2

Prepregs and Their Precursors

Felipe Wolff-Fabris, Hauke Lengsfeld, and Johannes Krämer

Over the last 70 years, prepregs have significantly influenced the technological development of high-performance fiber reinforced components. Today, these materials are globally prevalent and are used for the manufacture of composite parts in the aerospace industry, for high-speed trains, cars, boats, and many other applications. More than half of the global carbon fiber production is used to manufacture prepregs [1].

Yet, there are still segments in industry that are discovering the advantages of fiber reinforced composite materials over those of conventional materials, such as metals. Increasingly, combinations of metals and fiber reinforced plastics – so-called hybrids – are introduced.

This chapter will provide an overview of the design of prepregs on the materials typically used to manufacture them. In addition, we will introduce examples of the different generations of prepregs, including the current, modern prepreg systems.

With regard to performance, prepregs claim the undisputed leading position among high-performance composite materials (Figure 2.1). This class of materials allows the manufacture of ultra-lightweight yet highly load-bearing composite components. However, the figure also shows that the advantage in performance comes at the cost of productivity (see also Chapters 4 and 5). Therefore, this technology is mainly used for very small to medium-sized production runs. In these scenarios, component performance and production cost can be easily reconciled using prepreg materials (Figure 2.2). Despite their lower productivity compared to infusion techniques, prepregs excel in terms of their simple and safe processibility.

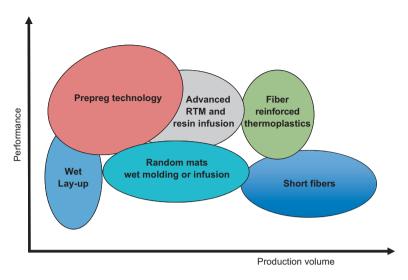


Figure 2.1 Performance and production volume of prepregs compared with other technologies

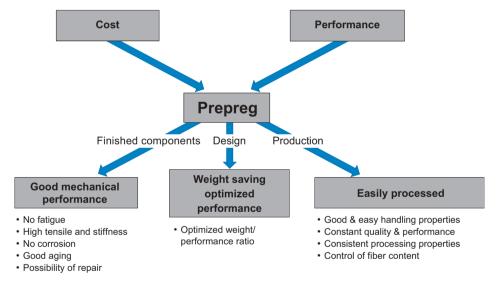


Figure 2.2 Prepregs as key materials for high-performance components

The costs of prepreg materials are determined by the requirements the finished component has to meet. Prepreg costs for the production of aviation components cannot be compared to those for components for wind turbines. The latter application is a good example for the fact that manufacturing and labor costs can be lowered by utilizing prepregs with high areal weight rather than using infusion technology. Using prepregs with areal weights of up to 2000 g/m² allows for high lay-up

efficiency (even by hand) and faster completion of the component. While the matrix is already part of the prepreg and only has to be cured, dry semi-finished products require the additional step of infusion with the matrix resin.

■ 2.1 Structure and Preparation

A prepreg (*pre*-im*preg*nated fibers) is a semi-finished product consisting of a highly viscous matrix and continuous reinforcing fibers. The material is typically wound on rolls and comes in two variations:

- Unidirectional (UD) prepreg (fiber reinforcement in only one direction)
- Fabric prepreg (orthogonal fiber reinforcement)

In order to manufacture a prepreg, the fibers are wetted with the matrix material, resulting in a pre-impregnated semi-finished product (see also Chapter 3). The choice of matrix material includes thermosetting resin systems (TS) as well as thermoplastics (TP); however, thermosetting systems are more commonly used.

The cross section in Figure 2.3 shows the typical composition of a thermoset prepreg as it is delivered between a polyethylene film (PE film) and a release paper, ready for further processing. Some processing techniques, such as automatic tape laying (ATL, see Chapter 4), require a carrier material only on one side of the prepreg. Both the PE film and the release paper protect the prepreg from contamination, prevent sticking, and facilitate handling, e.g., during cutting. In the case of thermoplastic prepregs (TP prepregs), these separating and carrier films or papers are not necessary because the material does not bond to itself (see Figure 2.4).

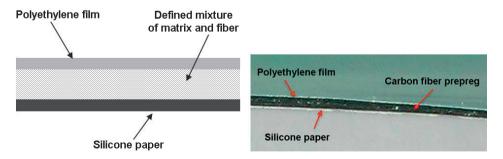


Figure 2.3 Typical thermoset prepreg cross section

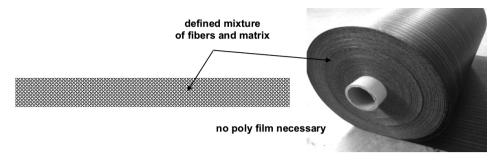


Figure 2.4 Typical thermoplastic prepreg cross section

The dimensions of the semi-finished product vary depending on application and type of material (UD or fabric prepreg). The roll width also depends on the width of the production line. Common roll widths and lengths are shown in Table 2.1 and Table 2.2.

 Table 2.1 Examples of TS-Prepreg Dimensions and Roll Weights

	UD prepreg	Fabric prepreg
Width in mm	6.35 (1/4") to 1500 (59")	900 to 1500
Length in m	up to 800	up to 200
Roll weight in kg	up to 80	up to 200

Table 2.2 Examples for Dimensions and Roll Weights of Thermoplastic Prepregs (TP)

	UD prepreg	Fabric prepreg (laminates)
Width in mm	6.35 (1/4") to 304.8 (12")	300 to 1000 mm
Length in m (UD) or mm (fabrics)	100 to 1000	ca. 40 to 60
Roll weight in kg	up to 250	up to 150

The ratio of fiber to matrix content is precisely defined for each prepreg, with narrow tolerances that depend on application. The tolerances for nominal resin content (RC) range from $\pm 2.5\%$ to as little as $\pm 1\%$. However, the resin content may be adjustable within certain limits, depending on application-specific requirements. A common choice is a combination of fiber areal weight and resin content that allows for a fiber volume content of approx. 60 wt.% after curing of the material. In many cases, resin is lost during curing in vacuum processes, and therefore the resin content in the semi-finished product is often adjusted to a higher value. Depending on resin content in the prepreg and/or in the composite component, the theoretical value of the cured ply thickness (CPT) changes. Excessive resin loss during the curing process may also lead to a smaller CPT than theoretically calcu-

renewed interest in research and development projects. Within a short time period, the carbon fiber manufacturing and processing industries have evolved into sophisticated technologies. Starting from a few selected materials and fiber composites, which were produced in very labor intensive, manual processes, today a variety of industries, including the aerospace and automotive industries, rely on low-weight, stiff, high-performance composites that could not be produced if it were not for prepreg materials and fully automated processes.

Thermoset prepregs were joined over time by thermoplastic-based prepregs. The latter's development and broad industrial use is more complex than that of thermoset prepregs due to the more complex processes involved.

3.2 Introduction: Manufacturing Methods

Prepregs, as semi-finished products containing pre-impregnated fibers (Figure 3.1), are a prerequisite for high quality and load-optimized lightweight fiber composites. The current manufacturing techniques and processes guarantee consistent quality of the prepregs, e.g., in terms of FAW and resin content, at a very high level. On the one hand, this simplifies processing for the manufacturer, and on the other it allows the reproducible production of high-quality components.

Prepregs always consist of a combination of a typically highly viscous matrix and a fiber reinforcement. Once the reinforcing material has been pre-impregnated with a matrix, it is considered a prepreg material. Both thermoplastic and thermosetting materials (reactive resin systems) can be used as matrices (see also Chapter 2) [2]. In the following, we will discuss the production of thermoset prepregs.

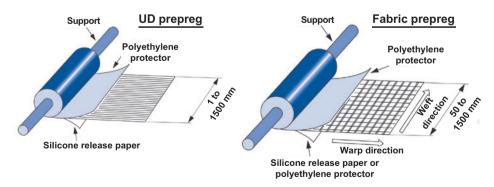


Figure 3.1 Delivery form of UD prepreg (left) and fabric prepreg (right) on supports [Courtesy: © Hexcel Corporation]

Fiber reinforcements are supplied in a number of different forms:

- uni-, bi-, and multidirectional fabrics
- fabrics
- non-wovens and random fiber mats

Depending on the reinforcing structure, processing techniques include creel sets (for rovings) and roll unwinders for fabrics.

Today, a number of different methods and machine concepts are available for the production of coating lines. They are able to use different fiber materials and combine them with a wide selection of matrix resins. State-of-the-art technologies include:

- solution coating processes (also called dipping (solvent) processes) (Figure 3.2 and Figure 3.3)
- hot melt processes (Figure 3.2)
- knife systems
- powder scattering (Figure 3.3)
- extrusion / slot die systems (Figure 3.3)

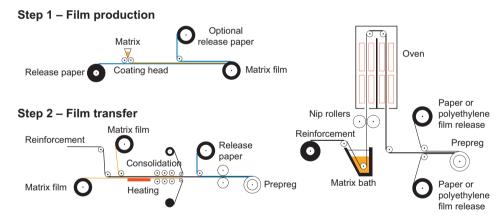


Figure 3.2 Manufacturing methods for thermoset prepregs, left: hot melt process; right: solvent process

Some processes, such as powder scattering, were initially developed for thermoplastic matrices, but later adapted to thermoset processing. However, these processes have not found widespread industrial-scale use. Today, there are two major impregnating methods in industrial practice: the dipping (solvent) process and the hot melt process [2].

4

Prepregs: Processing Technology

Hauke Lengsfeld, Javier Lacalle, and Thomas Neumeyer

■ 4.1 Introduction

In this chapter, we will describe the different technologies used to process prepregs and to transform them into prepreg components. We will introduce both manual and automated deposition methods as well as methods to cut and form prepreg materials.

One of the advantages of fiber reinforced materials is the fact that the fiber reinforcement can be strategically placed in the component to optimize the relationship between mechanical properties and weight.

Manufacturing methods using prepreg are particularly efficient because they achieve highest quality and most accurate fiber placement in the component. This also ensures optimum fiber volume content in the component, because the ratio of resin to fiber has already been coordinated in the prepreg. The layer structure may be deposited by hand or by automated processes.

In general, the processes used to manufacture composites are laminating and deposition processes that use flat, semi-finished products (e.g., prepregs) and deposit them in a specific sequence and in a defined orientation and shape on a mold or tool.

Today, there is a wide variety of processes available. There are two different approaches to classify these processes. First, considering the pressure applied during forming and curing leads to the classification of the most common processes as shown in Figure 4.1.

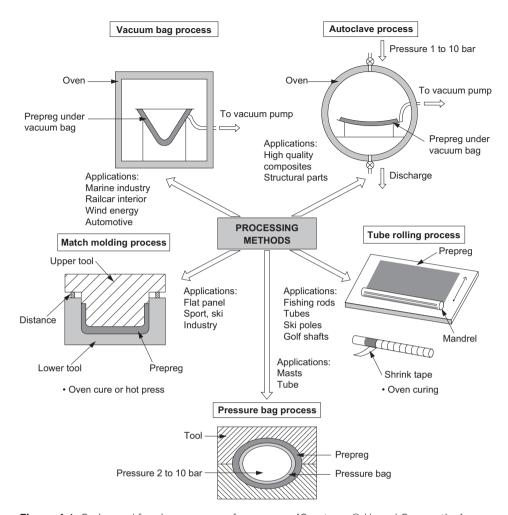


Figure 4.1 Curing and forming processes for prepregs [Courtesy: © Hexcel Corporation]

An alternative perspective considers the deposition and processing technologies that are used to process prepregs (Figure 4.2). This approach also includes the subsequent process of manufacturing a fiber reinforced composite part and provides a differentiated classification in the various technologies. While the pressure-oriented approach (see Figure 4.1) often includes the curing process, it is deliberately separated from the deposition and processing technologies. Curing is considered a separate step and thus includes the pressure processes shown in Figure 4.1.

During hand lay-up, the cuts are typically aligned using templates, leading edges, or markings on the edge of the mold to achieve sufficient deposition accuracy (positional tolerance) of the individual plies and to avoid incorrect deposition. Direct labeling of the finished cuts during cutting (whether manual or by cutter) prevents the interchange of cuttings during lamination. In addition, nowadays laser positioning systems are used that project the exact position and form of individual cuts on the lay-up area. These systems also prevent turning of cuttings and lay-up in the wrong orientation. The disadvantage of using templates becomes apparent when many different-sized cuts require the same high number of templates. With larger cuts, templates tend to become rather unwieldy. Another problem with hand lay-up of prepreg cuts is the sheer number of prepreg cuts necessary for the manufacture of complex components, which can reach several hundreds. This results in an additional logistics problem, especially when the cuts cannot be stored at room temperature but have to be kitted and frozen for storage.

Several parameters, including size, production rate, and the required accuracy and repeatability of the prepreg lay-up (form and positional tolerances) determine whether a component will be manufactured by hand lay-up or by an automated process. On the one hand, hand lay-up processes are time and personnel intensive; on the other hand, the high capital and operating costs of automated processes have to be considered.

In the past (until approx. 2004), large components, such as the vertical tail plane of the Airbus A320 and A330 series, were manufactured by hand lay-up of unidirectional tapes. For large components, the handling, exact positioning, and laying of long prepreg cuts without entrapping air is extremely difficult, and defects in the composite part are therefore hard to avoid. Therefore, the prepreg structure of such large components is typically manufactured using automated systems.

4.4 Automated Lay-up Technologies: Automated Tape Laying (ATL) and Automated Fiber Placement (AFP)

4.4.1 Introduction

Today, the automated laying of pre-impregnated fiber materials is a key technology for the manufacture of large composite components in the aerospace industry. For a number of years, automated tape laying has been used in conjunction with other technologies, such as hot-forming, to manufacture vertical tail panels, wing struc-

tures, stringers, spars, etc. Thermoset materials have traditionally been the basis for the production of composite parts.

However, the fast growing use of composite components both in aerospace and automotive applications, together with the increasing complexity of these components, has triggered the continuous growth in use and research of automated and highly efficient laying technologies, and the further development and additional formats of materials. Figure 4.16 and Figure 4.17 show the geometric complexity as well as the size of composite parts.

Also the increased use for productive, serial applications of other materials such as thermoplastics has opened a new development branch in the materials and processes.

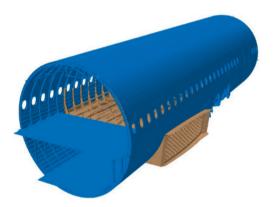




Figure 4.16 Carbon fiber reinforced composite fuselage structures [Courtesy: Airbus Operations GmbH]





Figure 4.17 Automated lay-up processes: ATL (left), AFP (right) [Courtesy: M.Torres Diseños Industriales S. A. U.]

■ 6.2 Tooling Materials

A variety of different materials is available for the manufacture of tools for the forming and curing operations of prepregs materials; these materials can also be combined, depending on the area of application.

Table 6.2 provides an overview of common tooling materials that will be described in more detail in the following.

Table 6.2 Examples of Tooling Materials

Material	Description	Type (examples)
Metals	SteelAluminumNickel-steel alloy (Ni-36)	 \$235 JR, \$355 JR ALMG 3/3.3535 INVAR 36, Pernifer 1.3912
CFRP (epoxy resin)	Fabric prepregQuasi-isotropic prepreg mat	Cycom® 7620,HexTOOL® M81
CFRP (BMI or BOX resin)	Fabric prepregQuasi-isotropic prepreg mat	 Duratool® 5270 HexTOOL® M61 Toolmaster BetaPreg
CFRP foam	Carbon foam	 Touchstone CFoam® 20
GFRP	 Dry fabric + resin, processed by resin infusion or hand lay-up 	
Other materials	 Wood Epoxy tooling boards Cellular concrete Sand casting compounds 	 OBO-Plywood, RETIstab Necuron, Rampf WB700, OBO-Modulan, TB650 Series Ytong Polymer bonded quartz sand

6.2.1 Metals

Metals are the easiest and most commonly used class of materials for the construction of tools for prepreg processing. This is due to their easy availability as well as their high load capacity. In addition, metal curing tools stand out for their robustness and thus high structural durability so that they can be utilized without difficulty for more than 1000 cycles. The surface of these tools is resistant to organic solvents and release agents, and even damage, such as scratches and dents, can typically be repaired easily.

Steel, aluminum, and ferronickel alloys are generally utilized, with steel and aluminum being the materials of choice because of their price and durability. Both materials exhibit a high coefficient of thermal expansion (Table 6.4) that needs to be taken into consideration during design of the tooling, in particular for high curing temperatures, in order to ensure its dimensional accuracy. Depending on tooling and application, thermal expansion may be desired, e.g., in order to facilitate for the finished component to shrink off the tooling during cooling (Chapter 8). Contour accuracy of 0.3 to 0.4 mm, even with large toolings (e.g., 20×5 m), can be achieved with metal tools at room temperature.



Figure 6.3 Steel tooling for the manufacture of rotor blades [Courtesy: Premium Aerotec GmbH]

A disadvantage of steel is its high weight, which complicates handling and impedes heat transfer. Metal curing tools are generally manufactured by contour milling, but also by preforming of sheet metal. In order to ensure the created geometry, in particular for a large tooling (e.g., thick profiled sheet), even at high temperatures and/or during handling (e.g., by crane), the geometry is often stabilized by a stiff sub-structure ("egg carton" structure). This sub-structure also facilitates safe handling and installation, e.g., of vacuum lines and hoisting points to lift the tooling via crane.

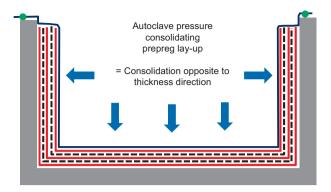


Figure 8.29 Consolidation and compaction inside tooling

Thus, the inner plies are forced to expand or to perform a relative movement in order to balance the change in length caused by the consolidation. However, they may not always be able to make these adjustments. The applied autoclave pressure (typically 7 to 10 bar) and the bonding between the plies by the prepreg resin render relative movement of individual plies impossible. Because the autoclave pressure is more effective on the plane than on the radii, the inner prepreg plies will bridge the radius to a certain degree, thus changing force progression and load capacity of the component (Figure 8.30). The continuous, inner line marks the actual, the dotted line the required fiber orientation.

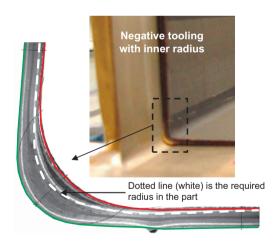


Figure 8.30
Micrograph of radius area showing the bridging effect of inner plies

This problem can be mitigated by one of several measures. For one, using a prepreg with a higher level of impregnation may minimize the consolidation. Another approach is the manufacture of a flat prepreg stack via ATL (rather than hand lay-up) and subsequent hot forming that would facilitate a pre-compaction of the stack prior to the curing process. Yet another, although somehow controversial,

method is the use of pressure strips (rubber or silicone corner profiles) in the radii. It is possible to effectively increase the autoclave pressure in this area using pressure intensifiers in the form of round cords. However, they often cause deep undesired indentations in the laminate or the formation of beads in the border area of the pressure strips.

Interrelations: Example of a Sandwich Structure

The interrelations between component design, material, and curing process and their implications will be described using a sandwich structure as an example.

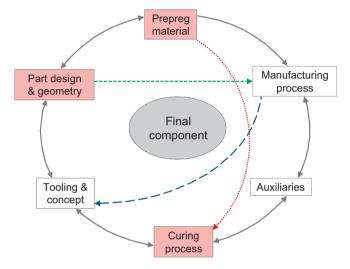


Figure 8.31 Effects of design, material, and curing process on component

PMI rigid foams (Evonik) can be used for the manufacture of Omega stringers (Figure 8.32). Typically, the formed foam remains in the component after curing of the prepreg, allowing for one-step curing of stringer and skin segment to be reinforced.

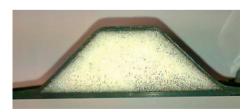


Figure 8.32Example of sandwich design: Omega-stringer with foam core

The cell walls of certain rigid foams do not exhibit sufficient dimensional stability under the temperatures (typically 180 °C) and pressures (7–10 bar) required for prepreg curing. Therefore, the pressure on the component is reduced to, e.g., 3 bar absolute.

Index

C **Symbols** CAD-CAM chain 190 1st-generation prepregs 23 2-film process 39 calendering unit 35 2nd-generation prepregs 23, 53 calibration 74 3rd-generation prepregs 23, 50 cantilever 84, 95, 115 4-film process 39 carbon foam 181 4th-generation prepregs 23 carrier films 81 carrier paper 89 cast nickel tooling 184 Α cationic polymerization 172 cellular concrete 188 activation 94, 111 AFP CFRP foam - bidirectional lay-up 109, 118 - carbon foam 181 - MCL (minimum cut length) 110 CFRP tooling 191 AFP (Automatic Fiber Placement) 101 cleaning 202 airpad 198 closed mold 196 closed mold curing 201 anhydrides 18 Aquacore 198, 199 coating unit 35 aspect ratio 3 coefficient of thermal expansion 182, ATL (automatic tape laying) 86 230 autoclave processing 153 column 84, 95, 115 comb and spreader bars 38 compact gantry 84 В compaction 94, 112 bismaleimide resins (BMI) 18 CPT 215 bleeding aid 151 creel 107 BMI 181 creel set 35 bridge 83, 95, 114 cross-linking density 151 bridging 112 C-spar 219 Brønsted acid 172 CTE 231 cured ply thickness 15, 215 - CPT 50

curing cycle 149, 150

curing mandrel 225
curing molds 196
curing technologies 149
- autoclave 149
- out-of-autoclave processes 149
cut edge test 211
cutting system 93
- AFP technology 110
cutting/trimming station 35
Cycom® 977-2 25
Cycom® 977-3 25
Cycom® 997 25

D

degree of crosslinking 17
design concept 217
DFP technology 26
differential design 220, 221
direct manufacturing of forming tools 190
DMTA 214
double diaphragm 138
drapability 79, 207
Duratool 181
dynamic mechanical thermal analysis 214

Ε

Ebalta 192
egg-carton structure
- sub-structure 182
electron beam 149, 152
electron beam curing 171
epoxy tooling block 188
epoxy tooling boards 181
excess resin 152
exchangeable head 99, 107, 117
exothermic 151
extrusion process 46

F

fabric prepreg 13, 33 feeding system 92, 109 ferronickel alloys 183 fiber areal weight 15, 204 fibers 20 fiber undulation 21 fiber volume content 15, 212

G

gantry 83, 95, 114
gelation 151
gel point 152, 208
glass transition temperature 214
glycidylated novolacs 17
guiding system 92
gusset filler 136

Н

handling characteristics - toolings 179 head change 108 head stock/tail stock 86 heat distribution 151 heating ramp 150, 151 HexPly® 913 **25** HexPly® 914 25 HexPly® 3911 24, 25 HexPly® 8552 25 HexPly® M21 25 HexPly® M21E 24, 25 HexPly® M56 25 HexPly® M65 25 HexPly® M77 25 HexPly® M91 25 HexPly® M92 25 HexTOOL 181 hot drape forming 137 hot forming tool 195 hot melt processes 34, 36 hydrostatic resin pressure 155

nomogram 231 non-crimp fabrics (NCF) 21
non-thermal 173 non-wovens and random fiber mats 34
OBO-Plywood 181 offline programming 73 omega stringer 236 online cutting 93 online inspection - AFP technology 113 open mold 196 open mold concepts 222 open mold curing 201 out-of-autoclave (OOA) 26 oven curing 157 overall lay-up width 116 overheating 170
phenolic resin 18 photoinitiators 174 plain weave 21 ply book 65, 72 polyether ether ketone 16 polyether sulfone 16 polyethylene film 13 polypropylene 16 positive design 217 positive mold 218 positive/negative design 217
positive tooling 179
pot life 150 powder coating process 43 powder scattering 34 pre-impregnated fibers 13 prepreg 11 - AFP 102 - areal weight 204 - ATL 88 - automated lay-up processes 76 - carrier paper 89

- drapability 79
- impregnation 78
- line 36
- manufacturing methods 36
- release and carrier films 81
- rigidity 78
- slitting 77, 104
- systems 23
- tack 103
- tape width 80, 89
- tow width 104
- types 15
- variations 48
press molding 159
pressure profile 155
processing technology 57
process simulation 73
productivity 119
- floor-to-floor 119, 120
- lay-up productivity 119, 120
- unit price 124
profile 136
pultrusion 133

Q

PVF film 205

quasi-isotropic 231 quasi-isotropic structure 185 Quickstep™ technology 152, 157

R

release agents 202
release and carrier films 102
release paper 13
resin content 15, 50, 204
resin flow 15, 204
resin viscosity 152
rigid/soft 201, 221
rigid/soft variation 222
robot 85, 96, 115

S

sandwich design 220 sandwich structure 236 satin weave 21 scrap 80, 104 shrink off 182 single diaphragm 138 single-diaphragm method 195 single-step integration 220 single tape 97 slit tape 22, 48 soft/rigid 201, 221 soft/rigid variation 224 soft/soft 201 soft/soft variation 220, 225 solution coating processes 34 solution route 207 solvent coating/solvent dip method 41, specific Young's modulus 6 SQRTM 144

т

table gantry 96, 115 tack 53, 103, 206 tacky tape 196 tape preparation 93 tape width 80, 89, 97 textiles 20 thermal characteristics - toolings 178 thermoplastic prepregs 26 thermoset prepreg 33 thermoset prepregs 23 time-transition-temperature 208 tooling contours 180 tooling materials 181 tooling technology 177 tool manufacture 190 Toolmaster BetaPreg 181 Toray 24, 25 total lay-up width 98 tow preg 22

towpreg 48, 49 tow width 104, 116 TTT-diagrams 208 twill weave 21

U

unidirectional prepreg 31

٧

vacuum bag 153 viscosity 208 volatile content 207 volatiles 207

W

water pickup 52, 53 water pickup test 210 winding station 35

Z

zero-bleed prepreg 15, 152