CORRELATION BETWEEN THE SURFACE ENERGETICS OF REINFORCEMENT AND MECHANICAL PROPERTIES OF CARBON/CARBON COMPOSITES

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Abstract

Surface energetics of reinforcement is one of the most important properties in case of adhesion of reinforcement in composites. For this study, PAN fibres were stabilized isothermally with three different timings (viz. 0, 1, 2 h) and eventually prepared fibres having different surface energetics were evaluated by DCA 322. Composites were made by using these stabilized fibres (designated as 0P, 1P, and 2P) with coal tar pitch as matrix precursor using match mould die technique. Green composites were carbonized upto 1000°C, then impregnated and heat treated to 1500, 2000 and 2600°C. Green composites as well as heat treated composites were studied for their mechanical properties. Microstructure as well as interfacial studies were carried out using optical microscope.

Optical microscopic examination of composite samples show that 1h treated fibres offer much better adhesion with matrix precursor and the matrix also exhibits an obvious increase in the anisotropic domain size in case of 2P composites. Density of stabilized fibres and also of green composites has been found to increase with stabilization time. Flexural strength of green composites prepared with 0 and 2h treated fibres decreases (123 MPa to 60 MPa). However, as a result of better bonding between fibre and matrix, in case of 1P composites, strength is always high except in green stage. An attempt has been made to correlate the surface energetics of fibre with mechanical properties as well as matrix microstructure of carbon/carbon composites.

1.0 Introduction

Carbon/carbon (C/C) composites are the ceramic materials used for high temperature applications because of their far superior thermo-mechanical properties compared to the conventional materials[1]. These are good reasons to make them practically the ideal material for use in aerospace applications, such as rocket nozzles, exhaust cones, heat shields etc. [2]. However, processing of C/C composites is a complex process influenced by surface chemistry and topography of reinforcement, char or coke yield of the matrix resin and the fibre/matrix interactions at the interface[3-6].

All these parameters are known to influence the performance of the composites. The interactions at the interface between the fibres and matrix are crucial in determining the mechanical properties of the composites. Coal-tar pitch is unique among carbon matrix precursors because of its low price and its flexibility to produce carbons with very different microstructures. A compromise between strong and weak bonding at the interface is necessary to optimise the efficiency with which fibre properties are utilized and the fracture toughness of the composites increased[7-8]. A strong interface is known to lead to a brittle fracture behaviour, whereas a weak interface permits fibre/matrix debonding and sliding and no proper transfer of load to the reinforcement.

One of the main disadvantages with C/C composites is their high cost. With the increased emphasis on lower cost of production of C/C composites, more attention is being directed toward lower cost fibres and the use of very high char yield resins and pitches as impregnants. This paper deals with the former aspect. Since PANEX fibres undergo chemical and physical transformations during pyrolysis along with the matrix, the microstructure of the matrix will be different than the carbon fibre based composites.

During pyrolysis of preforms, especially upto 1000°C there is a large relative shrinkage of the matrix precursor compared to carbon fibres, which have already seen a temperature of 1000°C and above. As such there is hardly any shrinkage in the fibres and the shrinkage of the matrix causes stress concentrations at the fibre/matrix interface. One can therefore observe matrix cracks, fibre damage and therefore lower strength of the resulting composites. The advantage in using oxidised PAN fibres. 'PANEX', thermally stabilized upto 250°C only, besides their low cost is that they also undergo considerable shrinkage along with the matrix pitch and chances of stress related cracks are rare. However, the shrinkage will be influenced by the surface energetics of the fibre, which may inhibit the free shrinkage of the matrix. This will further influence the mechanical properties of the composites.

Very few studies have been reported on the oxidised PAN fibres based carbon/carbon composites using either phenolic resin or pitch as matrix precursors [5,9-11]. A systematic approach is therefore required to understand the role of surface energetics of the precursor PANEX fibres and the subsequent development of microstructure in the matrix and its overall influence on the mechanical properties of the resulting C/C composites. Present study is one such attempt in this direction.

2.0 Experimental

2.1 Preparation of PANEX Fibres

Polyacrylonitrile (PAN) fibres tow containing 6000 monofilaments of 1.2 d'tex each and diameter about 12.5 µm obtained from M/s Courtauld's, U.K. were used in the present study. These were first converted into PANEX fibres on a continuous scale by oxidising PAN fibres under different stabilization conditions viz: oxidation temperature 250°C and stabilization time 0, 1 and 2h respectively. About 500meters of PANEX fibre was prepared for each batch. Table-1 shows various physical characteristics of the stabilized fibres, while Table-2 shows the surface energetics for each batch. One can clearly notice that the three samples exhibit completely different characteristics and therefore lead to different behaviour of the resulting C/C composites.

2.2 Preparation of composites using PANEX fibres :

Unidirectional composites of size 130 x 5 x 4 mm^3 (approx.) were made by reinforcing separate batches of PANEX fibres with coal tar pitch as matrix. The specifications of the pitch are given in Table-3. A standard match mould die technique was used to prepare several batches of green composites A,B and C, corresponding to 0, 1 and 2h PANEX fibres as reinforcement. These composites were then subjected to various heat treatment temperatures viz. 600, 1000, 1500, 2000 and 2600°C, in ultra high purity nitrogen atmosphere to observe the transformation in the composite microstructure at each stage.

2.3 Characterzation of the composites :

Mechanical properties of the fibres as well as that of the composites were measured on an INSTRON 4411 model. Density of the fibres was measured by sink float method while that of the composites was determined using Archimedes principle. Insitu dilatometry of the PANEX fibres as such and that of the green composites was carried out on Mettler TA-4000 thermal analyser upto 1000°C. Surface energy of the PANEX fibres was determined by measuring dynamic contact angle using CAHN DCA 322 system. Polarised light microscopy of the cross-section of the polished samples of the composites was carried out on an Olympus rotating stage optical microscope, to understand the microstructure of the C/C composites at all the heat treatment temperatures.

3.0 Results and Discussion

3.1 Characteristics of the PANEX fibres :

Table-1 shows the characteristics of the three PANEX fibre samples identified for reinforcement. Column 2 of the table shows that the aromatization index increases with oxidation time showing that 2h sample is the best stabilized one. This is also reflected in the DSC results of the sample which show the value of ΔH to be only 82 kJ/mol for 2h as compared to 973 kJ/mol for 0 h sample suggesting it to be least stabilized of the three. Likewise other properties like tensile strength and the density also show linear trend indicating gradual structural changes in the three samples. Similarly the surface energy of the fibres shown in table-2, especially the polar components of the surface groups which are responsible for interaction, shows a variation from 3.8 dyne/cm to 10.24 dyne/cm for 2h sample and does not follow the trend as in Table-1.

The difference in the characteristics of the fibres should form different bonds with the matrix coal tar pitch in the green stage and the effect should very much be reflected in the shrinkage behaviour of the composites when subjected to pyrolysis, especially upto 1000°C. In order to observe the effect minutely, in situ dilatometry of the green composites was planned. Shrinkage of the PANEX fibres was followed along the length whereas in case of the composites it was measured in both the directions i.e. parallel as well as perpendicular to the fibre tows. This could give an idea about the total volume shrinkage of the composites.

3.2 Dilatometry of the composites :

The green composites prepared from all the three PANEX samples were subjected to thermo-mechanical analysis on Mettler TA-4000 thermal analyser, to understand the in situ shrinkage behaviour during pyrolysis. The dilatometry was carried out in notrogen atmosphere and the heating rate was kept at 5°C/min.

Figure 1(a) shows the shrinkage behaviour of the PANEX fibres alone while Figs.1 (b) and (c) show the shrinkage behaviour of green composites parallel and perpendicular direction of the reinforcement. As expected, the fibres stabilized for 0 h show maximum shrinkage while the 2h stabilized sample shows minimum shrinkage. Interestingly, similar trend is not followed if one looks at the curves obtained for the composites [Fig.1 (b) and (c)]. In order to correlate these curves with the behaviour of the interactions at the fibre matrix interface, total shrinkage, following these curves, in different temperature ranges are reproduced in Table-4.

As shown in Table-4, one finds that in the longitudinal i.e. parallel to fibre direction there is maximum shrinkage i.e. about 9% in case of composites A and C in the temperature range 0 to 400°C. On the other hand the shrinkage in the case of fibres itself is only -3% and + 0.5% respectively. That is there is additional shrinkage of 6% and 10% in the case of composites, suggesting strong fibre matrix interactions. This is also in tune with the larger values of surface energies for these fibres (Table-2). In case of composite B the additional shrinkage is only 2.5%. It can therefore be inferred that in case of composite B, the fibre matrix interactions are different. In the temperature range 400-1000°C there is almost no significant difference in the numerical values as well as the general trend of the shrinkages in the parallel direction.

Similarly in case of shrinkage in the perpendicular direction, there is a large difference in the values between the composites ranging between 9 to 37%. The difference is almost 4 times between A and B and 3 times between B and C, and here too the difference is more pronounced upto 400°C alone. If one looks at the combined effect of the longitudinal and the perpendicular shrinkage it is clear that there is large volume shrinkage in case of composites A and C and very little in case of composite B. The density of composite B should therefore be minimum. However, as shown in Fig. 2, the density of composite B is maximum at 1000°C. It can therefore be concluded that the interactions in the fibre and matrix in composites B are such that there is much less evolution of volatiles comparatively. Density for composite B is therefore maximum. The char yield or the weight loss during co-carbonization of the PANEX and the pitch matrix is in the order 43%, 39% and 45% respectively which confirms this view point. Since the evolution of the volatiles in the composite C is maximum, its density is minimum at 1000°C.

3.3 Mechanical Properties of the composites :

Figure-3 shows the comparative bar chart of the flexural strength and flexural modulus of the composites A, B and C after heat treatment at different temperatures. As discussed above because of the better bonding between the fibre and the matrix in case of composites B, it shows highest values for strength at each stage of heat treatment. The influence is more pronounced in flexural modulus of composite B and is significantly higher comparatively.

3.4 Optical microscopy of the green as well as carbonized composites :

Fig.4 (a-c) shows the optical micrographs of the composites A,B and C treated at 600°C. Composite A shows the development of fine mosaic texture of the matrix. Composites B and C show essentially medium coarse to coarse mosaic texture of the matrix. There are areas where some flow type behaviour of the matrix pitch is also observed in composite C. One important point of notice is the difference in the diameters of the fibres in the three samples. Although the difference in the diameters of the PANEX fibres is not significant (Table-1), in the composites the diameter of the fibre in composite A, as measured from image analyser, is 9.5 μm as compared to 7.4 μm in composite B. Fig. 5 shows plots of diameter of the fibres in the composites subjected to different heat treatment. The higher diameter of the PANEX fibres in composite B could be attributed to strong fibre matrix interactions which do not allow the fibre to shrink along its cross section. The same behaviour was also observed by the authors earlier [6]. However, between 1000°C and 1500°C the matrix microstructure generally turns into a coarse mosaic type with flow type microtexture of the matrix in the pockets which are not influenced by the fibre energetics i.e. areas which are comparatively farther from the fibre surface. The diameters of the fibres, as expected, is also reduced considerably.

Composite B, which shows maximum strength shows only a coarse grain type matrix microstructure for all the heat treatment temperatures upto 2600°C (**Fig.**6-8). More importantly one does not observe matrix microcracks, as has generally been the case for Carbon fibre based C/C composites. This confirms the advantage with PANEX fibres which undergo co-carbonization along with the pitch and therefore stresses due to mismatch of fibre matrix shrinkage during pyrolysis are much less in these composites.

Beyond 1500°C it is quite evident that the fibres start developing anisotropy and the sample treated to 2600°C clearly shows the development of radial type of microtexture in the fibre cross section. This is quite unusual of PAN based carbon fibres, which generally show onion type microtexture. Radial type microtexture of the fibres as reinforcement is more preferable for high performance composites.

4.0 Conclusion

The study clearly reveals the importance of having optimum surface energetics of the reinforcement which will lead to strong C/C composites. Experiments are in progress to densify the composites to at least 1.8g/cc for the evaluation of ultimate mechanical properties of PANEX based C/C composites.

5.0 Acknowledgement

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References

1. "Carbon-carbon composites" (Ed. G. Savage) Pub: Chapman and Hall, London, 1993.
2. Thomas, C.R. - Overview-What are carbon-carbon composites and what do they offer ?, Chapter 1 in Essentials of carbon-carbon composites, 1994.
3. L.M. Manocha and O.P. Bahl, Carbon, **26** (1988) 13.
4. L.M. Manocha, E. Yasuda, Y. Tanabe and S. Kimura, Carbon, **26** (1988) 333.

5. E. Fitzer, K.H. Geigle and W. Huttener, Carbon, **18** (1980) 265.
6. T.L. Dhami, O.P. Bahl and P.K. Jain, Carbon, **33** (1995) 517.
7. Fitzer, E., Carbon, **25** (1987) 25.
8. Kowbel, W. and Shan, C.H., Carbon, **28** (1990) 287.
9. V. Markovic and S. Marinkovic, Carbon, **26** (1988) 329.
10. L.M. Manocha and Ketan G. Patel, Proc. 23rd Biennial Conference of Carbon Pennsylvania, **vol. II** (1997) p. 418.
11. V. Markovic and et.al., Proc. 15th Biennial Conf. on Carbon, Pennsylvania, 1980, p.272.

Table 1: PANEX Fibres characteristics

Fibre Type	A.I.	Weight g	Diameter μm	Enthalpy kJ/mol	T.S. MPa	Y.M. MPa	Density g/cc
0 h	51	0.7524	11.81	973.9	401	1405.4	1.30
1 h	60	0.7690	11.67	475.3	249	739.3	1.43
2 h	75	0.7626	11.44	82.2	206	390.6	1.49

Table 2 : Surface energy of PANEX fibres

	Cosθ(advancing)		**Geometric Mean Method (dyne/cm)**		
	Water	MI	Disp.	Polar	Total
0 h	0.231+0.018	0.693+0.011	31.58	6.55	38.13
1 h	0.136+0.006	0.704+0.016	33.52	3.80	37.32
2 h	0.331+0.021	0.678+0.011	29.38	10.24	39.62

Table 3:Properties of pitches

Characteristics	Preforming pitch	Impregnating pitch
Softening point (°C)	98	85
Quinoline insoluble (%)	9.9	0.6
Toluene insoluble (%)	29.1	21.0
Coking value (%)	57.4	51.0

Table 4

Percent change in length in PANEX fibres and the green composites (from Fig. 1)

Temperature	0-400°C	400-600°C	600-1000°C	0-1000°C
PANEX fibres Parallel (longitudinal)				
PANEX 1	-3.0	-2.5	-4.0	-9.5
PANEX 2	-1.5	-2.3	-3.8	-7.6
PANEX 3	−0.5	-2.5	-4.0	-6.0
Green composites Parallel				
Composite A	-9.0	-3.5	-3.3	-15.8
Composite B	-4.0	-3.0	-3.3	-10.3
Composite C	-9.8	-2.7	-2.7	-15.2
Green Composites Perpendicular				
Composite A	-37.0	-7.5	-3.0	-47.5
Composite B	- 9.5	-7.0	-5.0	-21.5
Composite C	-27.0	-3.0	-2.0	-32.0

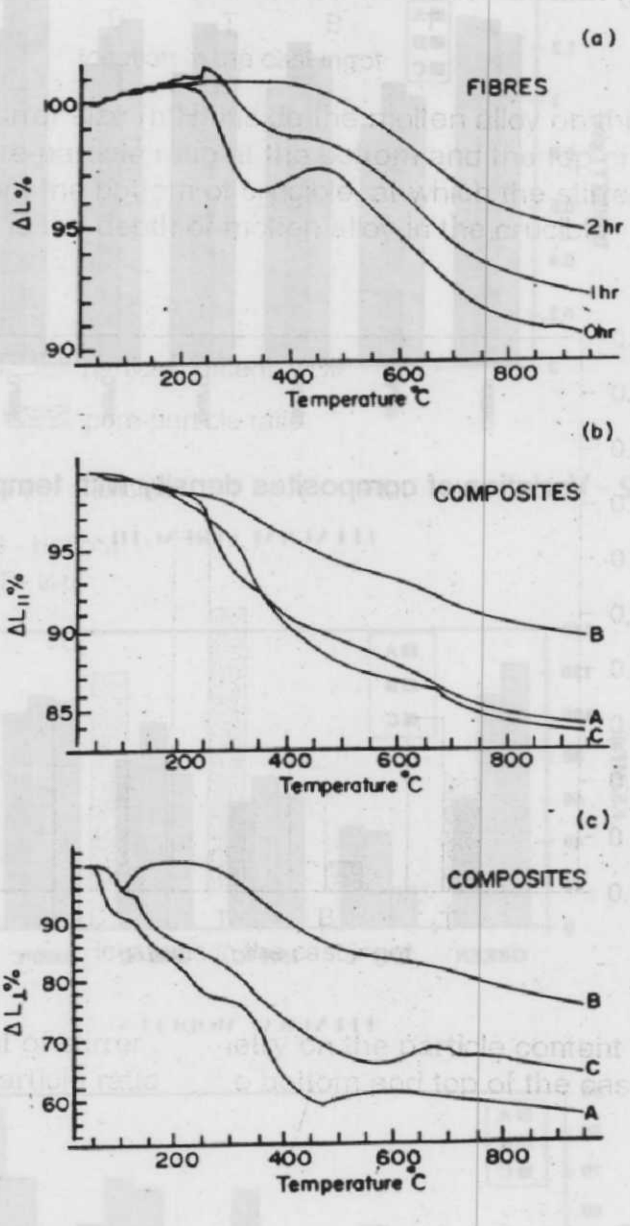


Fig. 1 - Dilatometry of panex fibres and the green composites

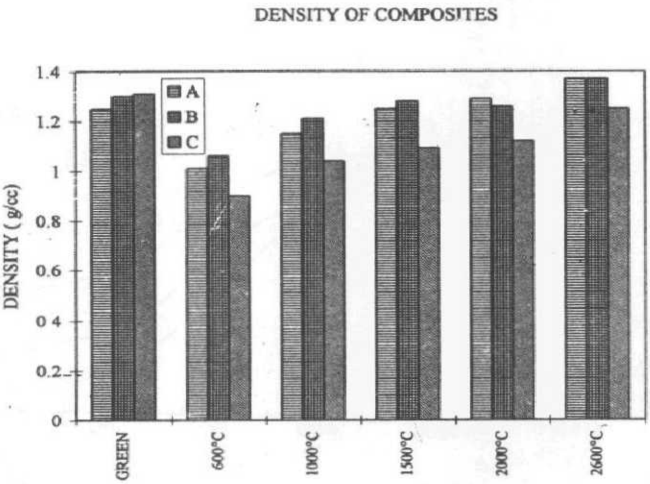
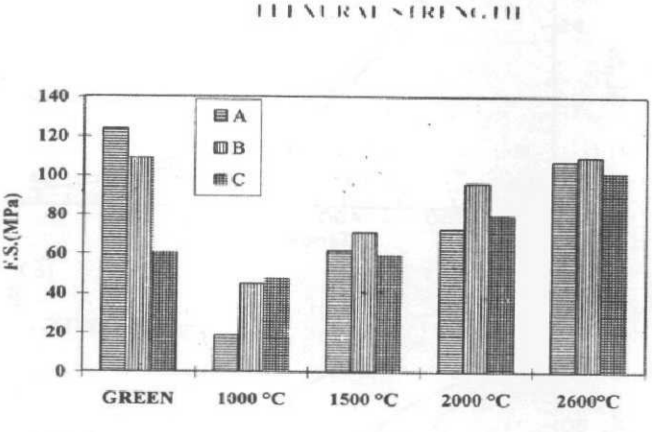


Fig. 2 - Variation of composites density with temperature.



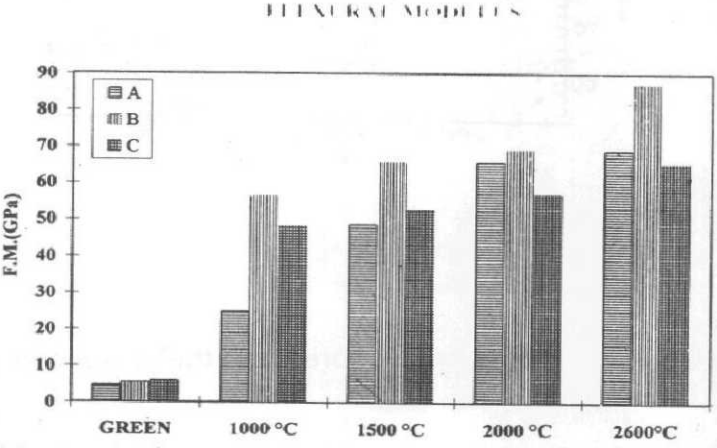


Fig. 3 - Mechanical properties of composites after heat treatment at different temperature.

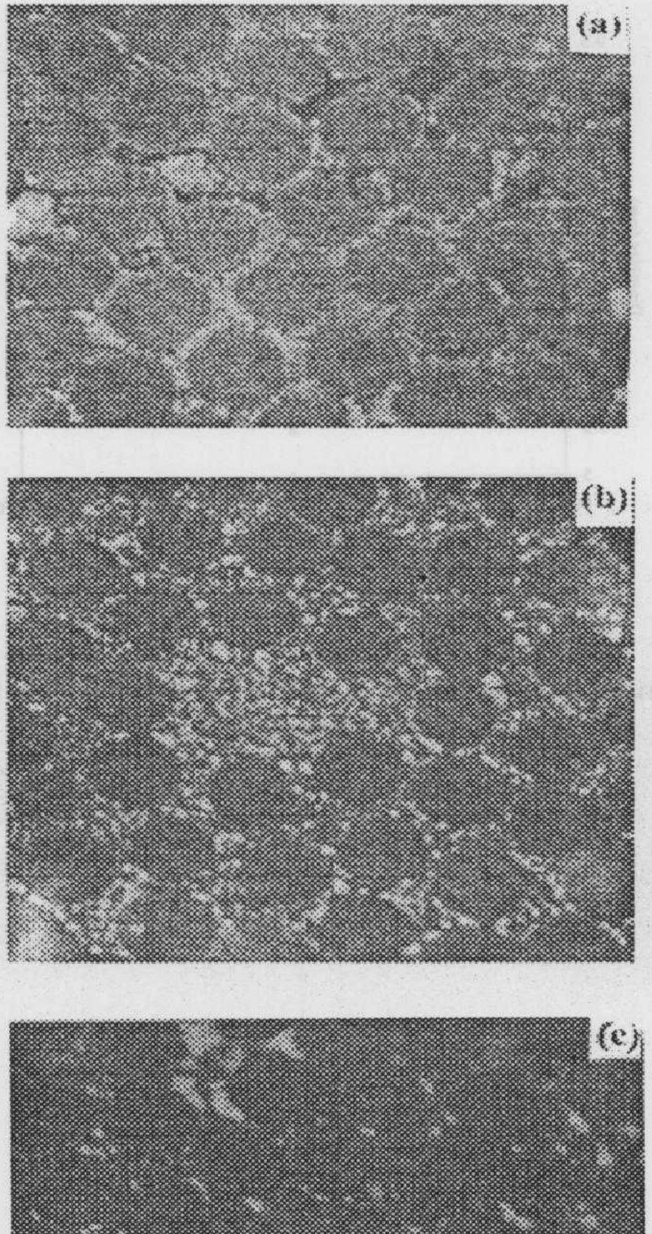


Fig. 4 - Optical Micrographs of composites HTT 600° C

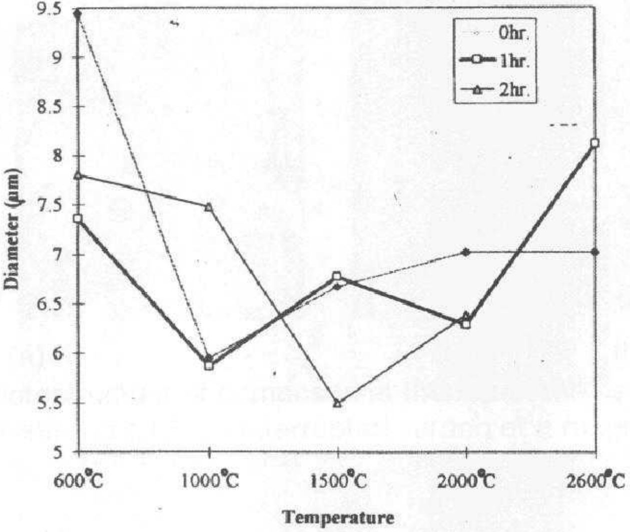


Fig. 5 - Changes in the diameters of the PANEX fibres in the composites at different HTT

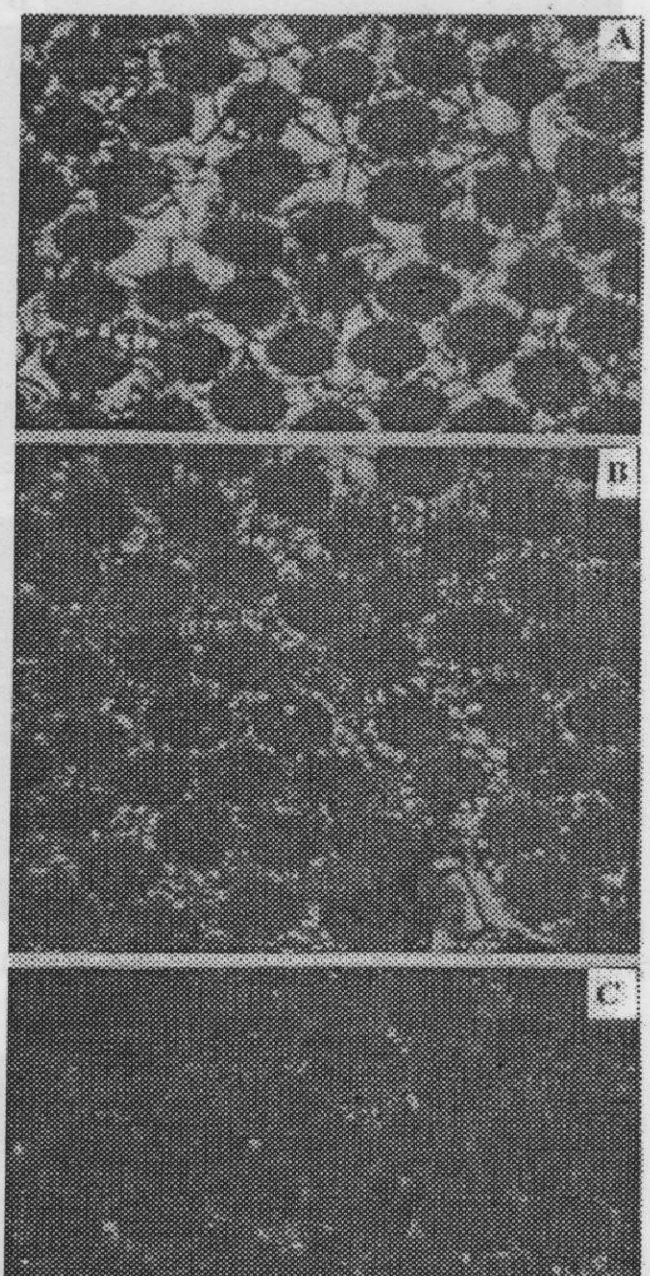


Fig. 6 - Optical Micrographs of composites HTT 1000° C

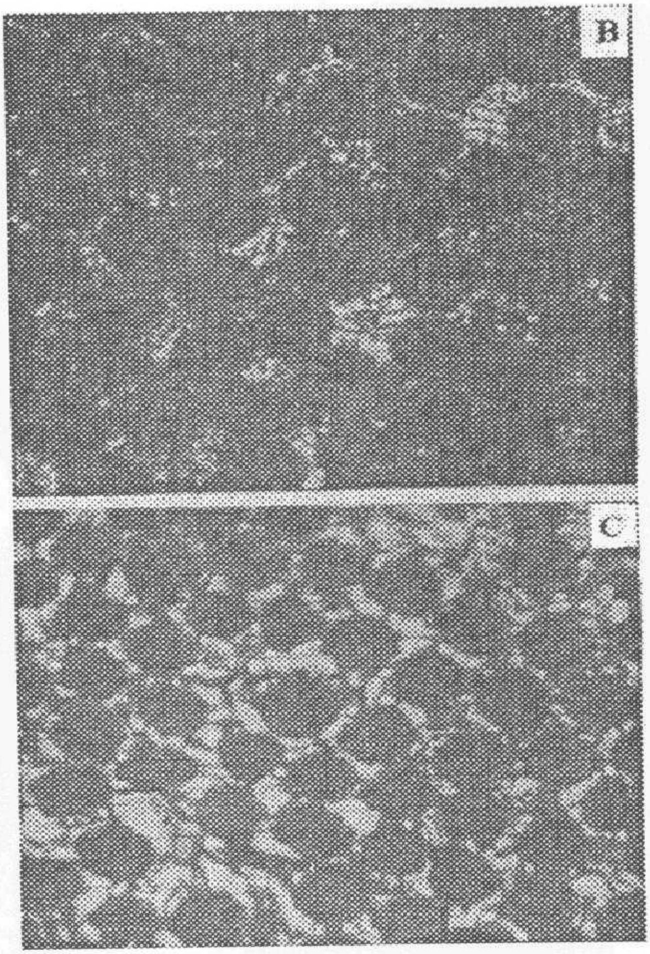


Fig. 7 - Optical Micrographs of composites HTT 1500° C

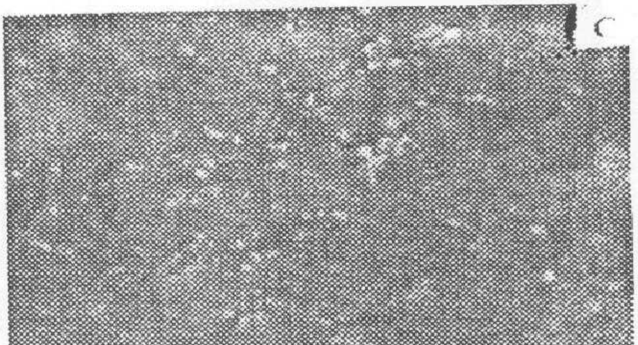


Fig. 8 - Optical Micrographs of composites 'C' HTT 2600° C