# AT ELEVATED TEMPERATURES

E. FITZER and M. HEYM

Institut für Chemische Technik Universität Karlsruhe, W.-Germany

### 1. Introduction

The development of high strength continuous fibre materials from light weight elements enables us to fabricate high performance composites having mechanical properties similar to steel, but at the same time a density which is five times lower.

In fig.1 the tensile strength and YOUNG's modulus of commercially available continuous low density fibre materials is shown. The black areas correspond to the different va-rieties of carbon fibres. It can be recognized that carbon fibres with strength up to 4000  $\rm MN/m^2$  or moduli above 50.10^4  $\rm MN/m^2$  can be fabricated. For room temperature applications most of these fibre materials are already successfully used, mainly as reinforcing component in epoxy matrix. Boron fibres are also tested as reinforcement for aluminium. However at present there is no structural application of fibre reinforced composites. at elevated temperature say above 150°C, because the true potential and applicability of temperature resistant fibre reinforced composites is not yet known sufficiently.

Therefore we studied the fabrication, the chemical stability and the mechanical properties of unidirectionally fibre reinforced composites with the most promising fibre/ matrix combinations at ambient and especially at elevated temperatures, that means up to  $500^{\circ}$ C in air. The study includes carbon fibre reinforced phenolic resin and various polyimide resins, carbon fibre- and boron fibre reinforced aluminium and carbon-carbon (C/C)- composites. Carbon fibre reinforced epoxy composites prepared from a commercial C/Epoxy-prepreg (FIBREDUX 911) have been tested for comparison with composites with high temperature resistant polymer matrix.

#### 2. Experimental

The polymer matrix composites have been fabricated by impregnating surface treated carbon fibre yarns with resin solutions and wet winding them into the shape of prepregs. The prepregs have been precured and subsequently hot molded to receive bars (2x5x160 mm) which have been postcured up to the final strength. Three different kinds of polyimide resins have been used: Resin 212 is a processable condensation polyimide which releases acetic acid during hardening; P 13 N is a prepolymer which undergoes imidization at curing temperatures between  $210 - 260^{\circ}$ C and crosslinkage of the nadic acid endgroups above  $290^{\circ}$ C. Kerimid 601 is a poly-bismaleinimide. The phenolic resin consists of a novolac, which has been hardened with hexamethylentetramine.

The C/C-composites which have been used for tests at elevated temperatures were prepared by liquid infiltration of the carbon fibre yarns with molten coal tar pitch (softening point 63°C) as carbon matrix precursor. The fibre content was controlled by hot pressing the infiltrated carbon fibres into laminates. The laminates were baked up to 550°C under elevated nitrogen pressure and subsequently upto 1400°C under atmospheric pressure. The porous carbon composite framework obtained after carbonization was reimpregnated with pitch and recarbonized four times which is sufficient to reach maximum strength. Further details on this technique have been published by FITZER et al. (1972).

Boron fibre reinforced aluminium samples have been prepared using commercially avai lable tapes with B4C-and SiC-coated boron fibres. In these tapes the fibres are held in position on an aluminium foil (6061) by plasma sprayed aluminium (6061). The tapes were combined in an eutectic bonding process.

Carbon fibre reinforced aluminium composites have been prepared by infiltration of carbon fibres which were coated with nickel or silver as wetting promoter with molten aluminium at temperatures of about 700°C. The influence of the different wetting agents on the composite fabrication process and the composite properties as well as the effect of SiC, TiN, TiC-coatings on the carbon fibres as diffusion barriers between carbon and aluminium during composite fabrication and especially during application at elevated temperatures will be discussed.

### 3. Results

In table 1 the room temperature properties of the different studied composite materials are compiled. It can be recognized that the fibre strength is almost completely utilized in the case of C/epoxy-, C/phenolic-,B/aluminium- and C/C-composites. The incomplete fibre strength yield for composites with polyimide matrices is caused by a residual porosity due to the release of condensation products or traces of the used high polar solvent during postcuring.

The interlaminar shear strength is very high in epoxy and phenolic matrix composites and comparatively low for polyimidematrix composites. In the case of aluminium matrix composites interlaminar shear strength is so high that the short beam test could not cause delamination. The given values therefore have to be regarded as minimum values, the real shear strength is lying higher.

The flexural strength of the composites as function of the test temperature is shown in fig.2. It can be recognized that C/epoxy composites loose their strength completely up to a test temperature of 200°C. C/Resin 212-composites show a better strength retention especially between 200 and 300°C. Most surprising is the excellent elevated temperature strength of C/phenolic-composites which is similar to that of B/aluminium-composites. As can be recognized the absolute room temperature strength of B/aluminiumcomposites exceeds that of C/aluminium-composites but the difference in strength va-nishes at a test temperature of 450°C. The strength of C/C-composites does not decrease at all with increasing test temperature, thus being superior to all other composite materials at temperatures above 400°C. The fracture behaviour of the different composite materials at room temperature and at elevated temperature will be discussed.

Futhermore the behaviour of the composites during long time exposure in air at elevated temperatures under static flexural load will be shown. It turns out that improve ments of the mechanical temperature resistance of B/aluminium composites can be realized by age hardening of the matrix. The chemically caused temperature limits will be pointed out by microscopic analysis of heat treated composites and the dependence of the composite strength on the barrier function of B4C-and SiC-protective coatings on the boron fibres will be discussed.

Thermogravimetric measurements of the oxidation behaviour of C/C-composites at elevated temperatures in air have shown that these composites are sensitive against oxidation already at temperatures above  $350^{\circ}$ C. Methods for improving the oxidation resistance of C/C-composites have been studied which allow an application of C/C-composites in oxidizing atmosphere up to  $500^{\circ}$ C.









Katrix	Epoxy	Phenolic	Kerimid	P 13 N	Resin 212	Aluminium			Carbon
Fibre vol. fraction v/o	55	58	56	60	60	45	49	60	50
Fibretype	T 300 B	Mag.HTS	Mag.HTS	Mod.IIS	Mag.HTS	Graf.HM	B∕B <sub>4</sub> C	B/SiC	Mod.I
Flexeral strength 10 MN/m <sup>2</sup>	158	155	127	112	135	115	163	172	95
Fibre strength yield \$	96	`99	84	78	· 83	78	82	96	100
Flexural modulus 10 <sup>4</sup> MN/m <sup>2</sup>	11,5	12,4	12,6	11,4	13,0	24,0	16,8	20,0	15,4
Strain to failure	1,5	1,2	1,1	1,1	1,1	0,45	1,0	0,9	0,6
Interlam. shear strength MN/m <sup>2</sup>	83	88	44	56	57	(55)	(75)	(75)	25
Bulk density 103 kg/m3	1,45	1,50	1,45	1,45	1,42	2,16	2,5	2,55	1,65

## Reference:

- E. FITZER, B. TERWIESCH, 1972 Carbon 10, p. 383
- Tab.1: Mechanical room temperature properties of unidirectionally fibre reinforced composites