PYROLYSIS BEHAVIOUR OF PANEX BASED POLYMER COMPOSITES

*T.L. Dhami, R.B. Mathur, H. Dwivedi, O.P. Bahl and M. Monthioux**
Carbon Technology Unit, National Physical Laboratory, New Delhi 110 012 INDIA
** CEMES, Toulouse, FRANCE*

Introduction

Carbon/carbon composites are the ceramic materials used for high temperature applications because of the their far superior thermo-mechanical properties compared to the conventional materials(1). Performance of c/c composites depends on the reinforcement properties, nature of the matrix and fiber/matrix interactions. However, processing of C/C composites upto 1000°C is a complex process influenced by surface chemistry and topography of reinforcement, char yield of the matrix resin, fibber/ matrix interactions and processing parameters etc.(2-5). Recently c/c composites have been developed using oxidized PAN fibres(6-8) as reinforcement. Present study describes the pyrolysis behaviour of oxidized PAN fibres('PANEX', developed in our laboratory) based c/c composites upto 1000°C.

Experimental

Courtelle 6K, 1.2 d'tex PAN fibers were oxidized isothermally at 250°C with increasing dwell time yielding samples A,B,C and D respectively. This ensures samples possessing different surface energies. These fibers were then characterized for surface energetics, elemental analysis, nature of surface groups and pyrolysis behaviour. UD composites of size 100 x 5 x 4 mm were developed using samples A-D as reinforcement and coal tar pitch as the matrix by match mould die technique. Green composites were pyrolysed upto 1000°C in inert atmosphere and characterized for dimensional changes , longitudinal as well as cross sectional,and their weight loss.

Results and Discussion

Table 1 gives the elemental analysis of samples A to D. It shows that the amount of oxygen present in the bulk fiber increases from 7% for sample A to 21% for sample D. However, ESCA results show the presence of oxygen on the surface in the form of surface groups like C-O, C=O, which varies between 7.8% to about 14% (table-2) and reaches a saturation value for sample B. This clearly indicates that the amount of oxygen present in the bulk fiber is totally different from the amount of oxygen present on the surface of the fiber. Table-3 shows the surface energy of the PANEX samples determined by using DCA 322 . It is evident that both the dispersive and polar components are almost same for samples A and B whereas these are lower for sample D.This is in agreement with the ESCA results (table 2) wherein the amount of polar groups e.g. C=O and C-O is much lower for sample D .

Fig. 1 shows the pyrolysis behaviour (free shrinkage and weight loss) of PANEX samples upto 1000°C in an inert atmosphere. The shrinkage along the length varies between 8 to 10% whereas the cross sectional shrinkage along diameter is around 30%. The shrinkage behaviour during pyrolysis of the composites is shown in Fig.2. It is evident that the shrinkage along the longitudinal direction varies between 8 to 10% and almost matches with that of PANEX fibers(fig.1) indicating that fiber/matrix interactions do not play any role in the shrinkage along this direction. However, cross-sectional shrinkage in case of composites varies between 14 to 18%. The cross-sectional shrinkage in case of oxidized PAN fiber based composites is effected by the (i) cross-sectional shrinkage of the oxidized fiber (ii) shrinkage of the matrix resins and (iii) strength of fiber/matrix interactions which further depend on surface energetics of the fiber and surface chemistry of the matrix resin(2). If the fiber/matrix interactions are weak, the shrinkage of fiber as well that of matrix will behave independent to each other. Strong fibre matrix interactions , on the other hand, will not allow the fiber to shrink towards its center as observed earlier by the authors(6). These interactions will rather pull the matrix carbon towards the interphase. This is the reason why the cross-sectional shrinkage for samples A to C is higher as compared to sample D which has lower surface energy comparatively (table 2). This confirms that fiber/matrix interactions effect to a large extent the cross-sectional shrinkage during the pyrolysis of the composites.

The weight loss pattern will be affected by two opposing factors : weight loss of PANEX fibres and weight loss of matrix carbon which will be effected by strength of fiber/matrix interactions. The stress at fiber/matrix interface effects the polymerization of matrix resin and increases the char yield to some extent as has been observed earlier(6). In the present study the weight loss of PANEX fiber based composites is in the range of 40 to 45%(yield 55-60%) It has already been observed that yield of matrix(coal tar pitch) alone is around 45%. As evident from Fig.1 the weight loss of

PANEX fiber during pyrolysis is around 50%. The increase in the yield of the composites clearly brings and the role played by fiber/matrix interactions during pyrolysis.

Conclusion

The amount of oxygen present on the surface of PANEX fibers in the form of surface groups is different from that present in the bulk. The fiber/matrix interactions which influences the mechanical properties of carbon/carbon composites effect to a large extent the pyrolysis behaviour (cross-sectional shrinkage as well as weight loss) of composites. The shrinkage behaviour along the longitudinal directions is mainly governed by the shrinkage of PANEX fibers alone.

Acknowledgement

Authors wish to thank the Indo-French centre for the Promotion of Advanced Research for sponsoring the project No. 1408-1, under which these studies have been carried out and also to ICSI, CNRS, Mulhouse, France, for carrying out surface energy studies on DCA 322.

References

1. "Carbon-carbon composites" (Ed. G. Savage) Pub: Champman & Hall, London, 1993.
2. O.P.Bahl and T.L. Dhami, Proc. Int. Conf. Carbon & Carbonaceous composite materilas, Malenvice, Czech Republic, 10-13, 1995 (editors K.R. Palmer, D.T. Marx and M.A. Wright) Pub: World Scientific, p. 255.
3 L.M. Manocha and O.P. Bahl, Carbon 26 (1988),p.13.
4. L.M. Manocha, E. Yasuda, Y. Tanabe and S. Kimura, Carbon 26, (1988) p.333.
5. E. Fitzer, K.H. Geigl and W. Huettner, Carbon 18, (1980) p.265.
6. T.L.Dhami, O.P. Bahl and P.K. Jain, Carbon 33, (1995) p.517.
7. V. Markovic and S. Marinkovic, Carbon 26 (1988) p.329.
8. V. Markovic et al. Proc. 15th Biennial Conference on Carbon, Pennsylvania, 1980, p.272.

Table 1 : Elemental Analysis of Panex Fibers

Sample	%O	%N	%C	%H
PAN	4	23.6	66.2	5.8
A	6.9-8.1	23-23.1	64-65	4.9-5.0
B	9.8-10.8	22.2-22.3	62.6-63.3	4.4-4.5
C	19.1-20.8	20.3-20.5	56-56.2	3.0-3.1
D	21.0-21.4	20.6-20.7	55.5-55.2	2.7-2.8

Table 2 : ESCA analysis of Panex fibres

% Elements	PAN	A	B	C	D
C	82.5	72.2	71.0	73.2	69.5
O	7.8	11.5	13.9	12.5	13.9
N	9.5	15.2	13.5	14.0	15.1
Si	0.1	1.1	1.6	0.3	1.4
%Groups					
C-O	27.9	33.7	26.5	26.8	24.4
C=O	4.3	8.1	10.9	7.7	8.4

Table 3 : Surface Energetics of Panex Fibers

Sample	Disp γ_S^D	Pol γ_S^P	Total
A	33±2	27±1	60±3
B	34±3	26±1	60±4
C	---	---	---
D	29±2	22±3	51±5

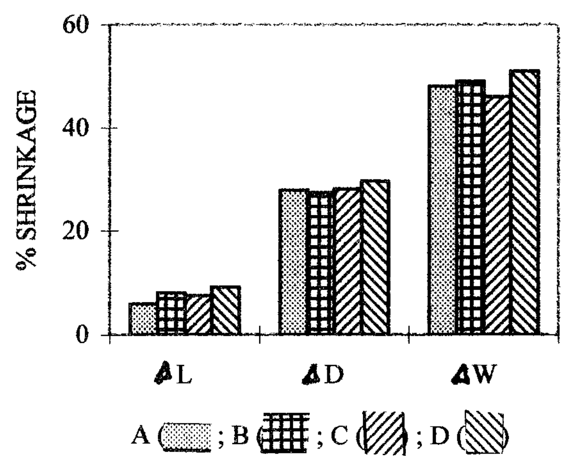

Figure 1 : Pyrolysis behaviour of Panex fibres.

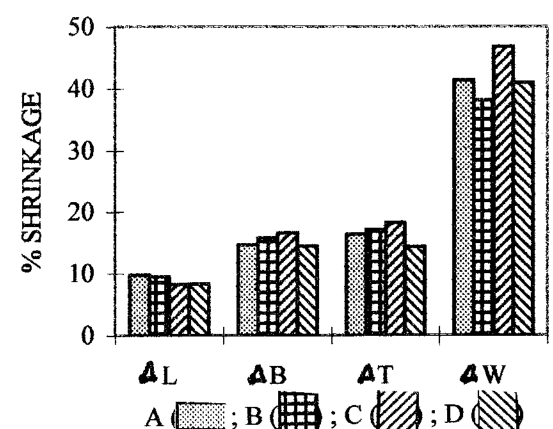

Figure 2 : Pyrolysis behaviour of Panex composites.