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THE EFFECTS OF MATRICES FORMULATION ON MECHANICAL PROPERTIES OF  
EPOXY GLASSFIBER PREPREGS

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TITLE : " The Effects of Matrices Formulation on Mechanical Properties of Epoxy Glassfiber Prepregs ".

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ABSTRACT : The correlation between chemical composition of epoxy matrices and mechanical behaviour of prepregs is discussed in this paper.

The chemical composition is evaluated through instrumented analysis techniques which are described, such as :

Infrared Spectrophotometry (IR) as first screening of the matrices

High Pressure Liquid Chromatography, for determination of ingredients in the formulation in a quantitative way.

Differential Thermal Analysis: to define the thermal properties.

The mechanical properties are determined through static and dynamic tests carried out under different experimental conditions.

This paper shows the results obtained on 4 glassfiber prepregs. Two of them, having similar chemical composition, give comparable results, whereas the third and the fourth ones present significant differences in terms of fatigue, high temperature behaviour and failure mode because of their different matrix compositions.

## 1. INTRODUCTION

The application of composite materials for high performance components and for primary aircraft structures requires deep investigations for the evaluation of their properties, which depend on chemical and physical characteristics. While the behaviour of the fibres is well clear, the influence of chemical composition of the formulations on the mechanical performances of the materials was so far not sufficiently investigated.

With the aim of correlating the chemistry of the resins to the mechanical properties, four epoxy matrices impregnating three types of glassfibres ( namely E, R, S<sub>2</sub> glass ) have been studied and in this paper the results are reported.

After a first screening of commercially available materials these prepregs were chosen, because they exhibited very interesting matter of investigation. The selected resin systems are 125°C curing epoxies and conform to MIL-R-9300 . In the following sections the results of mechanical tests are presented, which are aimed at putting into evidence the matrix behaviour, such as high temperature (82°C) tensile static tests and fatigue tests on + 45° fibre orientation laminates. The results of the tests confirm the validity of this approach.

## 2. EXPERIMENTAL METHODS

### 2.1 Chemical Investigation

The usefulness of chemical investigations for the characterization as well as for quality assurance procedures of epoxy based composites is known; these analysis are carried out through instrumented techniques both for separating and identifying the chemical composition of the matrices and for defining the most suitable cure cycle.

Carpenter (1) had defined a generalized approach to the separation, identification and characterization of non-metallic materials, which still can be adopted. Described here below are three techniques used in Agusta .

### INFRARED SPECTROPHOTOMETRY (IR)

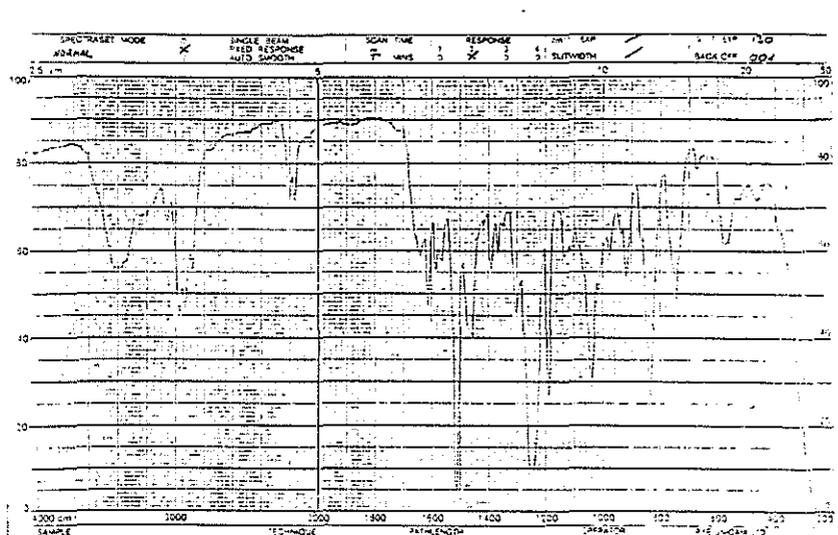


Fig. 1 Typical IR Spectrum

This technique is highly useful for the rapid identification of polymeric matrices, because each functional group of the molecules absorbs infrared energy at characteristic wavelengths, which give the so called "fingerprints" of the analyzed materials.

A typical IR Spectrum is shown in Fig.1. The wavenumbers of interest are tabulated in Tab.1. The samples preparation has been described in a previous paper (2)

Tab. 1 Wavenumbers of interest in IR

GROUPS	NAME	INGREDIENT	WAVENUMBER (cm <sup>-1</sup> )
N-H	Ammine	Accelerator	3400-3200
O-H	Alcohol	Epoxy chain	3600-3200
C-H	Aromatic	" "	3030
C-H	Aliphatic	" "	2850
C≡N	Nitrile	Catalyst	2200
C=C	Phenil	Epoxy Chain	1610
C-O-C	Epoxide	" "	1300-1200
S=O	Sulphate	Catalyst	1100

#### HIGH PRESSURE LIQUID CHROMATIGRAPHY (HPLC)

HPLC is the most powerful and versatile tool in the separation identification and quantitative evaluation of the components present in the resin mixtures. Separation is based on polar intermolecular interactions between the stationary phase less polar and the more polar mobile

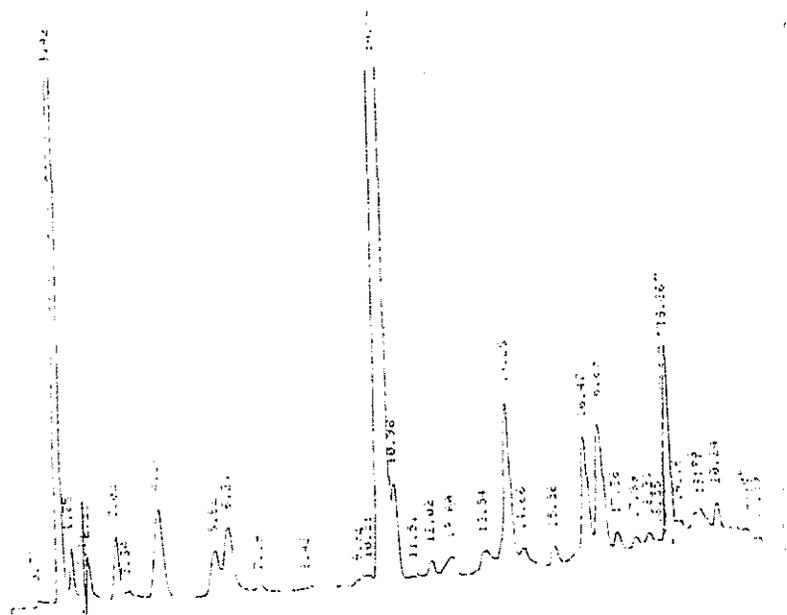


Fig.2 Typical liquid chromatogram

liquid phase and it occurs due to different partition of the molecules between the two phases. In this way particles of high polarity are eluted by the polar mobile phase, those of low polarity are retained in the non polar solid phase. This is called reverse phase partition chromatography, because through gradient elution a high degree of separation is provided. A typical liquid chromatogram of one of the investigated resins is shown in Fig. 2.

A Pye Unicam LC3 equipped with a gradient elution system and with a variable wavelength UV absorbance detector was employed. The column was a  $\mu$ Bondapak C<sub>18</sub> ( Waters Ass. Trademark ), the integrator for peaks integration and data formatting was HP 3388 A. The adopted experimental conditions are a suitable modification of the Dark's method (3) An amount of prepreg is dissolved with a suitable solvent in order to obtain a known concentration solution (1mg/ml). The analysis conditions are given in Tab. 2

Tab.2 Analysis conditions for HPLC

Injecte quantity	10 $\mu$ l
Mobile phase	linear gradient of water and acetonitrile (ACN)
	Time 0 = 60% H <sub>2</sub> O/40% ACN
	Time 15 min = 100 % ACN
Wavelength	230 nm

DIFFERENTIAL THERMAL ANALYSIS ( DTA )

DTA is effective for determining the thermal effect ( $\Delta H$ ) associated to the curing process, the phenomenologic kinetics of the polymerization, the Glass Transition Temperature ( $T_g$ ) of the resin mixture.

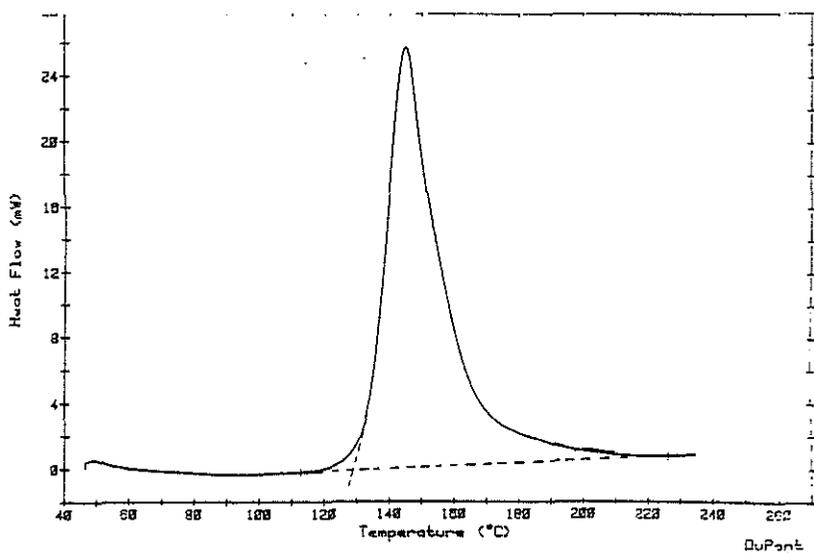


Fig.3 Typical exothermic peak ( polymerization)

Determinations relevant to the present work have been carried out on a Du Pont Thermoanalyzer using the following heating rates: 10°C/min with 0.2. °/inch  $\Delta T$  sensitivity for  $\Delta H$  measurement and 2°C/min with 0.2° /inch  $\Delta T$  sensitivity for  $T_g$ . A typical exothermic peak accompanying the polymerization reaction is shown in Fig.3

In Fig. 4 a  $T_g$  curve obtained by DTA scanning is reported. The sample was coming from the laminate used for the mechanical test and mentioned below as material A.

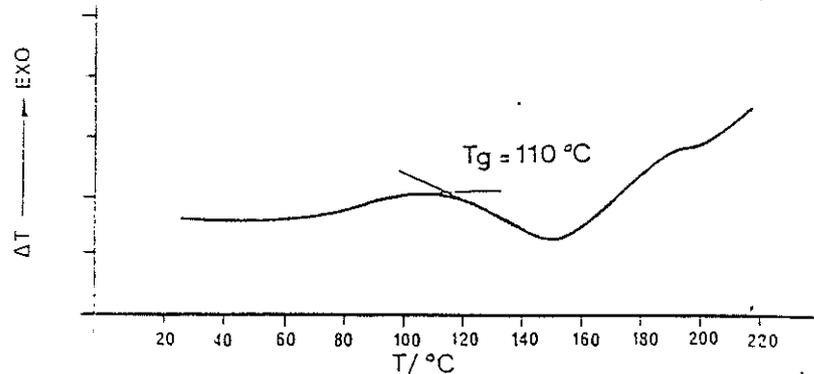


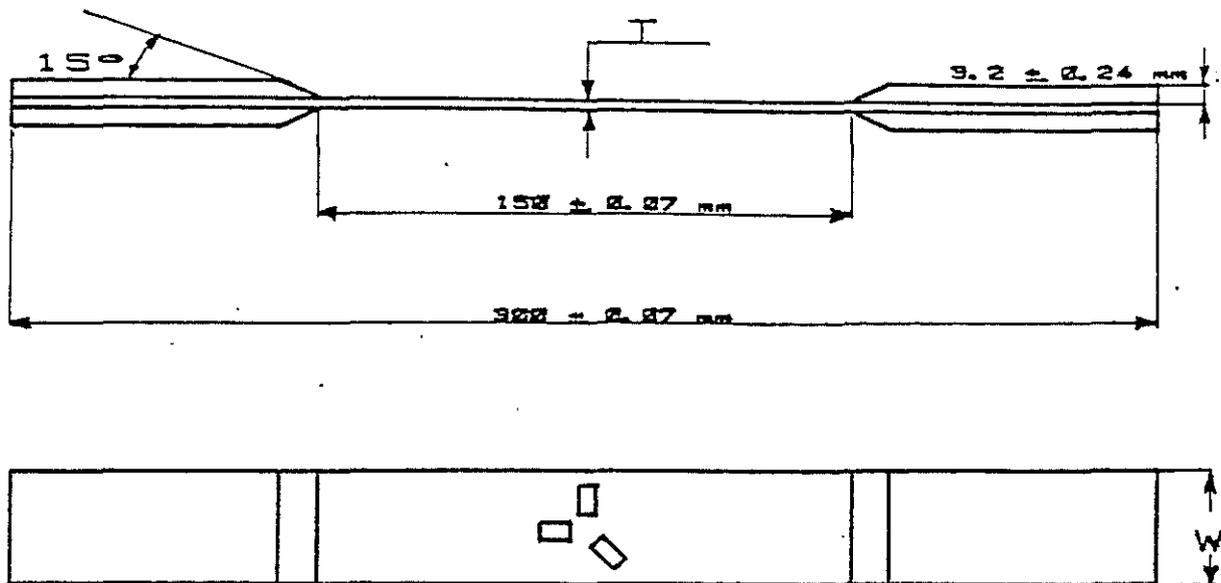
Fig.4 Typical  $T_g$  curve ( Mat.A laminate sample)

## 2.2 Mechanical tests

Static tensile tests were performed on parallel edge laminate specimens having 3 different fibre orientations ( namely 0°, 90°, 45° ) to measure the basic tensile material properties. The specimens and their dimentions are also shown in detail on Fig.5. The specimens were cut from laminates obtained from the various prepregs after curing either in autoclave or under press with curing conditions typical for such materials ( optimization of cure cycles recommended by manufacturers . Physical properties were within the specification limits (Fig.5). The specimens were instrumented with strain-gauges to allow elastic constants measurements (2).

Fatigue test specimens had the same shape and physical properties of static specimens. Two different lay-ups were tested in fatigue (namely 0° and + 45° fiber orientations) as detailed in fig 5. Specimens for fatigue tests were not instrumented.

Static tests were performed on an Instron testing machine at constant crosshead speed of 0.5 mm/min. For elevated temperature static tests a climatic chamber was used, set at 82°C and automatically controlled with 1.5°C of accuracy. Specimens before load application were conditioned at the prescribed temperature for at least 30 min. Load and signals from three strain-gauges were recorded



RESIN CONTENT: 33±2% By weight;Max void content 3%			
FIBRE ORIENTATION	N° OF PLYS	WIDTH mm	THICKNESS mm
0° (Static and fatigue)	7	12.7±0.24	1.2±0.24
90°(Only static)	14	25.4±0.24	3.0±0.24
45°(Only static)	14	25.4±0.24	3.0±0.24
± 45° (Only fatigue)	14	25.4±0.24	3.0±0.24

Fig.5 Specimens geometry and physical properties

Fatigue specimens were tested on servohydraulic machines in load control, until complete failure. Load waveform was synusoidal with 0.1 ratio (R) between minimum and maximum. Frequency was 6 cycles per sec. Several loads were tested to obatin S-N curves.

## 2. TEST RESULTS

The IR analysis showed that all the resin mixture, that in the following are conventionally called Mat. A, Mat.B, Mat.C, Mat.D, are Dicyandiamide (Dicy) catalized and no form of Bromine reacted is present within the structure. The data determined through DTA are collected in Tab.3 were  $\alpha_0$ , is the degree of matrix B-staging.

Tab.3 DTA Analysis results

MATERIAL	$\Delta H(0) \text{ Jg}^{-1}$	$\alpha_0$	$T_g \text{ } ^\circ\text{C}$
A	120	0	110
B	242	n.a.	107
C	270	0	120
D	230	0.13	105

The phenomenologic kinetics have been obtained by means of an iterative procedure (4); a kinetic order one was calculated for all the materials..

These data provide useful information and they can be correlated to mechanical properties described below. In general no significant differences were observed among the materials, whose thermal properties look very comparable.

The results of HPLC determination are summarized in Tab.4. Beyond the Dicy, whose presence in all the materials has been qualitatively disclosed through IR, other common ingredients are DGEBA (Diglycidylether of Bisphenol A) liquid with  $n=0.2$  and DGEBA solid with  $n=1$  or higher.

Tab. 4 HPLC Analysis results (quantities in %)

COMPONENTS	MAT A	MAT B	MAT C	MAT D
DICY	4	7	6	5
MONURON	-	4	-	3
DIURON	3	-	3	-
DGEBA liq	16	42	20	66
DGEBA sol	11	-	14	15
TGMDA MY720	8	-	57	-
NOVOLAC	58	47	-	-
ELASTOMER	-	-	-	11

Although they come from different suppliers i.e. in mat A DGEBA liq is DER 331 ( Dow Trademark ) and in B mat. DGEBA liq. is EPON 828 ( Shell trademark ), they exhibit very close performances.

Following these considerations the chemical composition of mat A and B look very similar, both DGEBA derivated and Novolacs are combined; in material C the presence of MY 720 ( CIBA Trademark) is significant because it is a tetrafunctional epoxy monomer very reactive, which leads to stiff and brittle structures; prepreg D is peculiar , because in its formulation there are only DGEBA derivatives plus an elastomeric componenet. The elastomer has been titrated by wet analysis , because it is insoluble in the solvents used for the mobile phase.

The results of static tensile tests carried out at room temperature and at elevated temperature are summarized in Tab.5, where initial tangent values of elastic constants and ultimate strength values are reported for the materials investigated in this work. The values are averages obtained from 10 tests.

Tab.5 Static tests results (all figures in MPa)

	Mat.A+S <sub>2</sub> Glass system		Mat.B+S <sub>2</sub> Glass system		Mat.C+R Glass system		Mat.D+R Glass system	
	RT	82°C	RT	82°C	RT	82°C	RT	82°C
E <sub>xx</sub>	46000	44700	44100	46500	46700	47600	42500	37600
E <sub>yy</sub>	13500	9700	14200	10200	15500	10800	13400	8800
G	5200	4100	5700	4100	5700	4100	5400	2800
ν <sub>xy</sub>	0.27	0.28	0.27	0.3	0.29	0.3	0.26	0.3
σ <sub>0</sub>	1580	1360	1400	1320	1200	1300	1300	1000
σ <sub>90</sub>	42	34	46	29	64	44	51	18
σ <sub>45</sub> <sup>*</sup>	70	53	75	49	90	53	90	24

The average stress/strain diagrams for every set of tests are shown on Fig.6 (room temperature tests) and on fig 7 (elevated temperature tests ).Although such diagrams do not always cover the whole test (mainly because of strain gauge bonding failure)up to complete failure, they are quite meaningful in outlining the typical behaviour of the four investigated materials.

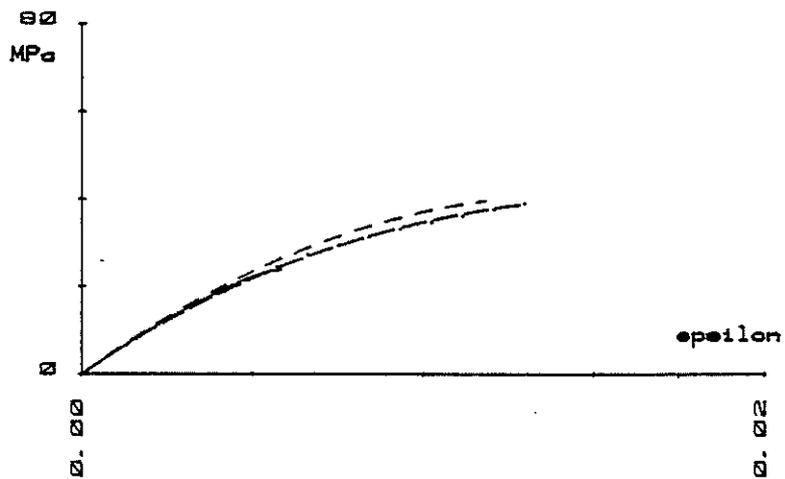
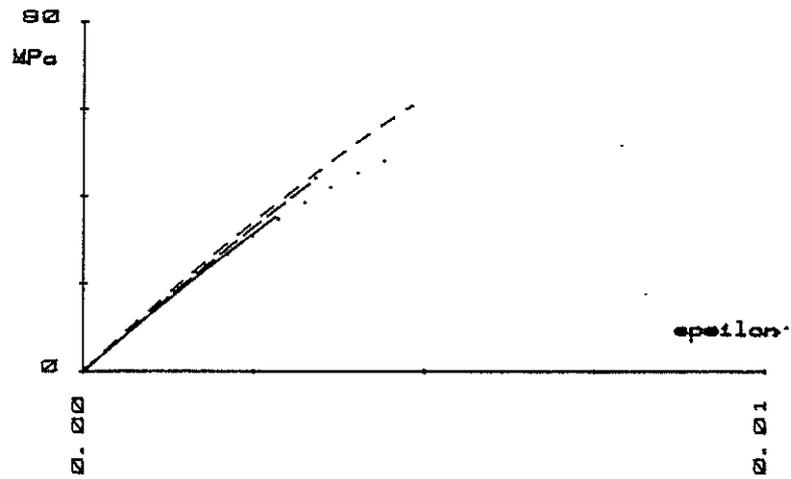
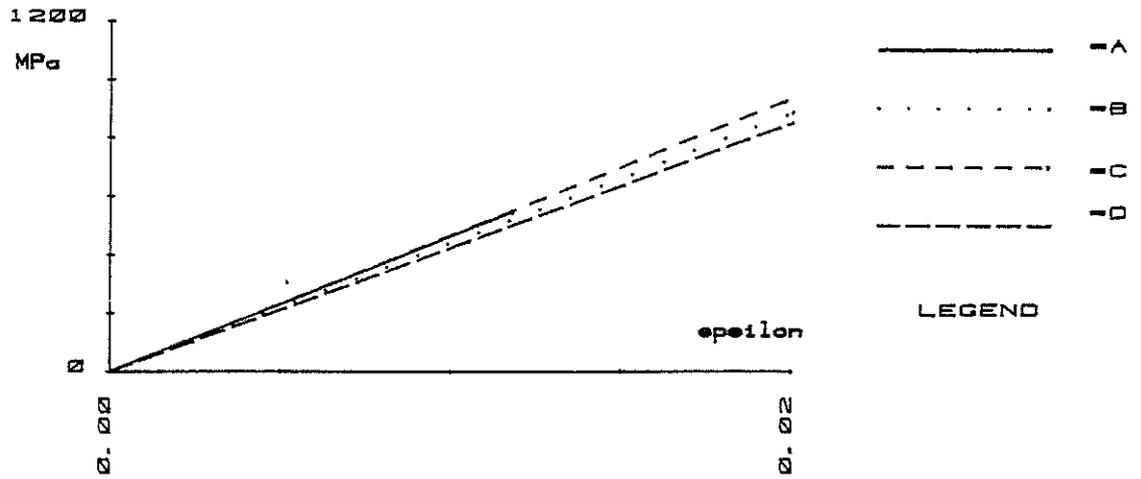


Fig.6 Tensile stress/strain curves ( $0^\circ$  and  $90^\circ$  spcm) and shear stress/shear strain curve for bias  $45^\circ$  spcm at room temperature (Average curves)

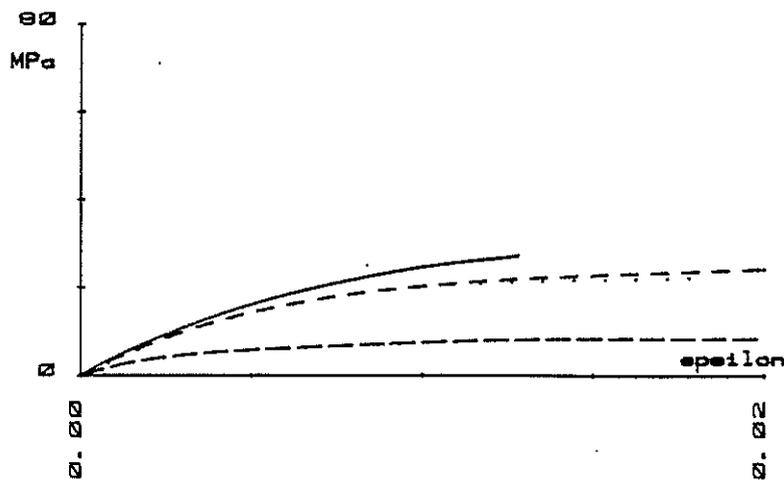
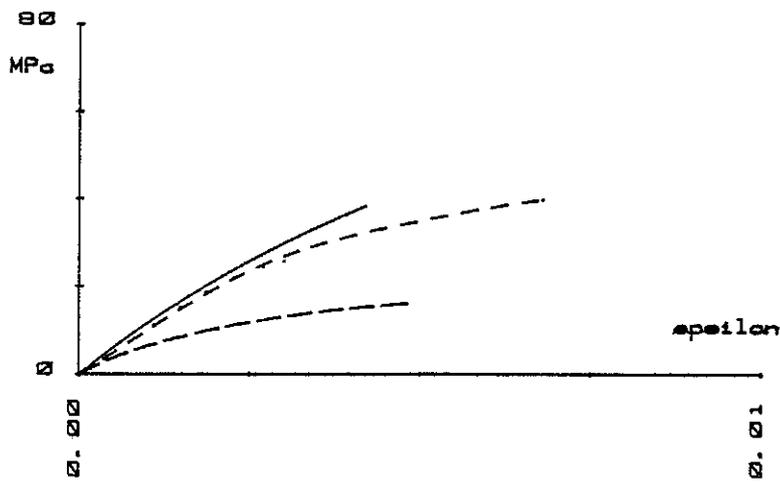
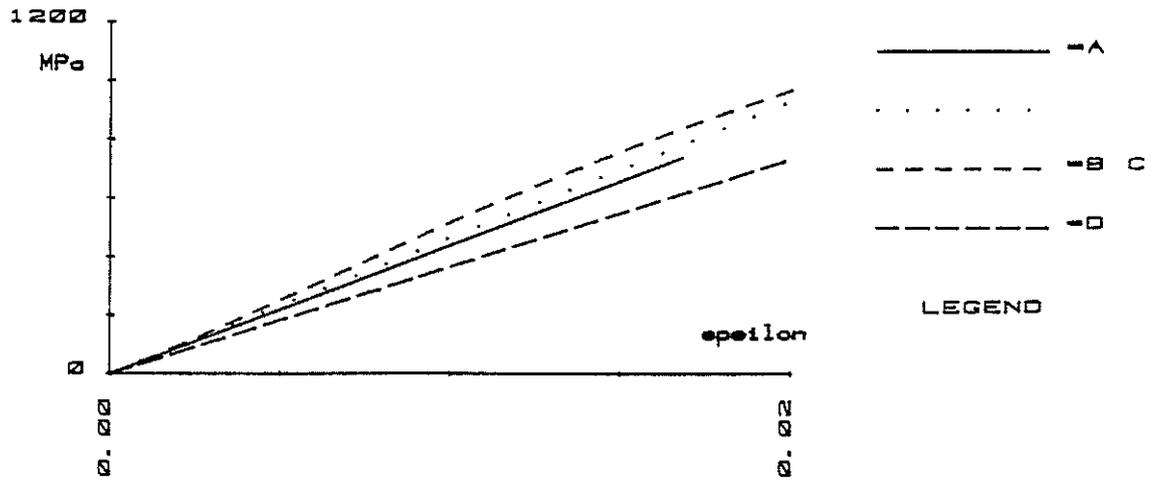


Fig.7 Tensile stress/strain curves ( 0° and 90° spcm) and shear stress/shear strain curve for 45° bias spcm at elevated (82°C) temperature. (Average curves)

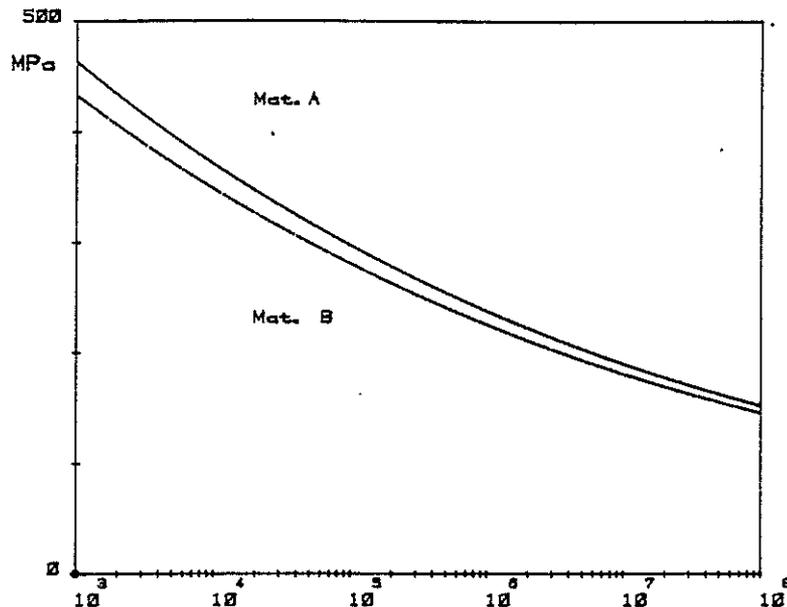


Fig.8 Mat. A Resin/S<sub>2</sub>Glassfibre,mat.D Resin/R Glassfibre  
Fatigue tests results : S-N curves of 0° spcm

The results of fatigue tests, run on 0 specimens of Mat.A resin/S<sub>2</sub>Glassfibres and Mat.D Resin/R Glassfibres are shown on fig.8. The S-N<sup>2</sup> curves of these two materials are very close, because in this direction of loading the behaviour is fibre dominated.

For a better understanding of the resin behaviour in fatigue, tests on +45° specimens with the same kind of fibres (E-Glass) were performed. Fig.9 shows S-N curves of Mat. A and Mat.B resin E-Glass composites, which behaved in a very similar way.

On Fig.10 S-N curve of material D resin E-Glass composite is reported. The different fatigue behaviour of D-Resin composite compared to the other two is evident from the high scatter of results.

### 3. DISCUSSION

Static performances at room temperature of all investigated materials can be considered close one to the other, because test conditions were not particularly selective. Two main comments can be formulated. First: matrix dominated properties of Mat.A and B are reduced in comparison to Mat.C and D. This is consistent with the chemical composition of the resins of such preregs, which are quite similar, though a full explanation of the difference in ultimate values should require further investigation. Second: fibre dominated properties of mat.C are lower than expected. Considering the failure mode of the four materials, an explanation to the latter remark can be hypothesized. Fig.11/a, 11/b, 11/d are S.E.M. fractographies of Mat.A, B, D failures when loaded perpendicularly to the fibers. They indicated a good adhesion between fibres and resin, whereas Fig. 11/c shows bare fibres, which means poor linkage at the interface on Mat.C.

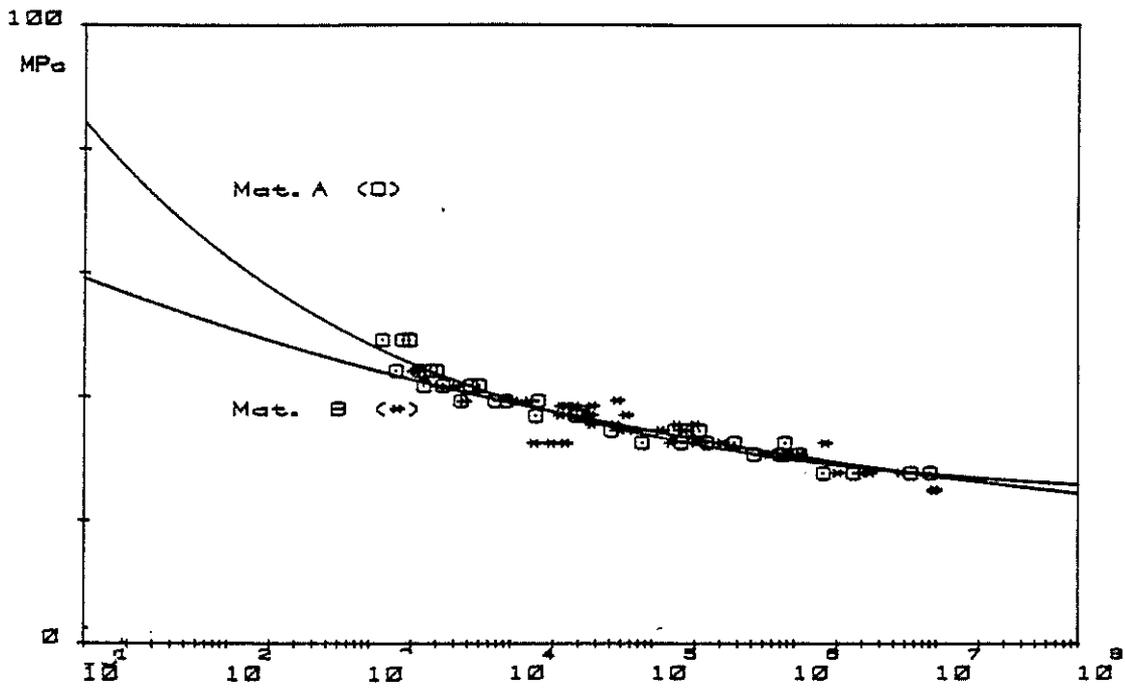


Fig.9 Mat.A and Mat.B resin/EGlass (+45°)  
Fatigue tests results: S-N curves

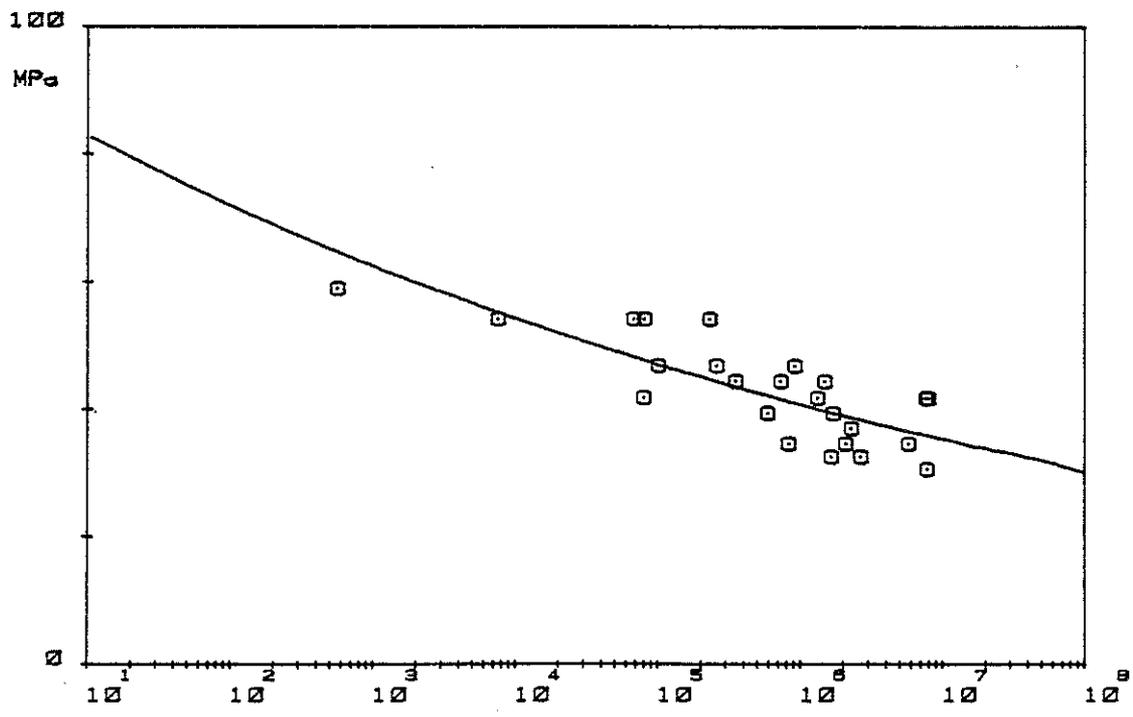


Fig.10 Mat.D resin/EGlassfibre (+45°)  
Fatigue tests résultats:S-N curve



Fig. 11/a



Fig. 11/b



Fig. 11/c



Fig. 11/d

Fig. 11 S.E.M. fractographies of failed 90° specimens.  
Fig. 11/a/b/c/d show Mat. A, B, C, D respectively

Looking at the chemical composition of the matrices we try to explain this phenomenon saying that the high degree of reactivity, also confirmed by DTA, of Mat. C due to the presence of MY 720 monomer leads to a stiff and brittle resin which hardly can accommodate the deformation of the fibres and allow load to be transferred from fibre to fibre.

High temperature static tests evidenced a substantially poor performance of Mat.D both in terms of stiffness and strength in the resin dominated properties. The presence of the elastomer within the resin is known to affect the elastic properties and to reduce the temperature application of the material; this effect is most evident if we look at fig. 7 for the properties dominated by the resin.

Another consideration concerns the presence in Mat.D only of monomer and oligomer having DGEBA structures. The epoxy rings in this case are placed at each end of the chains, which gives a decrease of crosslinking density, whereas monomers present in Mat. A and Mat.B, namely Novolacs, and that present in C material (MY 720) determine their good behaviour in elevated temperature conditions, having a higher degree of epoxy groups.

The similarity in behaviour of Mat.A and Mat.B in fatigue on  $+45^{\circ}$  specimens basically complies with the static properties. Mat.D peculiar behaviour in fatigue, characterized by an elevated scattering of results, can be substantially explained as a consequence of the poor temperature performance already mentioned, in conjunction with the highly dissipative effect of the elastomer during repeated cycling at 6 Hz, leading to local heat generation and increase in temperature. Fatigue tests at high stresses were therefore particularly affected and results scattering is to be attributed to the enhanced influence of uncontrolled experimental conditions (test stops, laboratory temperature) due to the above outlined phenomena.

#### 4. CONCLUSION

The results of mechanical tests presented here were interpreted according to the chemical analysis. They allowed to recognize three degrees of behaviour:

-Prepregs A and B exhibit good mechanical performances in agreement with the chemical formulation of their matrices.

-Prepreg C shows good values of stiffness and strength but the matrix was found inherently brittle, due to the presence of the tetra-functional monomer, and the consequence can be observed in the failure modes.

-Prepreg D is very much penalized in its mechanical properties: the chemical composition of the mixture can explain the anomalous in fatigue, characterized by a high scatter of data and the properties drop at elevated temperature.

The validity of the composite material characterization through several different types of tests, as shown in this paper, is confirmed by the fact that none of the applied techniques or test methods can alone evidence all the peculiarities of a material.

Particularly for the application on critical structural and dynamic parts in helicopters we think that the deeper material knowledge allowed by chemical and mechanical tests is important.

## 5. REFERENCES

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