

UNIDIRECTIONALLY REINFORCED CARBON/CARBON-COMPOSITES
WITH POLYIMIDE AND PHENOLIC RESIN AS MATRIX PRECURSOR

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Introduction

Carbon-Carbon-(C/C)-Composites are usually fabricated by infiltration of carbon fibres with a solution of a thermosetting resin, molding the resulting prepregs to the final shape of the composite and carbonizing the resin binder. Thus a skeletal composite with carbon bridges between the monofilaments is obtained which is densified subsequently by gas phase impregnation with pyrocarbon (HILL et al., 1974). FITZER et al. (1972, 1974) succeeded to use coal tar pitch as primary binder precursor and to replace the CVD impregnation process by repeated reimpregnation/recarbonization cycles with pitch. Carbonizations of the pitch binder have been performed under elevated gas pressure up to temperatures of semicoke formation in order to provide high coke yield of the pitch and good adhesion between the fibres and the resulting carbon bridges. The final mechanical properties of C/C-composites prepared by the CVD and by the pitch process have been found to be equivalent and correspond to 100% utilization of the fibre properties.

With the aim to make the C/C-composite fabrication technology more economic FITZER et al. (1976) have found recently that the elevated gas pressure during baking of pitch bonded carbon fibre composites can be avoided if the used binder pitch is modified by sulfur addition. The sulfur acts mainly as dehydration agent for low molecular aromatic constituents and therefore increases the coke yield of the pitch without preventing mesophase formation.

Thermosetting resins however which are highly crosslinked and show strong adhesion at the fibre surface have been found to be unsuitable as carbon matrix precursor for carbon/carbon-composites in spite of their high coke yield (FITZER et al., 1971). The anisotropic shrinkage of the resin matrix during carbonization caused cracks in the formed carbon matrix which partially run across the filaments.

In the present study we tried to overcome the shrinkage problems using polymers with linear aromatic molecular chains such as polyimide and phenolic novolacs with special chemical composition.

Experimental

C/C-composites have been prepared using three types of resins as matrix precursors:
a processable, condensation type polyimide, releasing acetic acid during curing (Resin 212 by Yorkshire Chemicals)

phenolic novolac with hexamethylenetetramine as hardener (Resin A)

phenolic novolac with benzenesulfochloride as hardener (Resin B)

For the fabrication of C/C-composites prepregs have been made by impregnating the fibres with the molten resin (as in the case of the polyimide), with a 50%-solution of the resin (as in the case of Resin A) or with liquid prepolymer (as in the case of Resin B). The resulting prepregs have been precured, hot molded into laminates (3x5x160 mm) and hardened under pressure. Composites with phenolic resin have been postcured up to 250°C, those with polyimide resin up to 400°C. Subsequently the composites were carbonized in inert atmosphere with a heating rate of 10-15°C/h.

Commercially available carbon fibres in the carbonized (MODMOR II, SIGRAFIL HF) as well as in the graphitized (MODMOR I, SIGRAFIL HM) state have been used as reinforcement. All fibres were non surface treated.

Results

On the left hand side of fig. 1 the linear shrinkage of unreinforced bulk samples of the different resins during carbonization up to 1000°C is shown. It can be recognized that the unreinforced phenolic resin A and the polyimide resin have very similar shrinkage behaviour, the main part of shrinkage occurring in the temperature range between 400 and 600°C. On the right hand side of fig. 1 the cross-section shrinkage of composites with the different resins as matrix precursors and various fibre types during carbonization is shown. No shrinkage has been detected parallel to the fibre direction. It can be recognized from the figure that polyimide matrix composites show higher shrinkage during carbonization than phenolic matrix composites and higher shrinkage than expected from shrinkage values of the unreinforced resin samples. This behaviour can be explained by preferred orientation of the linear aromatic ladder molecules of the polyimide precursor parallel to the fibre axis and fibre surface which results in preferred transverse contraction. Furthermore it can be seen that the amount of composite shrinkage depends on the type of fibre. Especially composites with phenolic resin A as matrix precursor and graphitized carbon fibres (SIGRAFIL HM) shrink only 6% whereas those with carbonized carbon fibres (SIGRAFIL HF) shrink at about 15%. The low carbonization shrinkage in the case of composites with graphitized fibres is a result of the poor ad-

hesion between graphitized fibres and the carbonizing matrix which causes shrinkage gaps at the fibre/matrix-interface and reduces the macroscopic shrinkage. Composite samples with phenolic resin B as matrix exhibit very low carbonization shrinkage because this resin forms a foam-like structure with closed spherical pores upon curing.

The effect of the carbonization shrinkage on the flexural strength of the composites during pyrolysis up to 1000°C is shown in fig.2. It can be recognized that C/C-composites with MODMOR I-and-II-fibres and polyimide resin as matrix precursor have strength as high as 700 MN/m² after carbonization up to 1000°C without any impregnation. C/C-composites with phenolic resin A and graphitized (HM)-fibres have strengths of only 50 MN/m² but the structure of these composites provides very effective impregnation. In C/C-composites with phenolic resin A as matrix precursor and carbonized fibres fibre breakage caused by shrinkage stresses has been observed by scanning electron microscopy. However, no fiber damage occurred if phenolic resin B was used because the matrix shrinkage was reduced by the porosity.

The influence of 4 reimpregnations with resin or pitch respectively on the composite flexural strength is shown in table 1. Pitch impregnations have been found to be more effective in comparison with resin impregnations. The high strength of non-impregnated C/C-composites with polyimide as matrix precursor can be increased by 10 - 15% corresponding to a final value of 820 MN/m² after 2 pitch impregnations/recarbonization cycles. The highest final strength of 1100 MN/m² has been obtained in C/C-composites with phenolic resin A as matrix precursor, and graphitized (HM)-fibres although this fibre/matrix combination had the lowest strength before impregnation.

The influence of impregnations on the interlaminar shear strength and the influence of heat treatments up to graphitization temperatures will be discussed.

Furthermore it will be shown that the strength of C/C-composites with phenolic resins as matrix precursor can be increased if the carbonization shrinkage of the matrix is reduced by addition of graphitic fillers with suitable grain size.

References:

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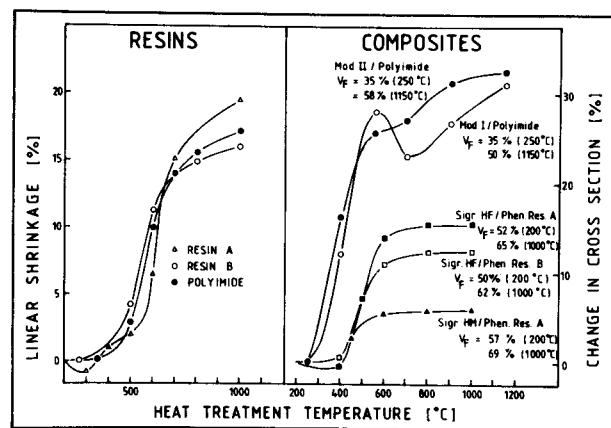


Fig.1: Linear shrinkage of resin bulk samples and cross-section shrinkage of UD-composites as function of HTT

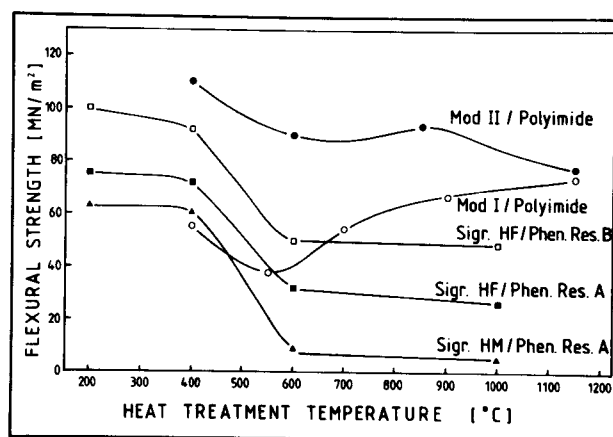


Fig.2: Room temperature flexural strength of UD-composites as function of the final HTT

RESIN	FIBRE	FIBRE CONTENT [%]	FLEXURAL STRENGTH [MN/m ²]			YIELD OF FLEX. STRENGTH [%]		
			0	4	4	0	4	4
			RESIN IMPR.	PITCH IMPR.	PITCH IMPR.	RESIN IMPR.	PITCH IMPR.	PITCH IMPR.
RESIN A	Sigr. HF	65 %	270	490	520	18,9	34,3	36,4
	Sigr. HM	69 %	59	850	1100	4,3	61,6	80,0
RESIN B	Sigr. HF	62 %	490	-	920	36,0	-	67,5
POLYIMIDE	Mod. II	58 %	730	-	820*	52,4	-	59,0*

* reached after 2 impregnation cycles.

Tab.1: Flexural strength of UD-C/C-composites (carbonized up to 1000°C) without and with reimpregnation/recarbonization-treatment using resin and pitch resp.