MECHANICAL CHARACTERISTICS OF RESIN/CARBON COMPOSITES INCORPORATING VERY HIGH PERFORMANCE FIBERS

G. HELLARD - Design Office - AEROSPATIALE TOULOUSE
J. HOGNAT and J. CUNY - Central Laboratory - AEROSPATIALE SURESNES

ICAS-84-3.1.2

Abstract

For some time now, the search after carbon fibers with higher performance has been made and begins now to beer fruit as one can find on the market very high performance fibers which can be used right away to reinforce resin/carbon composites. During the same time, the developments achieved in the field of impregnating resins has been more modest except in the case of so called "Tough" resin systems used to improve impact resistance properties most often to the detriment of other mechanical characteristics.

The intent of this paper by analyzing in depth the damage and deterioration mechanisms of those materials is to review the contribution of very high performance fibers to resin/carbon composites mechanical properties.

1 - Introduction

Organic matrix carbon composite materials are ever more widely used in aeronautical structures both on aircraft, helicopters, ballistic and tactic missiles.

Whilst retaining a high level of safety, these materials, in relation to conventional aluminum alloys, provide the following advantages :

- a higher fatigue resistance,
- a higher corrosion resistance,
- an often appreciable weight gain,
- lower maintenance requirements.

Even though the first generation materials at present qualified are proving entirely satisfactory in use, despite certain disadvantages such as :

- Hole sensitivity,
- low impact strength,
- brittleness,

for certain heavily loaded structures at present being studied, they are beginning to show their limitations at the expected weight gain.

In this case, competition with the new aluminum/lithium alloys, which are beginning to appear on the market and which give on improvement in specific performances (strength and rigidity) of about 10% over commercial alloys, is becoming fiercer and fiercer.

Parallel with this new developement of light alloys, the improvement in the organic matrix carbon composites is beginning to make itself felt, since second generation materials with improved properties are now appearing on the market. These materials use :

- very high performance fibers,
- modified resins with improved toughness,

in relation to the first generation resins, which should increase in particular the impact strength of the composites.

Using both documented results and the results of tests carried out in our own laboratories, we shall attempt to evaluate the potential of these new materials with regard to the performance of future composite structures.

We shall restrict ourselves to dealing with high strength carbon composites and organic resins curing at 180°C, and using prepregs with unidirectional continuous carbon fibers.

2 - Problems posed by prepregs

Before entering into a detailed comparison of composite materials at present in use and those of the second generation with improved performance, we felt it would be interesting to point out the problems of the prepreg, a semi-finished product associating both fiber and resin.

It would be wrong to think that the association of a "good fiber" and a "good matrix" would logically result in a "good composite".

We thus noted the following two interesting cases which should lead the manufacturers of prepegs to study very carefully the association of fiber and resin.

1st case

We noted for a same fiber associated with two resins of the same type (TGMDA/DDS) the tensile properties on the unidirectionnal composites gave strength figures of between 1500 and 2200 MPa, being a difference of more than 45% (see Fig. 1).

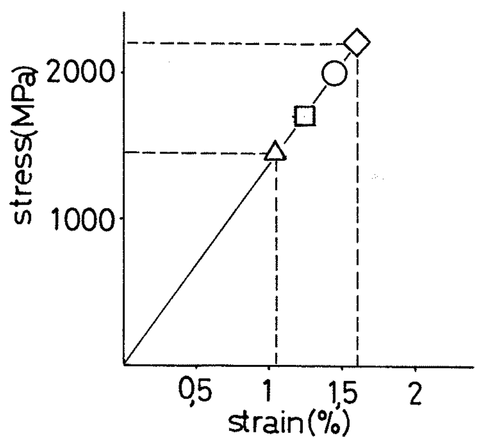

Fig. 1 : Unidirectionnal composites (same graphite fiber and same type of matrix)

2nd case

Similarly, the association of the same fiber and the same resin can result in mechanical tensile properties of between 1500 MPa and 2000 MPa, being a difference of 35%, depending on whether the fiber is unsized or sized.

In both cases, the compatibility either of the matrix with the fiber, or the matrix with the sizing, leads to composites materials where the presence of interfaces and interphases may influence the mechanical characteristics of the composites even when the latter is working more in the "fiber mode "than in the "resin mode", as is the case with tensile of unidirectional composites.

3 - States of the art composite materials

3.1 Basic products

3.1.1 Fibers (Fig. 2)

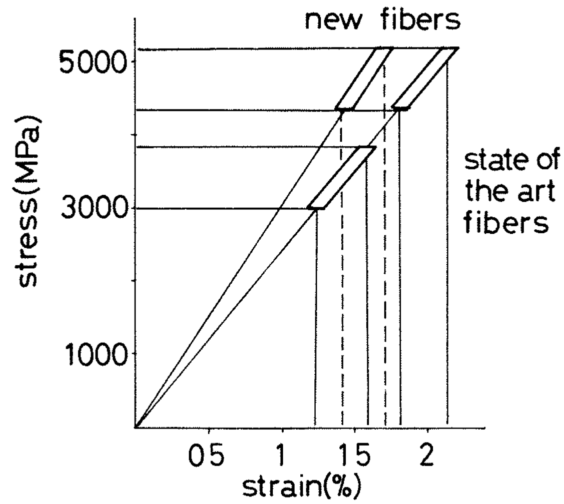

Fig. 2 : Graphite fibers tensile stress versus strain

These all have substantially the same modulus value which is around 240 000 MPa with ultimate tensile strength of between 3000 and 3500 MPa, and elongation at rupture of 1.1 to 1.4%.

3.1.2 Matrices (Fig. 3)

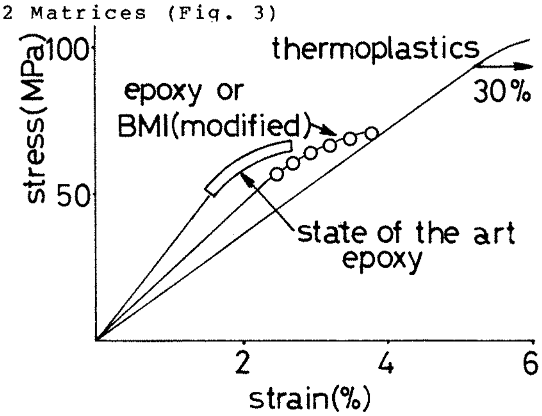

Fig. 3 : Matrix : tensile stress versus strain

In most cases, these are epoxy matrices of the TGMDA/DDS type. Their ultimate tensile strength is around 55 to 70 MPa for values of elongation at rupture of between 1.5 and 2.5%.

3.2 Mechanical properties of composites

3.2.1 Unidirectional laminates (Fig. 4)

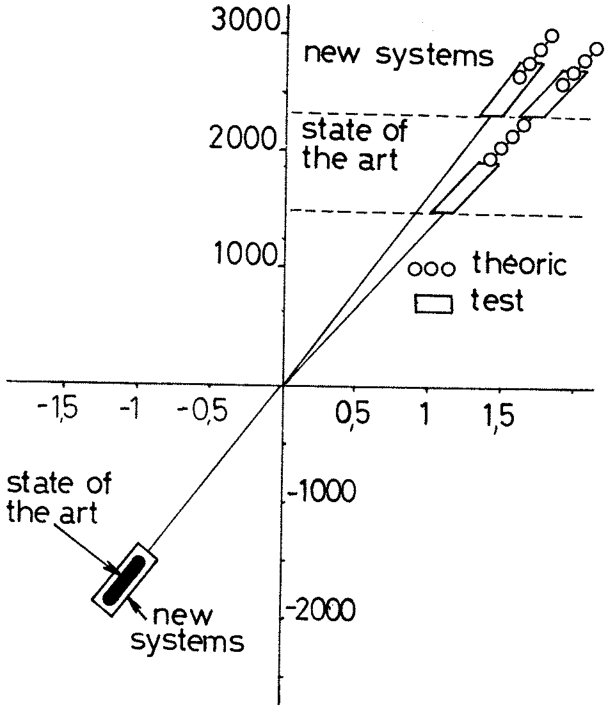

Fig. 4 : Unidirectionnal characteristics tensile and compressive tests

Along the axis of the fiber, the tensile strength varies between 1400 and 1800 MPa for elongation values at rupture of to 1.4%.

The rule of mixtures shows that these materials are not 100% efficient, since with a composite comtaining 60% volume of fibers, one could have expected between 1800 and 2300 MPa.

Under compression, the strengh varies between 1300 and 1600 MPa.

Perpendicular to the fibers, the tensile strength is much less impressive : 55 to 70 MPa, for elongation values of between 0.6 and 0.8% (Fig. 5).

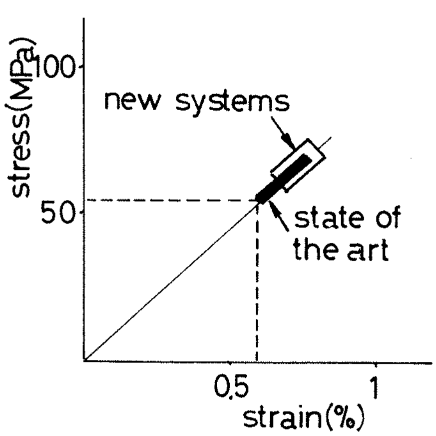

Fig. 5 : Unidirectionnal 90° tensile

3.2.2 Cross-ply laminates

a) Tension

The use of multilayer cross-ply laminates is the most case of the majority of structures. Although in this case the ultimate tensile strength values are often proportionnally the same as those of the fiber working in the direction of the stress, one must point out the fact that the poor transverse strength of this type of material leads to very early damage appearing well before the final destruction.

This damage takes the form of matrix breaks in the plies furthest out of alinement with the stress and can also, for certain stacking sequences result in delamination prejudicial to the strength of the material (Fig. 6).

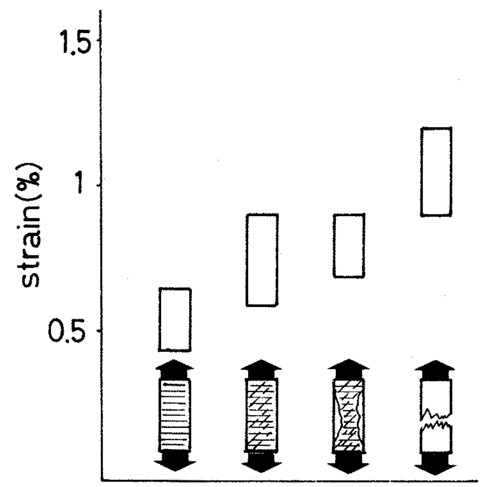

Fig. 6 : Damages before failure on cross-ply composites

b) Impact strength

The brittle nature of the TGMDA/DDS base matrices resulting from their high degree of reticulation, also leads to other problems connected with the impact strength of these composite materials.

For low-energy impacts, although there is no visible damage to the composite, there is however relatively important inter-layer delamination inside the composite, jeopardizing the structural integrity.

This is shown up by residual compression strength after impact which gives a good indication of the damage suffered by the cross-ply laminate (Fig. 7).

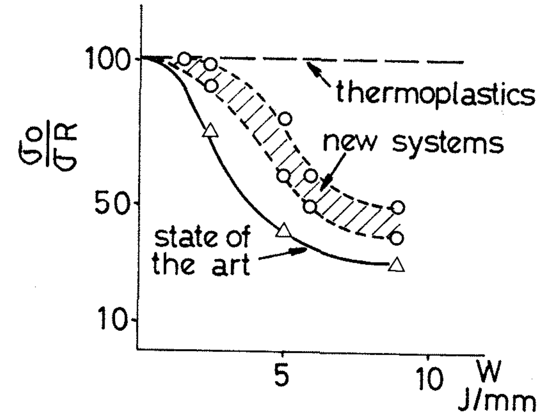

Fig. 7 : Damage tolerance : compression after impact

c) Effect of holes

Finally we should point out that this type of material which has no plastic zone prior to breaking, gives relatively high hole coefficients (dropping characteristics) under tension loading, which vary according to the diameter of the hole.

4 Future of the state of the art composites

The present generation of composite materials was introduced gradually starting with the simplest part subjected to the smallest load up to more complex structures.

In the case of the design of new more complex and more heavily loaded primary structures, at present being studied, we meet sizing problems linked to the limited properties of the materials at present used and in particular to the hole strength.

In the case of heavily loaded structures, it is necessary to use large thicknesses, and thus considerable attachment part diameters thus resulting in heavily penalizing hole coefficients.

A weight balance using these first generation materials shows a gain of about 10% in relation to conventional light alloys and none in relation to the new aluminum/lithium alloys.

In this case, the use of composite structures will only be advantageous if there is :

- a change in design, at the expense of very high production costs,
- a change in material, and in this case we have reason for holding out great hopes in the new preimpregnated materials to appear on the market.

5 - The new generation of composite materials

5.1 The new fibers (Fig. 2)

The market now offers on a large scale carbon fibers with a strength of between 4400 and 5000 MPa for elongation figures of between 1.4 and 1.7% or 1.7 and 2%, depending on the type of fiber, which gives us an improvement of around 30% over the first generation of fibers.

5.2 New generation matrices (Fig. 3)

There are three types :

- modified epoxies,
- modified bimaleimides,
- thermoplastics.

These various matrices were chiefly created with the aim of improving the impact strength of the matrices presently used while retaining their thermal properties as much as possible.

Generally, the modulus of the new thermosetting resins is slightly lower, with slightly improved ultimate tensile strength and elongation at rupture, in relation to the first generation of resins.

The elongation at rupture of the matrix, which is one of the important factors in the matrix when attempting to improve the impact strength, increases from 2 to 4%, but these elongations are still far from those of high performance thermoplastic matrices which have elongations of around 7% in the elastic zone and up to more than 30% at rupture, whilst their tensile strength and modulus is the same as for thermosetting resins.

5.3 Mechanical properties of the new fibers with first generation matrices

The basic questions to be asked when creating improved performance composites are the following :

- Can one use new fibers in conjunction with first generation matrices ?
- Must new fibers be associated with new generation resins ?

With regard to the tension tests carried out on unidirectional composites made from high performance fibers and first generation resins, the results show that the increase in the characteristics is not proportionate to the increase in the characteristics of the fiber, the efficiency in relation to the law of mixtures only being 70%, chiefly due to limite of the load transfer in a brittle resin with low values of elongation at rupture.

As regards the other properties listed in chapter 3 for the state of the art materials, it seems likely that all the properties of the resin will not be improved, that is :

- Crosswise tension at the same level of stress,
- Damage prior to breakage which would occur at the same instants,
- Identical impact strength in particular for low-energy impacts only causing delamination in the composites.

The only positive point would be an ultimate strength slightly improved, with hole coefficients in the same order as for the composite materials at present in use.

In order to obtain optimum efficiency from these new fibers, it is therefore necessary to associate them with matrices more suited to transferring the loads than those of the first generation.

5.4 Mechanical properties of new fiber and new generation resin composites

5.4.1 Unidirectional materials

a) Tension

Along the axis of the fiber, the tensile strength varies according to the type of fiber, between 2200 and 2700 MPa for elongation values of 1.3 to 1.6 or 1.5 to 1.9.

The use of new resins shows an increase in the fiber/matrix efficiency in relation to the first generation resins, without howerer achieving the optimum : the law of mixtures would imply breaking stresses of between 2600 and 3000 MPa for this type of fiber (Fig. 4).

b) Compression

For compression, the properties do not seem improved in relation to those obtained with lower performance fibers.

Two hypotheses may be put forward for the low compressive strength of new generation composites :

- use of less rigid resins,
- decrease in the diameter of the new fibers (5 micron filament instead of 7 to 8 microns), which may cause buckling earlier on (Fig. 4).

c) Perpendicular tension

Perpendicular to the fibers, despite the use of less brittle resins, the tensile strength is not improved to any significant extent (60 to 75 MPa for elongation values of 0.6 to 0.8%) (Fig. 5).

5.4.2 Cross-ply laminates

a) Tension

When compared against the tensile properties obtained with unidirectional materials, those achieved by cross-ply laminates are retained, and the ultimate tensile strength is improved by more than 50%. The same is observed with punctured cross-ply laminates (Fig. 8).

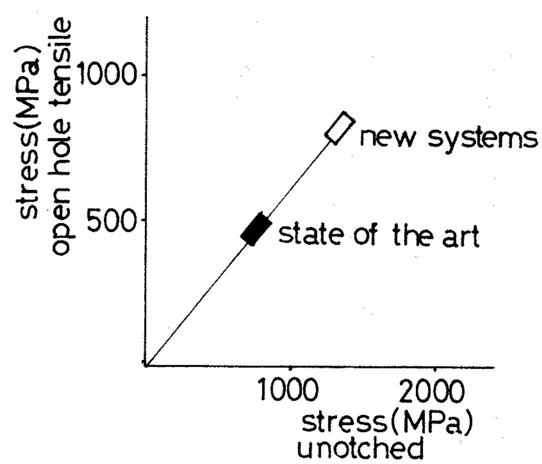

Fig. 8 : Cross-ply layers (43%-43%-14%) unotched tensile versus open hole tensile Ø 5 mm

It should be noted that, though the ultimate tensile strength is improved in relation to first generation materials, due to fiber quality, the problem of damage before break still remains.

- Thus, for a material (with alternate plies laid out in a (± 30°$_2$90-$\overline{90}$)$_s$ sensitive to edge effects (delamination), subjected to a tensile load, delaminations appears for the same stress as in the first generation materials, even though the ultimate tensile strength is improved by more than 50% (Fig. 9).

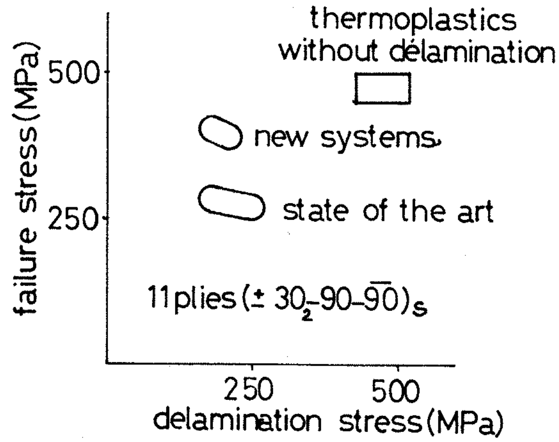

Fig. 9 : "Free edge delamination" tensile stress failure versus tensile stress delamination

The same phenomenon can be observed on a material with isotropic lay up (0, ± 45-90)$_s$, also prone to delamination (Fig. 10).

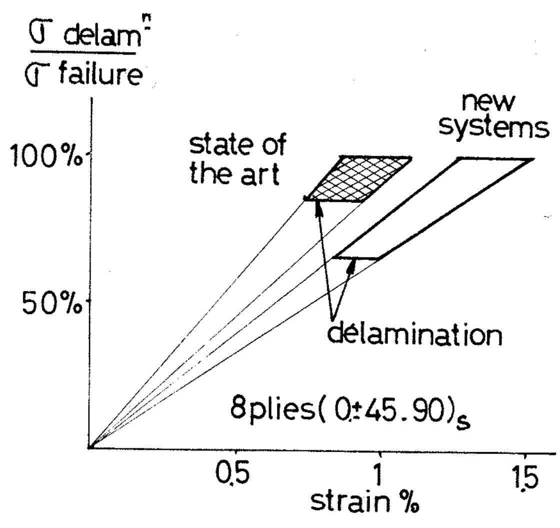

Fig. 10 : "Edge delamination" strain versus $\frac{\text{stress}}{\text{stress failure}}$

Finally, an examination of the damage undergone by the above mentioned punctured cross-ply laminates after rupture in tension reveals numerous matrix cracks throughout the material, whereas only the rupture area was affected in older materials. In both cases, the areas far from the holes are stressed to 50% of their capacity.

These three concrete examples show that the appearance of damage in relation to rupture is lower in the new generation materials, as compared to the older generation composites. This leads us to ask the following question :

- will it then be possible to subject these materials to the same ratio F/R of fatigue stress as was previously done, without incurring irreversible composite damage likely to impair the strength of the structures ?

It seems almost certain that, in the future, the structures will somehow be oversized, in order to avoid the consequences of these phenomena and then the expected gain, if only the tensile strength is considered, will be partly lost in these safety margins.

b) Impact strength

The improved properties of the new generation resins (ultimate elongation greater than for the state of the art resins) do not seem sufficient to significantly improve the resistance to low-energy impacts which only provoke composite delamination.

Only the high performance thermoplastic resins are likely to meet this requirement and solve the impact strength problem (Fig. 7).

CONCLUSIONS

Composite carbon-resin materials with improved properties are necessary for heavily loaded structures.

The new generation fibers are now produced on an industrial scale and they are endowed with interesting mechanical properties.

These fibers must be associated with new generation high adhesiveness matrices, so as to simultaneously :

- solve the problems linked with maximum mechanical efficiency,

- improve damage tolerance, and in particular impact strength.

The results obtained so far show that the improvements in the resin properties are not yet commensurate with those introduced in the fibers and therefore many damage resistance problems are still to be solved. These shall negatively affect the dimensioning of the structures.

Today, only the high performance thermoplastic matrices can help in solving this problem. These matrices, however, require that detailed studies be conducted concerning :

- their properties, as compared with those normally obtained with thermosetting resins,

- their utilization, which is likely to reduce manufacturing times and costs but introduces other problems (new technologies have to be developed, the type of structural parts which can be manufactured must be defined, problems relating to ply layout have to be solved, etc...).

The improvement of the thermosetting materials mechanical properties, which has already been initiated must be continued, the target being the properties of the thermoplastics.

In this way, the composites would be endowed with unequalled tensile properties, but the use of ever finer fibers and ever more flexible matrices seems incompatible with good compressive strength.

Thus some tradeoff will have to be achieved. But, may be, we are evolving towards two different materials, one with high tensile strength and another with high compressive strength.