MESOPHASE PITCHES AS MATRIX PRECURSORS OF CARBON FIBRE REINFORCED CARBON

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INTRODUCTION

A study on mesophase pitch as matrix precursor of carbon fibre reinforced carbon (CFC) has recently been presented [1]. It was shown that (i) a mesophase pitch with about 30-40 vol% mesophase spherulites can be infiltrated into a fibre preform without a filter effect, and (ii) surface oxidation of the carbon fibre and (iii) stabilization of the pitch after infiltration are of significant importance. The present study is focussed on two objectives: (1) the nature of the mesophase pitch, and (2) the stabilization treatment, which was performed at elevated oxygen pressures.

EXPERIMENTAL

For basic studies on pressure stabilization, a Tenax HTU fibre (not surface oxidized, fibre (A)) and a Tenax HTA fibre (surface oxidized, fibre (B)) from AKZO were used. For studies by variation of the mesophase pitch the Tenax HTA fibre was not available any more and replaced by the AS4 fibre (surface oxidized, fibre (C)) from Hercules.
The mesophase pitches were synthesized from the Ashland A240 petroleum pitch at an argon pressure of 1 MPa. Further synthesis conditions and some properties of the mesophase pitches are summarized in Table 1.

Table 1: Properties of the pitches used for infiltration of fibre preforms

a	b	c	d	e	f	g	h
1	▼	400	3.0	4.4	3.6	3.0	46.9
2	▲	440	3.5	53.8	31.3	32.5	60.3
3	■	460	0	22.1	8.7	5.0	53.8
4	◆	490	0	49.6	31.9	20.0	63.8

a - number of the pitch; b - symbol used in figures; c - pyrolysis temperature, °C; d - residence time, h; e - content of insolubles in tetrahydrofurane (Soxhlet), %; f - content of insolubles in N-methyl-pyrrolidone, %; g - mesophase content, vol%; h - coke yield (institute method), %

Pitch (2) is similar to that used by Christ [1]. Pitches (1) and (3) may be termed as "mesogenic" pitches (mesophase content ≤ 5 vol%). Pitch (4) has a similar NMP-I content like pitch (2), but a much lower mesophase content, a result of the synthesis conditions.

Composites of 140 · 6 · 2 mm with a fibre volume fraction of 60% were fabricated according to the procedure reported in [1]. Molding temperatures were 300°C (pitches (1) and (3)) and 360°C (pitches (2) and (4)).
Stabilization treatments were performed in an autoclave with pure oxygen. The composites were carbonized at 1000°C and graphitization-treated at 2100°C in flowing argon (ambient pressure).

RESULTS

Fig. 1 shows a typical result of the relative mass gain of the matrix after stabilization (fibre (B), pitch (2), 1 MPa oxygen pressure). The mass gain can be correlated with Fick's second law (t_0 corresponds to $\Delta m / m_0$ until final temperature is reached). The kinks in the curves are ascribed to a complete stabilization of the matrix. With additional oxygen uptake, the matrix is over-stabilized (see later).
Another typical result is presented in Fig. 2. It shows a correlation between the coke yields of the stabilized matrices and the relative mass gains after stabilization (fibres (A) and (B), pitch (2), 1 MPa oxygen). To a first approximation the correlation is independent on stabilization temperature and time. Over-stabilization can be recognized in a decreasing coke yield with excessive oxygen uptake. The influence of the fibre is obvious. Similar correlations between mass gain, complete stabilization, and coke yield were also found with the further pitches. An example is given in Fig. 3 (fibre (C), pitches (1) to (4), 1 MPa oxygen). The maximum coke yield with the mesogenic pitches (1) and (3) is slightly lower; it is achieved with higher oxygen uptakes.
A correlation between the swelling of the composites parallel to the pressing direction after carbonization and the relative mass gain after stabilization is presented in Fig. 4 (fibre (C), pitches (1) to (4), 1 MPa oxygen). Swelling is strongly reduced by stabilization. Minimum swelling is achieved in the range of complete stabilization. By over-stabilization swelling is intermediately increased but then it is decreased again (results with fibre (B), pitch (2), not shown).
As both maximum coke yield and minimum swelling of a composite are found at the same oxygen uptake corresponding to complete stabilization, the bulk density of the composites after carbonization is also maximum after that stabilization treatment. They vary between 1.35 g/cm³ (pitch (3)) and 1.45 g/cm³ (pitch (2)).
After graphitization treatment the flexural strength of some composites was determined. The results are

shown in Fig. 5. The flexural strength increases with increasing relative mass gain after stabilization and, surprisingly, also with a relative mass gain which is beyond optimum stabilization (pitch (3)). Further studies with over-stabilized matrices have to be performed in order to confirm this conclusion. It is remarkable that an excellent result was found with a mesogenic pitch, which can be infiltrated into a fibre preform much easier than a spherulitic mesophase pitch.

SUMMARY

Fabrication of CFC with mesophase pitch as matrix precursor was shown to be a complex process, although some general correlations between the extent of stabilization and the pyrolysis or carbonization behaviour of the stabilized matrix, respectively, exist. Flexural strength values found after graphitization treatment look promising.

ACKNOWLEDGEMENT

Financial support of this study by the German Research Foundation (DFG) is gratefully acknowledged.

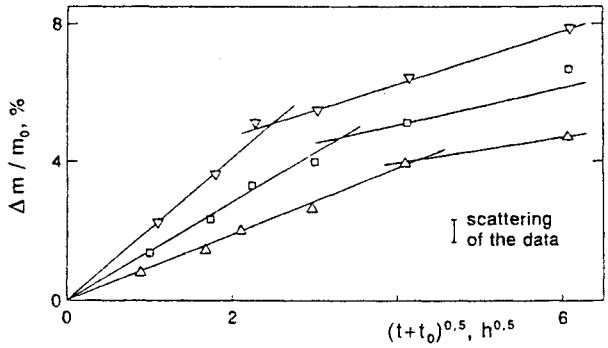

Fig. 1: Relative mass gain of the matrix in dependence on the square root of time ($t + t_0$); 1 MPa oxygen. ▲, 160°C, t_0 = 0.8 h; ■, 180°C, t_0 = 1.0 h; ▼, 200°C, t_0 = 1.2 h.

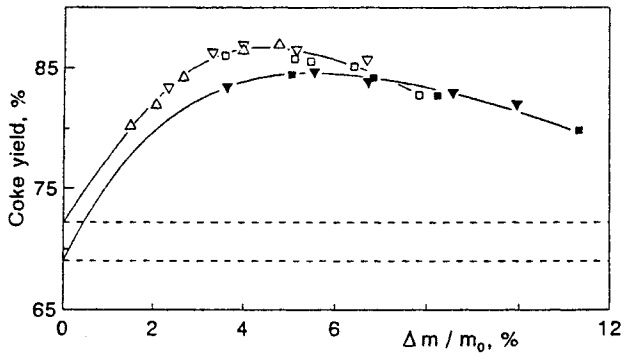

Fig. 2: Coke yield of the matrix after carbonization at 1000°C in dependence on the relative mass gain after stabilization. Full symbols: fibre (A), open symbols: fibre (B); symbols see Fig. 1.

REFERENCE

[1] K. Christ and K.J. Hüttinger, *Carbon* 31, 731 (1993)

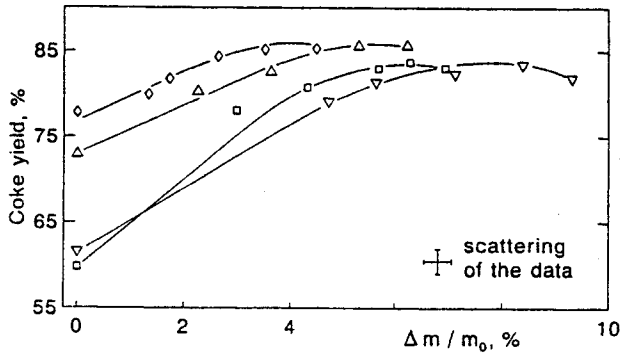

Fig. 3: Coke yield of the matrix after carbonization at 1000°C in dependence on the relative mass gain after stabilization at 200°C, 1 MPa oxygen; symbols according to Table 1.

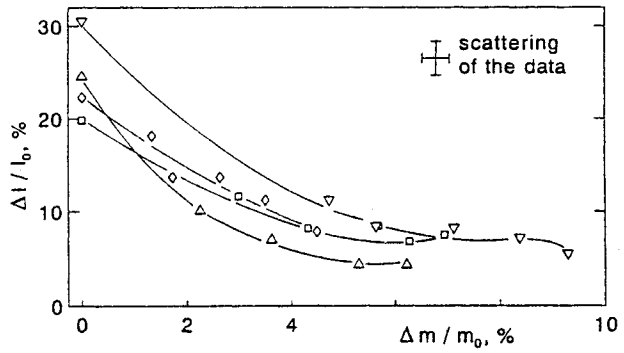

Fig. 4: Swelling of composites after carbonization at 1000°C in dependence on the relative mass gain after stabilization at 200°C, 1 MPa oxygen; symbols according to Table 1.

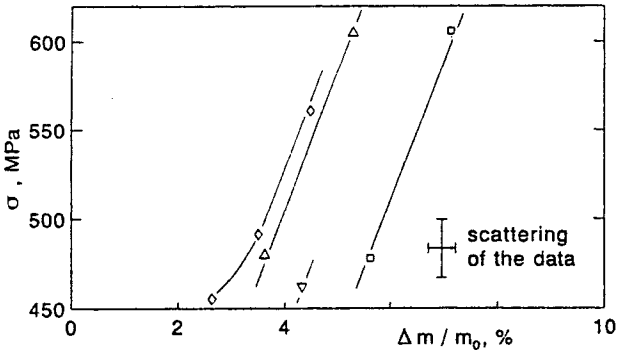

Fig. 5: Flexural strength after graphitization in dependence on the relative mass gain after stabilization at 200°C, 1 MPa oxygen; symbols according to Table 1.