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"TORAYCA" T1000 ULTRA HIGH STRENGTH FIBRE AND ITS COMPOSITE PROPERTIES

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SUMMARY

High strength and intermediate modulus carbon fibre "Torayca" T1000 was developed. Tensile strength of the fibre measured with resin impregnated strand specimen was higher than 7GPa, tensile modulus of elasticity was 294GPa, and ultimate strain at failure was 2.4%. High tensile strength of the fibre was well reflected to strength of T1000 composite. When combined with adequate resins, 3.5 to 3.8GPa of composite tensile strength and more than 2% of strain at failure were achieved. Engineering technologies of this high strength fibre manufacture were applied to high modulus grade fibres of 390 and 450GPa modulus and as a result "Torayca" M40J and M46J were developed.

INTRODUCTION

High specific strength and modulus of elasticity are unique characteristics of CFRP, and therefore, it has been replacing metals to some extent for the application where reduced weight is required. Since tensile properties of a reinforcing fibre dominate those of the composite materials, increase of strength and modulus of carbon fibre is fundamental to improve the performance of composites. Since 1971, Toray Industries has developed the carbon fibres of versatile tensile properties, and those are shown in Figure 1.

In 1984, intermediate modulus and high strength fibre "Torayca" T800H was added to the family of the products, and research works to obtain more higher strength fibre have been continued. A challenging target of the strength was set up to higher than 7GPa, and modulus was focused on so-called intermediate modulus of 300GPa. The fibre which met this target was successfully developed and it was named T1000, "Million Fiber" from its strength level of one million

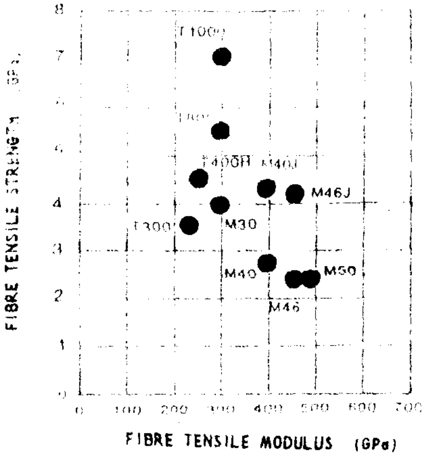

Figure 1 "Torayca" carbon fibres

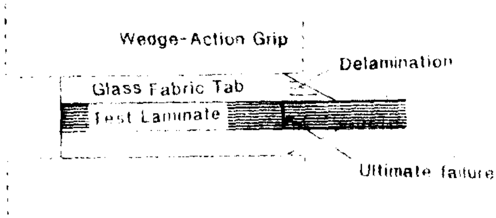

Figure 2 Location of failure at tensile test of T1000 composite

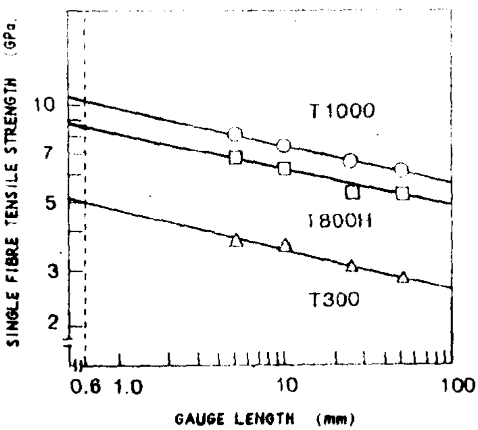

Figure 3 Tensile strength measured with single filament specimen

psi (pound per square inch).

Combination of engineering technologies to manufacture the high srtength fibre and high modulus fibre could provide new area of higher strength and higher modulus fibre. This concept was demonstrated by introducing M40J and M46J having substantively higher strength than the existing high modulus grade fibre M40 and M46.

EXPERIMENTAL

Carbon fibre

For this study, "Torayca" T800H and T300 were used as baseline materials for T1000, and M40 and M46 for M40J and M46J respectively. All those are carbon fibres manufactured by Toray. Fibre tensile properties were evaluated with single filament specimen and resin impregnated strand specimen. The single filament strength was measured with gauge length of 5 to 50mm and strain rate of 4% per minute in accordance with ASTM D3379-82. The resin impregnated strand properties were measured as specified in ASTM D4018-81 Method II. Impregnating resin was "Bakelite" ERL4221-BF,MEA, which was recommended in the ASTM, and curing conditions were 130°C for 35minutes.

Composite

T1000 composites were prepared by combining with five different epoxy resin systems of 180°C cure type. Properties of the resins are shown in Table 1. The resin systems of #3601, #3630 and RX850 were limited to investigate the effect of resin properties on 0° tensile strength of composites.

For M40J and M46J, 120°C cure type epoxy resin coded #2500 was used.

Fibres were impregnated with resins to form unidirectional prepreg tapes. Prepregs were cut and laid up to meet required size and thickness for each testing items, then cured in an autoclave to obtain laminated panels. Preparation of test specimens and testings were carried out in accordance with the test method specified by Boeing C.A.C.(1).

Modification of 0° tensile testing method

Initially tensile testing of T1000 composites was performed by using a conventional wedge-action type grip by the method cited in Reference 1. The resulting tensile strength, however, was not so good as expected from fibre strength of T1000. In this testing, delamination between glass fabric layers in tabs occurred, and failure of CFRP laminate followed within tabbed section as shown in Figure 2. These phenomena were not encountered in case of T300 and rarely observed in case of T800H. When a specimen was strained near 1.6%,

TABLE 1
Properties of cast neat resins

Resin system	Strain at failure (%)	Modulus of elasticity (GPa)	Glass temperature (°C)
#3601	2.1	3.7	230
#3620	4.0	3.4	220
#3632	4.9	3.7	215
#3630	6.0	3.5	180
RX850	12.0	3.0	161

TABLE 2
Test specimen configurations, type of loading grip and 0° tensile strength of T1000 composites*

Case No.	Type of loading grip	Tab dimension** L (mm)	a (mm)	Laminate thickness (mm)	Tensile strength (GPa)	Fracture mode*** Gauge section	Tab section	Delamination in tab
Control	Wedge action	51	10	1.1	3.31	2/9	7/9	severe
1	l_e=55mm**			1.1	3.49	2/5	3/5	
2				0.83	3.49	6/6	0/6	
3				0.55	3.41	9/9	0/9	
		85	20					slight
4	Non wedge			1.1	3.49	5/5	0/5	
5	l_e=100mm**			0.83	3.48	3/3	0/3	

* Sample "Torayca" T1000/#3620

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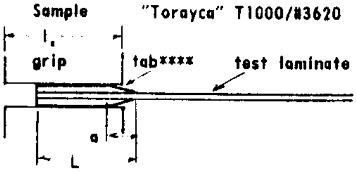

*** Ratio to number of whole specimens tested

**** Tab material GFRP woven fabric 0/90 lay-up
Tab ashesive 3M AF126

delamination at tapered area of the tab occured probably due to low toughness of GFRP tab material. The failure within tab section might come from excessive clamping force through the wedge caused by high axial load of T1000 composites. To solve these problems, following modifications were made;

[1] use of longer tabs made of tougher resin GFRP
[2] decreasing laminate thickness
[3] use of non-wedge type hydrostatic grips

Table 2 shows the results of improvements. These improvements were effectual to make test specimens break normally and to obtain strength values as expected. Conditions of Case No.2 in Table 2 was adopted and used for T1000 composite throughout this experiment.

RESULTS AND DISCUSSION

Fibre properties of T1000

Table 3 summarized the fibre properties of T1000. 7GPa of tensile strength, 294GPa of tensile modulus and 2.4% of strain were achieved by testing with resin impregnated strand specimens. To veryfy validity of this very high fibre strength, analytical study was done. Fibre tensile strength in the form of individual single filament was measured for different gauge length.
Results were illustrated in Figure 2 as a function of gauge length. Single filament strength of T1000 was superior to those of T300 and T800H. According to Rosen (2), strand strength of filaments in composites was given as strength of bundles at an ineffective length. Assuming the ineffective length of 0.6mm after Noguchi and coworkers (3) (4), strand strength was calculated. As shown in Figure 3, the observed strand strength of 7GPa for T1000 was in good coincidence with the calculated strength from data of single filaments.

Composite properties of T1000

Composite properties of T1000 are shown in Table 4, compared with those of T300 and T800H. Tensile strength of T1000 composite for 0° direction was 3.5GPa, almost twice of that of T300, and strain at failure was as high as 2%. It is noted that the strength depends on type of matrix resin combined with the fibre. The strength values measured with various resins are plotted in Figure 4 as a function of ultimate strain of neat resin. The composite with resin of 12% strain showed tensile strength of 3.85GPa at fibre volume content of 60%. Use of adequate resin system is, therefore, a necessary condition for T1000 to reflect its high strength to composites. It is also worthy to note that the very high strength values for T1000 composites were obtained by improved testing conditions with modified load-introducing sections.

TABLE 3

Properties of carbon fibre "Torayca" T1000, T800H and T300

Property	Unit	T1000	T800H	T300
Filament diameter	μm	5.3	5.2	7.0
Density	g/cm³	1.82	1.81	1.77
Filament count	—	12000	12000	12000
Mass per unit length	tex	480	445	800
Tensile strength*	GPa	7.06	5.59	3.53
Tensile modulus of elasticity*	GPa	294	294	230
Tensile strain at failure*	%	2.4	1.9	1.5

* Resin impregnated strand method

TABLE 4

Mechanical properties of unidirectional composites of T1000, T800H and T300

Carbon fibre		T1000		T800H		T300
Property	Unit	#3620	#3632	#3620	#3632	#3620
0° Tensile strength	GPa	3.49	3.55	2.95	2.94	1.70
Tensile modulus	GPa	158	158	160	165	135
Tensile strain at failure	%	2.0	2.0	1.7	1.7	1.2
0° Compressive strength	GPa	1.70	1.65	1.60	1.70	1.60
0° Interlaminar shear strength	MPa	110	95	120	115	125
90° Tensile strength	MPa	60	50	60	60	60
Tensile modulus	GPa	9	9	9	9	9
Tensile strain at failure	%	0.7	0.6	0.7	0.7	0.7

Fibre volume content 60%

TABLE 5

Mechanical properties of unidirectional composites of "Torayca" high modulus grade fibres

Property	Unit	M40J	M40	M46J	M46
Unidirectional composite					
0° Tensile strength	GPa	2.15	1.18	2.06	1.08
Tensile modulus	GPa	210	215	245	255
Tensile strain at failure	%	1.0	0.5	0.8	0.45
0° Compressive strength	GPa	1.17	0.88	1.07	0.83
Compressive modulus	GPa	196	196	230	235
0° Interlaminar shear strength	MPa	80	88	78	75

Fibre volume content 60%

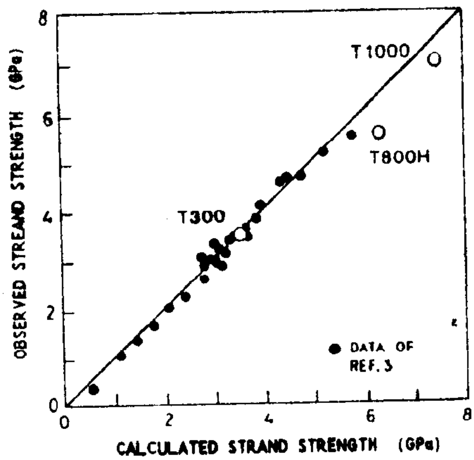

Figure 4 Relation between observed strength and calculated strength of resin impregnated strand

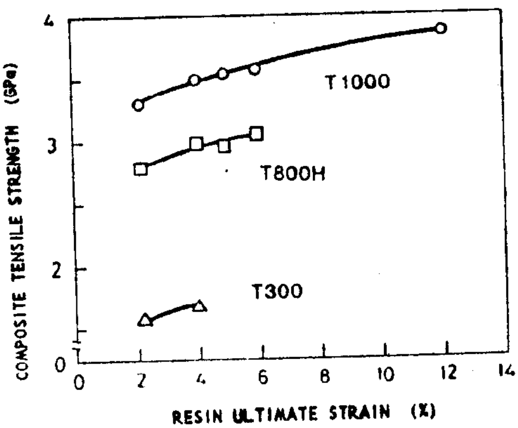

Figure 5 Relation between 0° tensile strength of composites and ultimate strain at failure of cure resin

Other properties, such as 0° compressive, 90° tensile and interlaminar shear properties are given in Table 4. They were almost same as those of existing fibres composites.

Filament wound high pressure vessels are one of promising applications for T1000 fibre, and evaluation programs are underway.

Composite properties of M40J and M46J

One of drawbacks of high modulus grade fibres is lower strength of their composites compared to high strength grade and intermediate modulus grade. M40J and M46J were originated to improve composite performances of the existing M40 and M46, respectively. As shown in Table 5, these new fibres performed excellent as expected, and 0° tensile strength of 2GPa was substantively higher than that of T300 composites and nearly two times higher than that of M40 and M46 composites. It should be noted that not only tensile but compressive strength became higher compared to the existing high modulus grade fibres.

CONCLUSION

1. Very high strength and intermediate modulus carbon fibre "Torayca" T1000 was developed. Fibre strength of 7GPa, modulus of elasticity of 294GPa and strain at failure of 2.4% were achieved. 0° tensile strength of T1000 epoxy composite was 3.8GPa, which is almost twice of the baseline T300 composites, and more than 2% of strain at failure was attained.
2. High strength and high modulus carbon fibre "Torayca" M40J and M46J were developed. 0° tensile strength of their composite materials was about 2GPa, almost twice of that of M40 and M46, and 0° compressive strength was also improved.
3. To measure tensile strength of very high strength composites made of T1000, adequate test specimens or testing devices should be introduced such as test specimens tabbed with longer and tougher tabs, decreased thickness of CFRP laminates, and/or non-wedge type hydrostatic grips.

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GLASS MATRIX COMPOSITES, MANUFACTURE AND PERFORMANCE DATA

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SUMMARY

Various reinforcement fibers -such as carbon fibers and SiC fibers- have been successfully incorporated into a glass of borosilicate matrix to obtain composites, which have shown high levels of performance, and excellent retention of their stiffness and strength properties, form R.T. to 500° C. These composites can be prepared in the same way than the one used for reinforced carbon epoxy composites, i.e. impregnation of fibers in a slurry, drying and then stacking up the plies. The last step, densification of the glass matrix is different by the higher temperatures and pressure needed. So, flexural strength as high as 1100 MPa for the carbon fiber glass matrix composites have been obtained, from R.T. to 500° C, and about 900 MPa for the SiC fibers glass matrix composites. These materials, with densities from 1.9 to 2.5 have shown potentialities of development for use in structural parts where high temperatures are reached.

INTRODUCTION

One of the limitations on the use of organic composite materials is their service temperature. We can assess that these composites may not be used above 350°C, except during very short exposure times. Such temperatures are met on external structural parts of missiles exposed to intense aerodynamical flows. Then, the use of metallic materials -such as steel or titanium alloy- is often required.

Meanwhile. development of metal matrix composite materials or glass and glass-ceramic composite materials show interesting capabilities.

These last two composite materials offer the best prospects for temperature of 500° C, even 1 000° C, depending on the type of glass used.

Work on these composites has been going on for a few years and has demonstrated their potentialities /1/.

Effectively, it can be of interest to compare a batch of materials in terms of flexural specific strength -Fig.1- or Young's specific modulus. These materials'densities are summarized in table 1.

TABLE 1 - Density of different materials

Steel	Titanium alloy	Metal matrix composites	Glass matrix composites	Epoxy/graphite composites
7.8	4.8	1.8 to 2.6	1.9 to 2.4	1.56

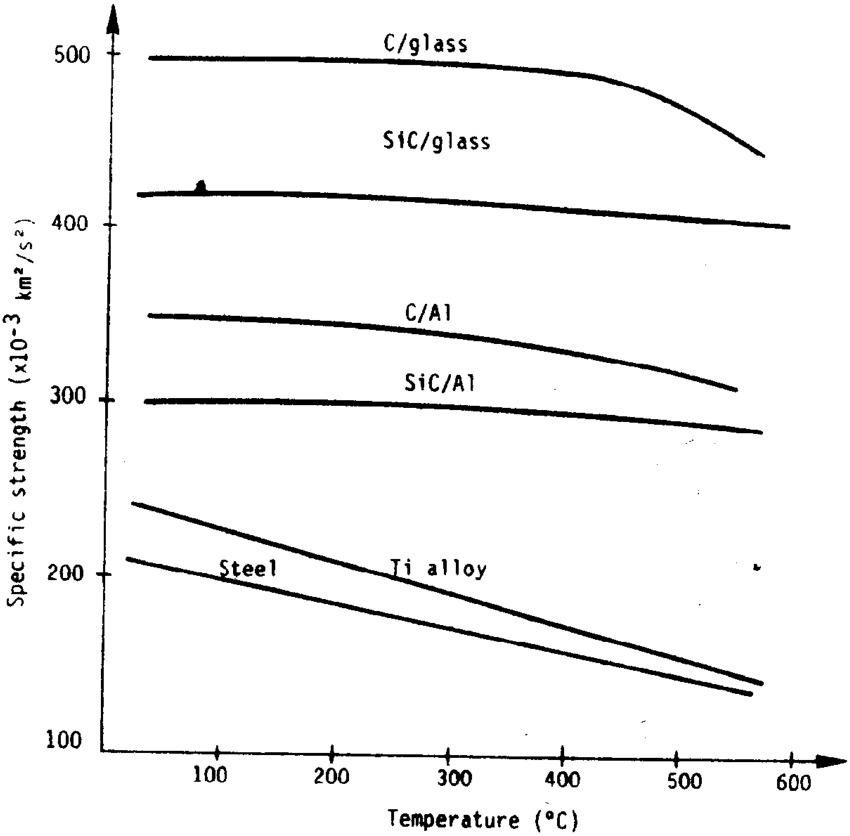

Fig. 1. Specific strength in flexion (3 points bending) for metallic and non -metallic materials.

Composite materials concerned are essentially reinforced with continuous. fibers.

We describe hereunder the process of elaboration of glass matrix composites and give the results of mechanical testing performed.

REINFORCEMENTS AND MATRIX

Fiber reinforcements

The reinforcing fibers used are continuous fibers of high tensile strength carbon or intermediate modulus carbon, or silicium carbide SiC. They all are commercial products.

No specific surface treatment has been applied on the filaments. Data usually available on the fibers we incorporate in the matrix are listed in table 2.

TABLE 2

Properties of the reinforcing fibers.

Fiber Type	Density	Number of filaments	Ultimate tensile strength	Young modulus	A %
High tensile strength- COURTAULDS XAS	1.80	12 K	3 100 MPa	230 GPa	1.4 %
HERCULES I.M. 6	1.76	12 K	4 800 MPa	310 GPa	1.7 %
NIPPON CARBON SiC	2.55	0.5 K	2 400 MPa	200 GPa	-

Matrix

Among the different glasses which may be used we selected first a borosilicate type glass, capable of temperatures exceeding slighty 500° C.

Such glasses like AS (alumino silicate) or LAS (lithium-alumino silicate) have not been retained, though allowing superior temperature of utilization, respectively 700° C and 1 000 to 1 200° C, but with a consequence, that the temperatures during fabrication process have to be largely increased.

The main data on the borosilicate glass are listed in table 3.

TABLE 3

Main characteristics of the borosilicate glass.

Major constituants	Minor constituants	Density	Strength in traction	E	Max. Use temperature	Working temperature
B_2O_3	Na_2O	2.27	100 MPa	65 GPa	600° C	1 040° C
SiO_2	Al_2O_3	-	-	-	-	-

The glass is used in a powder form, with a particule size as little as possible. A borosilicate glass has :

- a low coefficient of thermal expansion
- a good resistance to thermal stresses(Pyrex)
- a good chemical resistance

Glasses are, by definition, amorphous solids which rheological behavior is characterized by some fixed points which bind some standard levels of viscosity versus temperature.

For example, for the borosilicate glass, we can define :

- the softening point, for a viscosity of $10^{7.6}$ poise, at a temperature of 770° C
- the working point, for a viscosity of 10^4 poise, at a temperature of 1 040° C.

A thermal analysis showed that the glass transition zone of this borosilicate glass was between 515° C and 540° C.

COMPOSITE FABRICATION

A typical schematic of the process for continuous fiber is shown in Fig. 2.

First, we prepare a prepreg by impregnation of the fiber tows with a slurry, which contains mainly :

- the glass powder
- a solvent (alcool) and water
- a binder dissolved in water
- a wetting agent

The fibers are then rolled up on a mandrel to form a tape (Fig. 2a) which is dried to eliminate the solvent (Fig. 2b), that allows an easier handling of the prepreg.

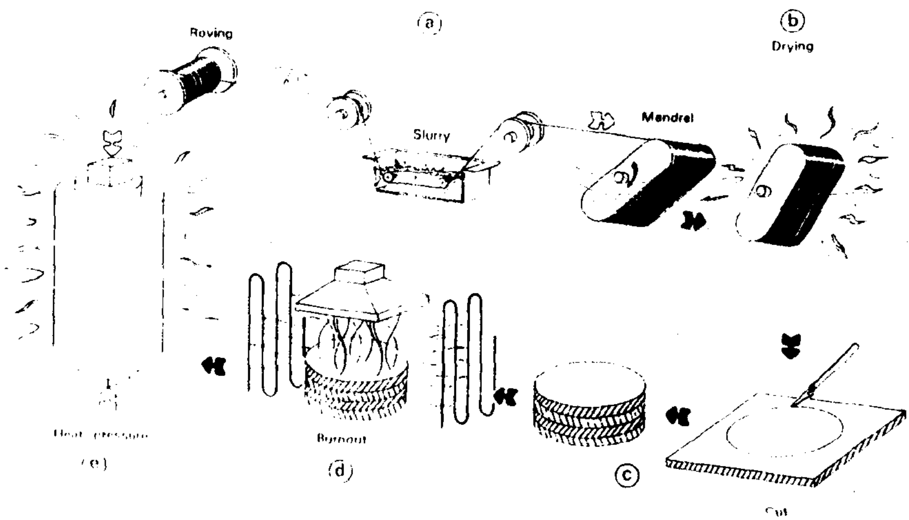

Fig. 2. Schematic of the process for the glass matrix composite elaboration.

Then the plies can be cut and stacked in a shaped die (Fig. 2c). It is necessary to heat at a sufficient temperature to eliminate all the organic compounds (Fig. 2d) ; a limitation on the heating temperature has to be set to avoid oxydation of carbon fibers if they are used, and if we are not in inert atmosphere. We can notice that, in the former description, these glass matrix composites are prepared in a manner totally similar to that used for resin matrix composites.

In the final step (Fig. 2e) the densification of glass powder occurs in a high capacity press, at a temperature which allows the glass to soften sufficiently to correctly wet the fibers. It is necessary to work in an inert atmosphere.

For the type of glass used, a temperature of 1 250° C is required at pressure of about 8 MPa.

GLASS MATRIX COMPOSITES

Carbon fiber reinforced glass matrix composites

The majority of elaborated composites were unidirectionnally reinforced, with a few ones of the crossply type (0° - 90°).

We measured on these samples the mechanical properties from ambient temperature to 500° C. We determined their strength in flexure (three points bending), their interlaminar shear strength (short beam shear strength) and Young's modulus. The modulus is obtained by a dynamical method : the sample is clamped and driven in a flexure mode, and by utilization of the frequency at the resonance peak, Young's modulus is extracted.

Data are listed in table 4 for the H.T.S. fiber composites(62 to 66 volume percent fiber) and the I.M. fiber composites (68 volume percent fiber).

TABLE 4

Mechanical properties of H.T.S. and I.M. carbon fiber glass matrix composites

Interlaminar Shear strength	R.T.	500° C	Flexural Strength	-40° C	R.T.	500°C	Young's Modulus	R.T.	500°C
H.T.S. Carbon	38 MPa	36 MPa	H.T.S. carbon	1240MPa	1240MPa	1237MPa	H.T.S. carbon	158GPa	154GPa
I.M. carbon	30 MPa	30 MPa	I.M. carbon	1022MPa	1030MPa	970MPa	I.M. carbon	160GPa	160GPa

Thus, we notice that performance of these composites appears modest as compared to those of resin matrix composites, which exhibit generally 1 700 to 1 800 MPa as ultimate strength in flexure test for a high strength carbon fiber reinforced one.