (e.g. yacht hulls) would not be able to pay very high 'aerospace' prices for tooling capable of operating at around 200 °C.

This spawned a new technology, quite separate from its aerospace ancestry. In the UK, companies such as the Advanced Composites Group and SP Systems developed a new family of prepregs which offered:

- high quality from a vacuum bag process;
- achievable processing temperatures (from about 50 °C);
- acceptable costs.

It was these developments that opened up prepregs to ‘middle industry’.

5.2.2 Advantages of prepreg materials

A prepreg material essentially combines the properties of the reinforcing fibre, which for textile composites may be in the form of woven or non-crimp fabric, with a high-performance epoxy resin matrix. The main advantages are:

- optimum fibre volume fraction;
- minimum variability;
- easy to cut accurately, either by hand methods or machine;
- controllable tack to allow plies to stay in place during fabrication;
- plies hold their shape and can be placed accurately;
- simple vacuum bag processes are available using tooling and processing techniques that are familiar to the industry.

The main disadvantages are that prepregs tend to be more expensive than separate resin and fibre systems, and need to be frozen for long-term storage.

5.2.3 Processing of prepregs

Almost any polymer matrix composite requires some degree of heat and pressure to complete the cure. The first prepregs were consolidated using a matched die moulding process to achieve the pressure, and an oven to achieve the temperature. Today, many of the prepregs used in some parts of aerospace and related industries still require autoclaves for consolidation and cure at relatively high temperatures of around 200 °C. The autoclave is necessary to achieve the minimum possible level of voids within the structure, giving the highest quality. The high-temperature cure is traditionally necessary to give useful working temperatures in the finished composite of between 120 and 150 °C.

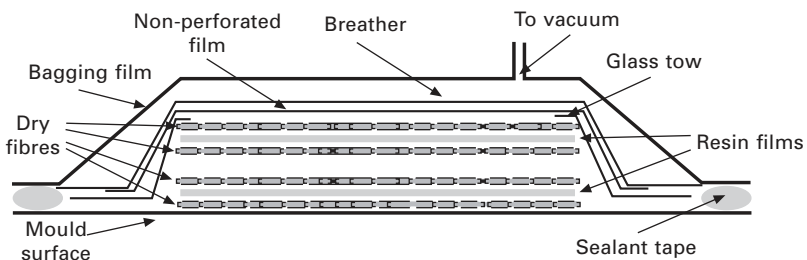
When prepregs were developed that could be cured under a vacuum at modest temperatures, they became useful in a much wider range of applications. Prepreg technology became available to many industries where specialist equipment such as the autoclave was not available and temperatures of 200 °C could not be achieved. Some of these prepregs were originally designed

as tooling materials where the low weight and high stiffness of composites, particularly those based on carbon fibre, were advantageous, but the parts were often too large for high-temperature autoclave cure. Very large structures, including the hulls and masts of America's Cup yachts, could be produced from prepregs, using vacuum bags and large simple ovens (effectively heated sheds) to cure the composite.

Modern prepreg systems offer extreme flexibility and can be processed under any conditions that can achieve the equivalent pressure to one atmosphere and the cure temperature (typically 50 °C upwards). Far from being restricted to autoclaves, modern processing techniques include:

- vacuum bagging;
- pressing;
- internal pressure bags;
- diaphragm moulding.

A typical, simple prepreg process is the SPRINT™ process illustrated in Fig. 5.1. For conventional prepreg, the only difference is that the resin films are integrated into the fabric rather than the discrete layers of resin shown in the diagram. The mould surface is treated with a proprietary release coating. The prepreg is then stacked on top. Once the lay-up is complete, the prepreg is covered with a release sheet. Some material systems may need this to allow resin to bleed through into the breather felt. The breather layer is necessary to allow even application of the vacuum. If it is not present, the vacuum will pull the bag tight to the surface and some areas will 'lock-off' and not see the full vacuum. Glass tow vents are placed at intervals around the periphery of the laminate to allow air, but not resin, to exit. Finally, the whole stack is covered with the vacuum bag, which is sealed to the mould, generally using a mastic tape. Ports are required to vent the bag to the vacuum pump, and to fit a pressure gauge to monitor the process. For parts that require the very highest quality or some specialist prepreg systems



5.1 Process stack for the SPRINT™ process. Conventional prepreg is similar, other than that the resin is integrated into the fabric rather than the discrete layers central to the SPRINT™ concept. Figure reproduced by kind permission of SP Systems Ltd.

which require a very high process pressure, the mould may be placed in an autoclave, which will apply pressures of several atmospheres. While the autoclave does offer very high quality, it is a very expensive piece of equipment with correspondingly high overheads, and its benefit for the bulk of composite applications is questionable. The industry is generally developing processes and materials that avoid the need for autoclaves. Once the vacuum is established, the part will be cured in an oven. Most prepregs will require a cure temperature of between 50 and 200 °C.

5.2.4 The cost equation

The initial cost of purchasing prepreg materials can be around double that of separate resin and fibre systems. However, since prepregs are generally easier to use and better controlled than ‘wet’ systems, the cost of the finished part may not be very different. [Table 5.2](#) compares the use of a typical, low-temperature prepreg with more conventional wet systems.

For small parts, prepregs are often most suitable as the quantity of material is low and precise handling becomes an important issue. For very large structures, processes such as resin transfer moulding (RTM) and vacuum infusion (VI) (see [section 5.3](#)) may generally be more appropriate, owing to the significance of materials in the cost equation. In between these extremes, the manufacturer will have to consider the true cost of all the elements contributing to cost – not just that of the material. A final consideration is the manufacturer’s normal preference. For instance a company that normally uses prepreg would incur considerable hidden cost in retraining its staff to use RTM or VI.

5.2.5 Hybrid systems

In recent years there has been a new family of materials developed, which are essentially a combination of conventional prepregs and the dry infusion process, which uses alternating layers of dry fabric and resin film. Materials such as SPRINT™ from SP Systems look very similar to conventional prepreg, but apply the resin to one side of the fabric, rather than distributing it through the thickness. The advantage of this is that the fabric itself provides pathways to allow all of the air to be extracted under vacuum, before the resin is heated to the point that it starts to flow. This produces a high-quality, low-voidage composite without the need for high processing pressures and autoclaves. [Figure 5.1](#) illustrates the process ‘stack’, and a complete boat hull bagged up and in process is shown in [Fig. 5.2](#).

Table 5.2 Comparison of advantages and disadvantages associated with prepreg with wet lay-up

	Prepreg	Wet lay-up
Material cost	High. Often difficult to obtain in small quantities.	Medium to low.
Tooling	Relatively high cure temperatures mean that some thought must be given to the tooling materials. Even at 50 °C some woods, paints and plastics start to become unstable.	Room temperature cure allows the use of most low-cost materials.
Consumables	The lack of free resin often allows consumables such as breather fabrics, to be reused.	Resin will tend to prevent reuse of consumables.
Cutting	Prepreg fabrics are very stable due to the presence of the resin. It can be cut with anything from a knife to an NC machine. Very accurate cutting is possible.	Dry fabrics tend to be unstable and unravel at the edges. This makes cutting to size very difficult, resulting in a trimming problem after cure. Stabilised fabrics are available but are expensive.
Control of fabric	Prepreg fabrics are stable, easy to lay with precision and drape well.	Wet fabrics can be difficult to lay down evenly and are almost impossible to position precisely. Stabilised fabrics can be difficult to drape.
Surface finish	Excellent with suitable tooling.	Can be difficult to reliably achieve a good surface finish.
Component quality	The controlled resin implicit in the use of prepregs results in very consistent fibre volume fractions and laminate thickness.	Although it is possible to produce very high-quality parts by wet lay-up and vacuum bagging, the repeatability is very dependent upon the experience of the operator.

5.2.6 Conclusion

There is little doubt that, from structural considerations, prepregs offer a material system that will produce a consistent part of very high quality. The negative side of the equation is cost, both in terms of the initial cost of the material and its storage and cure requirements. Only an analysis of the parameters of a particular part within the context of a particular manufacturer will indicate the cost effectiveness of the material.



5.2 A large boat hull being manufactured using the SPRINT™ process. Figure reproduced by kind permission of SP Systems Ltd.

5.3 Liquid moulding of textile composites

Of all the potential conversion routes for textile-based intermediates, liquid moulding is arguably the most flexible, combining the small batch flexibility with the low emissions and higher quality levels of prepreg, without the high on-costs associated with those materials. Liquid moulding describes a family of closed mould processes whereby a dry reinforcement is impregnated with a liquid thermosetting resin. [Table 5.3](#) summarises the most widely used processes and terminology.

Apart from some of the technical reasons for using liquid moulding, it is also of strategic importance that liquid moulding is used almost exclusively for producing engineering sub-assemblies or complete structures – rather than semi-finished goods – with the cost benefits associated with eliminating this intermediate stage. A materials cost save of 40% might be expected, compared with prepreps.

A large part of the flexibility lies in the facility to change textile architectures to suit the application (for processing or performance reasons) without the need to re-engineer the upstream process (as would be the case with prepreps, compounds, etc.). This also offers the only sustainable route (for thermosets) for non-mainstream fabrics – 3D weaves, braids, etc.

Table 5.3 Glossary of terminology related to liquid moulding

RTM	Resin transfer moulding – positive pressure, matched mould variant with polymer resins.
VARI	Vacuum assisted resin injection – adaptation of RTM using vacuum sink to enhance pressure gradient.
SRIM	Structural reaction injection moulding – adaptation of RTM using reactive processing equipment and techniques, usually for urethanes.
VI, VARTM, RIFT, SCRIMP	Vacuum impregnation processes using one hard tool plus vacuum membrane. Usually involves flow-enhancing medium. Some variants are patent protected.
RFI	Resin film infusion – (usually) through thickness impregnation by stacking films and fabrics, increasing materials available in kit form.

The mainstream liquid moulding applications are RTM products in the automotive industry and elsewhere in industrial goods. The principal resins are unsaturated polyester (for automotive body structures) and epoxies or bismaleimides for aerostructures. Several monographs were produced in the mid-1990s which provide a general introduction to the field^{1–3}. The last decade of the 20th century was marked by a moderate increase in the RTM market and a much wider acceptance of the technology for low-volume applications. This can be attributed to a combination of legislative changes concerning styrene emissions and cost reduction exercises in the transportation industries. The technology has matured considerably during this period with the emergence of materials, computer-aided design (CAD) systems, tooling solutions all more or less tailored to the process. The developments might be largely summarised as the refinement of polyester RTM and the evolution of a parallel technology, equally robust for high-performance aerospace resins. Less well known, perhaps, have been attempts made over the same period to adapt the technology to thermoplastics resins – notably polyamides and polyesters, an intriguing possibility as this market segment continues its buoyant growth.

The purpose of this section is to summarise the basic science and technology of RTM and to review the important developments which have taken place post-1995 in the related fields of resin film infusion (RFI), structural reaction injection moulding (SRIM) and vacuum infusion. More fundamental issues related to process modelling are described in [Chapter 7](#).

5.3.1 Resin transfer moulding (RTM)

Key features

Matched moulds

Low pressure processing

Structural and cosmetic parts

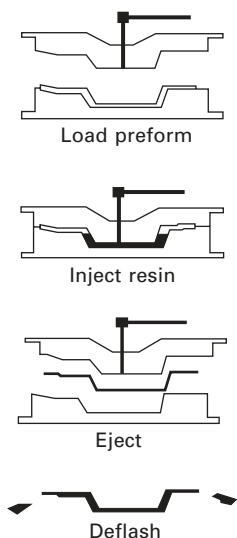
Low-volume applications

Darcy's law:

$$Q = \frac{KA}{\mu} \frac{\partial p}{\partial x}$$

where Q = volumetric flow; K permeability, A cross-sectional area, p pressure and x distance (parallel to flow direction)

The basic process (Fig. 5.3) involves a positive pressure resin supply and a pair of matched moulds. The fabric charge (preform) is loaded, the mould closed and resin is introduced at superatmospheric pressures (2–20 bar is typical). Darcy's law is usually assumed to apply and the time taken to impregnate the preform therefore depends on the pressure gradient, the resin viscosity and the hydraulic conductivity or *permeability* of the fibre bed. Impregnation times range from a few minutes to several hours and the resin needs to be formulated taking this quantity into account. The resin may be supplied via a simple pressure pot or, more usually, some form of positive displacement pump.



5.3 RTM process schematic.

The process can be configured in many ways, depending upon the application and the industrial environment. However, a typical manufacturing cell would involve low stiffness tooling (glass fibre reinforced plastic, GRP, or nickel shells) backed by a fabricated stiffening structure with peripheral clamping. A pneumatic, reciprocating pump would deliver polyester resin, dosed with a low-temperature initiator and passed through a static mixer en route to the mould. The mould may be heated by resistance elements or fluid-carrying pipes; either may be embedded within the mould structure. Porting is essential to admit the resin and to vent the air. These may be inside or outside the main cavity; the latter is often preferable for cosmetic parts to avoid witness marks. Single injection ports are the norm, although it is possible to use multi-porting (e.g. for large area mouldings), but special care is obviously required to avoid air entrapment where flow fronts coalesce.

Unsaturated polyester and epoxy resins account for the majority of applications, the major constraint being viscosity – 0.5 Pa s represents a practical upper limit. Higher viscosity systems such as aerospace epoxies or bismaleimides may require reactive diluents or substantial preheating in order to bring them into this range. Such systems (and other hot-setting formulations) are generally handled as premixed, one pot systems while low temperature curing resins (especially unsaturated polyesters) are dosed with peroxide initiators on-line.

Reinforcements for RTM include a wide range of mats, fabrics and non-woven structures. In-plane permeability is the dominant property for most applications and virtually all intermediates will fall within the range that can be processed. Notable exceptions are forms based largely on monofilaments (owing to the hydraulic radius effect) and many chopped strand mats (owing to the tendency for fibre washing which arises from highly soluble binders). It should be noted also that permeability is a strong function of wetted area (and therefore fibre volume fraction), as well as fibre orientation.

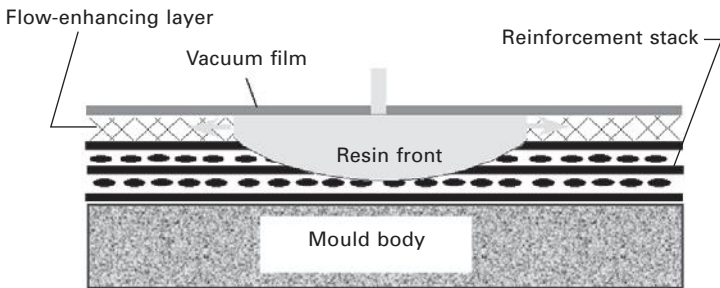
Various proprietary products are used to create high-permeability regions as processing aids. Perhaps the simplest approach is the elimination of alternating tows in, e.g., a woven or multiaxial warp knit fabric, with obvious consequences for mechanical performance. Alternatives include polyester monofilament netting, as used widely during infusion processing (see below) or so-called flow enhancement fabrics, notably Injectex[®] which includes a proportion of warp-bound tows to create relatively large inter-tow conduits for resin flow.

5.3.2 Vacuum infusion (VI)

Key features

Control of styrene vapour
 Thickness, V_f control
 Elimination of prepregging stage
 High consumables cost

In this process (Fig. 5.4) the upper half of the mould pair is replaced with a vacuum membrane. This reduces the tooling cost significantly and provides an increasingly important fabrication route for large structures where the throughput requirement is small. The key advances over open-mould alternatives are control of volatiles, thickness and fibre volume fraction (V_f) and resin consumption. Although the basic technology is more than 50 years old, recent industrial interest has been strong and driven almost exclusively by legislation on styrene emissions. In this context, the benefits of vacuum consolidation such as higher and more consistent volume fractions are significant, but secondary considerations.



5.4 Vacuum infusion process schematic.

The usual infusion set-up involves a GRP mould operated at room temperature. The fabric is laid-up by hand, followed by the ancillary materials – peel ply, breather felt, infusion mesh and vacuum membrane. Sealing relies on mastic tape, as with conventional vacuum bag moulding, and the facility to pull an effective vacuum. While the impregnation process is relatively fast for most set-ups (owing largely to the infusion mesh), the overall manufacturing time may be quite similar to those for wet laminated products. This is because the mould preparation – reinforcement, infusion mesh placement and bagging – are all critical, manual operations. Nevertheless, infusion continues to make inroads into the wet laminating sector, largely driven by legislative pressures.

Resins for vacuum infusion are generally low-viscosity variants on standard (i.e. laminating resins) epoxies and polyesters. The flow requirements are no

more demanding than for conventional RTM, although the process is usually done at room temperature and so there is not usually a temperature-related viscosity reduction. One of the consequences of moulding at sub-atmospheric pressures is the danger of degassing. Infusion temperatures are generally sufficiently low to inhibit styrene boiling but the risk of pulling dissolved gases out of solution remains. This is the subject of a useful discussion by Brouwer *et al.*⁴, who recommend degassing the resin before infusion in the presence of a nucleating agent (e.g. ScotchbriteTM) or sparging (bubbling through an air stream at reduced pressure).

Given the limited pressure gradient (since the maximum pressure difference between source and sink is usually 1 atmosphere) most operators rely upon an infusion mesh to create a high permeability zone at the surface of the laminate. Typically, this consists of a knitted monofilament which combines high porosity with low transverse compliance to provide the important flow gallery which makes for reasonable infusion times. Multiple infusion mesh layers are also beneficial – these may be either distributed or contiguous, although obviously this adds to consumables costs since the mesh is not generally reusable and creates a sacrificial resin film.

High-permeability zones, such as those created by the infusion mesh, mean that the flow within a typical laminate with any significant thickness will be three-dimensional. Flow leads at the surface and lags at the underside – the so-called lead-lag effect. This has several consequences:

- The infusion needs to continue until the lagging face is thoroughly impregnated.
- The infusion mesh may need to be cut back from the vented edge of the part to allow the flow front to recover.
- The magnitude of the effect will vary with the reinforcement style and the laminate thickness.

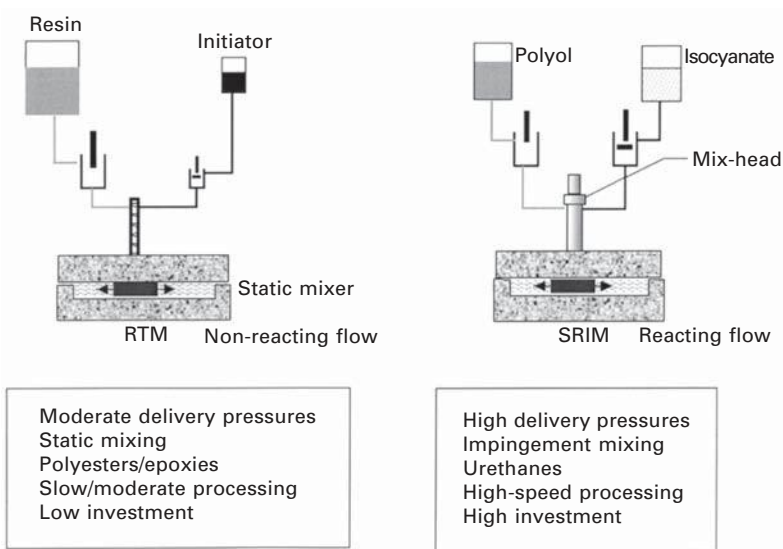
One further consequence of vacuum-driven processes of this sort is the indirect control of laminate thickness. During impregnation, the local thickness depends upon the pressure difference across the vacuum membrane and the transverse compliance of the reinforcement. Both factors will vary with time and position because, firstly, the pressure inside the bag depends upon its distance from the injection point and secondly because the transverse compliance varies with saturation and (probably) with time also. Practically, this means a gradual reduction in laminate thickness from the inlet to the flow front. A small ‘ditch’ may also be observed at the flow front because of the increased compliance of the saturated reinforcement. The evolution of the thickness post-filling is determined largely by the process control strategy. Many operators will bleed resin from the laminate to increase the fibre fraction and reduce the void fraction. Andersson⁵, for example, notes the progressive consolidation during this phase.

5.3.3 Structural reaction injection moulding (SRIM)

Key features

Polyurethane processing
High capital costs
High throughputs

SRIM is essentially the marriage of reaction injection moulding and RTM (see Fig. 5.5). Because the injection involves monomers, the viscosity is low enough to enable extremely short filling times – a few seconds is typical. Although, in principle, many polymers can be processed this way, the important commercial applications involve polyurethanes and polyureas. The automotive industry is more or less the exclusive market for SRIM products – semi-structural items such as fascias, bumper beams and interior trim panels are all current. Although the technology applies equally to ordered textile structures, most of the reinforcement that is processed this way involves various forms of non-woven. This reflects partly the performance criteria for current applications; also the need for rapid impregnation and fairly high washing resistance at fairly low fibre volume fraction.



5.5 Comparison of RTM with SRIM.

SRIM also offers some possibilities for processing of thermoplastics. The earliest system for polyamide 6 was developed in the early 1980s and is usually termed NYRIM. This involves the anionic polymerisation of γ -caprolactam, and was developed originally by Monsanto⁶⁻⁸ and later sold to

DSM. The main market for these materials is industrial cast polyamides (although some operators also incorporate milled glass reinforcement). A more recent formulation for polyamide 12 was developed by EMS Chemie⁹, using a liquid initiator for laurolactam polymerisation (although the same system can be used with carolactam to produce PA6). Studies at EPFL¹⁰ have examined a continuous version of the process for producing semi-finished goods via reactive pultrusion, where this somewhat demanding process can be operated in a steady state. Liquid moulding processes involving thermoplastic polymers are described in more detail in section 6.4.

5.3.4 Resin film infusion (RFI)

Key features

B-staged resins

Incremental vacuum bagging technique

Low throughputs

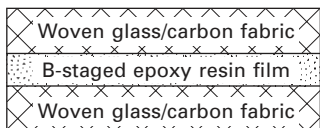
The introduction of several commercial ‘kit’ systems has renewed industrial interest in RFI, particularly in the aerospace and marine industries. RFI was initially patented in 1986 by Boeing¹¹ but has not received widespread technical interest outside the aerospace industry, where some work has been performed on composite wing stiffeners. Several semi-finished products have been introduced that package fabric and resin film together in a variety of ways.

The conceptual process involves interleaving fabric and B-staged films in the appropriate ratio before bagging and autoclaving in a similar fashion to prepreg processing. While offering ostensibly lower materials costs to conventional prepregs, progress was hindered by poor availability of suitable resins and limited understanding of the practicalities. Few systematic studies have been published although there has been some research effort in both the USA¹² and Australia.

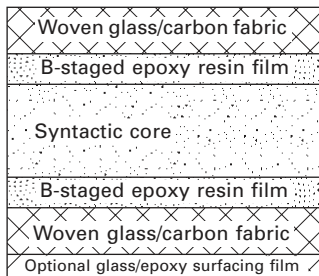
In response to industrial demands for materials cost reduction and in an effort to preserve existing markets, several materials suppliers now offer materials in kit form for RFI-type processes. Such products are sometimes termed semi-prepregs, since the fabrics are either partially impregnated or are tacked to a B-staged resin film. An increasing number of product variants includes surfacing films, syntactic cores, etc., and some of these are illustrated in Fig. 5.6. Here there is some overlap with the ‘hybrid systems’ described in section 5.2.5.

Whichever approach is used to combine the fabric and resin, several common and distinguishing features can be identified:

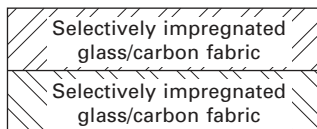
- The presence of integral breather channels within the dry portions of the fabric.



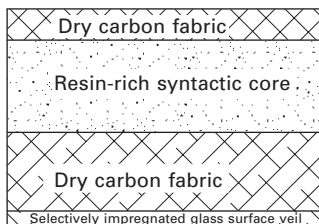
Fibre-resin-fibre RFI system



RFI body panel system



Selectively impregnated RFI system



Selectively impregnated RFI body panel system

5.6 Schematic representation of RFI kit systems.

- In some cases, superior draping characteristics to conventional prepregs due to the incomplete impregnation.
- Relatively short lay-up times, since the laminate is generally designed to be laid up as a single ply.
- The relatively short flow paths mean that minimum viscosity resins are not required and so higher molecular weight products can be used than are typically necessary in RTM.

As with conventional prepregs, the materials are designed to be processed using vacuum bag and oven or autoclave. Heat and pressure are applied and the resin flows the short distance, either in the plane or through the thickness of the fabric, before crosslinking fully.

Applications include low-volume manufacturing of automotive body panels, wind turbine blades and high-performance marine structures. Body panel systems incorporate typically a syntactic core containing glass microspheres. This reduces panel mass and enables, e.g., carbon fabrics to be used cost effectively. Cosmetic body panels may also include a satin weave cloth to mask fibre strike-through or a sandable surfacing film. Frost *et al.*¹³ have made an initial comparison of several commercial systems.

Most of the published research focuses on process simulation, usually evolved from RTM simulation codes. Loos¹⁴ presents results for a composite

stiffener based on their 3D RFI process model, simulating flow front position, impregnation time, temperature distributions, resin viscosity, degree of cure, preform deformations, fibre volume fractions and final cured shape. Other studies include those of Blest *et al.*¹⁵, Antonucci *et al.*¹⁶ and Sevostianov *et al.*¹⁷ which deal specifically with cavitations and resulting void formations in RFI.

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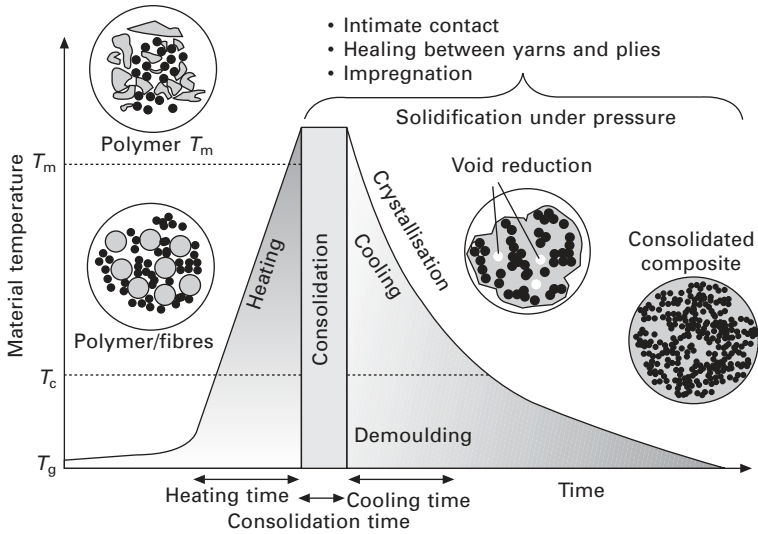
M D WAKEMAN and J - A E MÅN SON,
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6.1 Introduction

Thermoplastic-based composites differ from thermoset-based composites due to the nature of the matrix because the often time-consuming chemical reaction (crosslinking) is not required during the processing of thermoplastics. Harmful chemical emissions are generally reduced during processing. The considerable shelf-life of thermoplastics is also an advantage because sub-ambient storage is not required. Thermoplastic composites offer increased recyclability and can be post-formed or reprocessed by the application of heat and pressure. A large range of tough matrix materials is also available.

The manufacture of components from textile thermoplastic composites requires a heating process, either directly before the final moulding process, where an oven plus a cool tool is used (non-isothermal processing), or in a hot mould (isothermal processing). This is needed to raise the polymer matrix temperature sufficiently above the melt temperature (T_m) to reduce viscosity for impregnation of the textile structure during the final conversion process. The application of pressure to give intimate contact and hence heal adjacent yarns and plies, reducing void content, completes consolidation followed by cooling, under pressure, to solidify and crystallise the matrix to finish the cycle (Fig. 6.1)¹. Heat transfer thus forms the principal boundary condition governing process cycle times, with a corresponding potential for lower conversion costs. These basic steps define the many processing techniques that can be used to transform different material forms into the final product, where considerable flexibility exists to heat and shape the textile composites. One limitation for manufacturing techniques that results from the continuous, well-ordered and close-packed fibre architectures is that these materials do not flow in the same way as a fibre suspension to fill a tool, but must instead be deformed by draping mechanisms (see Chapters 3 and 4). Where flow does occur, this is local to the fibre bundle or, in certain cases, across the stationary fibre bed.

However, this limitation notwithstanding, a wide variety of both materials



6.1 Thermal cycle for thermoplastic composite processing (adapted from Månson *et al.*¹). T_m = melt temperature, T_c = crystallisation temperature, T_g = glass transition temperature.

and processing techniques have been developed for both niche applications and components produced at high volumes. Several commercially available aligned fibre forms are available that are suitable for conversion by a variety of processes and this market sector has an estimated growth rate of 20% per annum.

This chapter starts with an overview of the impregnation and consolidation processes for thermoplastics that have driven both materials development and the choice of final conversion process. This is followed by a summary of thermoplastic composite pre-impregnation manufacturing routes, and a review of final conversion processes for textile thermoplastic composites. The chapter concludes by reviewing forthcoming processing techniques for hybrid textile composite structures.

6.2 Consolidation of thermoplastic composites

6.2.1 Impregnation

The impregnation of fibre beds with thermoplastics is inherently more difficult than with equivalent processes for most thermosets owing to the high viscosity of thermoplastics at melt temperature. For example, polypropylene (PP) at 195 °C has a viscosity² of 410 Pa s, which is over 500 times the upper limit of 0.8 Pa s for unsaturated polyester resin. Since flow can be approximated by Darcy's law, the time for impregnation of a fibre bed by a constant viscosity material is given by eqn 1³, where the impregnation time (or

pressure) can be minimised by reducing the mass transfer distance, x , or the viscosity, μ :

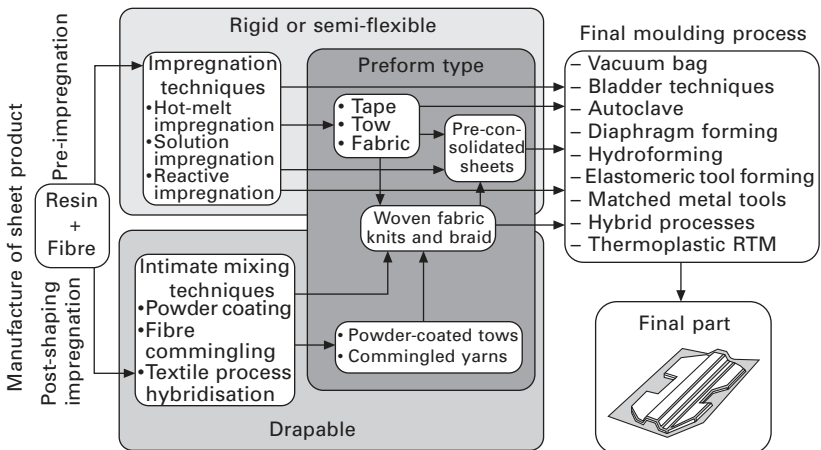
$$t_{\text{imp}} = \frac{x^2 \mu (1 - V_f)}{2K(p_a + p_c - p_g)} \quad 6.1$$

where:

- x = impregnation distance
- K = fibre bed permeability in the Z-direction
- μ = matrix viscosity
- p_a = the applied pressure
- p_c = the capillary pressure
- p_g = the gas pressure
- V_f = the reinforcing fibre volume fraction

Intimate mingling techniques reduce the impregnation (mass transfer) distance of the matrix into the fibre bed during processing, reducing consolidation pressures. There is often an associated increase in product cost with increasing homogeneity². Reduced impregnation times improve throughput and minimise thermal degradation of the polymer. Simple increases in pressure, during direct-melt impregnation for example, are likely to be counter-productive since this will also reduce the transverse permeability of the fibre bundles. Notably for lower viscosity systems, capillary pressure can play a role in the spontaneous wetting of fibres as low external pressure may be applied.

The starting distribution of fibres, matrix and porosity (defining the preconsolidation level) dominate the structure of aligned fibre materials, which fall into two principal classes (Fig. 6.2)¹. The first class consists of



6.2 Material routes, preform types and final moulding processes for aligned fibre thermoplastic composites (adapted from Manson *et al.*¹).

unconsolidated 'dry' mixtures of polymer and reinforcing fibre, for example as commingled yarn, which is flexible and hence suitable for further processing as a hybrid yarn into textile structures. In addition to the wide range of fibre architectures (woven and non-crimp fabrics, braids and knits), this has the advantage that textiles can be draped to a mould surface while cold. This offers ease of handling for isothermal processes. The disadvantage is that an often-considerable material bulk must be accommodated in the moulding process and that full impregnation and consolidation must occur in the final conversion process. The second class consists of partially or fully preconsolidated sheet, for example via film stacking and melt impregnation, which is subsequently semi- or fully rigid. This aids handling for non-isothermal processes where heating occurs in a first step followed by often automated transfer to the cool moulding tool, but inhibits the use of isothermal conversion processes because the material cannot be conformed to the tool in the cold material state.

Various techniques have been adapted for producing intimate fibre-resin combinations, including hot-melt impregnation, solution impregnation, reactive impregnation, powder coating, fibre commingling and textile process hybridisation. These are discussed in section 6.3.

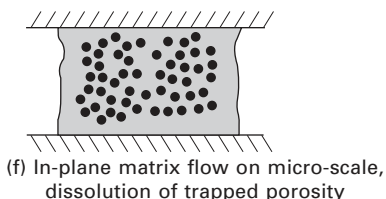
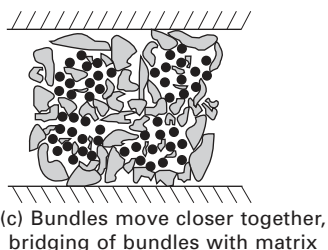
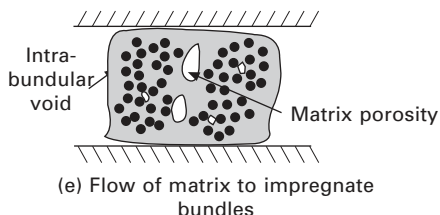
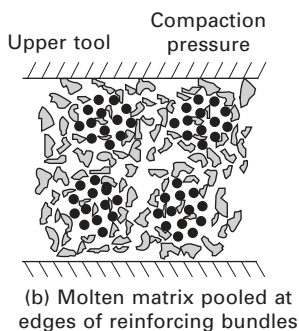
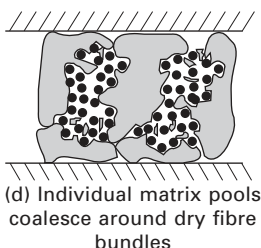
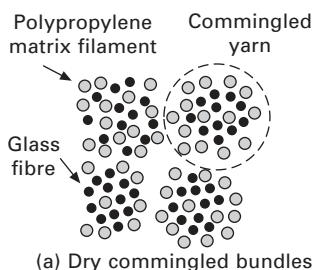
6.2.2 Consolidation of thermoplastic textile composites

The consolidation of thermoplastic matrix composites consists of three major steps: intimate contact, autohesion and fibre impregnation^{1,4}. Intimate contact is required between the surfaces of successive plies, which are initially rough with gaps consequently existing between the plies. The application of heat and pressure causes viscous deformation of the contact points and the degree of intimate contact is increased. The second step occurs after contact of the two surfaces with an autohesion bonding process occurring at the interface where segments of macromolecules diffuse and interpenetrate across the interface. The third step depends upon the initial impregnation state of the composite. Here impregnation of the fibre bed is either fully accomplished, or completed during the final stages of compaction. The deformation and flow mechanisms involved during the forming stage include resin percolation, squeeze flow or transverse flow, intra-ply shear and inter-ply shear.

The flow mechanism of resin percolation consists of a movement of matrix through the fibres and as such is not a deformation of the fibre arrangement. Without sufficient resin percolation, proper consolidation of the part will not occur, resulting in residual porosity. Squeeze flow or transverse fibre flow is a mechanism whereby parallel fibres displace transverse to the fibre direction due to the normal pressure applied across the laminate surface.

The consolidation stages taking place during final conversion depend on the initial degree of impregnation and consolidation when at process

temperature. The consolidation process is illustrated here through the example of commingled materials^{3, 5-8} which is shown schematically in Fig. 6.3. The polymer and reinforcing fibres are generally not distributed homogeneously within a yarn. Impregnation initiates after heating, with molten matrix pooled at the edges of the reinforcing fibre bundles. Increased compaction pressure moves the bundles closer together and bridging of bundles occurs with the matrix. Individual matrix pools then coalesce around the dry fibre bundles. Additional compaction pressure results in flow of the matrix to impregnate the fibre bundles and at full impregnation further increases in pressure may result in in-plane matrix flow on the meso-scale⁹. The time taken to impregnate the reinforcing fibre bundles depends upon the structure of the fabric, yarn dimensions and shape, number of fibres per yarn, fibre diameters and the quality of commingling².



6.3 Consolidation of commingled yarns.

6.2.3 Effect of fabric deformation on consolidation

The formation of complex shapes needs the material to have sufficient compliance at the processing temperature to deform to the imposed geometry. When the shaping operation occurs at room temperature (e.g. non-consolidated fabrics), this relies on the draping characteristics of the dry textile. When non-isothermal processes are used, the matrix is in the melt phase and lubricated fabric deformation occurs, with forming and consolidation often occurring in rapid sequence.

The basic deformation mechanisms that permit the material to conform are intra-ply shear and inter-ply shear (see [Chapter 3](#))⁴. The degree of conformability is controlled by the reinforcement architecture that dictates the component complexity. For biaxial reinforcements, the principal deformation is intra-ply shear, whereby the yarns are subject to in-plane rotation about their crossover points, enabling a woven textile to conform without wrinkling to a complex surface. Where multiple plies are present, inter-ply slip also occurs whereby the individual ply layers slip across one another when forming a curved shape.

A consequence of intra-ply shear is varying local superficial fabric density. In the simplest case, where the part thickness is not directly constrained (such as in a diaphragm forming or vacuum consolidation process), the laminate thickness will increase locally in the sheared region. The effect on fibre volume fraction (V_f) depends on the matrix distribution but will remain more or less unchanged. Where rigid tools are used, the cavity thickness is defined and a pressure gradient will result given the necessary force for compaction to the nominal thickness. Regions with greater shear will be subject to higher compaction pressures. In a rapid process, matrix solidification greatly inhibits in-plane flow. Thus the effects of the consolidation pressure variations are frozen in, which implies a variation in void fraction over the laminate. Aligned fibre composites with fibre contents of greater than 50% by volume can only adapt to gap tolerances of less than 5% of the original sheet thickness¹⁰.

The issue of non-uniform consolidation can be approached in three main ways. The first uses drape modelling tools^{5,11} to estimate the arising distribution of superficial densities or consolidated thicknesses. These data can be used to define the cavity thickness in a way that takes into account the fabric deformation. Thus the part would be produced with varying thickness but uniform V_f and at a uniform consolidation pressure. Although this approach is practical from a tool-making perspective, the non-uniform cavity is then dedicated to a specific fabric and its orientation with respect to the axes of the part. Part quality becomes highly susceptible to small deviations in fabric alignment and changes to the fabric specification would require the mould cavity to be reworked.

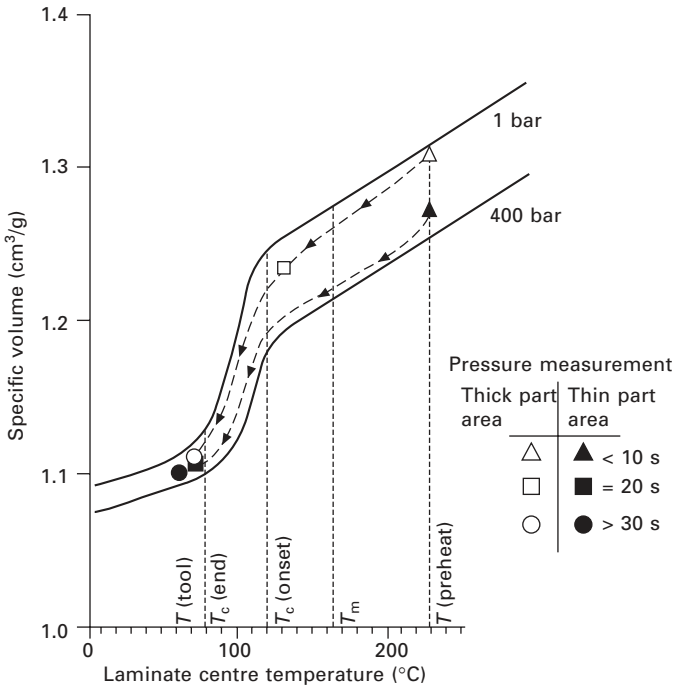
A more flexible alternative involves the manufacture of a deliberately compliant mould¹². Here one die is rigid, as before, while the other is cast from an elastomer, offering a useful solution for intermediate manufacturing volumes. Practical difficulties remain since the laminate thickness is not controlled directly, which has implications for subsequent assembly operations, and the elastomeric tool has a limited life and significantly lower thermal conductivity than the metal die, which makes for non-uniform cooling and solidification.

Arguably the most effective solution for high-volume press-based manufacturing is to use a multilayer material of fabric skins with a core structure. During forming, the fabric skins will shear in the usual manner followed by local squeeze flow of the core, which can be either a glass mat thermoplastic (GMT) type material or a polymer film^{13, 14}. Use of such a core enables variations in cavity pressure or V_f arising from the fabric deformation to be reduced, but with a lower overall V_f compared with aligned fibre materials. However, owing to its general proximity to the neutral axis, this does not significantly affect flexural stiffness.

6.2.4 Void content reduction

Composite porosity should be reduced to minimise quality variations and maximise mechanical properties. The tendency of preconsolidated sheet materials to deconsolidate, or ‘loft’ during preheating, or the bulky initial structure of dry textile structures heated to process temperature, results in trapped gas in the consolidating laminate. Much of the gas is expelled from the tool before the matrix viscosity reaches a limiting level. Porosity then reduces with increasing time at pressure to a final residual level. The decreasing temperature and increased pressure of the trapped gas results in volumetric reduction of the void volume, with polymer flowing into the original void cavity while the viscosity remains below a limiting threshold.

Voids can also form from crystallisation shrinkage due to the relation of pressure and temperature on specific volume during cooling. The volumetric shrinkage that occurs between the onset and end of crystallisation is shown in Fig. 6.4^{14, 15} for PP-based materials. Data points are superimposed on the pressure–volume–temperature (PVT) curves based upon a non-isothermal prediction that mapped through thickness temperatures¹⁶. This indicates that if pressure were released before the drop in specific volume (as crystallisation occurs), then any shrinkage from local crystallisation would not be accommodated by a laminate thickness change but by local void growth. Where one area of a tool, for example at a region of decreased thickness, cools first, the tool displacement to accommodate local shrinkage in thicker part regions will be limited by the thinner previously crystallised zone, with the shrinkage resulting in mid-plane voidage.



6.4 PVT relation for PP composite as a function of time with staggered cooling times for different laminate thickness (adapted from Janeschitz Kriegl *et al.*¹⁵).

The final phase of void reduction consists of the compressed gas diffusing into the surrounding polymer. Thermodynamic data suggest that individual molecules dissolve among the polymer chains¹⁷. For the case of PP, a given matrix element at 200 °C and 300 bar is capable of dissolving 15 times its own volume of air. The diffusion coefficient of air in PP at 200 °C results in a mean free path of 0.4 mm after 60 s for a diffusing molecule, indicating that the dissolved gas cannot escape out of the laminate during the short time of the high-temperature period. The diffusion mechanism is activated thermally, with the rate of dissolution decreasing as the laminate centre cools. The majority of trapped gas is hence dissolved into the matrix before solidification of the melt, with reduced dissolution below the melting temperature. Thus the impregnation state, any local thickness variations and the cooling rate will influence the final void content level and distribution in the part.

6.2.5 Internal stresses and spring-back phenomena

Processing conditions have a direct influence on the build-up of internal stresses in composites, and hence on the final component quality^{18–20}. The

morphology and mechanical properties of semi-crystalline thermoplastic composites are influenced by the cooling conditions applied during the solidification stage of the processing cycle. Increased cooling rates usually reduce the degree of crystallinity, give smaller crystallite sizes, increase the interlaminar fracture toughness, and reduce the transverse elastic modulus^{21, 22}. For example, rapid cooling of a composite surface at the end of a processing cycle induces temperature gradients through the part thickness, leading to internal stress build-up from heterogeneous and anisotropic shrinkage of the material. Non-isothermal solidification of semi-crystalline thermoplastic composites also gives rise to internal stresses due to crystallinity gradients.

Owing to changes in stiffness and thermal expansion between plies, internal stresses may also be generated as a result of the chosen stacking sequence²³. On a different scale, internal stresses can result from the mismatch of thermal expansion between matrix and fibre. Process-induced internal stresses may have undesirable effects on the performance of the end-product, reducing strength and initiating cracks or delamination, thereby leading potentially to premature failure of the composite. Internal stresses may also affect the dimensional stability of the part by generating post-processing distortions. Post-treatments such as annealing can be a solution to the problem of relaxing internal stresses in composite components, but the time and costs involved can be prohibitive.

6.3 Textile thermoplastic composite material forms

6.3.1 Thermoplastic matrix materials

Thermoplastic polymers differ from thermoset polymers in the way that the organic molecular units are bonded together. Thermoplastic monomer chains are held together by secondary intermolecular forces (e.g. van der Waals or hydrogen bonds) and mutual entanglements, rather than the covalent bonds (crosslinks) of thermoset polymers. Hence the intermolecular forces in thermoplastic polymers can be overcome by thermal energy and the polymer will reach a softened or molten state. Depending on the molecular structure, thermoplastic polymers are divided into the two groups of amorphous and semi-crystalline polymers.

Amorphous polymers have randomly oriented molecular chains, even in the solid state. The asymmetric chains (e.g. those with bulky side groups) inhibit arrangement of the chains into ordered crystalline structures. In semi-crystalline polymers, the chains are symmetric enough to be fitted into an ordered crystalline state. Due to the large molecular chain length, complete crystallinity (as in a low molecular weight substance) is not achieved and both crystalline and amorphous regions coexist in the solid. When a polymer is cooled from above the melt temperature (T_m), the chains lose mobility and

begin to interact segment by segment until glass transition (T_g) or crystallisation takes place. At T_g the molecular chains are locked in place and the polymer assumes a 'glassy' state. The molecular orientation of amorphous polymers in the glassy state is random due to the irregular chain structure. Semicrystalline polymers crystallise at temperatures well above the T_g and hence regions of amorphous and crystalline phase coexist in the temperature range between crystallisation and T_g . Crystallisation does not occur at a clearly defined temperature, but over a range, for example being shifted to a higher temperature with increased pressure, or reduced with an increased cooling rate.

As a thermoplastic polymer is heated above the T_m , a reduction in melt viscosity occurs. Given suitable impregnation techniques, this enables a variety of thermoplastic polymers to be used as matrix materials in textile composites, giving a wide range of thermal and mechanical properties (Table 6.1). Generally, the lower melting temperature polymers simplify processing, due to handling and drying issues. The following section describes a variety of approaches, shown schematically in Fig. 6.5, that are used to impregnate the reinforcing textile structure with the matrix polymer. Table 6.2 compares the mechanical properties of textile thermoplastic composites from a variety of sources, which should be taken as representative values rather than design data.

6.3.2 Bulk melt impregnation

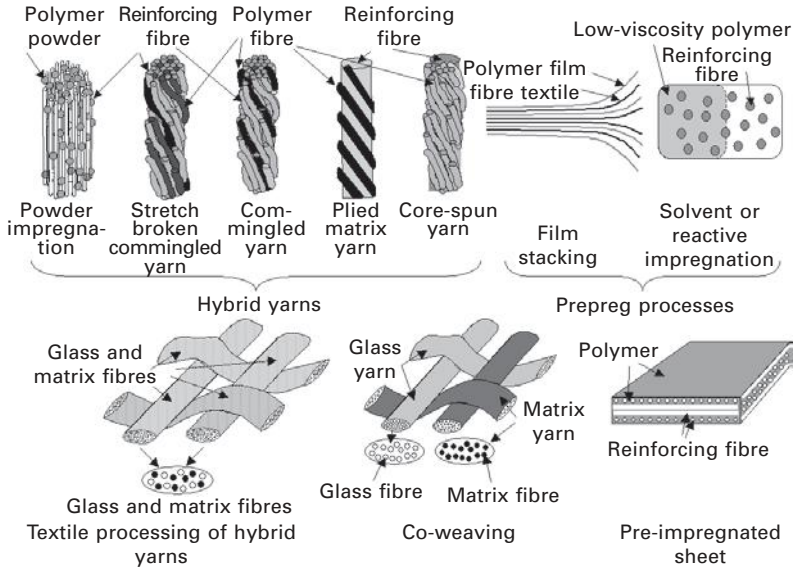
The polymer is introduced (usually as a film or extruded) between layers of reinforcement²⁶. The assembly is then pulled through a series of heated rollers that melt the matrix and reduce its viscosity sufficiently to enable impregnation. After a chilling roll, depending upon the thickness of the resulting laminate, the material is either collected on a rotating drum or sawn to a predetermined length. Double belt presses are often used (2–4 bar pressure) to achieve high-speed impregnation (5–8 m/min) and consolidation of semi-finished sheets²⁷, as is used commercially for GMTs²⁸ and textile thermoplastic composites²⁹. Impregnation quality (void content) is dominated by the pressure–temperature history of the polymer and the speed of the lamination machine³⁰. The significance of this depends upon the subsequent fabrication process (usually involving further void reduction) and the intended application. Melt impregnation is difficult or impractical for certain polymers due to their limited tolerance to the temperatures required for viscosity reduction. Thermal degradation, characterised by a reduction of molecular weight (where crosslinking does not occur), may initiate within a few degrees of the melt temperature, making this method of viscosity reduction impractical. While most systems²⁹ manufacture sheet product continuously, film stacking uses similar principles where fabrics are interleaved with polymer film and consolidated between heated dies or in a diaphragm-forming arrangement.

Table 6.1 Typical properties of unreinforced thermoplastic polymers used as matrix materials in textile composites (from MatWeb.com and adapted from ref. 24)

Unreinforced matrix	E_{ten} (GPa)	σ_{tens} (MPa)	$\epsilon_{\text{failure}}$ (%)	ρ (g/m ³)	Izod impact (J/cm)	T_g (°C)	T_m (°C)	T_{process} (°C)	€/kg
Polypropylene (PP)	1.4	31–42	100–600	0.91	31–42	–20	165	190–230	0.7
Polyethylene terephthalate (PET)	3.5	48–73	30–300	1.3	48–73	80	250	260–350	3.5
Polybutylene terephthalate (PBT)	2.5	56	50–300	1.3	56		235	240–275	3.2
Polyamide 6* (PA6)	3.0	35	min 50%	1.1	41–167	60	220	230–285	2.9
Polyamide 66* (PA66)	1.3	55	min 50%	1.1	51–96	70	260	270–325	3.1
Polyamide 12* (PA12)	1.1	40	min 50%	1.01	35–70	40	175	180–275	8.4
Polyphenylene sulfide (PPS)	3.4	48–87	1–4	1.35	48–87	90	285	310–335	8.3
Polyetherimide (PEI)	3.4	62–150	5–90	1.26	62–150	215	am	340–370	18–22
Polyvinylidene fluoride (PVDF)	1.0	24–51	12–600	1.76	43–80	–40	171	185–290	15
Polyetheretherketone (PEEK)	3.6	70–105	15–30	1.3	70–105	145	335	340–400	30–77

am = amorphous.

* As conditioned form



6.5 Techniques of combining thermoplastic polymers with reinforcing fibres for textile composites (adapted from Verpoest²⁵ and Wakeman *et al.*⁸).

6.3.3 Solvent impregnation

Solvent impregnation is an alternative to melt impregnation for generally amorphous thermoplastics, such as those used by Ten Cate³¹. Polymers suited to solution techniques include thermoplastic polyetherimide (PEI), polysulfone (PSU), polyethersulfone (PES) and polyphenyl sulfone (PPS) (<http://www.matweb.com/reference/abbreviations.asp>). The processing of a low-viscosity solution (*c.* 10wt% of polymer) facilitates impregnation and wetting of fibre tows or woven fabrics. However, handling problems occur including the containment of volatile organic compounds (VOCs) and the removal of residual volatiles (the final 5%) prior to fabrication³². Resistance to solvents is often poor and a sensitivity to stress cracking can result. When choosing composites based on amorphous resins, susceptibility to specific solvents needs to be assessed. Nevertheless, such materials are used in a range of engineering applications³¹. The most successful are those based on PEI, which has excellent fire, smoke and toxicity characteristics. The Ten Cate³¹ CETEX® range of PEI-based composites has been used in a variety of aircraft applications with Airbus and Fokker.

6.3.4 Commingling

In addition to reducing the viscosity term by heating, minimisation of mass transfer distances also aids impregnation. Commingling is an established

Table 6.2 Suppliers and properties of textile thermoplastic composite materials

Material form			Reinforcement	Matrix	ρ (g/m ³)	σ_{tens} (MPa)	E_{ten} (GPa)	$\epsilon_{\text{failure}}$ %	σ_{flex} (MPa)	E_{flexural} (GPa)
Sandwich material										
		M_f%								
Quadrant	GMTex 4/1	40	Glass	PP	1220	248	10.5	1.8	280	14.5
	GMTex 1/1 (commingled fabric skins, GMT core)	40	0–90° glass	PP	1200	120	4.9	1.9	160	7.2
Experimental	GF weave 4/1 + random glass core	30	Random core, fabric skins	PET	1620	184/82	12/6.9	1.8/1.5	–	–
Experimental	75% wt 4/1 commingled glass/PP + 500:m PP core	<75	PP film + fabric skins	PP	–	377	25	–	410	21
Aligned fibre materials										
		V_f%								
Plytron	GN 638T (melt impregnated, surface = 0° direction)	35	[(0,90) ₂] _s	PP	1480	360	16	2.5	300	16.8
	GN 638T (melt impregnated) tape	35	UD glass	PP	1480	720/11	28	1.9	436	21
Tech textiles	Thermopreg non-crimp interdispersed fibres, GF	35	Stitched 0/90 fabric	PP	1700	256	13	–	170	–
Vetrotex	Twintex, commingled GF/PP	35	bal. 2 × 2 twill weave	PP	1490	300	13	–	275	12

Table 6.2 (Continued)

Material form			Reinforcement	Matrix (g/m ³)	ρ (MPa)	σ_{tens} (GPa)	E_{ten} %	$\epsilon_{\text{failure}}$ (MPa)	σ_{flex} (GPa)	E_{flexural}
Vetrotex	Twintex, commingled GF/PP	35	4/1 weave	PP	1500	400	24/8	–	380/160	18/6
	Twintex, commingled GF/PP	50	UD	PP	1750	700	38	–	400	32
	Twintex, commingled GF/PET	50	1/1 weave	PET	1950	440	25	–	600	23
	Twintex, commingled GF/PET	50	UD	PET	1900	870	37.6	–	1025	37.7
Experimental	GF/PET	48	Warp knit	PET	–	87/6.6	8.2/3.5	–	747/25	35/4.6
	GF/PBT	56	0°	PBT	–	–	–	–	810	40.5
Porcher Ind.	Power impregnation at fabric level	52	2/2 twill carbon fabric	PA 12	–	–	–	–	603	44
Vestopreg		52	Bal. weave	PA 12	1850	350/350	26/26	1.6/1.6	500	22
Comfil	Commingled GF yarn	44	Twill 3/3	PET	–	260	22	–	–	–
	Commingled GF yarn, modified PET with lower T_m	41	Twill 3/3	PET	–	280	20	–	–	–
Schappe Techniques	Stretch broken commingled fabric at 20 °C	56	5HS carbon fabric	PA 12	1440	801	61	1.3	606	52

Table 6.2 (Continued)

Material form			Reinforcement	Matrix (g/m ³)	ρ (MPa)	σ_{tens} (GPa)	E_{ten} %	$\epsilon_{\text{failure}}$ (MPa)	σ_{flex} (GPa)	E_{flexural}
	Stretch broken commingled fabric at 80 °C	56	5HS carbon fabric	PA 12	1440	631	58	1.2	332	42
EMS Grivory	PA12/carbon (anionically polymerised)	54	2/2 twill carbon fabric	PA 12	1430	790	62.6	1.3	–	–
Cyclics	Cyclic CBT	–	UD carbon	PBT	1600	1565	115	–	1310	–
Dow	Thermoplastic polyurethane	–	UD glass (76% M_f)	ETPU	1910	1000	45	2.2	1150	45
Bond Laminates	TEPEX 101-glass FG290 (melt impregnated)	47	Glass twill 2/2	PA 66	1800	380	21	2.0	570	22
	TEPEX 201-carbon C200 (melt impregnated)	48	Carbon twill 2/2	PA 66	1500	755	52	2.1	745	44
BP	Curv (PP/PP composite sheet)	–	Polypropylene	PP	900	180	5	–	–	–
Gurit	SUPreM (powder impregnated UD 1 × 13 mm tape)	60	Carbon, UD	PEEK	–	2800	142	1.9	2000	120
TenCate	CETEX PEI-glass	50	7781 glass fabric	PEI	1910	465	30	–	625	26
	CETEX PEI- carbon	50	5H satin carbon fabric	PEI	1510	665	56	–	830	47

Table 6.2 (Continued)

Material form			Reinforcement	Matrix (g/m ³)	ρ (MPa)	σ_{tens} (GPa)	E_{ten} %	$\varepsilon_{\text{failure}}$ (MPa)	σ_{flex} (GPa)	E_{flexural}
TenCate	CETEX PPS-carbon	50	5H satin carbon fabric	PPS	1550	660	54	–	–	–
Cytec	APC-2 (melt impregnated) AS4 carbon	63	UD carbon	PEEK	–	2400/82	151/9.9	–	2280	138

UD, unidirectional; GMTex, textile reinforced glass mat thermoplastic; 500:m PP core, core of polypropylene 500 micrometers thick

textile process for intimately blending reinforcing fibres and matrix in a fibrous form. With the short flow lengths given by the hybrid yarn structure, the secondary consolidation and impregnation phases may occur at substantially lower pressure than those required for conventional melt impregnation. Since the hybrid yarns are both flexible and relatively stable, they are suitable for further textile processing (e.g. weaving and braiding) and the arising fabrics can be formed conveniently at room temperature. Also, given that the yarns are (generally) continuous, the reinforcement to matrix ratio can be controlled closely via the filament size and count of the two yarns. In general, the quality of the laminate is controlled by the intimacy of the blend and the uniformity of the hybrid yarn.

A patented commingling process^{33, 34} has been developed by Saint-Gobain Vetrotex for glass and polypropylene yarn (Twintex®). The manufacturing route consists of drawing and sizing glass fibres (as normal), which are then passed to an annular drawing head that is supplied with molten polypropylene from an extruder. Under pressure, the molten matrix passes through orifices that are distributed over an annular die plate and then drawn into multiple continuous filaments that converge with the glass fibres to produce commingled yarn at rates of 10–30 m/s. Blowers control air turbulence. Several strategies can be adopted to maintain yarn integrity including the use of film formers or encapsulants. Where photoactive size is used, the application of ultraviolet radiation prior to the winding phase triggers a chemical transformation of the size to improve the bonding of the composite yarn. This is especially important when downstream processes such as braiding are planned, since any rewinding operation tends to separate the constituent fibres depending on their different moduli.

An alternative approach patented by Schappe blends stretch-broken carbon fibres with polyamide 12 (PA12) staple fibres (EMS-GRIVORY, a business unit of EMS-CHEMIE AG) with the addition of a wrapping filament³⁵, which is available commercially. Multifilaments of reinforcement fibre (typically carbon) are stretch broken by passing yarns through rollers, where the roller speed varies between zones, producing a strip of discontinuous fibres of a controllable length (70 mm average). These fibres are then transformed on standard spinning equipment into the stretch-broken yarn³⁶. The staple matrix fibres and the stretch-broken reinforcement are then brought together via a machine having an additional stretching zone that produces an inhomogeneous strip of reinforcing and matrix fibres. Each strip is then combined with ten other strips on a similar machine and repeated a nominal four times. The strip obtained is then wrap-spun on a long fibre laminating system before final wrapping of the parallel fibres by a continuous multifilament of the same matrix as the commingled yarn. This system of yarn production eliminates the formation of fibres into helices that occurs during conventional twisted yarn spinning techniques. A higher degree of mingling is claimed for

this process than for competing methods. Additionally, the discontinuous fibres provide additional compliance during forming.

A final approach to commingling³⁷, developed for carbon and polyetheretherketone (PEEK) systems, involves separating the two yarns into open ribbons. The PEEK yarn cannot be opened via an air curtain and is instead passed around polytetrafluoroethene (PTFE) rollers to induce a charge of 6 kV, causing the carbon filaments to repel. The charged bundle is then drawn into a flat ribbon. The carbon yarn is opened with an air curtain into a ribbon that is then combined with the PEEK ribbon at a commingling bar at rates of approximately 0.5 m/s. This, it is suggested, gives a homogeneous distribution. From the commingling bar, the hybridised fibres are coated with size and wrapped on a take-up roll to form the final product. Mechanical separating elements that would limit commingling speed are eliminated.

6.3.5 Powder impregnation

The powder-coating approach blends fibres and matrix on an intra-bundle basis³⁸⁻⁴⁰ and is arguably more versatile than commingling in that powders may be more readily available than thermoplastic fibres. The process deposits and distributes the powder, most variants of which involve a suspension of particles in a fluid stream. The solid particles adhere to the fibres mainly by electrostatic forces. Success has been reported for fluidised bed processing, aqueous slurries and electrostatic methods of coating. In each case, the yarns are spread prior to coating to reduce the mass transfer distances. Individual yarns are then passed through an oven to sinter the powder on the fibre surface, creating resin bridges and a semi-impregnated tow that is then fully impregnated during the final consolidation stage. An advantage cited for powder impregnation is the dominant flow direction along the fibre axis that is in the direction of higher permeability (opposed to flow normal to the fibre with commingled yarn). Ideally, particles should be at a minimum the same diameter as the fibres, with the consolidation time proportional to the sixth power of the particle radius. The FIT (fibre-impregnated thermoplastic) process, initially developed by Atochem, impregnated fibre systems with polymer powder before extruding the same polymer as a sheath around the bundle. The yarn remained sufficiently flexible for textile processing. Commercial products^{40, 41} include unidirectional and cross-ply tapes and broad goods. Fibre contents range typically from 30% to 65%.

An alternative commercial approach involves powder coating unidirectional (UD) tows directly or fabrics after weaving⁴². In the case of fabrics, they are passed from rollers in a continuous (e.g. 10 m/min) process under a first powder dispenser followed by infrared heaters before a second powder dispenser and a final set of infrared heaters. The material is removed on a take-up roll and fabrics of up to 1000 g/m² (glass) and 600 g/m² (carbon) have been

processed successfully at V_f of up to 52% with polymers including PP, PA6, PA12, PPS, PEI and PEEK. Typical particle sizes are 25–100 μm . As with competing methods, the coated fabrics may then be consolidated further, laminated alternately, or the initially set product heated in a frame and stamped directly.

6.3.6 Co-weaving and warp-knitting techniques

Other techniques, which may be economic in specific circumstances, adapt existing textile technology and include co-weaving, inter-dispersed fabrics, split-film knits and plied matrix systems²⁵. Co-weaving combines yarns of the two fibres into a form possessing good drape characteristics, although an uneven reinforcement to matrix distribution may occur with generally longer impregnation times compared with a commingled system for a given set of processing parameters. The plied matrix technique⁴³ uses a polymer fibre woven around a bundle of reinforcement fibres offering improved distribution over the co-weaving technique. Glass and PP yarns have been inter-dispersed on line during fabric formation to produce drapable stitch bonded fabrics⁴⁴.

Another example is the warp knitting of polymer films with weft insertion of reinforcement fibres^{45, 46}. Split films are cheaper than conventional (spun) polymer fibres and are cut lengthwise into tapes that can be processed in a similar way to yarns. Weft-insertion warp knitting has been used in this way to produce multi-axial, non-crimp glass–PET (polyethylene terephthalate) fabrics. Typically, the split films are inserted in the weft, although there is no particular reason why they could not be warped also. A light stitching yarn (typically PET) provides fabric stability in the usual way. During processing, the textile is restrained during the preheat phase to resist shrinkage of the oriented polymer chains in the stretched ribbon as a return to the random coil orientation occurs.

6.3.7 *In-situ* polymerisation

An alternative solution is to impregnate the fibre bed using low-viscosity monomers (viscosities in the mPas range) with subsequent *in-situ* polymerisation that commences with activation of the monomer. Hence impregnation must occur before the viscosity reaches a limiting level. When polymerisation is complete, depending on the material and time–temperature transformation relationship, the part is cooled and the component released. Based on these principles, three main systems based around reaction injection moulding (RIM) technology have been adapted to impregnate textile composite structures via resin transfer moulding (RTM) or pultrusion processes, where monomer, activator and initiator systems are injected into a mould where polymerisation is completed in a few seconds or minutes, with the

polymerisation times generally shorter than for thermoset resin cure cycles⁴⁷.

Polyurethanes

When mixed, isocyanates and alcohols react to form polyurethanes, which are found as cross-linked thermoset or linear thermoplastic resins, depending on the selected molecular chemistry and the polymerisation process⁴⁸. Dow has developed thermoplastic polyurethanes for a reactive pultrusion process, known commercially as 'Fulcrum®'⁴⁹. Here the thermoplastic polyurethane resin, which can be repeatedly processed, shows a rapid molecular weight reduction when heated into the processing range. The lower molecular weight melt also has a low viscosity, enabling impregnation of glass fibres in the pultrusion process. After the impregnation stage, cooling rebuilds the molecular weight to a similar high level as the starting point. Reactive pultrusion line speeds of 10 m/min have been achieved. Additionally, the urethane chemistry is reported to give good fibre–matrix adhesion. Materials can be recycled via injection moulding.

Anionic polymerisation of polyamides

Polyamides, denoted by the number of carbon atoms in the monomer unit, can be obtained by the ring-opening polymerisation of lactams^{50–52}, representing more than 50% of polyamide production. Anionic mechanisms, enabling fast polymerisation, have been applied commercially (NyRIM) by DSM to polyamide via the RIM technique. This has been used for manufacturing articles via gravity casting, rotational moulding and RIM, with different initiators and activators. This material system has also been used to impregnate glass fibre textile structures in a RTM process, giving a glass fibre PA6 composite.

Traditional anionic polymerisation required the combination of two volumes of lactam preblended with catalyst and activator, resulting in a short pot-life where the materials slowly polymerised in the tanks. This was overcome through the development of a liquid activator system by EMS Chemie⁵⁰ that contains both activator and catalyst in solution. This has enabled the processing of laurolactam by an anionic ring-opening polymerisation reaction to produce either a fibre reinforced PA12 part directly⁵³ or a thermoformable pre-preg^{54, 55}. Polymerisation can be completed within minutes, with the type and concentration of initiator and activator together with the temperature influencing polymerisation kinetics and the final molecular weight. At 200 °C, the viscosity of this material prior to polymerisation is 1 mPa s whereas the molten PA12 has a viscosity at this temperature of 50 000 Pa s.

Cyclics technology for PBT, PET and PC

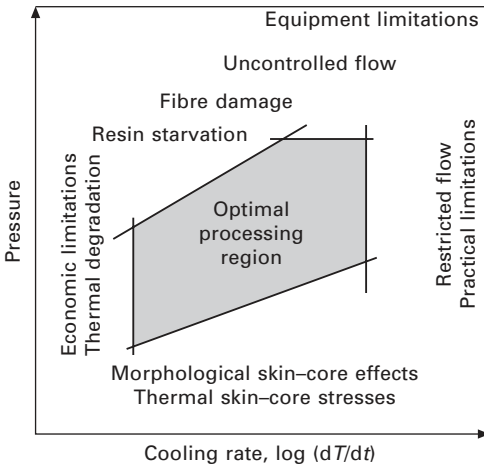
An alternative reactive thermoplastic system is produced by ‘cyclics’ technology⁵⁶. Reinforcement is impregnated with a low-viscosity thermoplastic resin (prepolymer) that subsequently reacts in the presence of heat and a catalyst to increase its molecular weight via conversion of its short molecular chains to a linear structure in a ring-opening polymerisation reaction. This technology has been demonstrated for polybutylene terephthalate (PBT) and polycarbonate (PC). Two different product forms are available: one-part systems that have the resin and catalyst premixed, and two-part systems where the resin and catalyst are supplied separately and mixed during processing. The prepolymer (CBTTM Resins) starts as a solid at room temperature, melts at 150 °C to a low viscosity of 150 mPa s, reducing further to below 20 mPa s at 180 °C. When mixed with specific tin or titanium catalysts, the PBT rings in cyclical form open and connect (i.e. polymerise) to form high molecular weight PBT thermoplastic. Full polymerisation is reported to occur from tens of seconds to many minutes, depending on the temperature and type of catalyst used.

6.4 Processing routes

6.4.1 Process windows for textile-based thermoplastic composites

A typical processing cycle for a composite with a thermoplastic matrix consists of heating the constituents above the matrix T_m , applying pressure for a time period to ensure appropriate consolidation, and finally cooling the material while maintaining the pressure. From a manufacturing perspective, considering equipment investment cost and production rate, it is desirable to process the part at the lowest pressures and with the shortest cycle times. Reducing cycle times requires exposing the composite to high heating rates prior to final shaping and high cooling rates during the solidification stage of the processing cycle.

Optimal processing conditions, in terms of pressure and cooling rate, may be defined by a processing window (Fig. 6.6)¹. The lower cooling rate limit is fixed by economic constraints, since long cycle times are costly. At high cooling rates, a considerable thermal gradient is imposed over the thickness of the composite part, which leads to both morphological skin–core effects and thermal skin–core stresses. If the polymer is exposed to excessively high temperatures during an extended time, thermal degradation mechanisms become increasingly important (and undesirable). Relations between different defect mechanisms, often governed by the internal stress build-up (voiding, microcracking) and cooling rates have been observed. An increased forming pressure, corresponding to the upper right boundary of the diagram, may



6.6 Generic process window for thermoplastic textile composites (adapted from Månson *et al.*¹). T = temperature, t = time.

suppress this defect initiation. The forming pressure upper boundary will be governed by the practical limit of forces applied by the forming equipment, as well as by the increased tooling cost for high-pressure processes. High forming pressures may also cause damage to the fibre bed (and changing permeability) as well as leading to local resin fraction reductions due to a high degree of in-plane macro-scale resin flow from the mechanically locked fibre bed.

Based around these boundary conditions, a wide variety of processing routes have been developed to process thermoplastic composites. These offer different combinations of cycle time, material suitability (semi-finished products such as partially impregnated sheets or as textile structures composed of, for example, commingled yarns) and the investment in capital equipment needed.

6.4.2 Low-pressure processing techniques

A range of low-pressure processing techniques have been developed that rely on the intimate fibre and matrix distribution before processing, either in a 'dry' commingled yarn material, or a preconsolidated laminate. The lower pressures reduce the investment in tooling and forming equipment, which is an important consideration for lower manufacturing volumes.

Vacuum forming of thermoplastic composites

Thermoplastic composites can be processed by vacuum forming in a similar manner to thermoset composites. Vacuum forming also enables thermoplastic

composites to be used in a hand lay-up type process. The produced part has only one surface with a finish that reflects the surface of the mould. Cycle times are a function of the heating route and sample size, ranging from 60 s⁵⁷ for carbon fibre (CF) reinforced PEEK, to 15 mins for glass fibre (GF)/PP plates⁵⁸ and to 24 h for a 7 m rigid inflatable boat⁵⁹. With a two-shift pattern, a typical production volume is 30 parts per day⁶⁰.

Taking the example of commingled yarn-based textiles, the first process step is to position the material into a mould. Techniques employed to hold 'dry' commingled fabrics to vertical mould walls and to subsequent layers include the use of hot air guns to 'tack' layers together and, for polypropylene-based materials, a pressure-sensitive polypropylene-based adhesive that is fabric coated onto the commingled textile, together with low molecular weight polyolefin spray contact adhesives (e.g. 3M-77). Core materials, which resist collapse at the composite process temperature and pressure, can also be incorporated, with typical materials including foams (e.g. Airex KapexC51), aluminium honeycomb and balsa wood. Release agents are often used to facilitate part release.

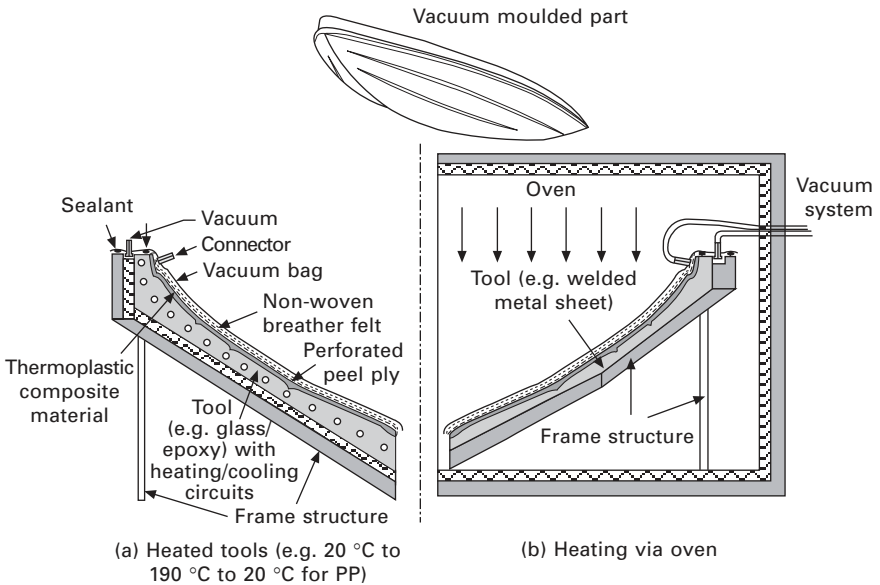
For well-consolidated parts (low porosity), a perforated peel ply (100 g/m²) and breather felt (non-woven nylon or nylon-PET of 100–300 g/m²) are used beneath the vacuum bag, which enables the air to be fully evacuated. The peel ply is in direct contact with the thermoplastic composite to prevent adhesion between the breather felt and the moulded material. The vacuum bag can consist of several materials, which for the case of polypropylene-based composites must have a melting temperature above 200 °C. Depending upon production volumes, a flexible nylon vacuum bag (50–75 µm) or a pre-shaped reusable silicone rubber bag is sealed against the surface of the tool. Reusable silicon membranes can be used to replace films, reducing consumable costs and the time needed to position the vacuum system. Typically only 100–150 parts total production volume are needed to offset the higher initial costs. Preformed silicon rubber forms enable a male tool to be used.

With a vacuum approaching 1 bar being applied for the whole processing cycle, the tool and material are heated under vacuum to the polymer's processing temperature (e.g. 185–190° C for PP), which is maintained for typically 10–20 min (dependent on the textile fibre and matrix distribution) for full impregnation. The tool is then cooled to below 70 °C (to reduce distortion and ease handling) with the vacuum pressure still applied, after which the vacuum bag is removed and the part released.

As this is an isothermal process where the mould temperature is cycled above and below the composite matrix T_m , the overall mould mass that is heated and cooled needs to be minimised. The mould material chosen depends on the number of parts to be produced, the cycle time desired, and the surface finish needed. Four general types of mould are used: high-temperature epoxy composite (3000–6000 parts/mould), welded metal sheet moulds (5000–

10 000 parts/mould), cast or machined aluminium (10 000–30 000 parts/mould) and electroformed nickel shell (50 000–100 000 parts/mould)⁶⁰.

Several methods are available to heat the evacuated tool depending on the size of the part, with the important requirement of a homogeneous temperature distribution. Heated tools avoid the need for a heated enclosure but are part-specific and generally used for part areas of 1–3 m² (Fig. 6.7a). However, tool durability is reduced due to differential expansion between the different mould materials and heating systems. Ovens offer a clean heating route, enabling a variety of components, including large structures, to be made from one heating system (Fig. 6.7b).



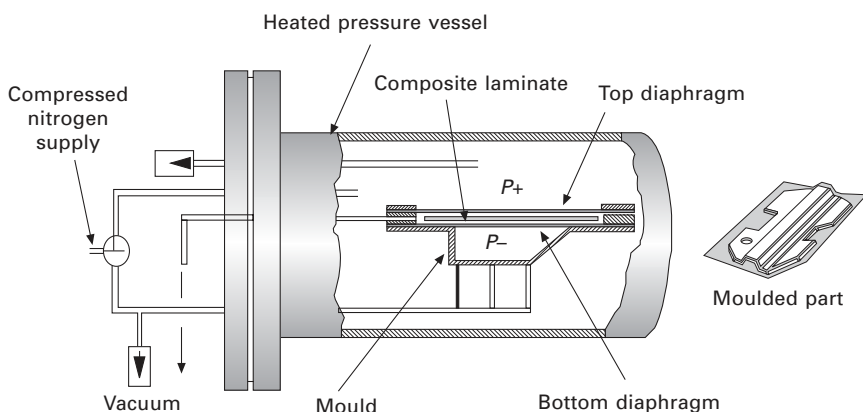
6.7 Vacuum bag processing of thermoplastic composites.

As an example of the vacuum moulding process, a rigid inflatable boat hull⁵⁹ has been produced from commingled glass and PP textiles. A mould material was needed that would withstand 500 production cycles. The contoured base is a cast mould equipped with heating and cooling systems. The texture and colour of the component can be changed using thermoplastic films that are placed on the mould surface. For such a production volume, neither metal nor nickel-shell tooling was cost effective and hence composite tooling was developed using a high-temperature divinylmethane diisocyanate tooling resin. This produces a high-quality gel coat surface and can be highly filled with metallic powder to improve the thermal conductivity. Where appropriate, a heating system can be integrated into the mould by either laminating in PTFE-coated resistance wires (e.g. 2500 W/m²) or copper tubes for hot oil.

In the case of the electrically heated mould, the resistance wires are fabricated into a grid that is draped just beneath the mould surface. Using an oil heating system, 40 min were required to heat commingled fabric across the boat structure to melt temperature. Pressure was applied for a further 40 min before the cooling cycle of 20 min where cold water was passed through the integrated copper tubes, giving a total process cycle time of approximately 100 min. This was reduced to 45 min for the electrically heated mould.

Autoclave forming of thermoplastic composites

In an extension of the vacuum moulding process, autoclaves offer similar advantages to ovens during the heating stage (heating of the assembled mould, textile composite and vacuum bag) with the ability to apply additional external pressure from 3.5 to 7 bar. This reduces void content and offers closer thickness tolerances, but reduces the number of parts made per day (Fig. 6.8)⁶¹. Forming is performed by raising the autoclave temperature to above the matrix T_m followed by an increase of the autoclave pressure to effect forming and finally cooling under consolidation pressure. During forming, the mould is subjected to hydrostatic pressure and the only force tending to distort the mould is the reaction to the diaphragm stretching, which in the case of polymeric diaphragms is very low. Thin section moulds with low thermal mass can be used.

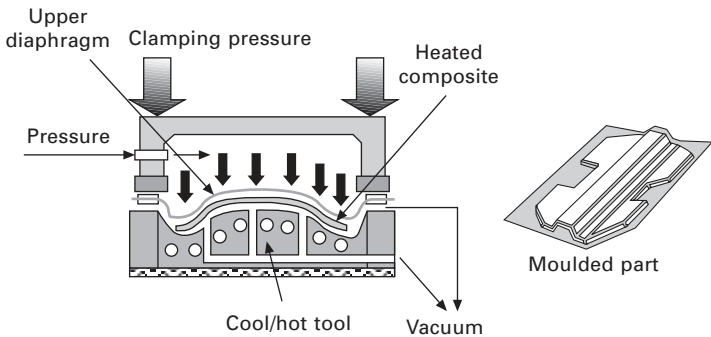


6.8 Autoclave processing (double diaphragm forming) of thermoplastic composites (adapted from Mallon *et al.*⁶¹).

Diaphragm forming

Diaphragm forming is a technique that consists of placing the laminate between two thin plastically deformable sheets, known as diaphragms. The diaphragms, when clamped around the mould edge, maintain biaxial tension on the laminate

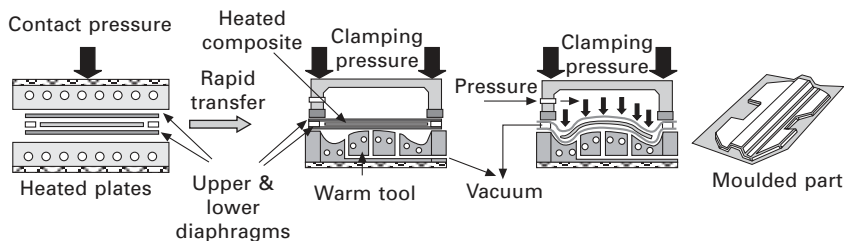
during deformation, consequently restricting laminate wrinkling, splitting and thin spots. The normal procedure consists of heating the whole mould, laminate and diaphragms to above the laminate polymer T_m , generally limiting process cycle times to 30 min or more. The combination of air pressure above the diaphragm, and a vacuum drawn from beneath the diaphragm forces the laminate to the mould geometry enabling the production of complex parts. Diaphragm forming can be performed either using compressed air or an autoclave. As an alternative to using two diaphragms, a single diaphragm placed over the preform can effect forming in a similar manner to double diaphragm forming (Fig. 6.9).



6.9 Isothermal single diaphragm forming of thermoplastic composites.

The diaphragms most commonly used are either polymeric or metallic⁶². Metallic diaphragms, such as superplastic aluminium, have been used for forming APC-2 (CF/PEEK) laminates. Polyimide films, such as Upilex-R (0.13 mm thick), have good elongation properties at temperatures up to 400 °C and have been used extensively. During forming, the laminate can slide within the diaphragms. As the diaphragms are stretched, surface friction between the laminate and the diaphragms transmits tensile forces to the laminate, creating out-of-plane support and suppressing wrinkling.

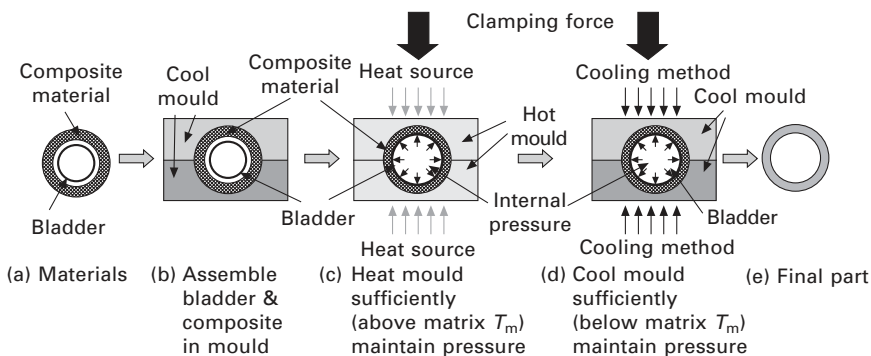
Recent developments have applied this technique to commingled glass and polypropylene textiles where panels have been produced using 0.5–1.0 mm thick silicone sheets. The composite fabrics and two silicon sheets are preheated in an initial stage between hot platens (210 °C) before rapid transfer to the forming unit and the application of positive pressure (7 bar) to form the material into a ‘female’ tool (Fig. 6.10). The silicon membranes are reusable, for between 500 and 1000 parts in polypropylene. This reduces cycle times to typically 2 min, as the temperature of the one-sided mould does not need to be thermally cycled.



6.10 Non-isothermal double diaphragm forming of thermoplastic composites – external heating in hot plates and rapid transfer.

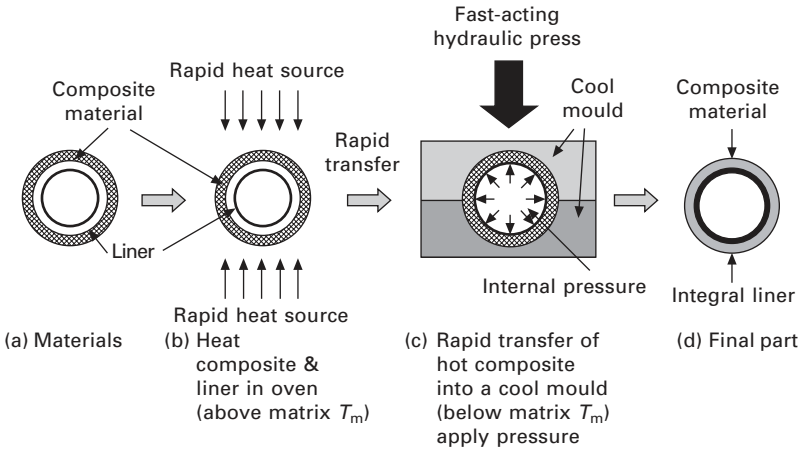
Bladder inflation moulding

The bladder inflation moulding (BIM) technique enables production of composite components with hollow geometries that have both high geometrical complexity and high intrinsic stiffness^{63–66}. BIM uses an outer mould and inner bladder to define the shape of the part. The low process pressures (~10 bar) permit the use of simple tooling, giving a process for producing thin-walled hollow composite parts with evolving cross-sections. Previous work has demonstrated bladder inflation moulding for small generic components, bicycle frames and handlebars, tennis rackets, suspension arms and pressure vessels⁶⁵. Two process variants of the BIM technique have been developed: (i) an isothermal process where the mould temperature and thereby the composite temperature is cycled above and below the composite matrix T_m (Fig. 6.11) and (ii) a non-isothermal process where the thermoplastic composite textile is preheated above the matrix T_m outside of the mould and then transferred rapidly to the cool mould for bladder moulding (Fig. 6.12).



6.11 A cross-sectional sequential view of the isothermal bladder inflation moulding process.

The isothermal BIM (isoBIM) process (Fig. 6.11) consists of assembling a thermoplastic composite braid around a bladder, which is pressurised



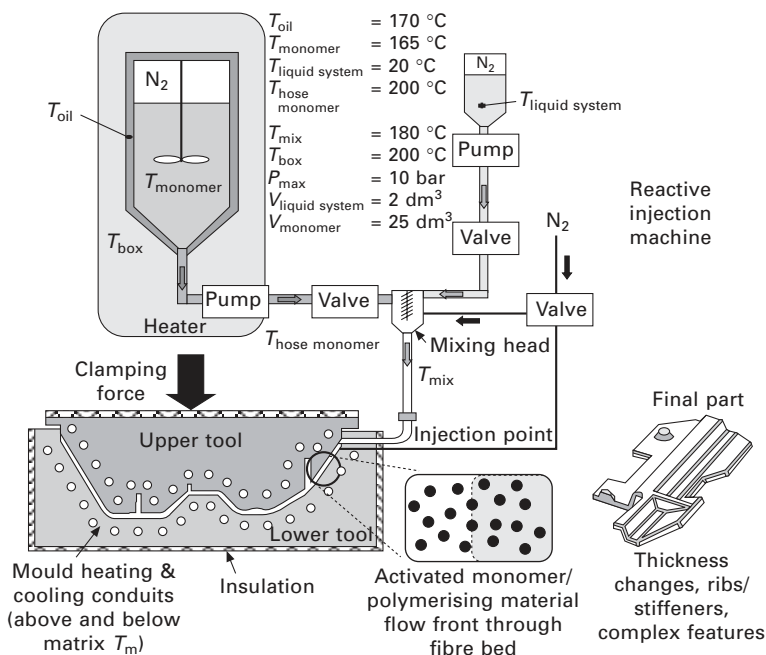
6.12 A cross-sectional sequential view of the non-isothermal bladder inflation moulding process.

internally via compressed gas. The bladder elongates elastically (silicon rubber) or plastically (thermoplastic extrusion blow mouldings) under the influence of the applied internal pressure and the braid is compressed between the bladder and a female mould. By heating the mould, the braid temperature is increased sufficiently above the matrix T_m in order to lower the matrix viscosity while maintaining an internal pressure inside the bladder to drive impregnation and consolidation. At process temperature, the pressure is maintained for the required period, after which the mould is cooled below the matrix T_m for solidification and crystallisation to occur. The internal pressure is then released and the part removed. In one example⁶⁵, eight-litre vessels (160 mm diameter) were produced from carbon fibre and PA12 commingled yarns in 12–15 min. The PA12 bladder, which formed an integral liner, was produced via extrusion blow-moulding.

To further reduce cycle times, suiting higher manufacturing volumes, a non-isothermal BIM (non-isoBIM) process has been developed^{65, 66} that eliminates the tool thermal cycling needed for the isoBIM process (e.g. 20 °C to 260 °C to 80 °C) (Fig. 6.12). The assembled PA12/CF commingled yarn and PA12 bladder were heated directly in a combined forced hot air convection (heating the bladder) and IR oven (heating the external braid to higher temperatures) and then transferred rapidly using a sled and rail system into a cool mould, maintained below the polymer melt temperature. A hydraulic press was used to close the tool and internal pressure was applied inside the bladder via a rapid pneumatic connection system to produce the part. This reduced in-mould cycle times to 140 s for a generic pressure vessel component of 85 mm diameter and 2 mm wall thickness.

Reactive thermoplastic RTM

RTM techniques that are commonly used for thermosetting resins are also applicable to reactive thermoplastic resins. Thermoplastic RTM (TP-RTM) has been used to produce both generic plates^{54, 55} and sections of a car floor pan⁵³. As an example, TP-RTM of a PA12 material consisted of the following steps, which are shown schematically in Fig. 6.13. The injection unit consists of two tanks, two gear pumps and two pipes conveying respectively the activator and the monomer from the tanks to the mixing head. The monomer is in the molten state; therefore tank, pump and pipes are maintained at 180 °C during processing. The liquid system remains at room temperature to avoid degradation. Both materials need to be held under nitrogen. Immediately prior to injection, mixing of the molten monomer and the liquid activator system (2.5%) occurs in a static mixing head.



6.13 Reactive thermoplastic RTM process, with the reactive injection machine illustrated for APLC12 materials (PA12 final polymer).

This particular monomer and activator system requires isothermal processing for economic processing. The mould temperature needs to be cycled from above the monomer T_m of 150 °C to a peak ranging from 200 °C to 250 °C (with higher temperatures increasing the polymerisation rate), followed by cooling sufficiently below the PA12 polymer T_m of 175 °C for demoulding.

An aluminium mould was used that enabled the production and study of 450 mm × 550 mm plates of 1–3 mm thickness. Using oil heating, less than 30 min was required to reach a mould temperature of 200 °C, and with water cooling, temperatures were reduced from 200 °C to 50 °C in 5 min.

The TP–RTM cycle consisted of the following steps. First, a release agent compatible with the anionic polymerisation was applied to the mould and two layers of a dried 5-harness satin carbon weave (440 g/m²) laid in the mould cavity [0/90]_s. Nitrogen was then flushed through the closed mould to remove oxygen and residual moisture. As the mould temperature exceeded 180 °C, activated monomer was injected into the mould. When the mould cavity was full with polymerising material, inlets and outlets were closed and heating maintained to enable complete polymerisation. The polymerised material then solidified during cooling, before final demoulding. The whole processing cycle required less than 60 min, with this being reduced to 15 min for a tool with faster heating circuits. This process has been used to produce a section of an automotive floor pan structure, offering the advantages of increased toughness and the ability to post form materials⁵³.

Injection-compression techniques have also been used to control crystallisation-based shrinkage and associated void formation to reduce porosity levels from 10% to 1%. Injection-compression processing applies a typical surface pressure of 55 bar during the cooling phase, using a shear edge tool.

The polymerisation of cyclic butylene terephthalate oligomers to form a PBT material system (offered by Cyclics⁵⁶) is also suited to TP-RTM. The prepolymers can be processed without cycling the mould temperature and will melt, polymerise and solidify when processed between 180 and 200 °C. With a prepolymer melting point of 150 °C, a processing temperature (mould temperature) of 180–190 °C is reported to give a compromise between higher rates of polymerisation and crystallisation. As the polymerised PBT has a melt temperature of 220 °C, the mould does not need to be cooled before part release. Cyclics® Corporation⁵⁶ claims to have demonstrated the use of CBTTM resins in the following textile composite processes: compression moulding, vacuum bagging, resin film infusion (RFI), RIM structural reaction injection moulding (SRIM), RTM and pultrusion.

6.4.3 High-pressure processing

Press-based processes, often involving separate preheating of the composite and then moulding in a cool tool, require higher forming pressures due to the short residence time in the tool under pressure during which final impregnation and consolidation need to occur. These processes have evolved to reduce costs and decrease cycle times for high-volume manufacturing. The alternative (isothermal) technique of cycling the tool temperature is less suited to high

production volumes, requiring large transfers of energy and resulting in generally longer cycle times and higher operating costs.

During non-isothermal processing, drapable textiles are still essential for maximum formability, but there is no longer a need for the composite product to have tack or drape at room temperature (forming occurs above matrix T_m), and a degree of mechanical handling integrity is desirable. The choice of fully impregnated, partially impregnated or unconsolidated material forms is an interaction of economics (eliminating pre-consolidation costs *vs.* potentially lower stamping times) and mechanical properties (cycle time *vs.* void content) and of practical handling considerations (degree of automation). Pre-consolidation eliminates the need to heat multiple layers of fabric, which must be assembled before stamping. Where fully pre-consolidated materials are used, the final stamping stage forces the material to conform to the mould geometry and (ideally) to eliminate any deconsolidation introduced during preheating. A comparison of stamp-forming with unconsolidated (dry commingled textile), partially pre-consolidated (40% porosity) and fully pre-consolidated CF/PA12 commingled yarn material showed increased laminate properties and reduced porosities for increasing levels of pre-consolidation, with the effect strongest at lower forming temperatures⁵⁴.

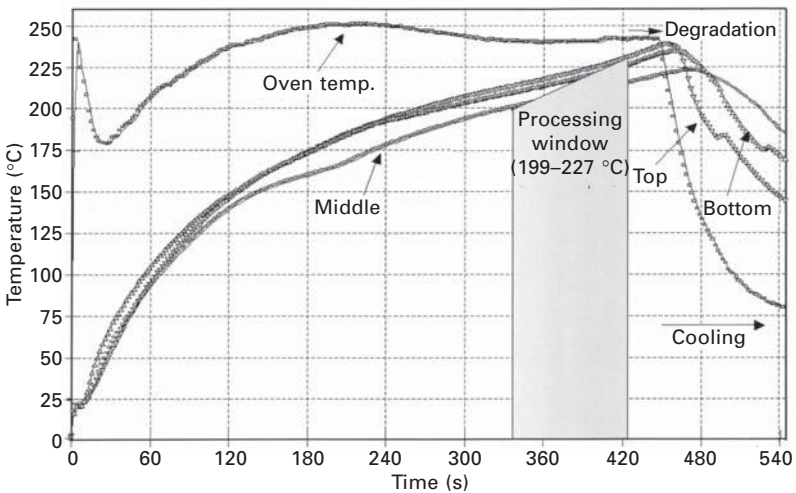
The following processing techniques, described after a brief examination of common preheating and blank holder technologies, are essentially all stamp-forming variants. After heating of the material to processing temperature, the primary forming mechanisms are the simultaneous phases of⁹ intra-ply shearing to facilitate fabric deformation, inter-ply shearing for shape accommodation (for two or more plies), viscous-friction between the plies and tool surfaces, pressure application for consolidation and removal of heat to permit solidification of the matrix.

Preheating technology for stamp-forming processes

Established industrial preheating techniques include infrared, hot air and air impingement heating, with contact heating, microwave, radio frequency and resistance heating (for carbon materials) under development⁶⁷⁻⁶⁹. Infrared heating⁷⁰ offers several advantages, including fast absorber heat-up times, programmable heating, controllability and higher energy efficiency. Problems occur with surface and through-thickness temperature inhomogeneities, which are oven design issues⁷¹. Circulated hot air ovens⁷² are best used for porous materials or pre-consolidated sheets that strongly deconsolidate. They have longer response times compared with infrared, but limit degradation from high flux levels at the composite surface and generally give a more even surface temperature distribution. Additionally, inert gases can be used to further reduce degradation. Air impingement ovens direct hot air at high velocity towards the composite blank and limit the upper temperature.

Infrared oven emitters radiate electromagnetic energy in the infrared region, with the laminate reflecting, absorbing or transmitting this energy. Heat transfer occurs when radiation is absorbed, increasing the random molecular energy. For example, carbon black pigmented PP shows minimal transmission, with 3% reflection and 97% absorption, irrespective of the wavelength, over the range of 0.8–3 μm ⁷³. This analysis needs to be performed for the specific polymer in question. Therefore, only as much energy can be delivered to the surface as can be transferred into the blank, without the surface overheating. The advantages of short wave emitters for PP are therefore limited to reducing response times and hence increasing the control potential.

A preheat processing window (Fig. 6.14) can be established as a period where the mid-plane of the laminate has reached the desired processing temperature for impregnation but without degradation at the outer surfaces. Different textile composite forms exhibit different heat transfer characteristics, for example, the range of pre-consolidation levels between a 'dry' commingled textile and a fully pre-impregnated laminate. Additionally, fully impregnated materials (fibre architecture dependent) will deconsolidate during heating⁷⁴ due to release of strain energy in the reinforcing fibres, the condensation of dissolved gas into voids of finite size¹⁷ and fibre to matrix adhesion effects. Hence during heating, the centre of the composite can become insulated because of its lofted structure. High matrix viscosities require heating to the maximum temperature possible to facilitate impregnation, while avoiding oxidative degradation, which results in chain scission of the macromolecules, and hence a reduction in the molecular weight. Matrix degradation occurs as a function of both temperature and time at temperature and frequently phosphite



6.14 Example of a preheat window for PP-based thermoplastic composites.

antioxidants are used⁷⁵ to minimise these effects during both preheating and the service life of subsequent products. As an example, gel permeation chromatography (GPC) has been used to define the upper processing window limit (with a given stabiliser package) for glass and PP laminates⁷³. Higher laminate temperatures reduced the time to the onset of degradation. For a standard infrared oven and for a laminate temperature of 220 °C, the preheat time adopted for the fabric blank of 145 s was within the onset of degradation at 200 s. At laminate temperatures of 180 °C, preheat times of greater than 10 min were possible.

Engineering polymers, such as PEI, require pre-drying before the main heating cycle, for example 4 h at 150 °C, to remove residual moisture. This is not necessary for commodity polymers such as PP.

Blank-holders and membrane forces

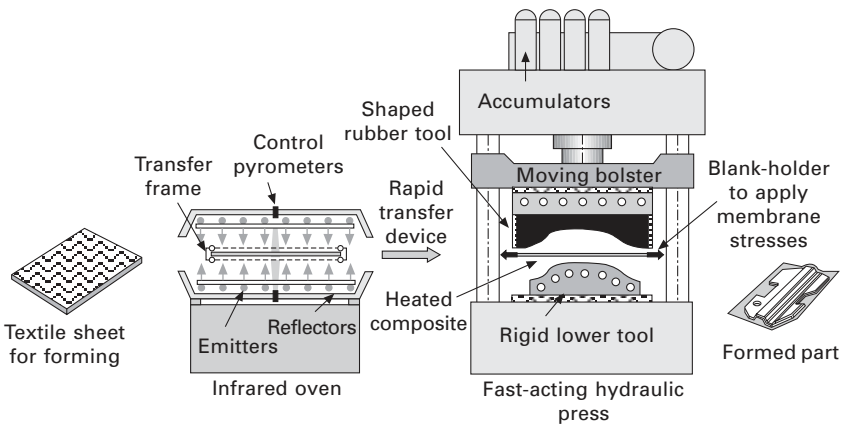
Blank-holders are a common feature of the stamp-forming processes discussed below, performing three principal functions. Due to thermoplastic memory effects, the matrix phase of certain composite textiles shrinks during preheating, requiring a blank-holder to hold the material. Additionally, to maintain fibre orientations correctly in the final part, an automated route is needed to transfer the hot and hence conformable material from the oven to the tool. Manual transfer is unsuitable because of the rapid convective heat loss and also localised conductive heat loss where the operator grips the laminate. Blank-holders thus restrain the material during preheating and also enable rapid (<10 s) transfer to the cool mould, which has been minimised in practice to 2–3 s^{10, 29}.

To maximise fabric drapability and reduce forming faults during moulding, a membrane stress should be applied to the fabric by a blank-holder, permitting higher shearing angles without visible wrinkling. For example, a 20 MPa membrane stress increased fabric shear angles from 35° to 60° without visible wrinkling¹⁰. As the fabric conforms to the tool, it is pulled through the blank-holder when the force needed to overcome the viscous friction at the fabric/blank-holder contact interface is less than the force needed to continue intraply shearing. The clamping load is transmitted to the fibre through the shear action of the resin, which will act as a lubricant depending on matrix temperature. Resistance at the tool/ply and ply/blank-holder interfaces is a function of the matrix film viscosity and Coulomb friction from the reinforcing fibre and tool contact. Increased pullout velocities and normal pressures increase the shear stress. Blank-holder temperatures should be lower than the material bulk⁷⁶; for PP-based composites, a blank-holder temperature of 125 °C improved quality versus 50 °C. An alternative to planar blank-holders is to clamp the fabric between rollers at selected zones, with the knurled roller surface fixing but not damaging the sheets¹⁰. The torque resistance of

the rollers inhibits draw-in of the material into the mould, with the normal pressure on the rollers controlled via pneumatic cylinders to vary retaining forces as a function of draw depth. This reduces heat transfer from the hot sheet to the blank-holder by the small contact surface of the rollers, reducing residual stresses where high membrane tensions are used.

Elastomeric tool forming

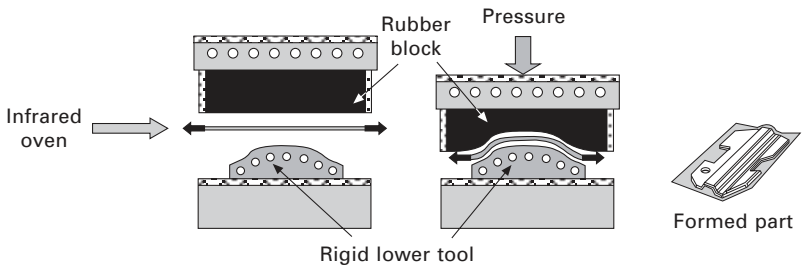
The upper tool used in this process consists of an elastomeric pad that can be contoured to match the shape of the lower mould for forming complex shaped components (Fig. 6.15). Elastomeric moulds deform elastically to a rigid lower mould under relatively low loading, but with low compressibility (constant volume). In the locked situation, elastomeric tools behave near hydrostatically, where an increase in the applied force on the mould transmits to a general increase in surface pressure on the whole laminate. Consolidation quality is influenced less by the part geometry than where two rigid moulds are used. Rubber moulds can be created from polyurethane or cast silicon rubber types (e.g. GE RTV630, offering high strength and tear resistance with inherent release capabilities). The laminate is preheated to above the matrix T_m and transferred rapidly into the mould. Blank-holders are used to control wrinkling. Closing of the mould deforms the laminate into the required shape and subsequently the component cools and solidifies within the mould. Marginally longer cycle times are needed than for matched metal moulds because of the lower thermal conductivity of the rubber mould. By changing the rubber tool geometry, the pressure distribution around the mould can be varied. The flexible nature of the mould accommodates composite material thickness variations caused by deformation of the laminate during forming.



6.15 Use of shaped elastomeric tooling for the stamping-forming of textile composites.

Elastomeric moulds are generally less suited to very high production volumes due to the reduced tool life compared with metallic moulds (contact with hot laminates and a low rubber thermal conductivity)¹².

The rubber pad may also be in the form of a rubber block (Fig. 6.16). This is generally suited to forming only simple shaped components, due to the limited local deformation of the rubber pad. Rubber block pressing provides high normal forces and surface tension but these are not uniformly distributed over the laminate. The local forming forces are determined by the shape of the die only, which counteracts closure of the press. Such processes have been widely used in production for Airbus and Fokker aerospace applications, in PEI and PPS-based textile composites (CETEX®).

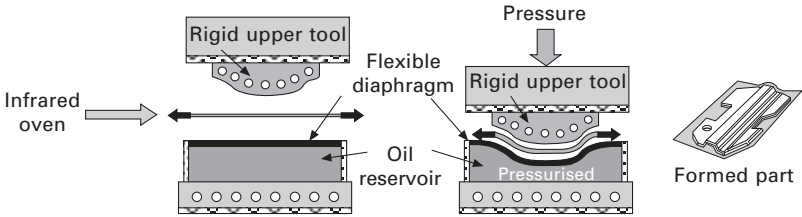


6.16 Deformable rubber block tooling for the stamping-forming of textile composites.

Hydroforming

The hydroforming process (Fig. 6.17) utilises fluid pressure (hydraulic oil) behind a rubber diaphragm to force a sheet of material into the shape of an adjoining mould. The cut textile preform is first located on the diaphragm that is fixed to the fluid filled chamber. The draw-cap is fixed in position and the punch lowered to form the part against the resistance of the fluid pressure. Both the punch and the fluid are held at the appropriate temperature and, after the required hold time, the pressure is released, the punch withdrawn and the part removed. The main advantage of hydroforming is the application of hydrostatic pressure and a uniform normal pressure over the laminate surface, during both forming and consolidation phases. This facilitates the deformation mechanisms of inter-ply and intra-ply shear while at the same time squeeze flow effects are not restricted. As a result, the formed part will not suffer from damage in high spots and sharp corners in the same way as can occur in matched die forming.

Hydroforming, like diaphragm forming, eliminates the need for mutually conforming dies and consequently the tooling costs are relatively low. Elastomers used in hydroforming are generally suited only to lower temperatures and hence, for higher temperatures, additional rubber sheets



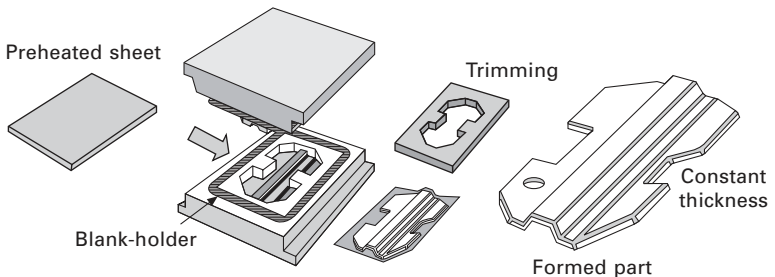
6.17 Hydroforming of textile composites.

have been placed over the preform before forming to prevent diaphragm rupture. Compared with diaphragm forming, hydroforming offers fewer possibilities to control forming forces on the laminate, but higher hydrostatic pressures can be imposed on the laminate surface.

Rapid stamp-forming with matched rigid moulds

The rapid stamping technique (Fig. 6.18) has been extended from more traditional techniques such as diaphragm forming for high-volume or cost-sensitive industrial sectors, notably the automotive industry. Metallic tools are necessary to achieve the high heat transfer rates needed to reduce cycle times. The process consists of preheating the textile in an oven to above the matrix T_m before rapid transfer to a cool tool where forming and consolidation take place. Blank-holders are used to control wrinkling. With consideration of the following issues, textile composites can be processed with matched metal tools using the techniques commonly used for GMTs:

- avoid obstructing deformation of the laminate when local pressure is applied too early;
- thickness differences due to intraply shearing must be predicted precisely (dependent on the fabric type and the initial orientation in the tool);
- the final consolidation will be different over the product due to different surface pressures during the consolidation phase (e.g. wall sections with lower normal pressures);
- fabric waste management and recycling.



6.18 Non-isothermal stamping of thermoplastic textile composites.

The required consolidation pressure depends on the tolerated porosity level, but 5–15 bar is typical^{3, 29}, and pressures above 40 bar (e.g. for GF/PP and CF/PEI) may promote resin percolation to the outer plies^{9, 77}. The forming rate has important effects during processing. Reported stamping rates include 25 and 210 mm/s for PP and PPS systems⁷⁸, and 12 to 166 mm/s for glass or carbon and PA12^{10, 54}. Higher stamping rates reduce material cooling and were found to increase hemisphere quality for CF/PA12 materials. Examination of four materials at rates of 10–100 mm/s, with right angle and cylindrical dish tools, showed that higher forming rates limited inter-ply slip, resulting in increased surface fibre buckling⁷⁹. The use of a rapid approach, followed by a relatively slow forming and consolidation period, has also been suggested. Mould temperatures are material (matrix) dependent and are recommended as: 80 °C (PP), 130–160 °C (PA), >160 °C (PPS), 230–280 °C (PEI) and 230–300 °C (PEEK). Cool moulds cause matrix solidification prior to complete part drape (limiting inter-ply slip) whereas materials conform fully at higher forming rates with warmer tools.

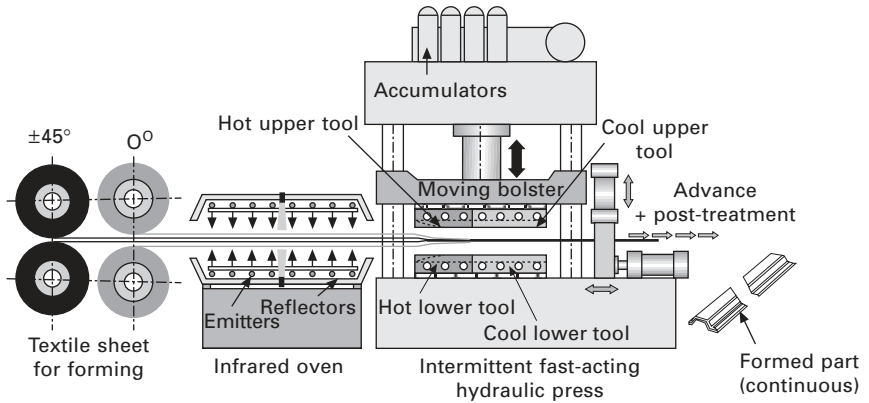
Continuous compression moulding

This is a derivative of the stamp-forming process where materials are fed into a preheat oven and then into an intermittent press with a heating and cooling zone⁸⁰. The process is normally automated. The material is pulled through the tool when the press is open and feed stops as the section of material in the tool is compressed. The tool then opens again and the material is advanced, by a step size smaller than the part size. Shaped flat sections, ‘U’ sections, ‘I’ sections and ‘II’ sections can be produced together with closed hollow sections. Shapes with a constant radius (in one degree of freedom only) can also be formed. The lay-up of the composite sheet used to feed the process can be varied, such that UD fibres can be located on the flange area, and $\pm 45^\circ$ fibres on the wall areas of an ‘I’ beam. Pressures of 25 bar are typically applied, and feed rates of 30–80 m/h are common. Part thickness of 5 mm is possible and 30 mm thick sandwich structures can be made. The process is shown schematically in [Fig. 6.19](#).

6.5 Novel thermoplastic composite manufacturing routes

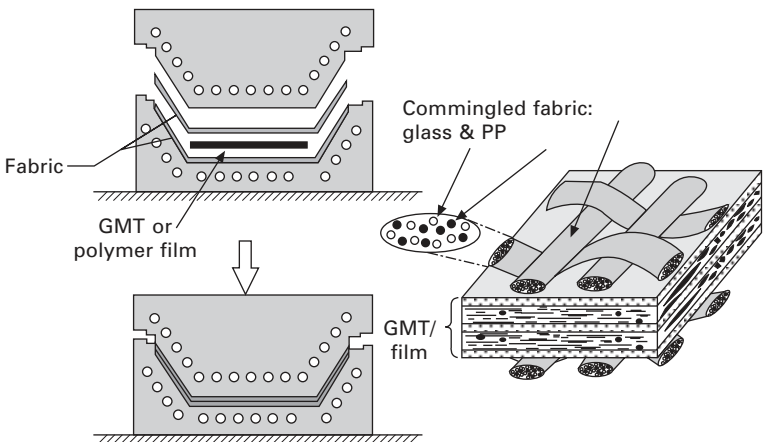
6.5.1 Co-compression moulding of textile preforms with a flowable core

In addition to adding thickness changes and functional parts (ribs and bosses) to a structural item, the compression moulding of fabrics is often made easier by incorporating compliant polymer film or GMT interleaves between



6.19 Continuous compression moulding for the stamping-forming of textile composites.

layers of fabric to overcome problems of thickness variations and areas of poor consolidation (Fig. 6.20)^{13,14}. While the flow-moulding core can reduce the overall V_f , it has a minimal effect on flexural stiffness. The polymer or fibre suspension flows in an open channel at the inter-ply region (insulated from the relatively cold tool by the outer plies), yielding pseudo-hydrostatic consolidation. This has been demonstrated¹⁴ for an automotive door module, producing a fourfold increase in modulus over monolithic GMT, with no cycle time penalty. An example of a material commercially available from Bond Laminates^{27,28} is 'flow-core' and Quadrant GMTex® where commingled fabric skins have been combined in a double belt press with a GMT core, which are now in series production for automotive applications. Another

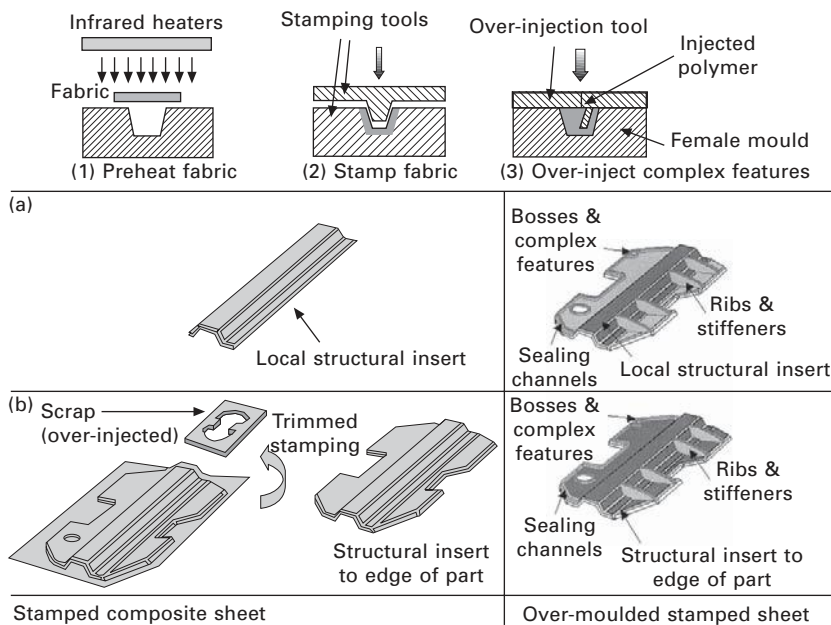


6.20 Co-compression moulding of textile composites with a compliant core.

solution is the extrusion of long fibre thermoplastics (LFTs) between commingled fabric skins prior to compression moulding⁸¹. This co-compression moulding technique gives a solution for applications that do not need textile reinforcement to the edge of the component, where the area of aligned fibre materials is smaller than the tool, eliminating waste and the need for blankholders during preheat and transfer stages. This has also been applied to more conventional sandwich structures using either polymeric foam or honeycomb cores⁸¹.

6.5.2 Over-injection moulding of stamped preforms

A hybrid moulding process, developed by EPFL-LTC^{83–85}, that enables composite stampings to be over-injection moulded (by direct recycling of waste prepreg material) is shown in Fig. 6.21. The combination of sheet stamping with over-injection moulding facilitates the combination of the intrinsic stiffness of sheet forming with the ability to include a high degree of integrated functionality via the over-injected polymer. The key issue behind the process is to achieve interfacial healing between the hot, over-moulded polymer and the warm textile composite stamping, with the requirement that the average temperature of the two is above the polymer T_m ^{86–88}. In practice, a standard injection moulding tool and melt temperatures (e.g. 50 °C and 240



6.21 Over-injection moulding of stamped textile composites: (a) rectilinear stamped sheet and (b) net-shape stamped sheet.

°C respectively for PP) can be used where the stamped insert is preheated off-line to a temperature below the polymer T_m (e.g. 150 °C for PP). This maintains the rigidity of the insert during transfer into the over-moulding tool and also gives the thermal requirements needed for *in-situ* fusion bonding. Ejector pins can be used to hold the sheet in position while the injection moulding tool fills. The pins are removed when the tool is full but before packing pressure is applied.

Figure 6.21(a) illustrates a route where the area of stamped sheet would be inside the edges of the part. Preconsolidated sheet would be heated and then hot draped to the tool geometry using a low-cost shaping tool. The preform would be reheated and then placed locally in the mould where it is needed. Hence a separate stamp-forming stage would not be used, reducing tool and press costs. The tool is then closed ready for the injection moulding cycle. Final consolidation of the sheet occurs from the over-moulding process. Thus the need for an external blank-holder is eliminated and rectilinear fabric sections can be used in the part. A limitation here is that sheet would not span the whole component, notably at non-linear edge regions. This approach has been used commercially for GF/PP material by PlasticOmnium to produce a rear bumper for General Motors.

Figure 6.21(b) shows a generic component where the stamped part covers the entire hybrid component surface. Here the textile composite is stamp formed in the standard manner. The stamping scrap, typically 30% of the part, is then ground and compounded with virgin polymer to adjust the fibre volume fraction for over-injection moulding. The net-shape textile structure is then placed into the over-moulding tool and ribs, bosses and other complex features are over-moulded.

6.6 Conclusions

This chapter has presented an overview of the interacting material/process/property relationship for thermoplastic textile composites for a variety of conversion techniques. A wide choice of raw material forms and final processing techniques suited to a diverse range of applications is commercially available. Hence textile thermoplastic composites have evolved considerably from the first generation of material forms with the slow and expensive techniques developed for the aerospace industry to a state where automotive production volumes can be considered or large marine structures be processed.

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