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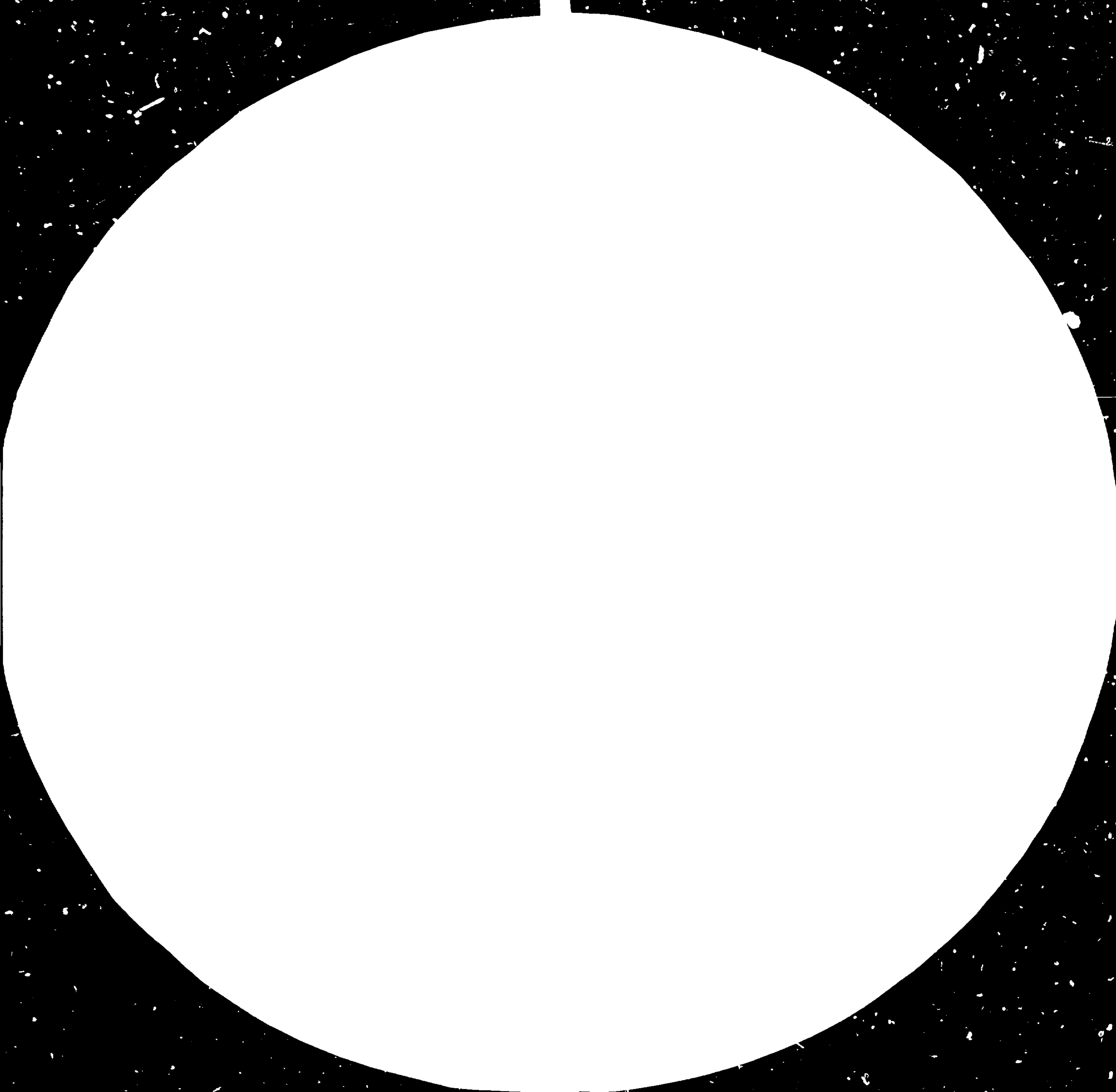

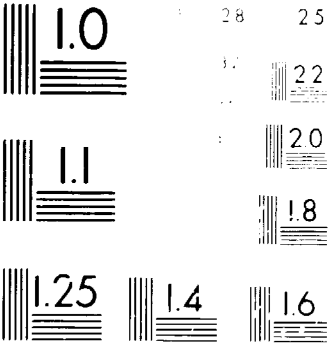
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REVIEW OF FABRICATION PROCESSES FOR HIGH PERFORMANCE CARBON COMPOSITES WITH SPECIAL EMPHASIS ON THE TECHNOLOGY OF PREPREGS*

(WET WINDING AND PREPREG TECHNOLOGIES)

by

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FABRICATION PROCESSES

The principal methods available for fabricating carbon fibre composites are:-

INJECTION MOULDING
PULTRUSION
WET LAY-UP
WET WINDING
VAC-BAG MOULDING
PRESS MOULDING
EXPANSION MOULDING
AUTOCLAVE MOULDING

Of these techniques INJECTION MOULDING is specific to short fibre reinforced resins - particularly thermoplastics - and is usually rather limited in the size of the component that can be produced. Because they do not contain continuous fibre, cannot contain very high levels of reinforcement and yield parts with relatively random fibre orientation - they cannot be considered as primary high performance composites. Nevertheless, this technique is the best for large numbers of limited size individual components, providing the required properties can be achieved and greater stiffness is required than obtainable with the glass reinforced equivalent.

PULTRUSION is a convenient method of manufacturing constant section solid profiles which are largely unidirectional. As such it is strictly limited to the relatively small number of applications requiring this type of composite in carbon fibre.

WET LAY-UP techniques are not widely used in carbon fibre fabrication technology. Firstly it is unsuitable for completely unidirectional lay up because of the problems in maintaining fibre orientation - it is thus limited to fabrics. Secondly, wet lay up is not such a controlled process - it is difficult to maintain consistent resin contents, it is difficult to obtain high fibre volume fractions and it is not convenient for the manufacture of honeycomb sandwich structures. The range of resins that can be used is limited and the cleanliness of the operation, both from workplace and handling points of view, is less than ideal. There have been some developments in aerospace using wet lay-up but usually this is combined with some form of pressure application during cure. The most likely prospects for carbon fibre wet lay-up in the long term are for repair work or selective stiffening of structures already made in glass, e.g. gliders, racing boats etc.

WET WINDING is an important technique but from the CFRP point of view has been mostly limited to pipes as torsion tubes or struts and stiffness reinforcement of pressure vessels and centrifuges. For those intended applications without an axis of symmetry and/or requiring non-geodesic winding or special mandrels, sophisticated computer winding programmes and controls become necessary rendering the whole technique highly specialised.

For simple constant section tubes high production rates can be achieved. Tubes 1500mm x 65mm with a wall thickness of 3mm can easily be wound in one minute. This order of speed, however, depends on the use of a roving guide which feeds several resin-impregnated rovings simultaneously and symmetrically to many points on the periphery of the mandrel.

The manufacturing sequence for such tubes is:-

Resin mixing
Fibre impregnation in dip bath
Winding on mandrel
Wrapping with polyester tape
Gelation
Curing
Mandrel withdrawal
Finishing
Inspection

Resin content is determined in part by nip-roll pressure to remove the excess after emerging from the impregnation bath and partly by very careful control of tension in the wrapping film to squeeze out any remaining excess.

Finishing operations usually consist of cutting to precise length, machining for end fittings if required, assembly of fittings and varnishing for a good finish. Inspection should consist of measuring dimensions, weight, natural frequency and static and fatigue strength as appropriate.

DRY WINDING and tube wrapping with either prepregged individual fibre tows or narrow tape or even full width prepreg tape is gaining in importance and even represents the main method for the manufacture of fishing rods and golf shafts.

For simple wound shapes as in the previous section, the resin mixing and impregnation stages are omitted, leaving an easier, cleaner operation. Where non geodestic winding is required tacky prepreg can greatly assist in holding the fibre in position. In either case it may prove a production advantage to warm the mandrel during winding.

VAC-BAG MOULDING consists essentially of using pressure up to one atmosphere to consolidate the prepreg layers in the manufacture of a part. This is achieved by using a vacuum pump to withdraw the air held between a mould tool, the prepreg and an impervious plastic film which is firmly attached to the mould. It is usual practice to heat the prepreg assembly in an oven to cure it, although heated tools may be used as well. This technique is very attractive where expensive autoclaves and presses are not available.

PRESS MOULDING is a fairly common procedure and employs matched tools, between which is placed the prepreg needed to make the part. Heat and pressure are applied in the press, the resin flows and cures and the part is demoulded usually after cooling. The tooling is often expensive.

EXPANSION MOULDING is a simple technique requiring some rather sophisticated products and careful part and mould design. The principle is one of producing basically male and female tools from special rubbers - usually silicone - and then laying prepreg between these tools as for press moulding. The whole assembly is then placed in a strong retaining box and placed in an oven at the curing temperature. The rubber tools are so designed that they expand up to the curing temperature when they then exert the correct pressure to consolidate the prepreg and produce a cured part of the correct dimensions.

AUTOCLAVE MOULDING is the principal technique for the production of aerospace carbon fibre composite parts. It operates in a similar manner to vac-bag moulding, except that it has the big advantage of being able to pressurise the part from outside the plastic membrane. This enables removal of air by vacuum inside the bag early in the cure cycle and then application of excess pressure on the outside to ensure good consolidation. The main problem is the high capital cost of the autoclaves in the first place.

PREPREGS

In five of these eight processes it is standard practice to work with the carbon fibre in a pre-impregnated form. In about 80% of the applications discussed so far the starting material for part production has been a prepreg.

(A) What are prepregs?

(B) Why are prepregs so important? - What are their advantages?

(C) Are they all the same? - What are the differences?

(A) A prepreg is a mixture of unidirectional or woven fibre and a preformulated resin in a particular weight ratio protected against contamination on one or both sides with easily removed separators.

Unidirectional prepregs are a standard width of 300mm but can be obtained from very narrow tapes (e.g. 5mm) up to 1200mm in special cases. The resin content and cured ply thickness can be varied as required but typical figures would be 34% resin and .125mm thickness. They are produced continuously and usually purchased as a 250 metre long reel.

Woven prepregs are manufctured at standard widths of 1 metre and 1.2 metres. The resin contents and weave styles may be varied as necessasry but typical would be a 5 harness satin weave fabric with 37% resin, moulding to approximately 0.28mm per ply.

They are normally purchased with one or two interleaving protective layers at a length of about 50 metres on a spool. This represents a handleable weight.

(B) Why are they so important? What are their advantages?

(i) They are the only practical way of handling true unidirectional fibre arrays

(ii) They give precontrolled resin to fibre ratio

(iii) They give predetermined total weight

(iv) No mixing of resins/hardeners/catalysts is required

(v) Tack and drape are designed into the product to ease the lay-up process

(vi) Pot life at room temperature will be weeks to months as opposed to a few hours for wet resin processes

(vii) Storage life deep frozen is months to years

(viii) Viscosity of the resin can be accurately controlled giving rise to easier processing, low porosity laminates and good bonding to honeycomb

(ix) A wide range of cure cycles and mechanical properties can be obtained

(x) Some prepregs with nett resin contents can be easily handled leading to much reduced cost

(xi) All handling and toxicity hazards are reduced

(xii) Assurance of resin/fibre performance can be given by Q.C. testing before component fabrication

(C) Are they all the same? What are the differences?

No they are not all the same. All prepregs possess some of the advantages listed above, but some possess the majority of them. The following section makes these differences clear by a detailed comparison of two distinct types and also poses questions which are necessary if the correct material is to be chosen for a given application.

PROCESSING ASPECTS OF MATRIX RESINS

Selection of the best prepreg for the fabrication and use of any given item can only be made satisfactorily after a number of features have been considered. Among the most important of these are:-

NATURE OF THE PART TO BE PRODUCED	CONSIDERATION
Simple unidirectional flat laminate	handleability? suitable for tape laying?
Multidirectional reinforcement	tack? fabric? suitable for tape laying?
Multicurvature	level of tack? fabric? adhesion? porosity? surface appearance?
Honeycomb sandwich	controlled flow? adhesion? porosity? surface appearance?
Size and complexity	out life? tack? consistent flow?
Thick or thin section - or both	cure reaction rate? zero bleed?

MECHANICAL PERFORMANCE REQUIRED	CONSIDERATION
Basic strength and moduli	adequate to make composite construction worthwhile?
Temperature limits	are these really known and realistic?
Environmental performance	What property loss when exposed to use conditions?
Adhesion to honeycomb	is separate adhesive film necessary?
Toughness	suitable for likely damage environment?
Fatigue	will it perform over the full life intended?
Flammability	will fire hazard be a problem? self-extinguishing?

EQUIPMENT AVAILABLE FOR FABRICATION		CONSIDERATION
Autoclave	-	versatile but expensive to purchase and operate?
Press - matched tool	-	probably less expensive plant but tooling often very expensive!
Ovens - vac bag, expanding rubber	-	cheapest method, when feasible!
Tape laying	-	save labour costs where suitable!

Cost

Although the price of prepreg is important many other factors must be taken into account as some of them will have a much greater impact on the cost of the finished item. These include:-

(i) shop floor handleability and shelf life
(ii) need for removal of excess resin
(iii) type of tooling required
(iv) complexity of moulding process
(v) reproducibility
(vi) scrap and rejection rates

There are a wide range of matrix formulations available to the user to select from but these can be divided basically into two types:-

Group 1	Those curing at 170°C - 180°C
Group 2	Those curing at 120°C - 130°C

each of these can be subdivided further into low viscosity and controlled high viscosity systems.

Group 1 tend to have the higher temperature and environmental resistance whilst Group 2 offers potentially lower processing costs resulting from the lower curing temperature, the possible use of plastic tooling and the best adhesion to honeycomb.

The majority of aerospace structural and semi structural applications use Group 1 materials although there are many demanding applications which are satisfied by those from Group 2.

GROUP 1 170°C - 180°C CURING SYSTEMS

In order to illustrate the different processing characteristics of epoxy matrices within Group 1 comparison will now be made between the widely used typical low and high viscosity systems. For the comparison to be convincing reference will be made to two CIBA-GEIGY products, FIBREDUX 914 and FIBREDUX 922.

FIBREDUX 914 is representative of the controlled high viscosity matrices and also possesses a long out-time at room temperature. It has been in use in Europe for some eight years and has gained wide acceptance with special emphasis on processing ease. The viscosity characteristics are obtained by careful chemical formulation and not by advancement of the chemical reaction by heat during the prepregging operation. Thus the viscosity is accurately controlled and is a permanent feature of the product which does not change rapidly with extended shop floor out-time.

FIBREDUX 922 is typical of the family of very low viscosity, short shelf life products on which a large number of civil and military applications have been based in the U.S.A. These matrices employ as the primary resin CIBA-GEIGY MY720, and as main hardener pp' diamino-diphenylsulphone. As this composition is quite reactive, even at room temperature, all resin mixing operations, prepregging processes, shipment, storage and shop temperatures have a major effect on its handling and processing characteristics.

The mechanical properties of the two systems are not greatly dissimilar with 914 having greater strain capability and toughness and 922 having the edge in mechanical performance above 130°C.

The following table and subsequent discussion covers the differences in the two systems and in particular those concerned with processing.

Processing properties of Fibredux 914 and 922

PROPERTY	FIBREDUX 914	FIBREDUX 922
CURE CYCLE	1 hr at 170°C Post cure optional	2 hrs at 177°C No post cure
OUT TIME/TACK AT 22°C	> 2 months	< 3 weeks
MINIMUM PROCESS VISCOSITY	45 Poises	1 - 2 Poises
DIRECT BOND TO HONEYCOMB	Yes	No
ZERO BLEED POTENTIAL	Good	Difficult
MAX TEMP/MECHANICAL PROPERTIES	130-135°C	140-150°C
VAC-BAG PROCESSING	Yes	Yes

CURE CYCLE

The ability to cure for one hour in an autoclave and then post cure in ovens separately can be an advantage, depending on autoclave capacity and the need to post cure. Conversely a full cure in two hours could also be considered an advantage. However, these cure cycles are the times taken once the curing temperature has been reached. In many instances complex heat-up schedules are needed for the low viscosity systems, including a dwell step in order for the reaction to advance, thus increasing the viscosity, before applying full pressure. This can be very difficult to control with certainty if an autoclave load consists of different size parts heating up at different rates. This is confused by the reaction occurring at different speeds at all temperatures in the heat-up cycle and great care must be taken to ensure that full pressure is applied before any part of the load is gelled.

914 does not react at any significant rate for processing purposes up to 100°C and is still slow enough to permit a dwell at 120°C - 130°C if necessary to ensure consolidation and resin flow from thick section parts. Apart from this possibility 914 has the ideal "straight-up" simple cure cycle.

The total cure time difference in the autoclave can be as much as one third in favour of the simple cure cycle as illustrated in the following temperature. pressure, time charts.

OUT-TIME/TACK AT 22°C

The tack of 914 diminishes slowly at 22°C and a substantial amount remains even after two months. Although no longer tacky the prepreg has been found perfectly usable after six months ambient storage. Additionally the tack is firm but not aggressive allowing the removal of misplaced prepreg without disturbing the previously laid plies.

The tack of completely fresh 922 is good, but rather sticky due to the low cohesive strength of the uncured resin. However, it diminishes fairly rapidly at 22°C and has effectively disappeared after four weeks. During this time the ability to tack to complex curves and to themselves and to be removed is constantly changing as are the flow properties of all these 720/DDS based systems.

It is thus clear that other than for relatively simple layups the advantages for this property lay with 914. There is no need on a production line to return unused material to deep freeze at the end of work time, no defrosting on restart, no resultant condensation of water and no fears of varying flow properties on a large, long lay-up time job.

MINIMUM PROCESS VISCOSITY

914 is over a magnitude greater in minimum process viscosity than 922. At first glance this may not appear an obvious advantage - in practice it certainly is.

Generally the viscosity of 914 is high enough to avoid the need for edge damming a composite part during processing as the resin flow is sufficiently low to avoid resin starvation and consequent voiding at the edges - this saves time and money. 922 definitely needs either edge dams or extreme care during lay-up as otherwise flow can be excessive.

Additionally, the viscosity of 914 permits full pressure to be applied at the outset of the cure cycle thus permitting the "simple cycle" previously referred to. The actual viscosity of 914 is high enough throughout the cure to ensure that "hydraulic" pressure is applied to entrapped air bubbles to effectively collapse them. With 922 the viscosity is far too low for this effect and results in the need to increase the viscosity by dwelling before full pressure can be applied with the nuisance and attendant problems this can cause.

DIRECT BOND TO HONEYCOMB

The viscosity of 914 is ideal for good filleting directly onto honeycomb on both the top and bottom faces and its chemical nature permits good adhesion. 922 is far too low in viscosity for this purpose and will flow from the top face down the cell wall to the bottom.

Since the 170 - 180°C cured resin systems are more brittle than those cured at 120 -130°C it is often preferred to use an adhesive film between the prepreg and the honeycomb. This move is essential with 922 but is optional with 914 whose adhesion in tension and shear is sufficient to "fail" most honeycomb in sandwich structures.

ZERO BLEED POTENTIAL

Zero bleed or net resin content prepreg is a very important aspect of processing because of its effect on finished part cost.

Prepreg is expensive and it is clearly uneconomic to buy it with the certainty of discarding a proportion of it through intentional resin "bleed out". Additionally and even more expensive is the cost of materials and labour employed to lay-up a suitable controlled resin bleed system - all of it being ultimately waste.

Two criteria are essential for a good, practical zero bleed prepreg system.

(1) The matrix must permit the formation of a good laminate with no excessive resin squeeze out or voiding and this is most readily accomplished by using a controlled flow, high viscosity formulation for the reasons previously discussed.

(2) The prepreg itself must be handleable.

The latter is not a big problem per se with woven fabric prepreg but with unidirectional reinforcement at 32-34% resin content by weight it can be a major difficulty. This is because at these low resin contents there is insufficient resin present with some systems to hold the fibres together transversely to permit practical handling. Thus the cohesive strength of the uncured resin is important here. In this case the strength of 914 as a result of its polymer content is many times that of 922 which contains only relatively low molecular weight ingredients. Indeed 914 unidirectional zero bleed prepreg is amply strong enough to be well suited to a variety of manufacturing techniques, including automatic tape laying and gives excellent mechanical performance when so processed. Unfortunately 922 is not as amenable to this approach.

MAXIMUM USE TEMPERATURE/MECHANICAL PERFORMANCE

It is no use having outstanding processing properties if the composite parts produced will not meet the design requirements and hence no decisions on matrix type can be divorced from mechanical performance.

As the two systems under consideration have such different processing characteristics their chemistry must be significantly different and it might be supposed their mechanical properties also.

Simply stated - the chemistry of 914 gives a slightly lower Tg capability than that of 922 (approx 195°C for 914, approx 215°C for 922) but its cured morphology results in a product with 50% higher strain and at least 100% higher fracture energy.

	FIBREDUX 914	FIBREDUX 922
Fracture Energy (J/m^2)	190	82
(Compact Tension)		
Strain to Failure	3%	2%
(Cast Specimens in tension)		

The "changeover temperature" for 914 and 922 is around 131°C. At this temperature the performance of the two systems are about equal in both the resin dominated properties such as short beam shear and resin influenced properties such as compression. Above this temperature, whilst both systems are losing strength, 914 decreases more rapidly.

VAC-BAG PROCESSING

It would be ideal if parts could be made under vacuum pressure only in an oven. This could prove economically attractive as well as opening up an almost limitless production capacity as ovens are usually readily available. Recent attempts to establish suitable conditions for processing aerospace type prepregs by this technique have proved promising and indicate that this may well become a practical approach for the production of even quite complex parts in the near future.

The arguments concerning the relative merits of the 914 and 922 type matrices hold good for all handling and lay-up operations but it is likely that all vacuum-only pressure cycles will need a significant dwell period in the curing process to permit the removal of more air. This is probably because there is less pressure to "collapse" remaining air bubbles as some level of vacuum must be maintained throughout the cure cycle - as opposed to autoclave cures where it is normal to "dump" the vacuum at an early stage. Both 914 and 922 have excellent "dwell options" and hence are capable of being processed by this technique - however, once again viscosity considerations favour 914.

One possible limitation of this technique is the likelihood that a maximum fibre volume of around 55% will be achieved with fabric prepregs due to the lower consolidating pressures involved. No such limitation is likely with unidirectional prepreg and thus all comments relating to zero bleed systems still apply.

GROUP 2. 120° - 130°C CURING SYSTEMS

This discussion would not be complete without reference to the Group 2 matrix systems which are widely used in aerospace and sports goods applications ranging from those which are less demanding to others which are critical, e.g. furnishings, fishing rods, helicopter rotor blades.

Apart from potentially lower processing costs this group attracts applications which need matrices with excellent toughness, impact strength, adhesion to honeycomb and fatigue resistance. Although they do not possess the maximum environmental properties of the higher curing systems, some are eminently suitable for applications requiring operating temperatures of 90-100°C.

Many of the existing lower temperature curing prepreg systems are old formulations developed for use with glass fabric for skinning honeycomb and as such were not designed to be structural over a very wide temperature/ humidity range, although the viscosities were controlled to permit good filleting. There are others which were primaril· designed for laminating applications and these tend to exhibit the lower viscosity characteristics of 922 with the resultant disadvantages.

All the previous considerations of processing aspects under Group 1 materials still apply but because of the lower cure temperature constraint it is more difficult to find prepregs in this group which have a long out life, controlled high viscosity and significant retention of properties at higher temperatures.

However, one such product is FIBREDUX 913 which has been produced and used in Europe for some eight years. It has an out time of two months at room temperature, is suitable for both laminating and direct bonding to honeycomb and retains a reasonable proportion of its strength under hot/wet conditions. In the following graphs it is compared with other existing low cure systems of the following generic type:-

(a) typical traditional glass fabric adhesive prepreg resin systems

(b) typical current semi structural aerospace specification resin systems

RESUME

In this review which, because of the complexity of the subject, must be somewhat general the intention has been to place most emphasis on the practical aspects of the handling and processing of structural prepregs.

In comparing these aspects of two standard widely used products, which by mechanical considerations are relatively similar there is little doubt that the long out life, controlled high viscosity system is the most attractive. Such products have big advantages over their widely used but now "old-fashioned", low viscosity, short shelf life rivals. The scope for cost saving at almost all stages of processing, coupled with a lower risk of rejected parts makes them economically very attractive and the experience of practical users confirm even more strongly the benefits they confer in production.

That a move towards this type of prepreg is now under way in the U.S.A. appears to substantiate the philosophy which led to these products being actively developed and used in Europe a long time ago in terms of "modern composite history".