JOURNAL OF MATERIALS SCIENCE 25 (1990) 4604–4606

Development of preforming pitch for carbon–carbon composites from coal-based precursors

R. K. AGGARWAL, G. BHATIA, O. P. BAHL
Carbon Technology Unit, Division of Materials, National Physical Laboratory, New Delhi 110 012, India

Preforming pitch, a special type of pitch, used for the matrix formation of carbon–carbon composites, has been developed from suitable coal-based precursors, using the techniques of distillation, condensation and polymerization. The effects of various processing parameters, namely the temperature and period of heat treatment, and the atmosphere (inert or partial vacuum) during the heat treatment, on the characteristics of the resulting pitch have been studied. Some of the pitches were subjected to field trials from which the characteristics of a good preforming pitch leading to a carbon–carbon composite of density around 1.8 g cm^{-3} have been identified.

1. Introduction

Preforming pitch is one of the most important raw materials in the development of carbon–carbon composites. Its function is to bond the flexible carbon fibres, taken as such or woven in the form of a two- or three-dimensional preform, into a rigid form, known as the skeleton, which is then densified by several cycles of impregnation, carbonization and graphitization to result finally in what is known as a carbon–carbon composite [1–4]. As one would expect, this preforming pitch is basically similar to the binder pitch used in the manufacture of conventional carbon products. However, because of the differences in the counterpart material in the two cases, namely, carbon fibres in the case of carbon–carbon composites and a filler coke in the case of conventional carbon products, and, therefore, because of the consequent differences in the production technologies in the two cases, the characteristics of the pitches required in the two cases are entirely different. Because carbon–carbon composites form a class of materials finding potential applications in defence and other critical fields, little is published in the open literature on their developmental aspect. In view of this, we initiated work in this direction which also included the development of special pitches, preforming as well as impregnating [2, 5–8]. The present paper reports the results of attempts made to develop the preforming pitch by the thermal and chemical (sulphur addition) treatments of two commercially available coal-based precursors, (1) a medium-hard grade coal tar pitch, and (2) a coal tar.

The preforming pitches, so obtained, were characterized with respect to softening point (SP) (ring and ball), benzene (BI) and quinoline (QI) insolubles contents, β-resin content, coking value (CV), and atomic C/H ratio. These were then used in the actual formation of carbon–carbon composites from which the specifications of the most suitable preforming pitch were evaluated.

2. Experimental procedure

The characteristics of the coal tar pitch and coal tar used in the present work are given in Table I. The attempts to develop the preforming pitch from the coal tar pitch precursor consisted of two types of experiments: (1) the thermal treatment of the pitch in a nitrogen atmosphere, and (2) the chemical treatment of the pitch in the presence of sulphur. In the former case, the coal tar pitch was heat-treated in a 3-litre three-neck flask of the assembly shown in Fig. 1, at a temperature of 400° C for periods of 8 and 16 h to obtain two preforming pitches (1 and 2) with softening points of 98 and 125° C, respectively, and other characteristics as given in Table II, and in the latter case, the coal tar pitch was heated in the presence of sulphur at a temperature of 180° C for a period of 16 h to obtain another batch of the preforming pitch (3) having the characteristics given in Table II.

The other attempt to develop the preforming pitch from a coal tar precursor consisted of heat treating the

TABLE I Characteristics of the coal-based precursors

Pitch	Characteristics	Coal tar pitch	Coal tar
1.	Softening point (R&B) (° C)	70	–
2.	Density (g cm^{-3})	1.30	1.18
3.	Coking value (%)	51.0	39.9
4.	Benzene insolubles (%)	28.8	15.4
5.	Quinoline insolubles (%)	10.1	4.2
6.	β-resins (%)	18.7	11.2
7.	Ash content (%)	0.27	0.16
8.	Elemental analysis:		
	Carbon (C) (%)	93.3	91.0
	Hydrogen (H) (%)	4.4	5.0
	Atomic C/H ratio	1.78	1.53

0022–2461/90 $03.00 + .12

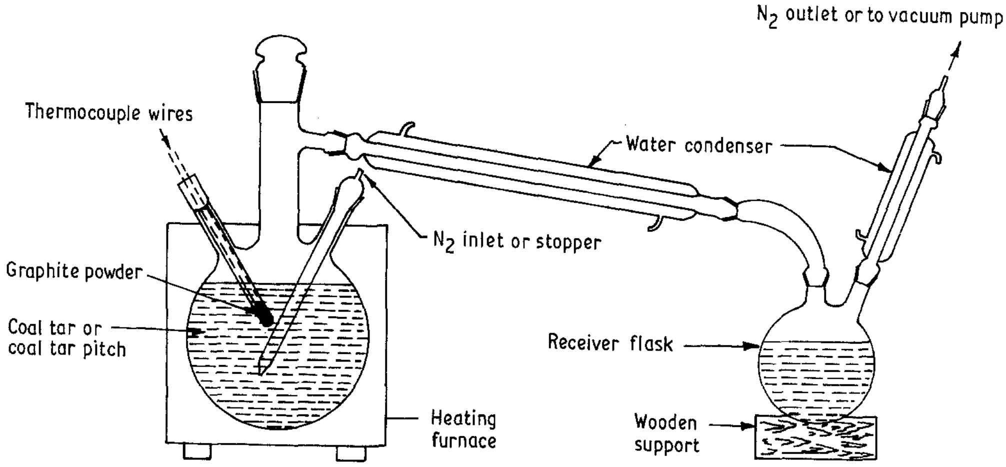

Figure 1 A drawing of the apparatus for the development of preforming pitch.

tar at temperatures of 350 to 390° C under a partial vacuum of 14 to 20 cm Hg for a period of 2 to 3 h, again using the assembly shown in Fig. 1. In this fashion, another three preforming pitches (4 to 6) were obtained, the characteristrics of which, along with the processing conditions used, are shown in Table III.

All six batches of preforming pitches were then employed in the development of carbon–carbon composites using a two-dimensional carbon fibre cloth, the results of which are described and discussed below.

3. Results and discussion

It is observed from Table II that the heat treatment of the coal tar pitch at 400° C for 8 and 16 h results in an increase in the values of all the measured characteristics. This is due to the removal of low molecular weight components of the pitch as well as due to the polymerization and condensation reactions occurring during the heat treatment. When green composites made from pitch 1 were carbonized, the skeletons were found to be fluffy, possessing an unreasonably low density of 0.9 g cm^{-3}, whereas pitch 2 led to skeletons of slightly higher density. These observations may be attributed to low values of β-resin content in these pitches. Therefore, the preforming pitches 1 and 2 were not considered suitable for making carbon–carbon composites. It was thought that further heat treatment of the coal tar pitch precursor would also not result in an improved pitch but only increase the benzene and quinoline insolubles content without increasing the β-resin content of the pitch.

When the coal tar pitch was chemically treated with 12% (by weight) sulphur, fast removal of hydrogen in the form of H_2S gas took place. Although this treatment resulted in an increase in the coking value, quinoline insolubles and benzene insolubles content, it did not improve considerably the β-resin content as is seen from Table II. Moreover, it is known that modification through sulphur addition has the disadvantage that some unreacted sulphur in the composite could cause puffing problems at around 1400° C. Therefore, the chemical modification of pitch with sulphur was considered unsuitable for making a good preforming pitch.

In the development of preforming pitch from coal tar, it is seen from Table III that all the characteristics of the resulting pitches (4 to 6) improve as the severity of the heat-treatment conditions (temperature, time and partial vacuum) increases. It may be worthwhile to mention here that compared to the process of heat treatment under a nitrogen atmosphere, the heat treatment under partial vacuum is a more efficient way of removing the low molecular weight components.

It may be noted that pitch 5 was much superior in quality compared to pitch 4 because of considerable improvement in β-resins and coking value without significant increase in the QI content. Both of these

TABLE II Characteristics of the preforming pitches obtained from the coal tar pitch precursor

Pitch	Raw material and heat treatment conditions	Characteristics of preforming pitches obtained				
		SP (°C)	CV (%)	BI (%)	QI (%)	β-resins (%)
1.	Coal tar pitch, 400° C, 8 h, N_2 atmosphere	98	55.3	35.0	12.5	22.5
2.	Coal tar pitch, 400° C, 16 h, N_2 atmosphere	125	62.2	44.6	16.8	27.8
3.	Coal tar pitch + 12% S (by wt)	–	68.0	52.2	25.4	23.8

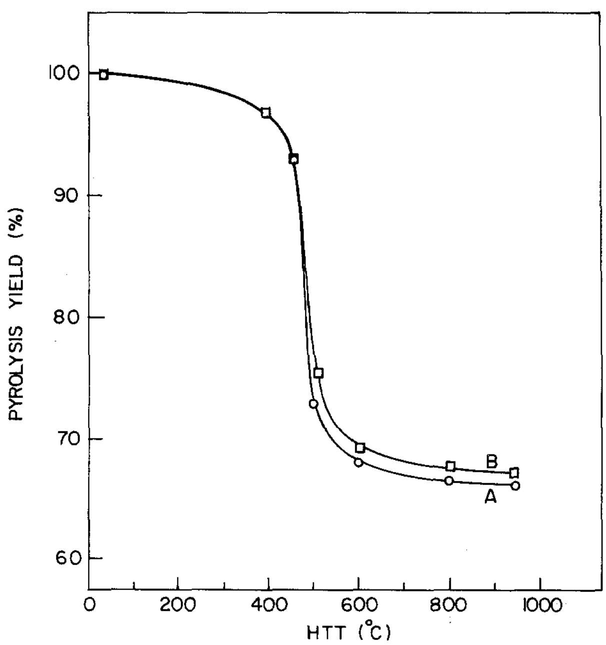

Figure 2 Pyrolysis yields of (A) the straight-made preforming pitch 5, and (B) a blended preforming pitch, as a function of heat-treatment temperature.

TABLE III Characteristics of the preforming pitches obtained from the coal tar precursor

Pitch	Raw material and heat treatment conditions	Characteristics of preforming pitches obtained				
		SP (°C)	CV (%)	BI (%)	QI (%)	β-resins (%)
4.	Coal tar, 350°C, 20 cm Hg, 3 h	123	59.6	36.4	10.2	26.2
5.	Coal tar, 370°C, 16 cm Hg, 3 h	170	67.5	51.5	13.5	38.0
6.	Coal tar, 390°C, 14 cm Hg, 2 h	190	77.0	63.0	25.0	38.0

pitches (4 and 5) resulted in good processability of the green carbon–carbon composites. However, on carbonization, pitch 4 led to a fluffiness in the carbon–carbon composites and consequently low apparent density in contrast to pitch 5 which resulted in dense carbon–carbon composites. The observations on pitch 4 could again be attributed to low values of β-resins and quinoline insolubles in this pitch as well as to its lower coking value compared to that of pitch 5.

When pitch 6 was used in making the green composites, difficulties were faced in the processing because of its significantly higher softening point and lower benzene solubles content. Further, on carbonization, this pitch led to delamination of the composites and a loss of their integrity, which indicated a poor wettability of the carbon fibres by the pitch. This poor wettability is due to unreasonably low content of the benzene solubles in the pitch.

In view of the above experimental results, it was concluded that a pitch, in order to be a good preforming pitch, should possess optimum contents of quinoline and benzene insolubles, and should possess a high coking value and high β-resins content. All these properties are needed to achieve good wettability of the carbon fibres by the pitch, and preserve the integrity or to prevent the delamination or distortion of the carbon–carbon composites on carbonization. Pitch 5 was found to satisfy all these requirements and led to carbon–carbon composites with final densities of around 1.8 g cm^{-3}.

It is worthwhile to mention here that while the temperature could be maintained within an accuracy of ± 5°C, fluctuations in partial vacuum did occur due to release of volatiles from the pitch, on which no good control could be maintained. In view of such practical difficulties in maintaining the partial vacuum and the heat-treatment temperature to the desired values, the characteristics of the resulting preforming pitches varied at times. Therefore, in such cases, blending of preforming pitches was done on the basis

TABLE IV Characteristics of the straight-made preforming pitch 5 and a blended preforming pitch

Characteristics	Straight-made preforming pitch 5	Blended preforming pitch
Softening point (R&B) (°C)	170	165
Coking value (%)	67.5	68.6
Benzene insolubles (%)	51.5	53.0
Quinoline insolubles (%)	13.5	14.2
β-resins (%)	38.0	38.8
Atomic C/H ratio	2.03	2.01

of "Law of Mixture" in such a way that the characteristics of the resulting pitch came close to the specifications of the preforming pitch 5. The validity of the blending process appears to be confirmed by the fact that the preforming pitch 5 and a blended pitch having similar specifications as given in Table IV, were found to have a similar TGA behaviour, as shown in Fig. 2.

4. Conclusion

The acceptable range of specifications of a good preforming pitch capable of producing carbon–carbon composites with a density of 1.8 g cm^{-3} are given below:

Softening point (R&B)	165 to 175°C
Coking value	65 to 70%
Benzene insolubles	50 to 55%
Quinoline insolubles	12 to 15%
β-resins	35 to 40%
Atomic C/H ratio	1.95 to 2.05

Acknowledgements

The authors thank Dr V. N. Bindal, Head, Division of Materials, for his keen interest in the work, and Professor S. K. Joshi, Director, National Physical Laboratory, New Delhi, for permission to publish this paper.

References

1. E. FITZER, "Carbon fibre reinforced all carbon composites", Proceedings of the 1st Indian Carbon Conference, New Delhi, 15-17 December, 1982 (Indian Carbon Society, New Delhi, 1984) p. 55.
2. L. M. MANOCHA, G. BHATIA and O. P. BAHL, *ibid.*, p. 325.
3. F. TAUZIN, "Carbon-carbon composites: Modern method of production", Extended Abstracts - International Carbon Conference, Bordeaux, France, 2-6 July 1984 (French Carbon Society, 1984) (Carbon '84) p. 197.
4. E. FITZER, *J. Chim. Phys.* 81 (1984) 717.
5. O. P. BAHL *et al.*, "Development of high density carbon-carbon composites", Proceedings of the International Carbon Conference, Baden-Baden, West Germany (German Ceramics Society, 1986) p. 738.
6. O. P. BAHL *et al.*, "Development of carbon-carbon composites for bio-medical application", Final Technical Report, DST-UNDP Project, June 1986.
7. O. P. BAHL *et al.*, "Development of high density carbon-carbon composites", Final Technical Report, Project sponsored by Defence Research and Development Laboratory, Hyderabad, August 1986.
8. R. K. AGGARWAL *et al.*, "Development of preforming pitches for carbon-carbon composites", Proceedings of the Seminar and Workshop on Carbon Fibres and their Applications, New Delhi, 15-17 December 1986 (Indian Carbon Society, New Delhi, 1986) p. 151.

Received 11 May
and accepted 10 October 1989