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The influence of adding pitch to resin as a matrix precursor on properties of carbon–carbon composites

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Carbon–carbon composites were prepared with commercially available carbonized and graphitized fibres, with a mixture of pitch and phenolic resin as a binder and pitch as an impregnant. The contents of pitch in mixtures were: 0, 10, 20 and 30 wt%. The influence of pitch content in the mixture and fibre type on mass loss, shrinkage and mechanical properties of the composites was examined. With an increase of pitch content mass loss and shrinkage increased, while mechanical properties decreased. After three densification cycles, flexural strength increased with increasing pitch content in the binder, especially for composites with graphitized fibres.

1. Introduction

In the conventional carbon–carbon composites fabrication by liquid impregnation, the matrix is emplaced by impregnation of fibres with pitch or with polymer resin [1]. The precursor for the liquid impregnation process should give a high carbon yield, a small linear shrinkage, weak interfacial bonds between fibre and matrix in the green composite, and the possibility of open porosity formation which could make further densification processes more effective [2–5].

Coal tar pitch gives a low carbon yield when carbonization is performed at atmospheric pressure. The carbon yield is improved by adding sulfur or resin, or by increasing the pressure of carbonization [6–8].

A high carbon yield is obtained during resin carbonization, but the volume shrinkage is high too [9].

Phenolics form covalent bonds between the hydroxyl groups of the resin and functional groups of the fibre surface, which improves adhesion [3]. Good chemical bonding between the fibre and matrix in the composite, together with high linear shrinkage of the phenolics, results in poor flexural strength [10]. This is explained by restrained shrinkage of the matrix precursor during the carbonization process causing high shrinkage stresses, pyrolysis cracks and, in the worst case, fibre damage. This is less pronounced when pitch is used as the matrix precursor.

The aim of this work was to gain an insight into the effect of adding pitch to resin as a binder on the mechanical and bulk properties of carbon–carbon composites, with respect to the carbon yield and shrinkage of the matrix precursor during pyrolysis and the densification process. The properties of the matrix without fibres, and the influence of fibre type, were examined, for a better understanding of the influence of adding pitch to resin on the properties of carbon–carbon composites.

2. Experimental procedure

The samples were prepared with commercially available PAN-based graphitized fibres (Sigrafil HM) and carbonized fibres (Torayca T-300). A phenolic resin–resol type and coal tar pitch, with a softening point (S.P.) of 80 °C, was used as the matrix precursor.

A unidirectional green composite was prepared by the wet winding technique, with the same number of fibres. Phenolic resin, or its mixture with the pitch, was used as a binder. Mixtures were handmade and the pitch content was: 10, 20 or 30 wt%. A mixture with 30 wt% pitch was unworkable. The samples were cured by hot pressing and after that were carbonized up to 1000 °C in a flow of nitrogen. After carbonization the composite was high temperature treated in vacuum at 1800 °C for 3 h.

For matrix examination, samples were prepared in the same way as composites but, without fibres.

Pure coal tar pitch was used for impregnation of composites. Evacuated samples were impregnated with molten pitch under pressure and then cured up to 600 °C, also under pressure. After that, the samples were carbonized up to 1000 °C and high temperature treated at 1800 °C. Three subsequent cycles of liquid pitch impregnation, carbonization and high temperature treatment were performed.

The volume fraction of the fibres in the cured composites was determined by dissolving the matrix in a hot solution of H_2O_2 and H_2SO_4.

Density and open porosity of the composites were determined using the hydrostatic balance method, with xylene as a liquid.

Mechanical testing was performed on an Instron machine. Flexural strength was measured in a three-point bending test on specimens 100 × 10 × 2.5 mm, at a span to depth, s/d, ratio of 32:1.

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Fractured surfaces were studied by scanning electron microscopy (SEM).

3. Results and discussion

Mass loss after carbonization (carb) and high temperature treatment (HTT) of the matrix precursor (MP) and of the composites with graphitized (C–I) or carbonized (C–II) fibres are compiled in Fig. 1. With an increase of pitch content in the mixture, mass loss after carbonization and high temperature treatment increases. The obtained results for the matrix precursor were not in agreement with results expected from the simple rule of mixtures (straight line in Fig. 1), which indicates some interaction between the pitch and the matrix. The mass loss of composites with graphitized fibres is smaller than of composites with carbonized fibres. Commercial fibres are usually surface treated, and there are more functional groups on the surface of carbonized fibres than on the surface of graphitized fibres [4]. This results in a higher mass loss for composites with carbonized fibres.

After high temperature treatment the composites with carbonized fibres and matrix with a pitch content of 10 wt % were decomposed. With an increase of the pitch content in the matrix precursor, mass loss and volume shrinkage, $\Delta V/V$, (except for the matrix precursor with a pitch content of 20 wt %) increase, see Fig. 2.

Functional groups from the fibre's surface react with –OH groups from phenolic resin and form strong covalent bonds. These bonds between the fibres and the matrix hinder shrinkage in the fibre direction during carbonization. Cross-sectional shrinkage, $\Delta A/A$, of composites C–I and C–II is shown in Fig. 2. Due to the larger number of functional groups on the surface of carbonized fibres, adhesion between these fibres and the matrix is stronger, which causes higher shrinkage of C–II during carbonization than C–I.

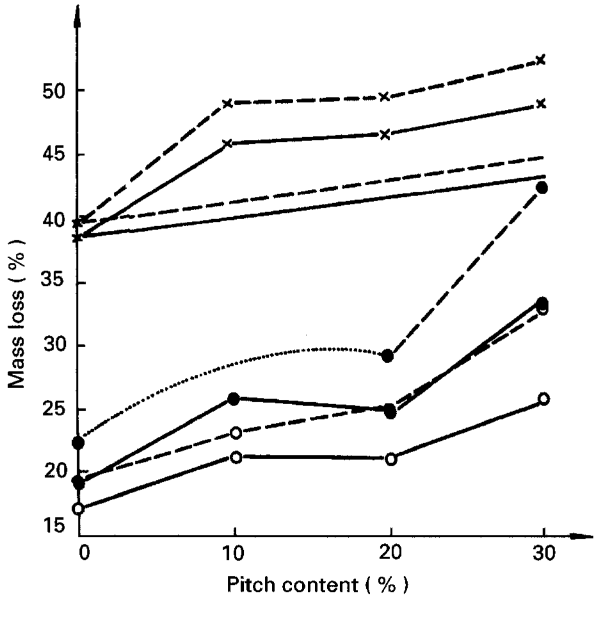


Figure 1 Mass loss after (—) carbonization and (– – –) high temperature treatment of (×) matrix precursor and composites: (O) C–I, (●) C–II.

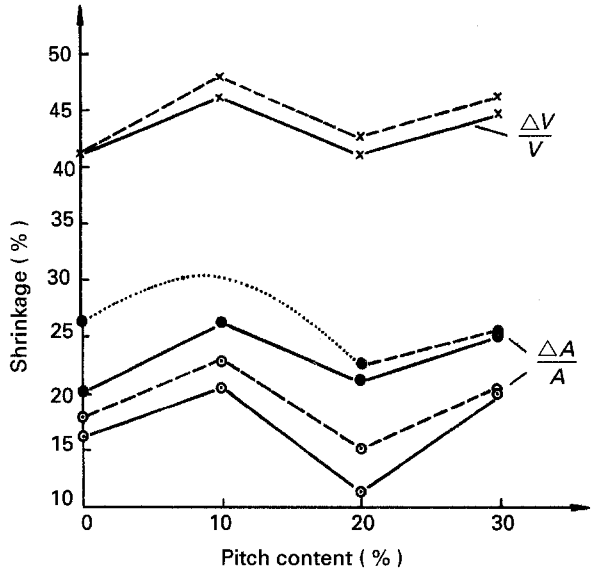


Figure 2 Shrinkage after (—) carbonization and (– – –) high temperature treatment of (×) matrix precursor and composites: (O) C–I, (●) C–II.

With an increase of pitch content in the matrix, cross-sectional shrinkage increases for both kinds of composites (except when the matrix content is 20 wt % pitch).

Although all the composites were made in the same way and with the same number of fibres, there exist some differences in the volume fraction of fibres in cured composites, see Table I. The matrix precursor with 30 wt % pitch does not completely impregnate the fibres, which causes a lower fibre content in the composite.

Pycnometer density of the matrix precursor after carbonization and high temperature treatment is shown in Table II. With additions of pitch up to 30 wt % the density of the matrix after carbonization is slightly lower than the density of pure resin. With an increase of pitch content density begins to increase, but it is still lower than for pure resin. This is unexpected because the density of pitch after carbonization and HTT is higher than the density of resin. This is probably a consequence of interaction between the pitch and resin. After HTT, the density of the matrix precursor increases with an increase of pitch content in the mixture.

Open porosity occurs when pitch is added, and increases with pitch content and with a rise of treatment temperature.

Densities, d, of C–I and C–II, after curing, carbonization and HTT are shown in Fig. 3a. Densities of C–I are higher than the densities of C–II after curing, carbonization and HTT, because of the higher density of the graphitized fibre (1840 kg m^{-3}) compared with that of the carbonized fibres (1720 kg m^{-3}). In almost all cases, density increases with an increase in pitch content. Composites with a pitch content of 30 wt % are an exception. These composites have the lowest fibres content (see Table I) and their densities are lower than expected.

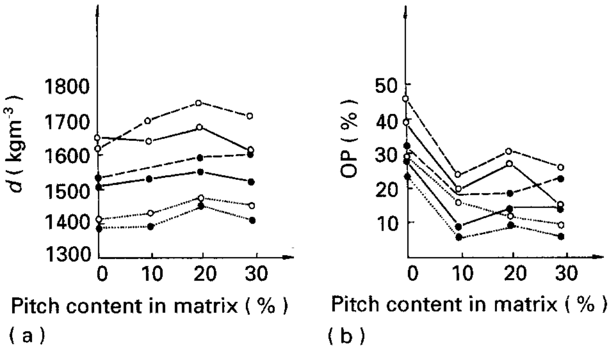
A rise in process temperature (curing, carbonization, high temperature treatment) influences an increase

TABLE I The volume fraction of fibres in cured composites

Pitch content (%)	C–I	C–II
0	41.98	40.14
10	39.33	36.18
20	42.42	42.75
30	33.14	32.21

TABLE II Density (d) and open porosity (OP) of matrix after carbonization and high temperature treatment

Pitch content (%)	d (kg m^{-3})		OP (%)	
	Carb	HTT	Carb	HTT
0	1490	1480	–	–
10	1450	1500	1.0	2.7
20	1470	1540	1.9	3.9
30	1480	1590	2.7	5.3



(a) (b)

Figure 3 (a) Density and (b) open porosity of composites after (-----) curing, (——) carbonization and (– – –) high temperature treatment: (○) C–I, (●) C–II.

in the density of the matrix, which results in an increase of composite density.

The open porosity (OP) is higher for composites C–I after curing, carbonization and HTT (Fig. 3b). In composites made with graphitized fibres, adhesion between the fibres and the matrix is weaker than that of carbonized fibres and, therefore, during carbonization, the matrix can easily shrink away from the fibres leaving behind a gap. This shrinkage gap between the carbon matrix and graphitized fibres is clearly seen in the SEM micrograph of the carbonized C–I composite (Fig. 4). In the case of carbonized fibres, surface groups from the fibres make strong bonds with phenolic resin. During carbonization these strong bonds inhibit shrinkage of the carbon matrix from the fibres (Fig. 5). This leads to the formation of cracks in the carbon matrix and voids between the fibre bundles. This results in a lower open porosity of composites with carbon fibres, than composites with graphitized fibres. After HTT, the matrix continues shrinking, which causes higher open porosity of composites, than after the carbonization process.

Adding pitch to phenolics decreases the adhesion between the matrix and the fibres, which decreases the formation of intramatrix cracks. Also, the carbonized fibres begin to separate from the carbon matrix, which is more pronounced with a higher pitch content in the matrix precursor (Fig. 6). The open porosity is lower when the matrix precursor contains pitch. The pitch present in the matrix precursor decreases stresses in the matrix, and in that way decreases the intramatrix cracks and the open porosity of these composites.

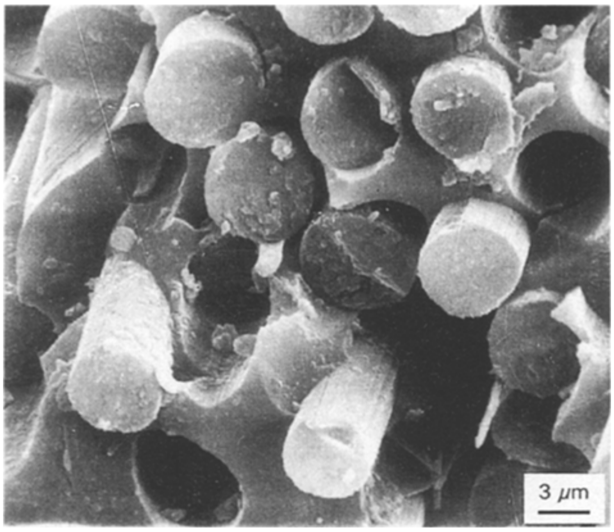


Figure 4 SEM micrograph of the carbonized C–I composite (10 wt % pitch content in the matrix precursor).

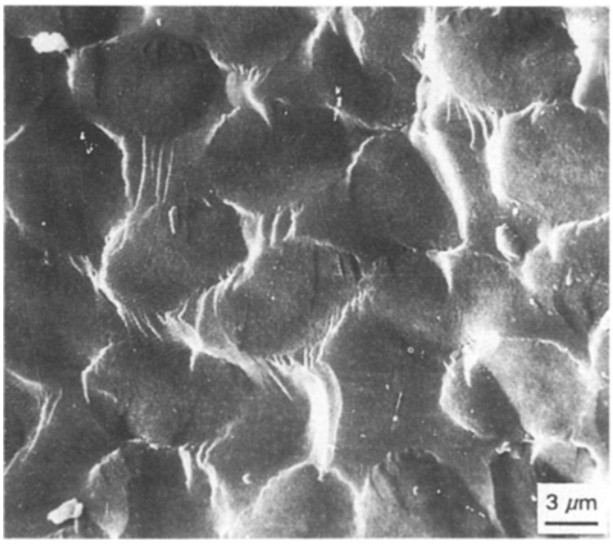


Figure 5 SEM micrograph of the carbonized C–II composite (10 wt % pitch content in the matrix precursor).

The open porosity is very important for the densification process. The higher the open porosity the more efficient is the densification process.

The mass yield after all three densification processes for composites with both types of fibres is presented in Fig. 7. Composites with graphitized fibres have a higher mass yield because their open porosity is higher. A higher mass yield means that more impregnant fills the pores and cracks in the matrix and gaps between fibres and matrix.

There exists a disproportion between open porosity of composites before and mass yield after the densification process (see Fig. 7). Liquid pitch fills the pores, but porosity is introduced by gas generation and dimensional shrinkages that accompany carbonization. Inequalities and anisotropies of fibres and matrix thermal expansion coefficients, introduces thermal stresses during baking, high enough to cause cracking on heating or cooling [11]. It would be expected for a higher open porosity of composite, that the mass yield would be larger. In the case where the composite contains pitch as a binder, open porosity is lower than in the case of the composite with pure resin as a binder. Also, there is an insignificant difference in the mass yield between composites, with or without pitch as a binder. This means that the presence of pitch in the matrix of the skeleton improves densification efficiency.

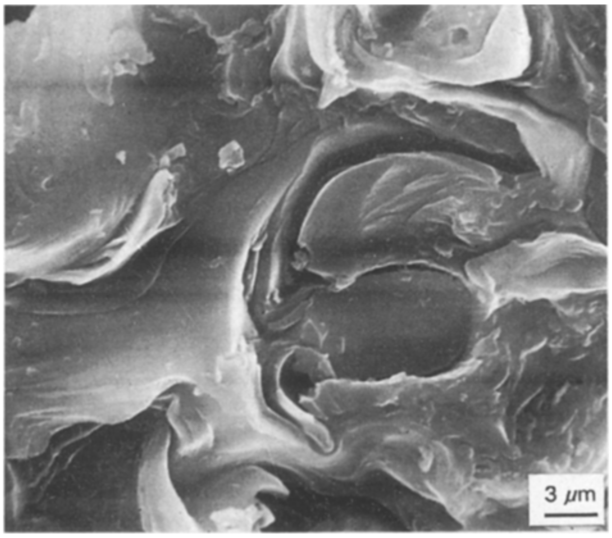


Figure 6 SEM micrograph of the carbonized C–II composite with 30 wt % pitch content in the matrix precursor.

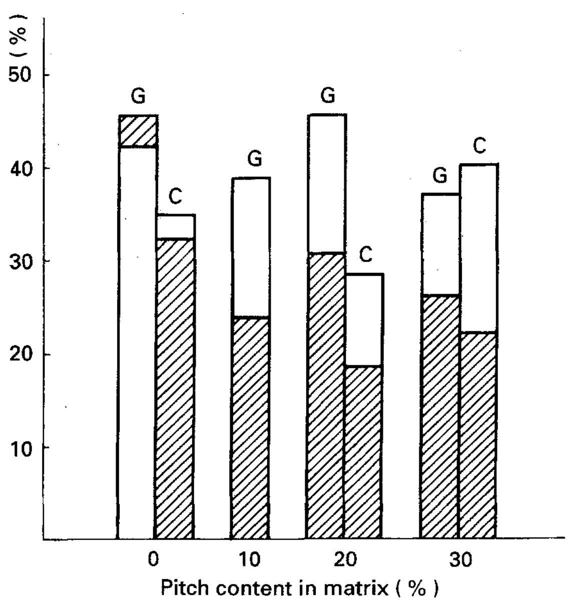


Figure 7 Available open porosity ▨ before the densification process and mass yield □ after the densification process for composites with graphitized (G) or carbonized (C) fibres.

The reason for this, may lie in inequalities of the thermal expansion coefficients of different cokes (pitch or phenolics precursor) of which the matrix consists, which improves crack formation on heating or cooling, increasing mass yield in comparison with accessible open porosity.

After the densification process, the density of the composites increases and open porosity decreases (see Table III). Even though the composites with pure resin as a binder have the greatest increase of density, $\Delta d/d$ and the greatest decrease of open porosity, ΔOP/OP, these composites do not have the highest density. This is because pitch is denser than phenolic resin, whether it is raw or carbonized, and skeletons with pure resin as a binder have lowest density (Fig. 3). Composites with added pitch are denser, before the densification process and, afterwards, these composites have higher densities. The higher the pitch content in the matrix skeleton, the higher the density. Also, C–I are denser than C–II because they are denser before the densification process.

The mechanical properties of the matrix without fibres were examined after curing and carbonization. After pyrolysis of pitch and resin mixtures these samples were broken. It was impossible to examine the mechanical properties of matrix without fibres after high temperature treatment. This is a result of inequalities in thermal expansion coefficients of resin and pitch. The results obtained are given in Table IV.

By adding pitch, flexural strength, σ_M, and modulus, E_M, of the matrix without fibres are significantly decreased. Such a matrix possesses heterogeneous texture (Fig. 8), and the presence of pitch

TABLE IV Mechanical properties of matrix without fibres after curing and carbonization

Pitch content (%)	σ_M (MPa)		E_M (GPa)	
	Cured	Carb	Cured	Carb
0	157.2	215.5	7.0	45.0
10	21.8	15.0	1.5	5.7
20	24.4	19.8	1.4	6.0
30	18.7	23.4	1.4	6.3

TABLE III Density and open porosity of final composites and their change after the densification process

Pitch content in skeleton	d(kg m^{-3})		$\Delta d/d$ (%)		OP (%)		ΔOP/OP (%)	
matrix (%)	C–I	C–II	C–I	C–II	C–I	C–II	C–I	C–II
0	1750	1650	8.0	7.8	23.6	18.3	48.4	43.1
10	1770	–	4.1	–	15.2	–	36.3	–
20	1840	1680	5.1	5.7	17.0	10.3	44.4	43.4
30	1800	1710	5.3	6.9	19.2	9.8	26.2	55.6

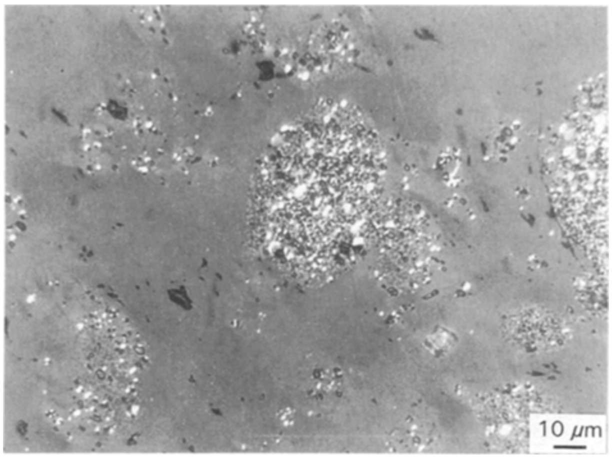


Figure 8 Optical micrograph of carbonized matrix precursor with 30 wt % pitch content.

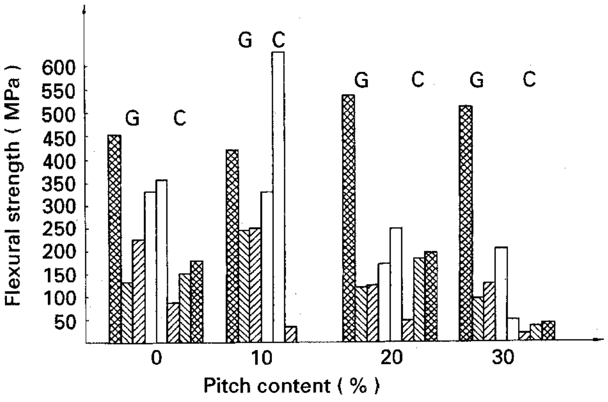


Figure 9 Flexural strength of composites with graphitized (G) or carbonized (C) fibres, after □ curing, ▨ carbonization, ▧ HTT and ▩ densification.

decreases bonding during resin polymerization decreasing the mechanical properties of the cured matrix. After carbonization there is no improvement in the mechanical properties of the matrix.

As has been presented previously, composites made with carbonized fibres possess stronger fibre–matrix bonding than those made with graphitized fibres. This is also reflected by the flexural strength of the cured composites (Fig. 9) [5]. By adding pitch as a binder (above 10 wt %) fibre–matrix bonding becomes weaker, and flexural strength of these composites is lower. By adding 10 wt % pitch as a binder for C–II, fibre–matrix bonding becomes stronger and the flexural strength is almost twice as high than for composites with pure phenolic resin as a binder. However, there is no significant change in flexural strength for C–I composites.

After the carbonization process, the composites show a decrease in strength. The stronger the fibre–matrix bonding in the composite, the greater the decrease in strength. Composites with good adhesion between fibre and matrix are prestressed, due to inhibition of shrinkage in the precursor during the carbonization process, along the fibre axis. This allows easy crack propagation perpendicular to the fibres, and causes poor flexural strength. So, C–II composites, especially with a 10 wt % pitch content in a binder precursor (highest fibre–matrix bonding in cured composite), show a drastic strength drop. On high temperature treatment, the prestress relaxes and fibre–matrix adhesion is not so strong. This influences the increase in flexural strength for these composites. Only for the composite with 10 wt % pitch content in the matrix precursor, was the prestress so strong, causing their decomposition upon high temperature treatment.

In such composites, cracks and pores are present mainly in the matrix, because the fibres and the matrix are well bonded. During the densification process, impregnation pitch filled these cracks and pores in the matrix (Fig. 10). This results in a small improvement in flexural strength of these composites with densification (Fig. 9).

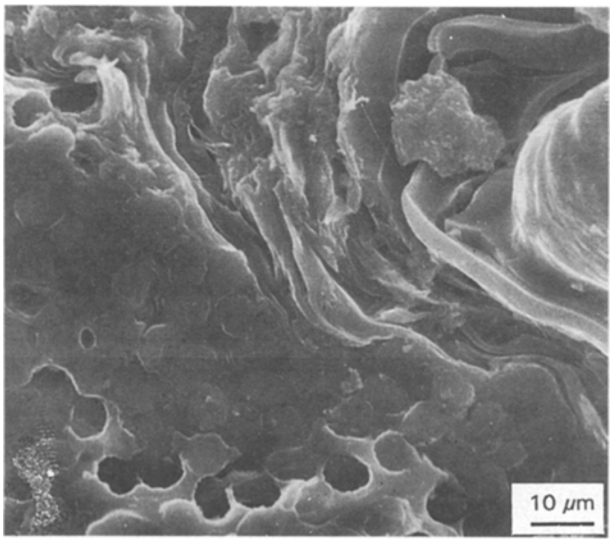


Figure 10 SEM micrograph of C–II after densification.

C–I composites have poor adhesion between the fibre and the matrix, and the fracture energy can be partly absorbed by a debonding process between the fibres and the matrix. This results in higher flexural strength of these composites than that of the C–II composites after the carbonization process (Fig. 9). Matrix properties will influence the mechanical properties of these composites [12]. After high temperature treatment, the shear strength of the matrix decreases and causes a decrease of the flexural strength of the composites. When the matrix precursor contains pitch (up to 20 wt %) this decrease of flexural strength is negligible.

These composites, besides intramatrix pores and cracks, possess gaps between the fibre and the matrix. This allows the impregnation pitch to fill them and to make bridges between the fibres and matrix (Fig. 11). This results in a proper distribution of stress among the fibres and improves flexural strength (Fig. 9). Therefore, the composites, whose binder precursors contain pitch, possess a higher mass yield in comparison with accessible open porosity, than composites with pure resin as a binder. This improves the flexural strength of these composites. C–I composites with a 20 wt % pitch content in the binder precursor,

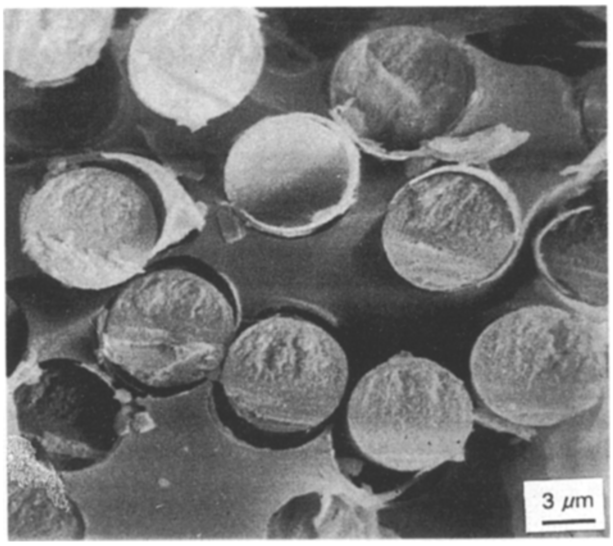


Figure 11 SEM micrograph of C–I after densification.

possess the largest value for flexural strength. C–I composites with a 30 wt % pitch content, show the greatest improvement of flexural strength.

4. Conclusions

The carbon binder between the structural fibre skeleton is weakest part of the composite. It is very important to choose a proper binder precursor or to modify the existent precursor. The fibre surfaces affect fibre–matrix interaction, which is very important in the densification of carbon–carbon composites.

The possibility of modifying phenolic resin with coal tar pitch as a binder or carbon fibres was explored.

Although adding pitch to a phenolic matrix without fibres decreases the mechanical properties, the mechanical properties of composites with these matrices increase, especially when graphitized fibres are used. Commercially graphitized fibres are more suitable for utilization because of a lower content of functional groups on the surface.

Adding pitch to phenolics decreases proper polymerization of the phenolics and decreases the number of –OH groups from phenolics which form strong bonds with functional groups from the fibres surfaces. This decreases the mechanical properties of the matrix, and bonding between fibres and the matrix influences the formation of gaps between them after carbonization. During densification, impregnant pitch fills these gaps forming new mechanical bonds between fibres and the matrix, which improves flexural strength. Adding pitch to phenolics also decreases the open porosity of composites by 38–48%. This decrease pertains to intramatrix open porosity. Gaps between fibres and matrix still remain, which allows better bonding between them after densification and improves strength.

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