University of the West of England
BRISTOL

Composite Materials – Topic 4: Pre-pregs and Pre-pregging

Contents

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1 Introduction

We have used the abbreviated terms which are used in common parlance for the title of this topic; if we were being absolutely correct we would call it pre-pregnates or pre-impregnated materials and the processes associated with pre-impregnation. One of the most significant steps in the evolution of the composites industry was the development of the pre-impregnation of materials, because it permitted the manufacture of higher volume fraction (Vf) components and allowed manufacture to take place in a cleaner environment with improved control of fibre volume fraction and void content. We propose to cover:

- terminology
- what are pre-pregs
- the materials associated with pre-pregs
- the pre-pregging process
- the advantages and disadvantages of using pre-pregs
- the composite manufacturing processes that use pre-pregs
- handling and storage
- associated test methods

1.1 Learning Objectives

At the end of this topic, you should be able to:

- explain the key terminology and its significance
- describe the pre-preg processes and assess their possible impact on the composite manufacturing stage
- differentiate between the technical and commercial benefits of using pre-pregs
- demonstrate a thorough understanding of the principal handling and storage condition for pre-pregs
- differentiate between the physical descriptions of the material, e.g. the interrelationship between fibre volume fraction, fibre weight fraction and areal weight
- explain and evaluate the importance of quality control with pre-preg materials

2 Terminology

Table 1 highlights the terminology commonly associated with this subject.

Table 1: Terminology associated with pre-pregs and pre-pregging

Term	Description
Pre-preg	The combination of reinforcement and resin (matrix) in a defined ratio, which can then be cured by the application of heat and pressure. Depending upon the resin system it can be stored under refrigerated conditions (−18°C) for 3–12 months.
Pre-pregging	The process by which pre-preg is made.
Run sheet	Found with each roll of pre-preg, detailing any faults and where they occur on the roll.
Resin weight	Generally abbreviated to RW% and used to express the amount of resin by weight in a material, especially a pre-preg. It is a most important property and is closely associated with areal weight, excess resin and resin flow. $RW\% = \frac{Weight\ of\ resin\ in\ a\ known\ area\ of\ pre-preg}{Weight\ of\ pre-preg\ of\ that\ same\ area} \times 100$
Faults	Defects detailed on the run sheet, which may relate to defects in the woven fabric, unimpregnated areas (dry patches), weave distortion, splits in UD pre-preg and other deviations from the specification.
Knife over roller	A pre-pregging process, sometimes called hot melt; it refers to the metering system used where a very accurately positioned blade controls the thickness of the resin film being cast. The thickness of the film, i.e. the amount of resin per unit area, in turn controls the RW% in the finished pre-preg.
Hot melt	See knife over roller.
Solvent process	A process for making pre-preg where the resin system is diluted in a solvent to aid impregnation and eliminate the need for heat to ensure the wet out of the filaments. After impregnation the solvent is removed in a heated tower.
Resin film	A thin film of resin cast onto a backer which is frequently a release paper. It also refers to a method for the manufacture of pre-preg where resin film(s) are cast and

	then the reinforcement is sandwiched between either two films or one film and a second release paper. This assemblage is then passed through a series of heated rollers to complete the impregnation. In addition it can refer to a form of adhesive where the adhesive is cast onto a release paper and is available as a thin film of various areal weights.
Fibre distortion	Can occur with all forms of reinforcement and refers to fibre not aligned in the appropriate direction. It can easily occur when pre-pregging satin weave fabrics unless great care is exercised.
UD	A reinforcement or pre-preg where the majority, generally 90–100%, of the fibres are aligned along the length of the material.
Tack	The ability of a pre-preg at room temperature to adhere to a mould tool surface; it is critical when applying the first ply on nearly vertical surfaces. Pre-pregs with excessive tack also pose severe problems to laminators in that the removal of the 'backers' (release paper or film) becomes problematical and leads to fibre distortion. Tack is very temperature sensitive, therefore it is vital that in any discussions relating to quality and the defining of tack, do define the temperature of any measurements. Tack is also affected by resin system type and quantity. The reinforcement can also influence tack.
Resin pools	Sometimes when the resin distribution is not even (the knife has to be lifted (knife over roller) to clear the gap where the resin film is forming or joins on the resin film are made), too much accumulates and forms a pool. This should be flagged as a fault.
Flag/Flagged	A method of indicating a fault on a roll of pre-preg. As the pre-preg is being made and a fault occurs, a marker (flag) is inserted at the edge of the roll and recorded on the 'run sheet'. It is a method of easily indicating the position of a fault.
Tracers	These are warp and/or weft threads, conspicuous by their colour, which are simultaneously interlaced into the fabric as it is being woven. Often red or green are used in a glass fabric, red or yellow in a carbon fabric i.e. a sharp contrast. They are there to assist lay-up in that they provide a clear indication of the fibre orientation and will clearly show fabric distortion.
Release paper	A paper treated with a material to impart low adhesion characteristics. Typical coatings are cured silicones or polythene. Used as the backing for a pre-preg or adhesive film. See Backer/Backing.

Backer	A generic term for release paper or release film.
Mouse	Slang term for a disposable temperature logger. Frequently used to monitor the thermal history of a pre-preg shipment.
Out life	The time that a resin, resin system, pre-preg, adhesive, hardener, catalyst etc. can remain at RT (room temperature 18–25°C) and still be processed to give optimum performance. Particularly relevant to pre-pregs.
Shelf life	The storage time at the manufacturer's recommended storage temperature for a resin, resin system, pre-preg, adhesive, hardener, catalyst etc. during which the material can be used and will deliver optimum properties, provided that the material in question has always been kept at the recommended storage conditions. See out life.
Areal weight	The weight per unit area, used throughout the industry to describe the 'weight' or 'surface density' of a fabric, UD or other reinforcement.
Pre-preg weight	The areal weight of the pre-preg i.e. the weight of reinforcement and resin system. **Note:** when some people refer to a 200, 280, 650 g pre-preg, that is **not** the pre-preg weight; it is the **weight of reinforcement**. When people are discussing areal weights and you are not sure whether they mean pre-preg or reinforcement weight, **ask!**
Resin weight	See RW%.
CofC	Frequently referred to as Certificate of Conformity or 'Cert(s)'. Do not confuse with a test report. All that a CofC states is that the product conforms to what was ordered and has been made by a documented and reproducible process. See **Glossary** (link at the top left of this page).
Interleaving	The paper or film placed on the upper surface of pre-preg to prevent adhesion to the next layer. Generally single sided (see single sided) and not required if a double sided backer is used.
'A' Stage	Not frequently used, generally associated with phenolics and refers to the early polymerisation stage of resin manufacture where little cross linking has occurred and the viscosity is still low; the resin will reticulate on a piece of sheet glass or release paper.
'B' Stage	A very important stage and can be described as an intermediate stage in the

	polymerisation process. Some cross linking has occurred, the viscosity has increased and the resin exhibits lateral tenacity in a UD pre-preg and will form a resin film without reticulation.
'C' stage	The final stage where the resin has become insoluble in most solvents and cure is almost complete.
Advance	A term used to describe the progression of a resin system through the 'B' stage process; if it advances too much then the resin will be difficult to mould i.e. require unacceptable levels of pressure to achieve the moulded thickness required.
Reticulate	Used to describe a resin when it is spread over a sheet of release paper and as a result of surface tension it forms into droplets and will not form a continuous film.
Resin system	Used to describe the resin (matrix) once the hardener/catalyst has been added.
Flow check	A test method where an agreed number of pre-preg plies of an agreed area are laid up moulded in a controlled manner (fixed bleeders and cure cycle). When cured the resin that has exuded from the edges of the stack is broken off and weighed and expressed as a % of the total cured weight of the stack. It can be used as a test to determine residual out life/shelf life of a pre-preg. The more the resin system has polymerised owing to ageing, the less the resin will flow.
Film thickness	The thickness of a resin film expressed in mm or mils (US).
Latent hardener	Many hardeners/catalysts will bring about polymerisation at room temperature. However, for pre-pregs we need the hardening (cure) of the resin system to be delayed until we wish to initiate it. The initiation can be accomplished by the application of heat, pressure, UV, electron beam or other processes.
Telescoping	When a roll of pre-preg is stored on end there is a propensity for the coils of pre-preg to start to slip down the roll, especially if it has been wound loosely. This always occurs after the roll has been started, because the winding tension has been released. The result is damage to the pre-preg.
Embossed film	A type of release film used on pre-pregs, especially those with a high degree of tack, the concept being that the embossing reduces the area of contact of the film with the pre-preg, making it easier to remove.

Pre-form	A series of plies of pre-preg that have been laid up out of the tool and are ready to load into the tool when it is ready (see **Glossary**: Horse (link at the top left of this page)).
Web	Nothing to do with the Internet! This is a term for any material, whether from a creel or roll, reinforcement, paper or film, that is fed into a machine for processing, such as the feeding of a woven glass fabric into a pre-pregging machine (the glass fabric is referred to as the web). Similarly, a collection of tows from a creel rack fed into a pre-pregging machine (the assemblage of tows would be called the web).
Ramp rate	The rate at which the temperature is changed during a cure or post cure, either up or down, and generally measured in degrees per minute (°/min) or degrees per hour (°/hr).
Fibre Volume Fraction (Vf)	An expression of the amount of reinforcement in the composite material by volume. Volume of reinforcement/volume of composite expressed as a percentage. Advanced composites always uses Vf and not Wf. Vf is one of the key criteria in the performance of a composite; UTS and Et are directly proportional to Vf.
Moulded thickness	Is used to describe the thickness to which a fabric can be squashed down and can be a useful guide when selecting fabrics. However, unless that thickness is qualified by a fibre volume it has little meaning. It is also linked to pre-pregs and defines the thickness that a ply of pre-preg will consolidate to at a given fibre volume.
Excess resin	Sometimes written XS resin. This is the amount of resin in a pre-preg which will be exuded from the moulding to give a composite of the correct fibre volume (Vf).
Void content	Generally expressed as a percentage and refers to the amount of voids in a laminate and can be determined by qualitative analysis and calculation. Void content will influence mechanical properties, especially inter laminar shear and fatigue.
Viscosity	A measure of how easily a liquid will flow. A liquid with a viscosity similar to water (water like viscosity) has an **extremely low** viscosity; one with a viscosity like tomato ketchup could be described as having a l**ow viscosity**; one resembling toothpaste as **medium viscosity**; and golden syrup (in a tin) as having a **high viscosity**. Please note viscosity can be measured accurately by a variety of techniques and is highly temperature dependent. How resin flows and behaves is called the rheology of the resin.
Zero bleed	A term used to describe a pre-preg where the amount of resin RW% is sufficient so

	that when the pre-preg is consolidated to the prescribed moulded thickness at a given fibre volume, no resin will be exuded (squeezed out) i.e. the pre-preg has no excess (XS) resin.

Each of these topics has a **glossary** linked to it. This is accessed from the menu link on the top left of each page.

3 What are Pre-pregs

Pre-pregs are the combination of reinforcement and resin (matrix) which is generally undertaken as a distinct process prior to manufacture of the component. We make this distinction because when resin and reinforcement are combined (wet lay-up), this could be considered as using a pre-preg; **it is not**.

- The combining of the reinforcement and resin is generally undertaken by a specialist company or department of a group, distinct from that which manufactures the components.
- The reinforcement may be continuous, discontinuous, woven or assembled. The resin system can be thermoset or thermoplastic. In the case of the thermosets, the pre-pregs have shelf lives of many months and those using thermoplastics have an almost indefinite shelf life. There are a couple of exceptions, and that applies to tooling systems in the pre-preg form; they often have short shelf lives, frequently a few months. Some tooling systems called pre-comps (short for pre-compounded) have shelf lives of weeks and out lives of days.
- As a general rule, the lower the temperature at which the resin system can be cured (the more reactive the resin system), then the shorter the shelf life. Many pre-preg tooling systems will cure at 55–60°C.
- Having combined the reinforcement with the matrix, the resultant combination is generally tacky and, to prevent the adjacent layers adhering to each other, inter-leavings or release films are used to separate the layers. To provide support to the pre-preg, especially UD (unidirectional), they are supplied on either a single-sided or double-sided release paper.

3.1 The Principle of Making a Pre-preg (Pre-pregging)

The principle of pre-pregging is simply to impregnate the reinforcement with a resin system, in the case of thermosets, and with a resin, in the case of thermoplastics (thermoplastics do not require hardeners or catalysts). To achieve this the resin system or resin has to infiltrate the filaments of the reinforcement to ensure that each of the filaments has a coating of resin. We have previously encountered fibre/fibre contact as a problem i.e. when there is an absence of resin (matrix) around adjacent fibres, thus preventing adhesion between them which precludes load transfer from fibre to fibre. In order that infiltration by the resin system can occur, then the rein must be of low viscosity (thin).

We can reduce viscosity in four ways:

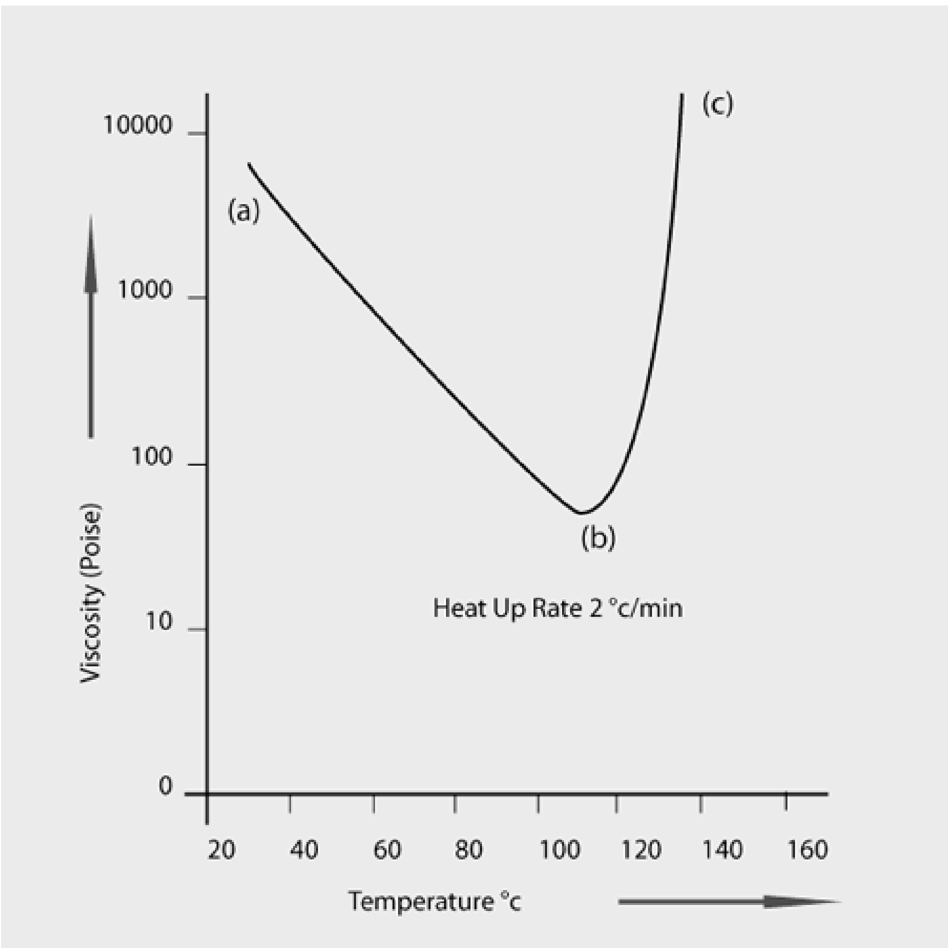
i. Start with a low viscosity resin and hardener.
ii. Heat up the resin system.
iii. Add a diluent (reactive or non-reactive).
iv. Dilute the resin system in a solvent.

3.2 Reducing Resin System Viscosity

Starting with a low viscosity resin system would appear to be an obvious solution. However, many of the hardener/catalysts are solids and to achieve the full spectrum of properties that we seek from a resin would be most unlikely to be achieved from just liquid resins. In addition when we come to mould the pre-preg we do not want all the resin to run out. Generally the resin element of the resin system is a compromise and is a blend of resins; this is particularly the case with epoxies. In seeking a low viscosity system for optimum impregnation we then complicate the problem by toughening the resin system (to improve the damage tolerance of the finished composite). Toughening is generally achieved by the addition of thermoplastics or rubber type compounds; such materials inevitably increase the viscosity.

Heating up the resin system appears an easy option to reduce the viscosity. However, because it is a resin system i.e. the hardener/catalyst have been added, then the heating process will start to bring about cure. As the cure starts so the viscosity will start to increase defeating the objective and also posing the risk of an exotherm.

Figure 1: A graph of viscosity v temperature



The addition of diluents may also appear as an obvious approach to viscosity reduction. However, reactive diluents are preferable as they cross link with the resin and hardener and become chemically bonded into the cured system, but they always remain a source of weakness when subjected to chemical/environmental attack. Non-reactive diluents tend to leach out from the resultant composite moulding, not only leaving it prone to environmental or chemical attack, but also bringing about embrittlement.

Dilution (lowering the viscosity) of the resin system with a solvent, followed by the impregnation of the reinforcement and then finally removal of the solvent, was one of the earliest methods of pre-preg manufacture and is still in use to-day; it has a several disadvantages:

i. Unless the solvent is reclaimed, this is a significant cost. Also, current regulations limit the discharge of Volatile Organic Compounds (VOCs) and solvents fall into this category.
ii. Inevitably there will be some residual solvent left in the pre-preg which can lead to the formation of voids during moulding.
iii. The removal of solvent is carried out up a vertical oven called a tower (see Figure 7), which can lead to fibre distortion in the pre-preg unless care is exercised.

On the positive side solvent impregnation:

- is quick
- is less capital intensive than film impregnation
- allows low areal weight fabrics requiring low resin weight contents to be more easily achieved than the hot melt or rein film processes
- allows the impregnation of very high viscosity or solid resin systems such as some of the phenolics

4 The Fibre Resin Ratio

The fibre resin ratio is one of the fundamentals of pre-pregs. Instead of applying resin to dry reinforcement, as in a hand lay-up operation, and being dependent upon the laminators to control the ratio of fibre to resin, the concept of the pre-preg manufacturing approach is to have this critical aspect already done by the pre-preg manufacturer. Therefore, as a composite designer/engineer, you need to be able to specify the pre-preg both in terms of fibre and resin type and also their ratio.

We have two fibre/resin ratios, one in the pre-preg and one in the moulded composite (which is our end product) and they are both defined in different ways.

In the pre-preg we talk of RW% i.e. a % by weight

In the moulded composite we talk of Vf (Fibre Volume Fraction) i.e. a % by volume

Fibre Volume Fraction (Vf) is defined as:

Advanced composites always uses Vf (fibre volume fraction) and not Wf (fibre weight fraction). Vf is one of the key criteria in the performance of a composite; UTS (ultimate tensile strength) and Et (tensile modulus) are directly proportional to Vf.

Resin Weight Content (RW%) is defined as:

This is generally abbreviated to RW% or Wr and is used to express the amount of resin by weight in a material, especially a pre-preg. It is a most important property and is closely associated with areal weight, excess resin and resin flow.

$$RW\% = \frac{Weight\ of\ resin\ in\ a\ known\ area\ of\ pre-preg}{Weight\ of\ pre-preg\ of\ that\ same\ area} \times 100$$

As the expressions above are expressed in different units (weight fraction and volume fraction) they cannot be mathematically manipulated (such as added or subtracted) so we need to convert them into a common format such as both being expressed as a weight percent. The determination of Vf is achieved by firstly determining the weight fraction of fibre (Wf) so if we revert to that statement or convert fibre volume fraction (Vf) back to fibre weight fraction (Wf), we'll be able to manipulate the two expressions.

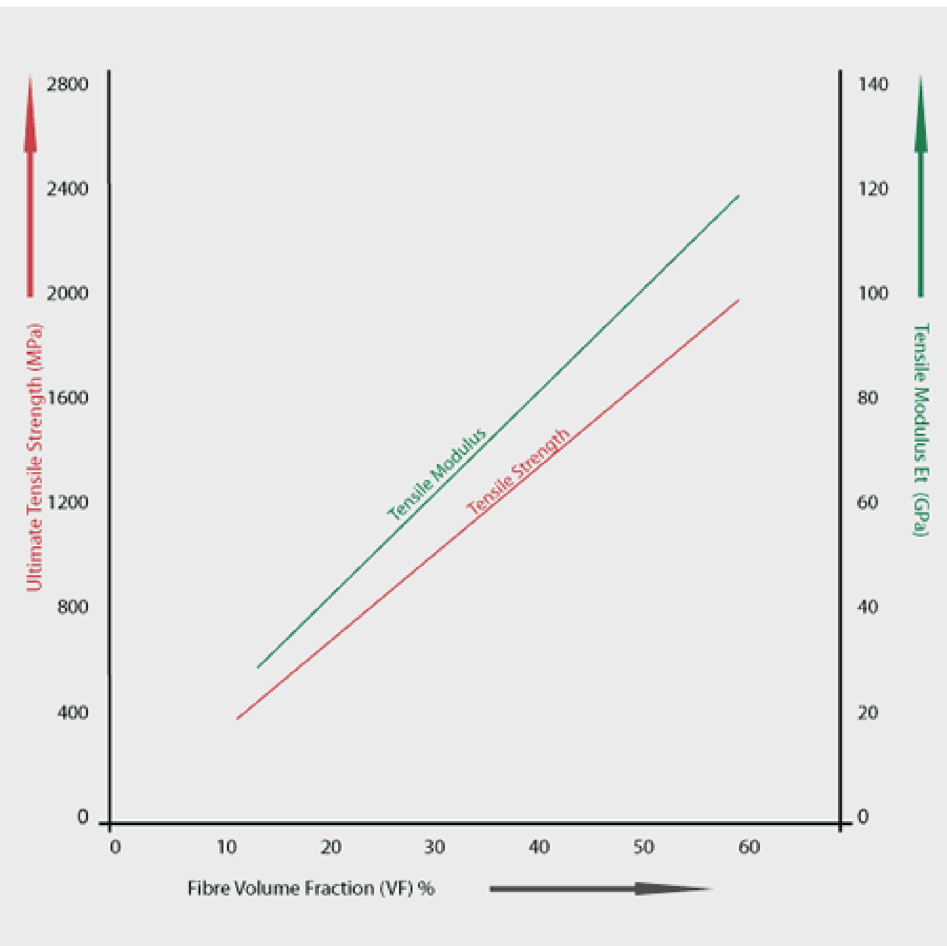
We can convert between the fibre weight fraction (Wf) and the fibre volume fraction (Vf) using the equations below:

$$V_f = \frac{W_f / \rho_f}{W_f / \rho_f + W_m / \rho_m}$$

$$W_f = \frac{V_f \times \rho_f}{V_f \times \rho_f + V_m \times \rho_m}$$

The importance of Vf is that it controls the strength (UTS) and the stiffness (Et) of the composite (see Figure 2 below): the more fibre there is in the composite, the stronger and/or stiffer it becomes, up to when we get fibre/fibre contact and the load transferring characteristics of the composite are lost. This is believed to occur at about 66%–68%, therefore most advanced composite structures are designed around a Vf of 55–60% i.e. to maximise the structural properties that the reinforcement can give for the minimum weight.

Figure 2: Graph of UTS and Et for a UD T300 type carbon 120°C core epoxy v fibre volume fraction (Vf)



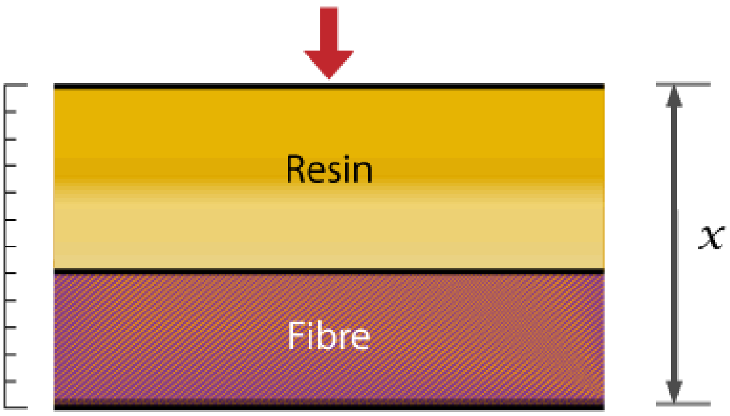
This gives rise to the term 'moulded thickness' which is used to define the thickness to which a pre-preg can be consolidated at a given fibre volume.

4.1 Moulded Thickness and its Relationship to Areal Weight

The moulded thickness is the thickness to which a ply of pre-preg will consolidate at a given fibre volume fraction (Vf). If we consider a hypothetical pre-preg (see Figure 3 (i)), imagine looking onto the end of one ply of pre-preg (it has been represented here as a UD, but this reasoning applies to all reinforcements). The pre-preg has quite a lot of resin in it and this is shown as 70 units (the term unit has been used purely for the purpose of explanation) and a quantity of fibre 50 units.

Figure 3: Schematic of a pre-preg

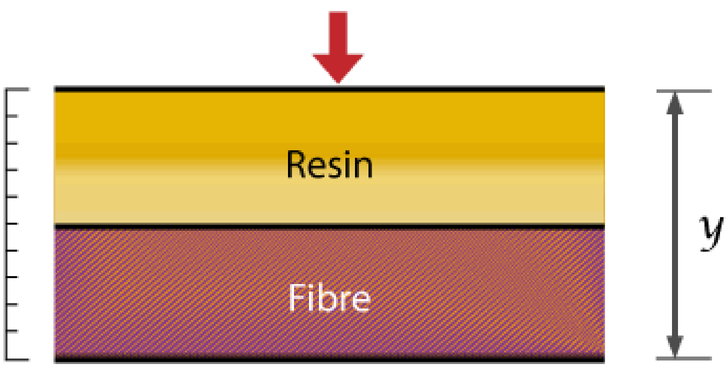
(i)



70 Units of resin

50 Units of fibre

(ii)

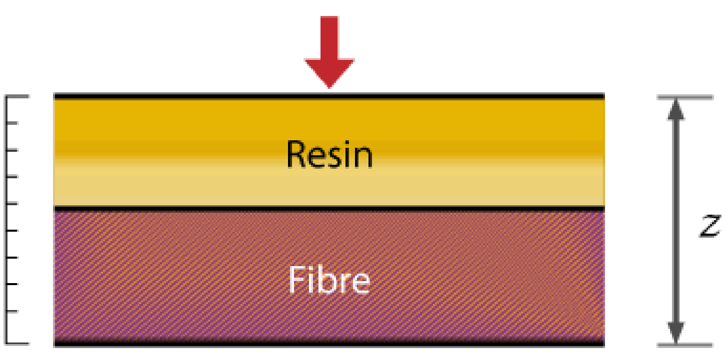


50 Units of resin

50 Units of fibre

$$\frac{50\ units\ of\ fibre}{50\ units\ of\ fibre + 50\ units\ of\ resin}\ x\ 100 = 50\%$$

(iii)



40 Units of resin

50 Units of fibre

$$\frac{50\ units\ of\ fibre}{40\ units\ of\ fibre + 50\ units\ of\ resin}\ x\ 100 = 55.6\%$$

If the pre-preg extends into the screen in all three (i), (ii) and (iii) diagrams for the same distance i.e. they are of the same length, then the only change in volume is brought about by the reduction in the cross sectional area.

And, assuming no fibre is lost when pressure is applied in the direction of the arrow, but resin is allowed to flow from the moulding to condition (ii).

Now if we were to stop the application of pressure and the resin stopped flowing and cured then we would have 50 units of both resin and fibre and, because all our diagrams have the same length, we have 50% Vf.

Imagine we could 'uncure' that resin and continue the pressurisation and consolidate it further to (iii), we now have a new volume which is described as 40 units of resin (more flowed out) and 50 units of fibre (none was squeezed out), giving a fibre volume fraction of 55.6% [50/(50+40)].

We have established a clear link between the Vf and the moulded thickness and, depending upon the amount of resin that we have in a pre-preg, we can change the moulded thickness to increase the Vf. **As noted earlier**, best practice suggests we want between 55 and 60% Vf.

There is also a link between the areal weight, the moulded thickness and the fibre volume fraction (Vf).

If we consider a sheet of pre-preg similar to the schematic Figure 3 (ii), but now we define the length and breadth as 100 cm × 100 cm and the thickness not as units but as 0.25 mm.

Then the volume of this sheet is 100 × 100 × 0.025 cm^3.

Note we have converted the thickness of 0.25 mm to 0.025 cm (mm are the standard units for pre-preg thickness in Europe, but we need to keep common units for calculation purposes).

If the fibre occupies 50% by volume and the density of the carbon fibre is 1.76 $g/cm^{3,}$ then the weight of fibre per square metre will be:

100 × 100 × 0.025 × 0.5 × 1.76 = 220 gsm

That completes the loop, so that now we can determine the moulded thickness that a reinforcement of known areal will have at given fibre volume.

The cured ply thickness or moulded thickness can be calculated using the formula below:

$$cpt = \frac{W_{fa}}{\rho_f \times 10 \times V_f(\%)}$$

4.2 Resin Weight Content

We have already defined resin weight content (RW%) and looked at the link between the areal weight of the pre-peg and RW%.

If the fabric weighs 100 g/m^2 and we want a RW% of 30% then the fabric must constitute 70% (100%−30%) of the pre-preg weight.

Therefore, if 100 gm of fabric constitutes 70% of the pre-preg, then the whole pre-preg i.e. 100% will weigh 100/0.7 = 142.9 g (fabric + resin).

We know the weight of the fabric is 100 g. Therefore, the resin weight in that square metre of fabric will be 42.9 g.

We can check this:

$$RW\% = \frac{Weight\ of\ resin\ in\ a\ known\ area\ of\ pre-preg}{Weight\ of\ pre-preg\ of\ that\ same\ area}$$

Therefore, we have 42.9 g of resin in a pre-preg of total weight of 142.9 g.

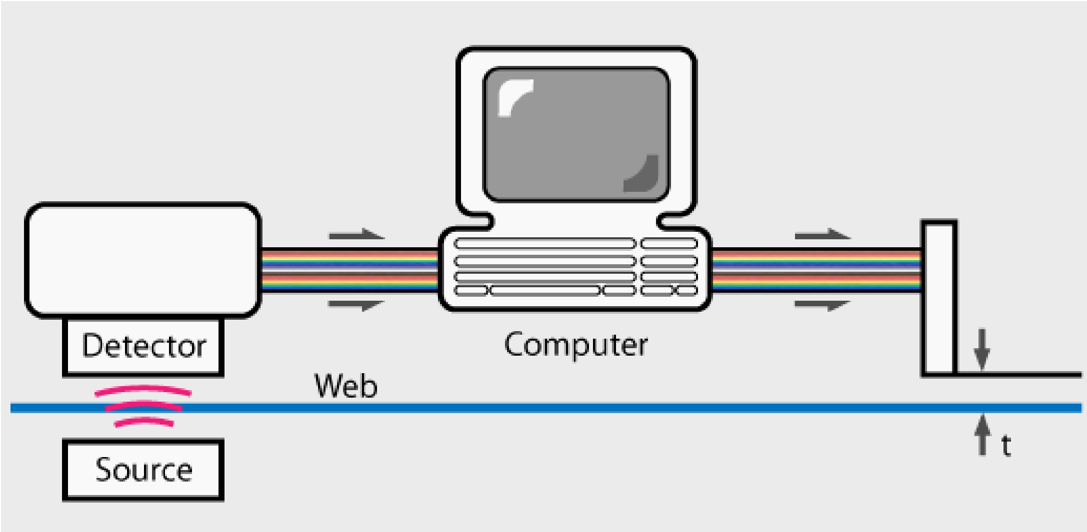
$$RW\% = \frac{42.9}{142.9} = 30\%$$

This is a relatively small amount of resin to be evenly spread over 1 square metre, i.e. we need to create a film 0.0035 mm thick and then impregnate this into the fabric. To create such a film is difficult and to achieve it commercially very difficult, therefore we have two options:

- pre-preg it by solvent impregnation, or
- accept a higher resin content

Film thickness is frequently controlled by a beta gauge (see Figure 4 below) with a closed loop feedback to the mechanism that controls the gap below the knife (knife over roller) or the coating head (resin film). Beta particles are fast moving electrons which are radiated from certain isotopes and this is called the source. Like all radiation, exposure must be limited. This can easily be achieved as the particles are easily screened by some thin plastic sheet. Disposal of the source or replacement must be in an approved manner. Measurement is by detection of the number of beta particles when no web is passing between the source and detector and when there is a web. Using the computer, this can be resolved into a resin film thickness (due allowance being made for the backing paper) and then via the feedback loop the gap (t) in Figure 4 is automatically adjusted.

Figure 4: Schematic of a beta gauge and feedback loop



A more complete description of these processing techniques will be provided later in this topic.

4.3 So Just How Much Resin Do We Want

In the preceding sections we have seen the relationship between moulded thickness and Vf and the relationship between areal weight of reinforcement and RW%, but we also need to understand the relationship between the fibre volume (Vf) and the RW%.

Stop and reflect 1

So how much resin do we want?

Notes 1

Notes 1

It's relatively simple to determine how much resin we want – enough to fill all the remaining spaces around the filaments and over the surface of the composite structure. We can express that more succinctly by assuming our theoretical composite structure has a volume of 100% and if the fibres are to occupy 60%, then 40% of the volume will be resin, assuming we have no voids.

For the moment we'll assume we have no voids, which we've achieved by using best laminating and moulding practice, and we are using an easy to mould epoxy system. So all we need is enough resin to fill the spaces and that is 40% by volume in this example; is that realistic? Yes, it is. During the moulding process we need to remove entrapped air which has come both from the pre-pregging process and the laminating process.

Previously, we discussed the need to resolve the Vf from a volume fraction to a weight fraction and this can be easily achieved knowing the fibre density and the composite density. The former can be readily established from the pre-preg supplier or the fibre manufacturers' data sheets.

We can ascertain a theoretical composite density from the law of mixtures assuming low or no voids:

1 .... $(V_f \times \rho_f) + (V_r \times \rho_r) = \rho_c$

Where:

V_f = fibre volume fraction – 60%
V_r = resin volume fraction
ρ_f = density of the carbon fibre – 1.76 g/cm^3
ρ_r = density of the resin (obtainable from the pre-preg supplier) – 1.21 g/cm^3
ρ_c = density of the resultant composite

If we assume no voids then the volume of the composite is 100% and consisting of only fibre and resin, therefore, $V_r = 100 - V_f = 40\%$

For this example we have assumed some typical properties for fibre and resin densities.

Substituting into equation 1 – $(0.6 \times 1.76) + (0.4 \times 1.21) = \rho_c = 1.54$ g/cm^3

Now to determine Wr (weight fraction of fibre):

$$V_f = W_f \times (\rho_c/\rho_f)$$

Rearranging the equation

$$W_f = V_f \times (\rho_f/\rho_c)$$

Substituting in some of the values from above

$$W_f = 0.6 \times (1.76/1.54) = 0.686 \text{ or } 68.6\%$$

We have assumed no voids or very low voidage, therefore if the composite contains 68.6% by weight of fibre, then the remainder must be resin (Wr resin weight content)

$$W_r = 100 - 68.6\ (V_f) = 31.4\% \text{ resin}$$

So if we have a pre-preg containing 31.4% resin or it has a resin weight RW% of 31.4% then we will have what is called a **zero bleed material**.

Stop and reflect 2

What is zero bleed?

Notes 2

Notes 2

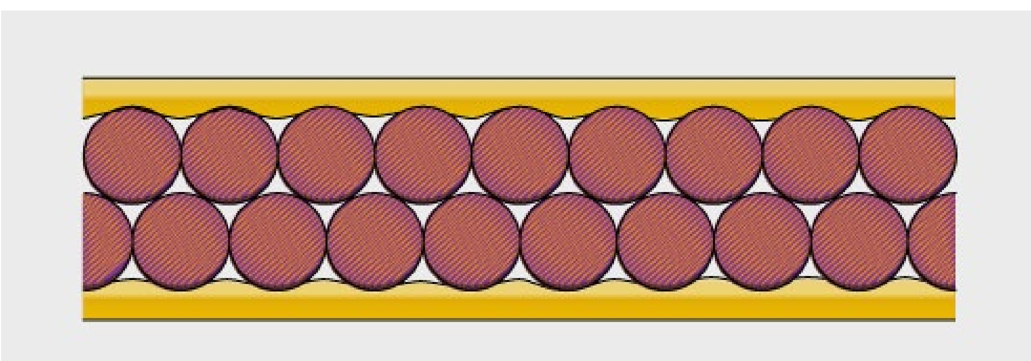
Zero bleed is a pre-preg that, when consolidated to the given moulded thickness and fibre volume, will not exude (squeeze out) any resin.

4.4 Excess (XS) Resin and Entrapped Air

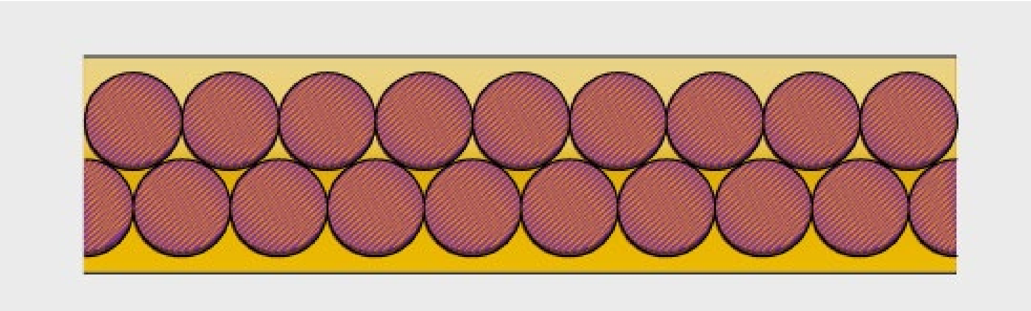
When applying resin, particularly by the resin film or hot melt process, air will be trapped between the fibre and particularly at the intersections of the warp and weft. (See Figure 5(i) and Figure(ii). (i) shows the condition that can arise with heavy weight tows or rovings or if the resin viscosity is too high. (ii) shows the perfect impregnation: all the filaments surrounded by a layer of resin.)

Figure 5: Schematic of a resin film not fully impregnating a fibre tow/roving

(i) Partial impregnation



(ii) Ideal impregnation



Note must be made here that the actual wetting out of the filaments does not have to happen at the pre-preg stage, but we must have the required amount of resin in the pre-preg to achieve fibre 'wet out' during the moulding process.

When we examine a relatively heavyweight pre-preg, say 650 gsm, removing a tow from the pre-preg cutting across the fibre to expose a 'clean end', we will see quite clearly that the resin after impregnation has not penetrated to the innermost filaments. At this stage this is not a problem, but full impregnation must take place during moulding to ensure we have a good composite.

Air will also be entrapped between plies during the lay-up regardless of good laminating practice and the inclusion of de-bulking in the lay-up process.

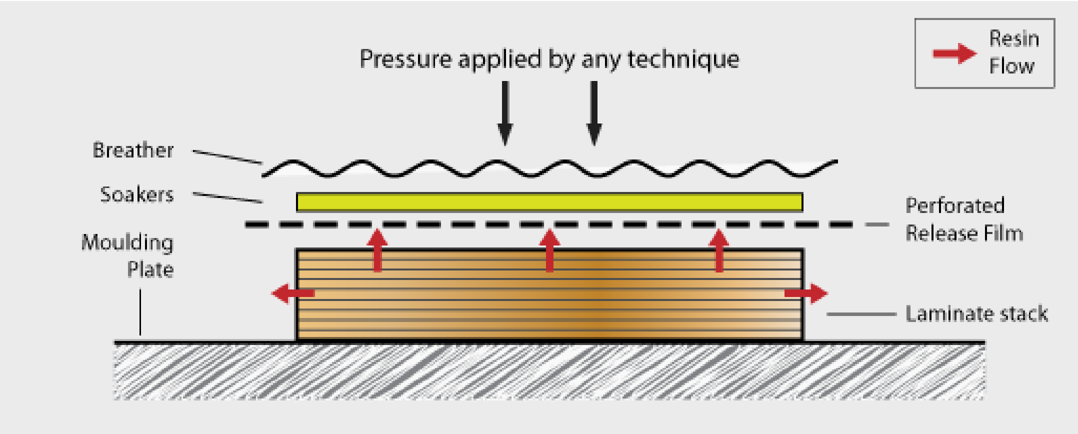
Depending upon the moulding pressures used, autoclave 4–7 bar or vac bag 1 bar, this will affect these small amounts of air (bubbles) entrapped. In the case of the higher pressures they will be squeezed to a very small size, but in the case of the vac bag moulding little change will take place to the size of the bubbles.

This is because, prior to the start of the moulding process i.e. the pre-preg is still at RT, the air inside the bubbles is at the pressure when they were formed during the pre-pregging and laminating processes which were carried out at atmospheric pressure i.e. 1 bar. Therefore using a moulding/consolidating pressure of the same pressure, which is all that can be generated by vac bag, will have very little effect on the size of the bubble. In fact the heating they are subjected to during moulding will increase the bubble size in accordance with the combined gas law.

$$\frac{P1 \; x \; V1}{T1} = \frac{P2 \; x \; V2}{T2}$$

Therefore if we can remove as much of the entrapped air as possible during the moulding process, then we'll have a greater opportunity to have a good moulding. During the moulding process as consolidation of the plies occurs, so resin will be exuded towards the edges of the moulding and through the surface of the moulding if a perforated release film is being used, see Figure 6 below.

Figure 6: Schematic of a laminate stack under pressure showing resin movement [The predominant flow direction is towards the edge.]



Therefore, it is advisable to have a little more resin (excess resin) than we require. However, if we have too much excess resin we can bring about fibre distortion (fibre wash) as it tries to escape or we'll have pools of excess resin over the surface of the moulding and/or it will be oversize (too thick), because we are unable to remove all the excess resin.

The definition of excess resin: Sometimes written XS resin. This is the amount of resin in a pre-preg which will be exuded from the moulding to give a composite of the correct fibre volume (Vf), assuming no voids.

Previously we saw how to determine Wf, thence Wr to give us a quantity of resin in the pre-preg that would give zero bleed.

100-Wf = Wr (the weight of resin required in the composite for zero bleed)

(Resin weight in the pre-preg – Wr) = Excess Resin

Where Wf is the Weight Fraction of Fibre and Wr is the Weight Fraction of Resin

Put another way...

Or cured RW% = initial RW% − Excess Resin

Now that we have resolved the terms for both resin and fibre into a common form either by weight or volume, we can quantify the excess resin. We know we must have Wr in the finished moulding and when we order the pre-preg we request a RW% or are advised what the standard RW% is. If as an example we request a RW% of 35%, then 35 – Wr = the excess resin.

4.5 So What is Considered an Ideal Amount of Excess Resin?

Stop and reflect 3

So, what is considered as ideal amount of excess resin?

Notes 3

Notes 3

What is considered an ideal amount of excess resin is a difficult question to answer and really depends upon the application, the moulding process, the level of cosmetic finish, the resin system in the pre-preg, the weight of reinforcement and the tolerance on the RW% allowed by the pre-preg manufacturer. We shall try and provide some guidelines, but this is where we need to seek guidance from one well versed in the moulding of composite parts.

Remember, these can only be guidelines as there so many variables.

As the areal weight of the fabric increases so the **amount** of resin increases. Resin weight (RW%) is a percentage of the overall pre-preg weight. Therefore, with heavier weight fabrics, it is expedient to reduce the RW%. The converse is true for lighter fabrics.

The industry standard for the tolerance on RW% is ± 3%; try to keep the supplier to that and even try and squeeze him/her to ± 2.5%. Obviously the tolerance becomes more important the heavier the areal weight of the reinforcement.

Let us just make sure we grasp that statement. On a 200 gsm fabric with a RW% of 34% and a tolerance of ± 3%, the quantity of resin in that pre-preg could be between 90–117 g, whereas if we apply that reasoning to a 650 gsm fabric we could have 292–382 g of resin.

Some moulders favour high RW% when they require a good cosmetic finish. Our experience is the quality of the finish is more influenced by the resin system than the quantity of resin; obviously it must not be resin starved.

The influence of the moulding process, i.e. the pressure and when it is applied, will determine the thickness of the finished part if no stops are used. If the pressure is applied too quickly then it can lead to much resin being exuded (lost).

Many resin systems are now considered to be 'controlled flow' i.e. during the heat up part of the cure cycle they do not drop below a certain viscosity. However, some of the bismaleimides and cyanate esters do tend to become very mobile (runny) during the heat up period and frequently a dwell period is recommended; this allows the resin viscosity to increase (it is in effect an *in situ* 'B' staging).

Resin system development has progressed considerably over the last ten years and now resin systems are available with variable cure cycles that can be tailored to the manufacturing process.

Pre-pregs which have a high modulus fibre as the reinforcement have less tack than a similar pre-preg (one of similar areal weight, resin system and RW%) which have a T-300 type or intermediate modulus type reinforcement. Therefore, a slightly higher RW% (+3%) would make lamination easier, especially the first ply. This anomaly is probably attributable to the very different surfaces of the fibre types. The T-300 and intermediate modulus materials are carbons, but HM fibre is graphite.

Remember, one of the functions of the resin (matrix) is to provide protection for the reinforcement, therefore any tendency for the surface of the finished part (moulding) to be resin starved is a serious potential weakness, especially in the long term. Therefore, a useful approach is to have the outer ply slightly more resin rich (higher RW%) than the inner plies, so when the pre-preg is delivered, check the RW% and 'ear mark' the higher RW% for use in the outer plies.

4.6 Resin Weight Distribution

We have discussed the resin weight content (RW%) of the pre-preg, but not considered from where it is sampled and how many samples are taken. As a user of pre-preg, we are looking for an even distribution across the roll and down the length.

Squares of 100 or 150 mm side are cut from the pre-preg at the start and end of the roll, which may be very dependent upon the areal weight of the reinforcement. At first glance this may appear an arbitrary approach, but it is about what can be easily lifted and comply with Health and Safety regulations.

Across the width of the roll is not too difficult, but it is worth asking how many samples were taken. When the resin is applied to the reinforcement it is frequently uniform in distribution, whether hot melt, film or the solvent process is being used. However, when the partially impregnated material is then passed through heated rollers to augment/complete the impregnation then there is a tendency for the resin to migrate towards the edges of the roll. If this is excessive then the overall RW% can be within spec, but large areas of the pre-preg can be 'shy' of resin.

We use the term 'shy' rather than 'dry' to infer that there is resin there, but not enough. When we have dry areas we can generally see loose filaments and can separate filaments from each other from within a tow or roving.

Samples are generally taken at the start and the end of the roll and reported on the run sheet as individual values so you can see whether any changes occurred during pre-pregging. Sampling from the middle of the roll is impractical as it would leave gaps from where the samples were removed. Also the stopping of the machine is not ideal as it can lead to resin rich areas, dry areas and partially cured patches where the pre-preg is in contact with heated consolidation rollers.

We have mentioned the use of beta gauges to control the thickness of the film, but it is still worth asking the supplier to report on his/her consistency along the length of the roll. Even taking an odd sample somewhere between the start or the end is not a bad idea.

4.7 The Final Piece of the Jigsaw – % Voids

We have considered the relationship of Vf to Wf in order to determine the amount of resin to achieve zero bleed. We now to take that a little further to see how these values relate to the percentage voids (one of the fundamental properties of a composite laminate).

We are familiar with the following terms:

Vf = Fibre Volume	ρf = Density of the fibre

Fraction Wf = Fibre Weight Fraction Vr = Resin Volume Fraction Wr = Resin Weight Fraction	ρr = Density of the resin ρc = Density of the composite

And we have used the following expression to determine Wf by rearranging it:

$$Vf = Wf \times \frac{\rho f}{\rho c}$$

For this calculation we can leave it as it is, and having determined Vf we can determine Vr in a similar manner:

100 – Wf = Wr

And

$$Vr = Wr \times \frac{\rho r}{\rho c}$$

Vf + Vr provided there are no voids should = 100% therefore we have the expression:

(1 – (Vf + Vr)) × 100 = % voids

4.8 Specialist Pre-pregs

One of the factors that slowed the uptake of composites was the difficulty in achieving a good finish and the ease of finishing. Composites was, and still remains, in many areas a labour intensive activity and the finishing of a composite part has been yet another area that has involved yet more labour. We use the term 'finishing' to describe:

- the filling of pin holes
- trimming edges
- sanding to improve the surface finish rather than the fitting of inserts, or
- bonding of metallic elements to the structure

Surface pin holing and entrapped air at the edge of the component have been typical problems. The problem was compounded when the industrial designers and marketeers saw the attractiveness of the weave pattern, particularly from carbon and carbon hybrid fabrics, as providing a selling point when operating in the consumer market, therefore it is sometimes necessary to have a virtually blemish free outer surface. This was never more so as composites became one of the favourite materials for the limited edition high performance sports cars.

Three factors seem to influence the surface finish:

i. The wetting of the mould surface.

ii. The viscosity of the resin.
iii. A route out for the air entrapped between the outer ply and the mould tool surface.

Wetting of the mould surface is very much a function of the release agent on the surface of the mould tool and the resin viscosity. If the release on the tool surface is too good, then the resin will not wet the surface evenly. Equally if the resin viscosity becomes too low then little wetting will occur, and if the air entrapped in the reinforcement and between plies cannot make its way to the edge of the moulding, then it will manifest itself as pin holes.

When pre-preg is moulded, the pressure is applied to the bag face and the entrapped air is then pushed through the lay-up towards the tool face and will remain there unless there is a path out of the moulding. One of the great advantages of the infusion techniques is that much of the air is pushed along by the resin front as it advances towards the exit manifold. By good positioning of the inlet and exit ports, much of the air entrapped in the dry reinforcement is removed because it has a pathway out.

In the mid/late 70s when controlled flow resin systems were unknown, some pre-preg moulders began to use low areal weight veils against the tool surface; this provided a pathway for the entrapped air and reduced the splintering at the edges of mouldings which so frequently occurs with cross plied UDs. This was an excellent approach, but when using woven fabrics the weave pattern was lost; such cosmetic detail was of no consequence to the structure, but not well received by the marketeers.

The mid 90s saw the launch of a variety of products designed to overcome the problems described earlier. This was achieved by having the resin of the first ply either as stripes or dots so that no hydraulic seal was created when the first ply was laid against the tool surface i.e. a pathway was left for the entrapped air to move to the edge of the moulding. Much of the drive for this good quality surface finish was coming from the specialist sectors of the automotive industry who were desperate to use composite materials in the body panels, but ended up with uneconomic levels of finishing cost. This rather specialist demand also sought reduced lay-up times in terms of the number of plies that were required for a body panel, and led to the development of pre-preg materials that have trade names such as Rapi-Ply™, 'Z' preg™ and Sprint™. They are all rather similar and consist of several layers of reinforcement, a relatively dry facing ply to provide a pathway for the entrapped air, and only partially impregnated reinforcements behind. The net result was a fairly thick pre-preg which could be laid into a tool, provided the curvature was not too great, and then moulded. The product was a virtually blemish free panel of sufficient thickness, hence stiffness, that could be used as an automotive body panel and accept a paint finish with the minimum of preparation.

For a printout of the equations used, click on Summary of equations.

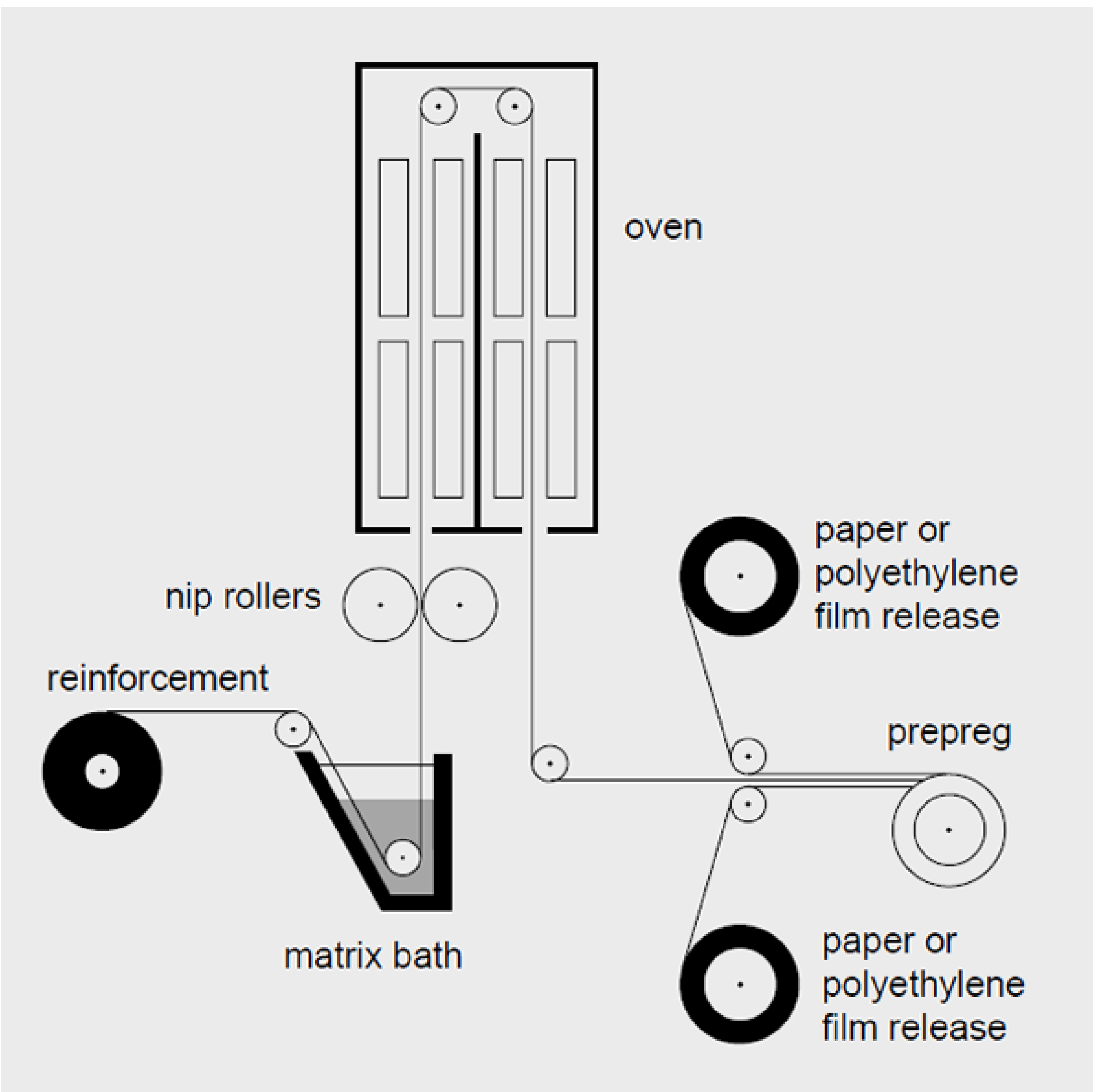
5 The Pre-preg Process or Pre-pregging

There are five fundamental pre-preg processes:

1. **Solvent impregnation – Tower**

   The resin system is diluted in a suitable solvent to reduce the viscosity and the reinforcement is passed through a bath of this solution (see Figure 7*).* It then passes through nip rollers to remove excess resin and then into a vertical oven to drive off the solvent.

   Figure 7: Solvent impregnation - Tower [© Hexcel (2005) *Prepreg Technology*, p.12. Kind permission to use given.]

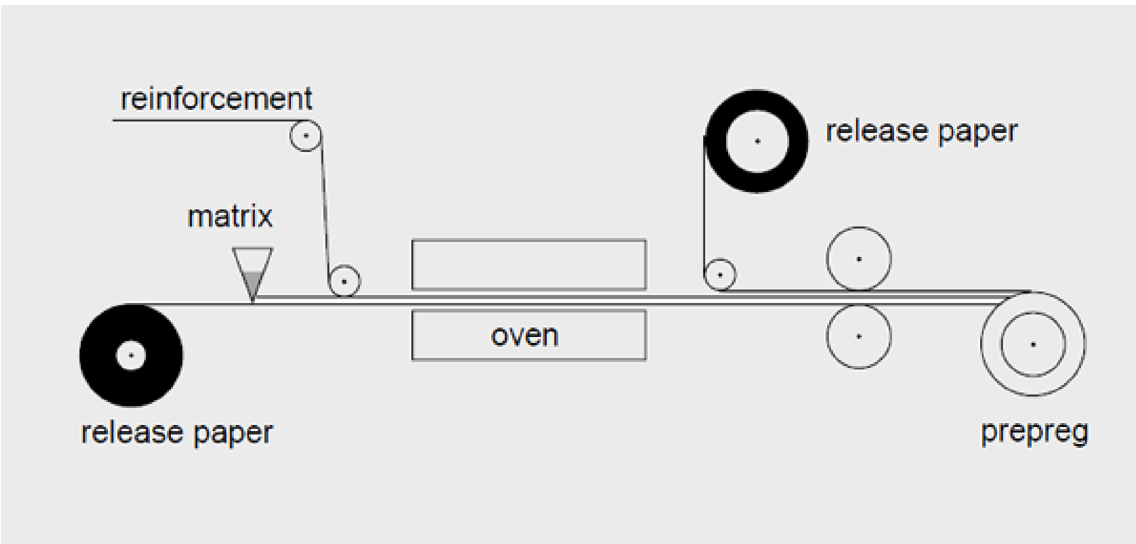


   The oven has a temperature gradient achieved by design and convection so that it is hotter at the top than the bottom. As the pre-preg emerges from the bottom of the oven it will have cooled considerably (is now less tacky) and release papers/films (backers) are applied and the assemblage is collected on a roll where an even and steady tension is ensured.

2. Solvent impregnation – Oven

The resin system is diluted in a suitable solvent to reduce the viscosity as in Figure 7 (above) and this solution is metered onto the web, and passed through a horizontal oven to remove the solvent. Release papers/films are applied, passed through nip rollers and onto the take-up system to create a roll (see Figure 8 below).

Figure 8: Solvent impregnation – Oven [© Hexcel (2005) *Prepreg Technology*, p.12. Kind permission to use given.]

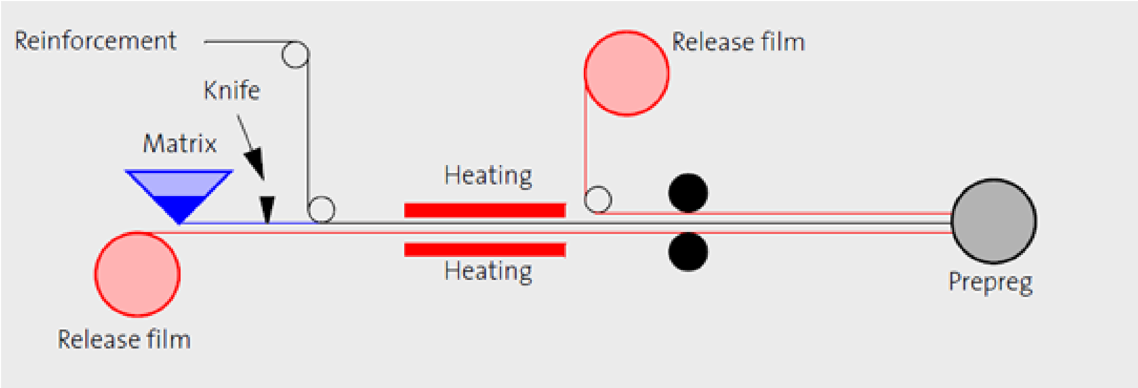


This technique has limitations. To prevent the web sagging it is supported by a release paper underneath, therefore when passing through the oven to remove solvent, only one face of the web is exposed to the hot air. If this method is tried with tows or rovings, a very gappy pre-preg will result as the surface tension effects of the solution will clump the fibres together and restrict them spreading. To close the gaps, total reliance is placed on the nip rollers.

3. Knife over roller impregnation

This is sometimes called 'hot melt', but it can be confusing as 'film impregnation' is a 'hot melt' process (see Figure 9 below).

Figure 9: Knife over roller impregnation [Source: Advanced Composites Group *An Introduction to Advanced Composites and Pre-Preg Technology*, p11. Kind permission to use given.]



The resin system is prepared in a 'B' staged form and charged to a heated reservoir in front of a heated steel blade (the knife). The knife is situated immediately above a large diameter (>300 mm) steel roller over which is passed a release paper of about 120 gsm. A gap is maintained above the paper and below the bottom edge of the heated steel blade.

In the previous paragraph we read of the resin being further heated; even though it is in the 'B' stage condition, it is vital, but must be very carefully controlled. Too much heat and the resin will begin to gel or even worse, exotherm, too little and the viscosity will increase and the resin system will not pass under the blade and form a continuous film on the paper. 'B' staging of the resin system prior to charging of the reservoir is also essential otherwise the film will reticulate.

Once a continuous film has been formed, the reinforcement can be fed onto the web; an upper release paper/film can then be applied and this assemblage is passed through a series of nip rollers to bring about impregnation. This stage is probably the most difficult to control in this process; it almost certainly needs more heat to drop the viscosity to achieve a reasonable degree of impregnation; too much and the resin will advance too much. The significance of this part of the process can be seen in Figure 9 which shows it as a single sided method of impregnation, therefore to achieve complete impregnation is difficult unless using light to medium weight (<400 gsm) reinforcements.

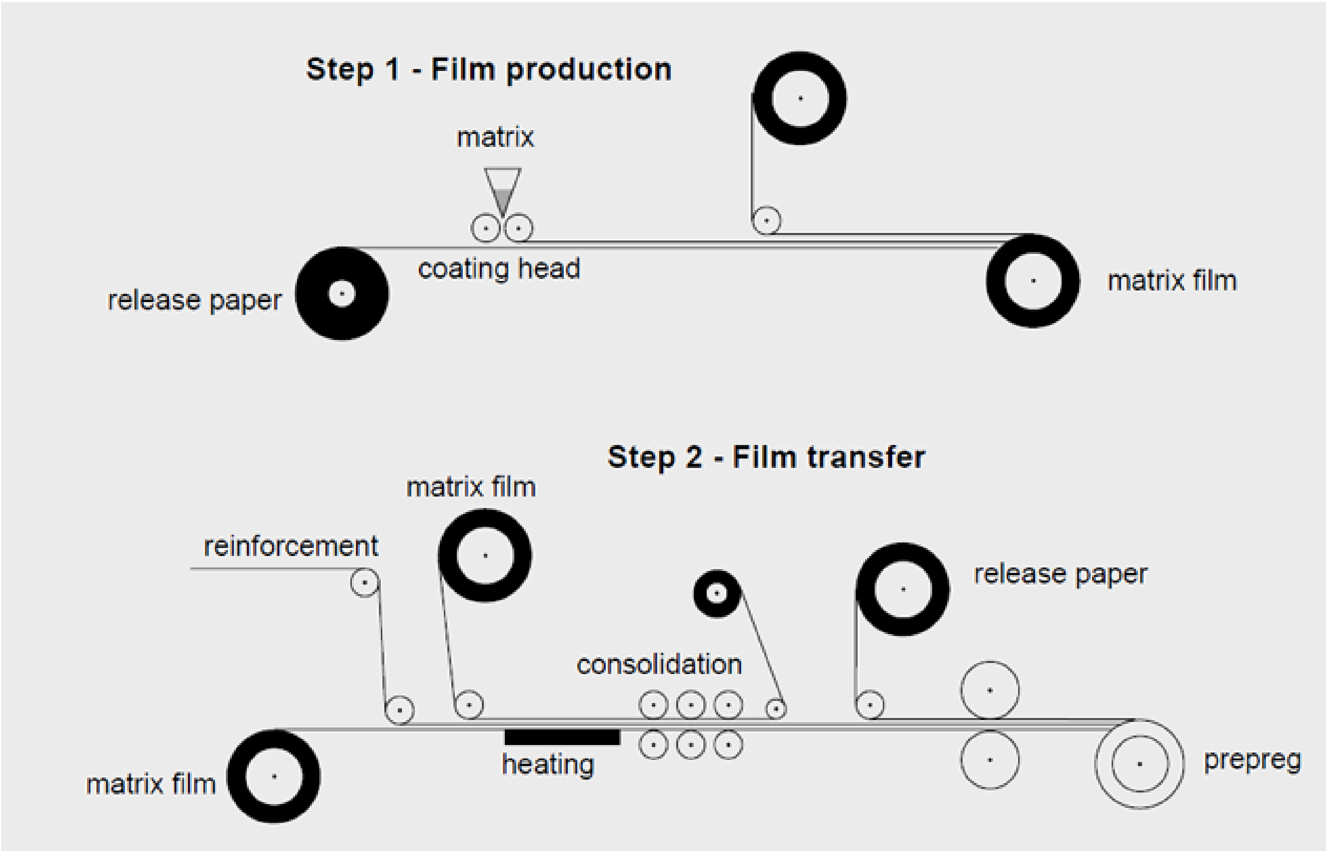
Remember, this is not about temperature, but about the quantity of heat that is imparted to the pre-preg through the nip rollers. The path through the rollers may be an 'S' path to provide greater contact i.e. more heat transfer. The speed of the pre-preg through the rollers will influence the quantity of heat that is able to transfer from the heated rollers. With most of these processes, although the schematic shows a pair of nip rollers, there are generally several all independently temperature controlled and the last set of rollers are frequently chilled.

On reading this we could conclude this is a high risk process, but in the right hands it isn't and it produces excellent pre-preg. It does have limitations when low RW% on lightweight reinforcements are required.

4. Resin film impregnation

This is a two stage process where resin films are prepared and then these are transferred to a pre-preg machine for the pre-pregging process (see Figure 10 below). This is the most capital intensive method, but it has significant advantages in that it offers single or double sided impregnation; generally double is used for the thicker reinforcements. Double sided impregnation is frequently faster than single sided.

Figure 10: Resin film impregnation [© Hexcel (2005) *Prepreg Technology*, p.12. Kind permission to use given.]



Here a resin film is cast onto a release paper, which can be done at fairly high speeds using classical paper coating technology. Film thickness has to be measured by beta gauge or other sensing device and then using this signal it is fed through a closed loop system to control the coating head and maintain the desired areal weight of resin.

Once the film(s) have been manufactured they are transferred to the pre-pregging machine and, using similar arrangements of nip rollers, impregnation of the reinforcement is achieved. This is followed by take-up onto a carefully tensioned and aligned roll.

For all of the processes capable of impregnating broad goods, it is essential that the plant alignment is very accurate, otherwise there will be a marked tendency for the pre-preg to 'run out' (cease to remain in the centre of the rollers) and will lead to rolls of material where the edges of the roll are not inline and RW% distribution falls out of specification.

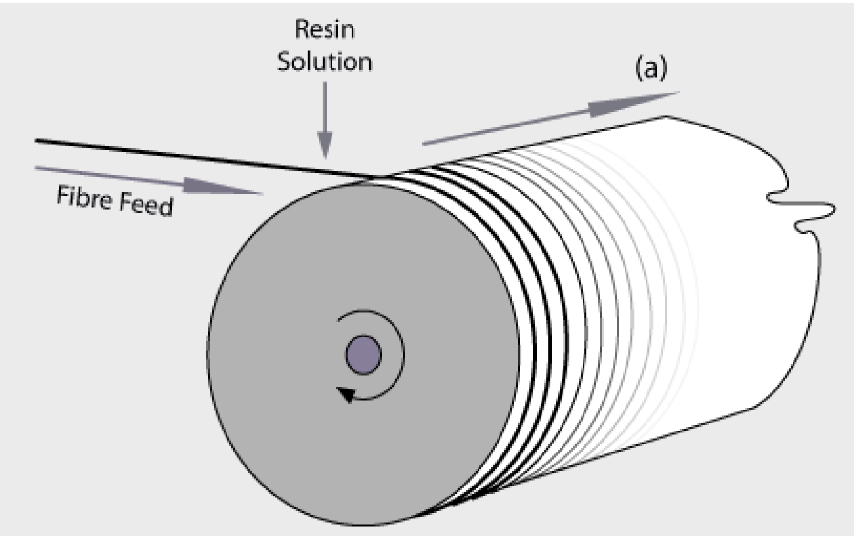
5. Powder Impregnation

This can be achieved by a variety of techniques. The first stage is the metering of a powder onto the tow/roving or narrow tape; this can be achieved by a dropping process or by electrostatic deposition. The powder now needs to be affixed to the tow/roving and this is generally done by passing through or by a heat source such as a very hot oven or IR (infra red) heaters. Sometimes, once past this heat source, the tow/roving or tape are inverted and the process repeated to place resin on the other side.

There are severe limitations for this process as a commercial general purpose pre-pregging process, but it has applications in certain niche markets.

Drum winding must be mentioned, but it is not a distinct method in that it can be used both for film or solvent impregnation. It is a small scale method absolutely ideal for small runs using high value materials (see Figure 11 below).

Figure 11: Drum winding



For a short demonstration of drum winding, see the YouTube clip on drum winding [approximately 4 minutes' duration]. Just click on the play button in the middle of the screen below. [If you want to increase the size of the screen, click on the YouTube button in the right of the video screen below and then use YouTube's buttons to adjust the size of the screen.]

The foregoing technical information is absolutely essential, but we also need to know whether there are any precautions that we should take in the handling of the material and that is contained in the MSDS (Material Safety Data Sheet); this should be supplied not only with the goods, but also under separate cover to the person responsible for such matters.

 This is an example of a typical Material Safety Data Sheet from the Park Electrochemical Corp.

Using a rotating drum with a fibre feed moving in direction (a) and a metered supply of resin solution, movement in (a) is driven by a load screen geared to drum rotation and resin solution delivery. The system can produce very accurate fibre areal weights and RW%.

The impregnation method can be changed and the drum wrapped with a resin film and the fibre wound on by the same geared mechanism, but a warm air jet and consolidation roller replace the solution impregnation system.

Pre-pregging may appear complicated, but it is relatively simple, requiring attention to detail, and personnel who understand the raw materials and are conversant with the reinforcement/resin relationships we have discussed. The area of real innovation is the development of the resin systems that are capable of delivering the performance in the composite that are required, but can be pre-pregged in a commercial manner.

6 Some of the Advantages and Disadvantages of the Various Processes

The use of solvents is not ideal:

i. Retained solvent in the pre-preg.
ii. The cost both in capital (solvent recycling) and the solvent cost.
iii. The cost of compliance to both existing and future environmental legislation.

Initially one might conclude that it is best not to use this process, but it is fast, ideal for lightweight reinforcements and tack free pre-pregs. Being fast it helps to offset the additional cost (solvent reclamation and solvent purchase) and our consumption of tack free pre-preg is staggering, because it is from this type of material that PCBs (printed circuit boards) are made.

In addition, many phenolic resin systems have to be pre-pregged by this route and the concern of retained solvent is irrelevant because the pre-pregs have to have a level of retained solvent to maintain their flexibility. Phenolic pre-pregs find widespread use for interior components in commercial airliners, mass transit systems and underground railway systems.

Contamination of the pre-pregging tower by fibres from previous materials, such as carbon fibres contaminating glass pre-pregs, would be an absolute disaster if the glass is to be used for a radome. Consequently it has to led to dedicated towers for carbon and glass.

The resin film process for large scale operation is ideal. Long runs of resin film can be made (huge economies are possible because it is the set up time that is the costly element of this process). Once the films are made they can be frozen and stored, being taken out as required for pre-pregging. This method has to be on a large scale owing to the diversity of resin systems, the widths of the web and the different areal weights of resin film required.

Resin films are brittle and will shatter when stored and handled in the frozen state (−18°C). Store them and handle them carefully until they have reached RT. This applies to core splice and other syntactic or syntactic/expanding systems.

Both knife over roller and resin film processes offer low retained volatiles generally <1%. This means that it is easier to achieve a lower void content in the moulding.

The drum winding method, although appearing rather antiquated, is ideal for small scale operation provided that material in the sheet form is acceptable. The 51″ (1.29 m) diameter drum which gives a 4 m long sheet is perhaps the maximum that is practical.

6.1 Pre-preg Forms

The most common pre-preg form is on a roll. Roll lengths vary with reinforcement cost but are generally 100 m. It is becoming ever more costly and even difficult to purchase shorter lengths unless you are a customer with preferential purchasing power (size or image). The core sizes on which the pre-preg is wound vary, generally 12″ or 300 mm for UD, and 3.5″ or 5.25″ for woven fabrics. All these dimensions are bore sizes. Such detail may appear trivial, but if you are setting up pre-preg take off racks on the shop floor to improve production efficiency or for feeding a Gerber type cutter, it is as well to be acquainted with the problem that will occur when pre-preg suppliers are changed and the core dimensions are dissimilar.

Woven fabric or UD pre-pregs can be slit into tapes and supplied on cinematograph spools. Alternatively, pre-preg tow can be supplied helically wound for filament winding or tow placement processes.

Generally pre-pregs are supplied on a single sided release paper (release characteristics on one side) with a release film on the upper surface. When a fabric pre-preg is wrapped onto the cardboard core at the wind-up/take-up stage, it is essential that the pre-preg remains flat and the fibres are not broken or cockled by creasing of the backers. If release paper was used on both the upper and lower faces of the pre-preg as it was wrapped onto the core so the outer release paper would control the wrapping process and the inner one (on the underside of the pre-preg) would crease and cause cockling of the fibre.

By using a less stiff material for the top surface of the pre-preg, this means that the paper on which the pre-preg lies controls the wrapping process and conforms to the cardboard core and the film is capable of stretching slightly to match the curvature.

UDs, as noted, are supplied on larger diameter cores than wovens, which allows the stiffer materials to conform more easily to the curvature and they are generally supplied without an upper release film. To preclude adhesion between wraps the release paper used is double sided. They are available as 300 mm and 600 mm wide pre-pregs; wider options would be available as a special order.

Pre-preg tape and tow are readily available for tape laying and filament winding applications; they are manufactured by slitting the wider (300 mm and 600 mm wide) UD pre-pregs. Once slit, they are then wound onto cinematograph type spools.

We need not even take delivery of the pre-preg roll, but receive it as a kit, cut and ready for laying up. It is essential to maintain good inventory control to ensure 'last in first out' (LIFO).

Our focus has been almost totally on the epoxy, BMI, PI type thermoset, but UPs are available both as Dough Moulding Compound (DMC) or Sheet Moulding Compound (SMC). These are generally highly filled systems (such as talc, calcium carbonate and metal stearates), reinforced with long strand discontinuous fibres, typically E-glass, to provide the strength and stiffness. The fillers reduce shrinkage which improve the surface finish and reduce cost, the metal stearates acting as a built in release agent for rapid de-moulding.

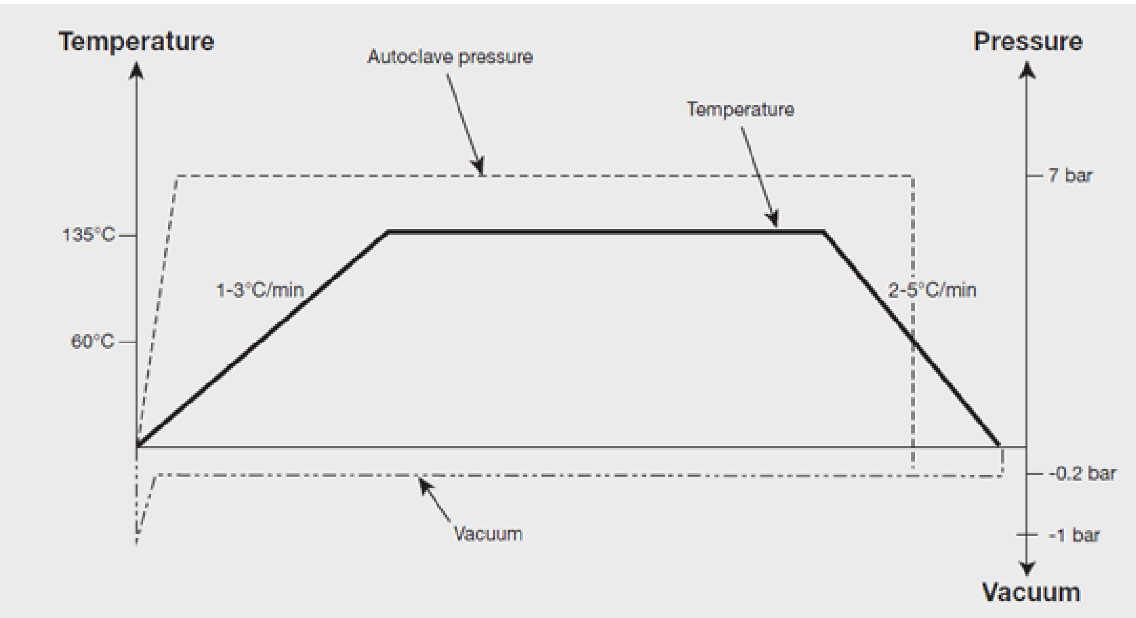
The catalyst is frequently BPO with an accelerator. This resin system is heat activated and has a very short cure time allowing high speed manufacture.

We must also consider co-mingled materials. They are discussed in *Topic 5: Reinforcement Forms*, but can fit equally well in this topic. They are formed by mingling filaments of thermoplastic resin into tows of a reinforcement, typically E-glass or carbon. The mingling ensures that the matrix is well dispersed and therefore able to wet out the filaments of the reinforcement. They can be moulded under vacuum pressure, but do require higher temperatures for consolidation than many epoxies of a similar operating temperature. In terms of 'green credentials' E-glass/PP is one of the most environmentally friendly pre-pregs to manufacture.

7 Curing Pre-Pregs to Manufacture Components

It is essential that the pre-preg manufacturers' recommendations are followed.

Figure 12: A typical cure cycle [© Hexcel (2008) HexPly® M35-4 Product Data, p2. Kind permission to use given.]



The three fundamental elements are the time, temperature and ramp rate of the cure as depicted in Figure 12 above. However, it is not the air temperature (the air surrounding the component during cure), nor is it the tool temperature that has to be monitored; it is the pre-preg temperature. Unless the pre-preg experiences the recommended temperature for the recommended period of time, then it is almost guaranteed that the resin system will be under cured.

The practicalities of inserting a thermocouple (TC) into a component are not realistic, therefore a dummy run prior to making the first part can be undertaken using a representative section of the component with an embedded TC and use the feedback from this embedded TC to drive the temperature controller of the heating device (oven, self contained tool). This then can become the cure cycle that is used to achieve the manufacturers' recommendations.

In following the manufacturers' instructions much of the hard work has been done, but it is well worth just considering what is going on in that pre-preg moulding. As the temperature rises, two effects are taking place with the resin system: one chemical; the other physical.

i. The chemical effect is the reaction between the resin and the hardener/catalyst which is bringing about cure. Remember, even at RT the reaction is underway albeit very, very slowly. Cure is conversion of the resin from a liquid to a solid infusible state. At RT the resin system (matrix) in the pre-preg is not liquid as we imagine a liquid, but a very viscous one (very thick).
ii. Meanwhile the physical effect is that the heat reduces the viscosity (thickness) of the matrix and it starts to become more like a liquid (see Figure 1). Try and remember these two processes are concurrent, not consecutive. The resin manufacturer has cleverly formulated the resin system so that the viscosity does not drop too low and the resin system becomes water

like; if it did it would easily run out and the composite part could become resin starved. These days many resin systems have controlled flow, i.e. their viscosity never drops too low (they never become too thin).

iii. At this early stage the physical effect is the dominant one. Even though the chemical reaction has begun, the hardener(s) selected by the resin chemist will have little effect on the resin at this stage. So with the matrix viscosity dropping, a critical aspect of the cure process begins to take place and that is the wetting out of the fibres, because unless this takes place the composite will not work.

iv. This juncture is especially important in the heavier weight (higher areal weight reinforcements), because frequently during the pre-pregging process the matrix has been at too high viscosity (thick) to fully penetrate all the fibres and wet them.

v. Now with the matrix at its lowest viscosity the chemical effect starts to dominate the physical one and we reach the onset of gellation or the gel point. This is where the viscosity of the matrix starts to increase rapidly, no more fibre wetting can take place because the matrix has too high a viscosity. The rapidity of the transition from thinnish liquid to solid is very quick (see Figure 1 (b)).

vi. We have encountered some new terms such as gelation, which is the process by which a gel is formed, and gel point, the position on the graph (see Figure 1 viscosity v temperature) where gelation occurs. This leads us neatly to a regularly quoted value – 'gel time'.

> The gel time is the time at a constant temperature for the matrix to convert from a liquid to a solid.

We now have a little insight as to what happens during the moulding (cure) cycle. Probably the most important elements we should remember are a ramp rate to ensure full fibre wet out; the critical temperature is in the pre-preg thermal insulation by the tool or bag face and thick sections in poor thermally conducting tools with rapid ramp rates can lead to exotherms, fire, loss of the part, severe damage or loss of the tool and damage to capital equipment.

Not only is it essential to follow the recommended cure schedule to achieve the desired properties, but if there was any question over the integrity/quality of the component we could always demonstrate that we had followed the manufacturers' recommendations.

8 Goods Receipt, Handling and Storage of Pre-Pregs

This section covers:

1. Nomenclature on the Box of the Pre-preg
2. What do we need to know?
3. Date of Manufacture (DoM)
4. Final Check for Goods Inward
5. Storage and Handling of Pre-impregnated Materials (Pre-pregs)

8.1 Nomenclature on the Box of Pre-Preg

The nomenclature on the box of pre-preg is generally written down by storekeepers often with little or no understanding of the terminology or its significance, therefore we must help them comprehend it so that they understand what has been delivered against what has been ordered.

It is impossible to give detailed breakdowns because each supplier has their own style. However, what is relevant is considering what is important to you. So ask the supplier for a breakdown of his/her code (some suppliers even use code for the reinforcement so it is impossible to determine the fibre type or weave style from the outside of the box).

8.2 What do we need to know?

The following information is usually contained in some form of product code, generally quite easy to understand, but to the uninitiated it can appear like a meaningless sequence of numbers. So we must ensure the supplier is able to explain to us how the following information is embedded in the product code/description:

i. Fibre type.
ii. Fibre form woven or UD.
iii. Areal weight of reinforcement.
iv. Weave style if woven.
v. Resin system.
vi. RW%.
vii. Width of material.

Some suppliers have a standard label detailing quite clearly all the relevant information topics, which is then completed for a specific pre-preg; consequently this is very easy to follow.

8.3 Date of Manufacture (DoM)

The date of manufacture (DoM) is generally a separate set of figures, almost always simply expressed such as 12 Mar 2010, so interpretation is not a problem. The problem lies on whether the date shown is the date of manufacture or the date of shipment. In the case of UK manufactured materials it is generally not of such a concern except for short shelf life materials such as tooling pre-pregs. However, in the case of imported materials it can be critical in trying to determine the amount of out life remaining on the material.

Most pre-pregs come with a shelf life of 6 or 12 months and an out life of 7 to 28 days. The lower temperature moulding resin systems have shorter out lives. Out life is just about being able to mould a material. Flow is not always the sole criteria for assessing whether the out life of a pre-preg has elapsed. Situations can arise where the flow remains in specification, and a good laminate results when the material is moulded, i.e. moulding to the required moulded thickness at the appropriate fibre volume and having a low void content. However, despite the flow being in specification, the material can have lost much of its tack, thereby rendering it very difficult to mould.

This can be overcome by the use of a mouse (disposable temperature logger). This is inserted into the pre-preg box at the time of shipment. The pre-preg supplier advises the customer in which box the logger has been placed so that on receipt of the goods the logger is retrieved and the data downloaded to a PC (personal computer) which then reveals the complete thermal history of the shipment (provided the boxes have not been separated in transit).

The labels bearing both the product code/description and the DoM are generally in three places: on the outside of the box when the pre-preg arrives; on the end of the core (if it is longer than the width of the pre-preg) or inside the bore of the core; and a third is generally loose inside the box so that we can attach it where we wish. Possibly the most important place is the bore of the core, because the core will be with the pre-preg right until the last metre is unrolled; consequently we always have an identity to the material.

However, a word of caution: if you re-use the cores for wrapping on a short length of pre-preg for storage, do remove the label in the bore and re-label it, otherwise traceability and identity of the material is lost.

8.4 Final Check for Goods Inward

What we ordered, what we have received, what the delivery/advice note, CofC and invoice all say, is it in agreement?

All very boring, all very essential and a totally impossible task unless you can decipher the supplier's product code.

8.5 Storage and Handling of Pre-impregnated Materials (Pre-pregs)

Emblazoned over the box in which these materials are delivered are two phrases:

Store at −18°C or below and **Don't Stand on End**

As we saw in *Topic 2: Matrix Materials*, once the hardener has been added to the resin we have what we call a resin system and this starts to react even at RT, therefore, to increase the shelf life of the pre-preg storage at a low temperature is recommended, and a temperature was chosen which is typical of the commercial freezer industry. The second warning, **Don't stand on End** is to preclude telescoping (see Section 2: Terminology of this topic).

Do heed this advice: pre-pregs can vary from £8–10/m^2 to over £150/m^2. Poor storage and handling can be very costly and it is frequently not just the loss of the material but the delay imposed on production to replace it. This ignores any penalty clauses enacted by the customer for late delivery.

In addition, when we open the pre-preg box we can see that the roll of pre-preg is supported at each end so that the roll does not rest on the bottom of the box and it is wrapped in a sealed non-moisture permeable film. Depending upon the supplier, different techniques are employed, but the concept is the same. If the roll was allowed to rest on the bottom of the box a flat would develop (because the roll will have reached RT during shipment and the matrix has softened) along its length which is almost impossible to remove unless the roll is rewound. Once the roll is refrigerated the 'flat' is now frozen into position and leaves distinctive crease marks on the pre-preg which can deteriorate into 'fish eyes' (a lenticular split or gap between tows/rovings, particularly common in badly processed or handled UDs).

Having been told to store the pre-preg at −18°C or below, when we remove the pre-preg from the freezer for use, condensation immediately forms on the non-moisture permeable film. Do not open or break that film; it is there to keep the moisture out. In *Topic 2: Matrix Materials* we mentioned the deleterious effect moisture can have on many hardener systems and the need to keep moisture off the pre-preg. If moisture is allowed to form on the pre-preg and this is then used to manufacture components, we have built in a source of voids, because during cure that moisture will be converted into steam.

What we need to do is leave the pre-preg roll in its non-permeable film until the roll has reached RT. The time for this to occur is debatable, but a minimum of six hours is acceptable. The best solution is to leave it over night: remember this must be reflected in the roll log of the pre-preg.

Thorough defrosting is essential especially with large rolls as the material is a good thermal insulator and the warmth does not readily penetrate to the core of the roll.

It is essential that every roll/box of pre-preg has a unique reference number that is maintained in a log book (metaphorical term for an electronic method, either manual/computer system, or by bar code). This should be established so that a warning flags up a reorder option within the lead time of the material and then a 'do not use' status and this can be easily reflected on the rolls/boxes as green (**use**), amber (**use first, need to order**), white (**quarantine**), reserving red for (**do not use – scrap**). Such a procedure saves much heartache at stock take as all materials with a red label have no stock value.

Stop and reflect 4

What is quarantine?

Notes 4

Notes 4

Quarantine covers a wide variety of cases in most quality manuals, but in essence it is material or product that cannot be used or sold, but which has value and should not be discarded.

We shall consider the narrower definition of quarantine where it is a raw material that has exceeded its shelf or out life (see **Glossary** (at the top left of this page) for Quarantine and Re-Life) but can be re-lifed, yet another term associated with the state of the pre-preg. Most pre-preg suppliers are conservative with their shelf lives and you can submit a sample of the pre-preg for retest by the supplier who will then issue a new certificate of conformity or extension to the one you hold, provided the material passes. There is a significant cost for this re-lifing, so it is important to check that the cost is justified rather than buying more material.

Always try to ensure you have some spare freezer capacity. Freezers often fail and seem to have a habit of doing so at about 4:30 on a Friday. Getting them repaired promptly can be very problematical. In a large organisation you can ensure you have 24 hour cover and a back-up plan as to what is done with the material. Remember as soon as the temperature comes above −18°C the out life is being used up and your pre-preg log must reflect this. In a small organisation even buying a chest freezer as a short-term solution may be the most cost effective route.

All freezers must have a record of their temperature and the ideal system is a seven day temperature recorder which will record all events, whether the facility is manned or not.

9 Why Use Pre-impregnated Materials?

We have encountered many warnings and problems in this topic which might arise from the use of pre-impregnated materials. However, they offered a huge step forward over wet-lay-up manufacturing:

i. Higher fibre volume fractions are achievable.
ii. Easier to control the moulded thickness of the component.
iii. Easier to control the fibre volume fraction.
iv. Lower void contents more easily achieved.
v. Better fibre orientation control.
vi. It is far easier to maintain the manufacturing area in a clean state.
vii. Very low VOCs provided the pre-preg is from a non-solvent manufacturing process.
viii. Opportunities to enter new markets where profit margins may be more attractive.

On the downside, the composite component manufacturer experiences:

i. Higher raw material costs.
ii. Up skilling of labour and the attendant costs.
iii. Significant investment in capital equipment.
iv. More expensive tooling.
v. Longer raw material lead times.
vi. Greater administrative costs to monitor out life and other quality issues associated with the manufacture of components from pre-preg.

With the emergence of various infusion techniques allowing the manufacture of very large structures and manufacture outside an autoclave (OoA) with fibre alignment, Vf and void contents approaching that of the autoclave process, the pre-preg route of manufacture is being challenged. The infusion method also eliminates the pre-pregging cost which means the raw material cost to the moulder should be reduced. Remember, this is the beauty of using composite materials: the designer/engineer makes the material whilst they are making the part; they have an almost infinite number of options.

10 The Testing of Pre-impregnated Materials

Certain tests can be carried out on both the cured and uncured pre-preg. These are usually undertaken by the manufacturer. They are:

i. Gel time.
ii. Retained volatiles.
iii. RW% (resin weight content).
iv. Flow.
v. Areal weight of the reinforcement.
vi. Tack is an important characteristic, but there is still difficulty in quantifying it. We need to keep a close watch on this as it can affect manufacturing (lay-up) times very significantly.
vii. Some additional testing relating to the chemistry and rheology of the matrix are routinely done.

Tests on the cured pre-preg excluding mechanical properties are also important, such as resin density and Tg.

Typical mechanical properties for moulded laminates and some details of the tests are given in the Hexcel publication: *Pre-Preg Technology* (2005).

11 Where are Pre-impregnated Materials Used?

It would be an endless task to describe all the applications; suffice to say that pre-pregs offer the designer and composite engineer a material from which they can virtually manufacture anything for almost any application provided that the environmental operating window is within the range of that pre-preg.

12 Summary

You have now come to the end of this topic on pre-pregs. You should be able to:

- explain the key terminology and its significance
- describe the pre-preg processes and assess their possible impact on the composite manufacturing stage
- differentiate between the technical and commercial benefits of using pre-pregs
- demonstrate a thorough understanding of the principal handling and storage condition for pre-pregs
- differentiate between the physical descriptions of the material, e.g. the interrelationship between fibre volume fraction, fibre weight fraction and areal weight
- explain and evaluate the importance of quality control with pre-preg materials

Please complete the evaluation form at the end of the topic as this will help us in our review of the topic.

13 Recommended Reading

Umeco, *An Introduction to Advanced Composites and Pre-Preg Technology*. Online. Available at http://www.umeco.com/~/media/Files/General%20guides/Introduction_to_Advanced_Composites.pdf [accessed 14/09/2012].

Hexcel (2008) HexPly® M35-4 Product Data. Online. Available at http://www.hexcel.com/Resources/DataSheets/Prepreg-Data-Sheets/M35_4_eu.pdf [accessed 14/09/2012].

Hexcel (2005) *Prepreg Technology.* Online. Available at http://www.hexcel.com/Resources/DataSheets/Brochure-Data-Sheets/Prepreg_Technology.pdf [accessed 14/09/2012].

Lubin, G. (ed.) (1982) *Handbook of Composites*. VNR Publishing.

14 Evaluation

General

1. Overall, how valuable has this topic been to you?

Extremely valuable ○ ○ ○ ○ ○ ○ Not at all valuable

Content

2. Doing this topic has enhanced my knowledge and understanding of the field.

Yes, greatly ○ ○ ○ ○ ○ ○ No, not at all

3. It was possible for me to make links between the content of this topic and my existing knowledge.

Yes, definitely ○ ○ ○ ○ ○ ○ No, not at all

4. The content was pitched at an appropriate level.

Yes, definitely ○ ○ ○ ○ ○ ○ Definitely not

Learning processes, organisation, materials and online environment

5. It was easy to access the learning environment and resources.

Yes, very easy ○ ○ ○ ○ ○ ○ No, not at all easy

6. The right amount of guidance was provided to get me started.

Yes, definitely ○ ○ ○ ○ ○ ○ No, definitely not

7. The activities helped me to improve my understanding.

Yes, a great deal ○ ○ ○ ○ ○ ○ No, not at all

8. Content and activities followed a logical sequence.

Yes, definitely ○ ○ ○ ○ ○ ○ Definitely not

9. It was easy for me to access help when I required it.

Yes, very easy ○ ○ ○ ○ ○ ○ No, not at all easy

Your comments

10. The best things about this topic were:

11. My suggestions for improving this topic are:

send

This evaluation is sent anonymously.