

LIQUID IMPREGNATION TECHNIQUES FOR CARBON–CARBON COMPOSITES

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1 Introduction

Carbon fiber reinforced carbon composites (C–C composites) are unique in providing materials with the highest possible specific thermal-mechanical properties. They have an additional value in that at high temperatures their excellent properties are not only retained but also improved as a result of a better structural order. However, the main problem with C–C composites, apart from their reactivity to oxygen at high temperatures, is their high cost due to the complexity and length of the fabrication processes. Consequently, C–C composites are currently used only in high-technology applications where no other materials are available. In recent years the search for ways to improve properties, reduce costs, and increase the efficiency of the processes involved in the preparation of C–C composites has been intensified. Unfortunately, easily available information is very limited because of confidentiality agreements, most of it being in patent form (Plotzker *et al.*, 1988; Hocquellet and Chenier, 1993).

The type and architecture of the fibers and the microstructure of the supporting matrix determine the physical properties of C–C composites. It is, therefore, important to understand the mechanisms that control the formation of the microstructure and its interaction with the fibers in order to be able to achieve the desired composite properties at the lowest possible cost and make full use of the electrical, thermal, and mechanical properties of the fibers (Meyer, 1994).

Two methods are at present used for the preparation of C–C composites: (i) liquid impregnation; and (ii) carbon vapor infiltration (CVI). A combination of the two methods is also used. Both have been described in detail in the literature (Savage, 1993a). Liquid impregnation, the topic covered in this chapter, is a two-stage method. Basically, in the first stage the fibers are impregnated with an organic precursor, giving rise to what is called a prepreg. Afterwards, the precursor is transformed into a carbonaceous matrix by thermal treatment (650–1,000 °C) in an inert atmosphere via a carbonization process. Depending on the application of the material, graphitization (>2,500 °C) may also be required. These stages have to be repeated until the desired density is obtained (Fig. 7.1). The other method, CVI, implies the cracking of a gas and the deposition of carbon onto the fiber substrate (Chapter 7 of this book). In general, liquid impregnation is considerably quicker and cheaper than CVI processing, and the equipment required, in an ambient pressure fabrication route, is not limited

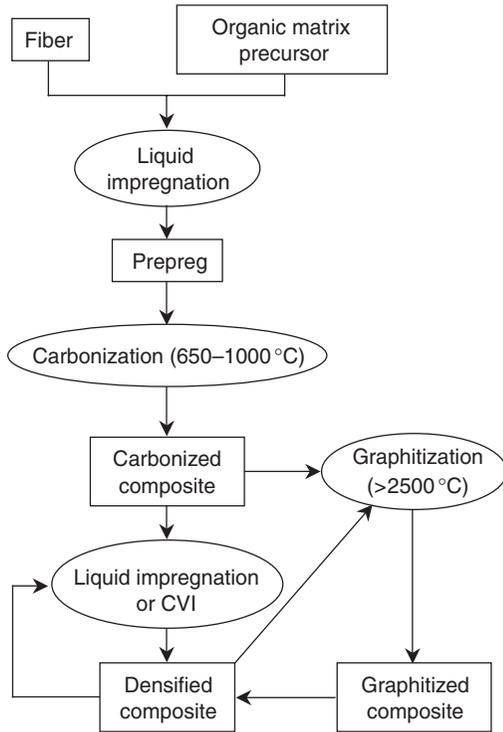


Figure 7.1 Flow diagram of C-C composite preparation by liquid impregnation.

by size or by the need for a large initial capital investment. The main advantage of the liquid impregnation procedure, however, concerns the great variety of matrix microstructures which can be produced, with the subsequent impact on composite properties.

The aim of this chapter is to offer a general view of the fundamentals of the liquid impregnation procedure and to point out the technical problems which may arise through eyes of the authors concerned. Special emphasis is given to the role of matrix precursors and the selection of the correct processing conditions for producing the desired microstructural features and composites with optimum properties. At the same time care is taken not to underestimate the important role of fiber in the properties of the composite. Ways of enhancing these properties through the carbon matrix precursor by means of preliminary treatment or by acting on the prepreg are also considered.

2 Impregnation technology

The technologies available for the impregnation of carbon fibers using a carbonaceous matrix precursor are similar to those used for fiber-reinforced plastics. Depending on the matrix precursor and the type of reinforcement (discontinuous, linear, planar, or n-D) many alternatives are available. Essentially, the procedures include: (i) passing continuous fibers through a solution of the matrix precursor; (ii) infiltration of a liquefied matrix precursor in a fibrous skeleton assisted by vacuum or pressure; and (iii) hot pressing of sandwiched fiber/matrix precursor mixtures.

2.1 Wet-winding technique

This is the most common technique used for preparing unidirectional C-C composites at laboratory scale (Fig. 7.2a). Basically, a continuous fiber bundle is made to pass through a bath which contains a liquefied matrix precursor. The impregnated fibers are then wound onto a mandrel under controlled tension. The winding processes differ from each other in the impregnation conditions chosen and the reinforcement scheme and type of winding path used (Borokh *et al.*, 1995). Depending on the impregnation conditions, winding can be wet

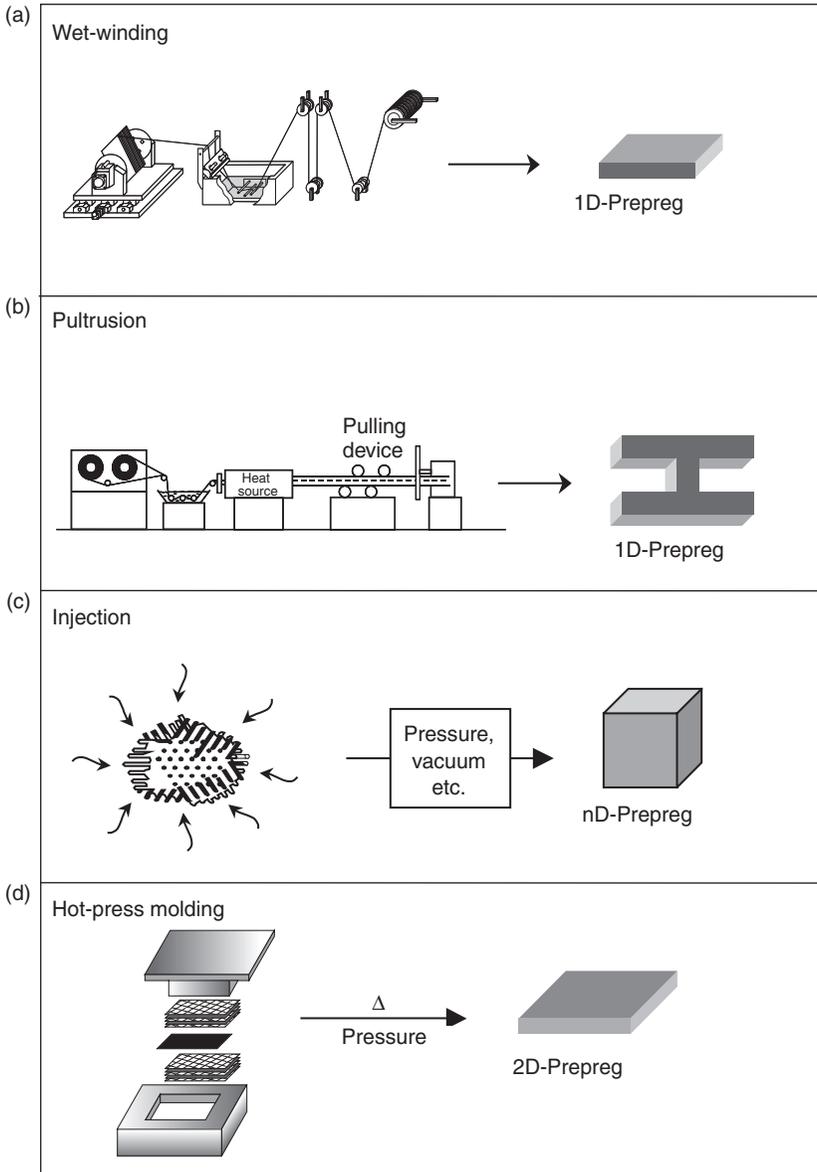


Figure 7.2 Impregnation techniques.

(impregnation is carried out during winding) or dry (winding is carried out on a preimpregnated, dried tape). Winding can also be performed with non-impregnated fibers followed by impregnation.

When using wet winding techniques, the impregnation conditions vary depending on the matrix precursor (Hirano *et al.*, 1993), i.e. a mixture of polymers and a plasticizer, melt pitch, liquid resins, pitch, or resin dissolved in an organic solvent, or fine particles suspended in the form of an emulsion (Hocquellet and Chenier, 1993). Two fundamental factors which must be controlled in this step and borne in mind when selecting the optimum conditions are: the alignment of the fibers and the homogeneous distribution of the matrix precursor. Correct fiber alignment is very important because small variations in the orientation of the fibers can mean additional stresses, which may lead to premature failure of the material. As an example, impregnation is relatively easy with solutions at low concentrations of the organic precursor. However, complete removal of the solvent is hard to achieve and it may produce fiber misalignment, as well as the generation of porosity during solvent removal.

The next step, after the impregnation process, involves curing and/or hot-pressing (depending on the matrix precursor), and then carbonization/graphitization. After this, other techniques (CVI, injection) are required in order to reduce the final porosity and obtain a high density material.

2.2 Pultrusion

This technique is derived from wet-winding. In this case, after being impregnated in a bath, the fibers are pulled through a heated die specifically shaped to produce the desired cross-section (Fig. 7.2b). Partial or complete curing occurs during the passage through the die.

2.3 Hand lay-up

Fibers are placed by hand into a mould covered by a released substance and then impregnated with a liquid precursor by means of painting or spraying and rolling. Rolling compacts the material and ensures the effective impregnation of the fiber by the matrix precursor, homogeneous distribution and the removal of air. The fibers may be in the form of random mats or woven fabrics. Layers of impregnated fibers are stacked up (lay-up) until the desired thickness is achieved. Carbonization is then carried out to obtain a stable porous structure. Again additional techniques are needed to obtain the desired final density.

2.4 Injection technique

This method (Fig. 7.2c) is generally used to impregnate preforms of carbon fibers produced by dry winding or braiding and also as a way to increase the density of the composite prepared by other techniques. The preform is dipped into the liquefied precursor or alternatively the precursor is forced into the pores of the preform by means of surface tension, gravity, atmospheric pressure or external forces such as gas pressure, centrifugal force, mechanical vibration, etc. (Borokh *et al.*, 1995). In some cases this is achieved with the help of a vacuum. Pore distribution in the preform and the rheological properties of the matrix precursor are the main factors that control this process.

2.5 Hot-press molding

This technique is frequently used at laboratory scale to prepare bidirectional C–C composites (Arianoutsos *et al.*, 1990). Woven mats of carbon fibers are stacked in a mold and sandwiched

by the matrix precursor powder (Figure 7.2d). The mold, matrix precursor and fibers, are heated together until the matrix precursor is thoroughly melted. At this point mechanical pressure is applied in order to place the melted precursor inside the mats and so ensure an effective impregnation. During pressurization, trapped air and excess precursor are forced out of the mold. After cooling, carbonization is required. Infiltration/carbonization cycles are repeated several times to achieve the desired density.

Unidirectional C–C composites are prepared in a similar way, using a powder coating process (Klett and Edie, 1995). Fiber bundles are separated by a vacuum spreader and then the individual fibers are coated with fine polymer particles in a fluidization chamber. The coated tow thus formed (tow-preg) is heated until the particles are fused to the individual filaments. Next the tow-pregs are cut, stacked and hot-pressed to form the final composite. This procedure may be specially desirable when using pitches with a high softening point and low solubility as matrix precursors.

Hot-press molding is also used as part of the process of preparation of unidirectional C–C composites by wet-winding. Laminated prepregs are stacked and then hot-pressed at specific temperatures, depending on the characteristics (chemical composition and rheological properties) of the precursor (Figueiras *et al.*, 1995; Casal *et al.*, 2001).

3 Densification efficiency

The preparation of C–C composites with the right density currently requires several impregnation/carbonization cycles, as mentioned above. This is because in the initial stages of the carbonization process of the organic precursor there is a major weight loss of volatiles which continues, to a lesser extent, throughout the process as the temperature increases, giving a porous material. The pores are produced, either in the initial stages of the preparation of the composite (impregnation process and molding), or during subsequent carbonization. Pores of the first type are usually open (Fig. 7.3a), whereas those developed on carbonization may be either open or closed (Fig. 7.3a). Carbonization pores may be developed either while the matrix precursor is still plastic or as a result of stresses (cracks) due to structural rearrangements or thermo-mechanical effects (Fig. 7.3b). Several studies have been carried out in relation with the characterization of porosity in C–C composites (Jortner, 1986; Granda *et al.*, 1998). All of these structural imperfections have an adverse effect on the bulk properties.

A knowledge of the parameters which control the efficiency and effectiveness of densification is essential for the optimization of the process. Experience shows that the first step of impregnation is not enough to ensure that all of the empty pores in a C–C composite are filled by the matrix precursor (Fig. 7.3c and d). An impregnation efficiency parameter, Y_i , can be defined as the relationship between the volume of impregnant introduced into the pores of the composite and the volume of the open porosity of the composite (eq. (1)). This parameter can be calculated from the increase in weight gain of the composite during the impregnation, ΔW_i , and the volume fraction of open porosity of the composite before impregnation, θ :

$$Y_i = \frac{\text{Volume of impregnant introduced}}{\text{Volume of initial empty pores}} = \frac{\Delta W_i}{\rho_p} \cdot \frac{\rho(0)}{\theta} \quad (1)$$

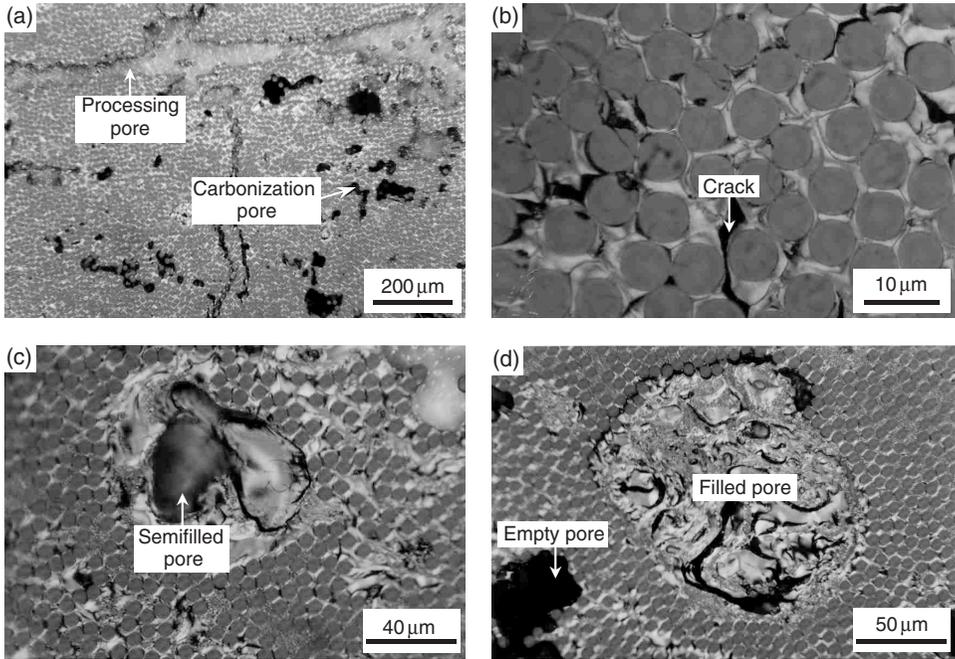


Figure 7.3 Polarized-light micrographs of cross sections of unidirectional C-C composites showing different types of pores: (a)–(b) undensified; and (c)–(d) densified composites. (See Color Plate IV.)

where ρ_p is the density of the impregnant at room temperature, and $\rho(0)$ the bulk density of the empty C-C composite. This expression can be generalized for the n -th step of impregnation as follows:

$$Y_i(n) = \frac{\Delta W_i(n)}{\theta(n-1)} \cdot \frac{\rho(n-1)}{\rho_p} \quad (2)$$

Several factors, related not only to the experimental conditions used but also to the characteristics of the network of pores developed in the composite (Fig. 7.3a) and the characteristics of the impregnant, affect the values of this parameter (Oh and Park, 1994; Granda *et al.*, 1998).

The density of the carbon matrix of the final composite depends on the experimental conditions used in the carbonization step and may differ somewhat from the density obtained when the matrix precursor is carbonized alone under the same conditions. This is because in the composite the thermally induced stresses tend to promote additional graphitization and densification of both fiber and matrix (Rellick, 1990).

Another aspect that should be mentioned is the relationship between the weight gain of the composite in the impregnation and the absolute increase in weight due to the n -th cycle of densification. One might expect the ratio of these magnitudes to be the carbon yield of the matrix precursor under the processing conditions. However, this is not completely true, because when carbonization takes place after impregnation, the phenomenon of matrix bloating may occur as a consequence of the release of volatiles. As a result, matrix yields

will be lower than anticipated knowing carbon yields from the impregnant, when carbonized alone. The physico-chemical properties of the precursor, the number of pores, the structure of the pore networks in the composite (size, shape, and orientation), and the experimental conditions used are the main controlling factors.

Studies of the densification efficiency of C–C composites with pitches (Oh and Park, 1994; Granda *et al.*, 1998) have led to the conclusion that impregnation efficiency increases, as the process is repeated due to a decrease in porosity, while retention efficiency follows an inverse trend due to the changes in the shape of the pores, as densification proceeds. Overall densification efficiency depends on impregnation efficiency and the effective carbon yield of the impregnating pitch. Pitch fluidity is the main factor controlling impregnation efficiency. Additionally, the tortuosity of the pores also plays an important role during the impregnation process. The use of pressure during carbonization reduces the release of volatiles and pitch bloating, leading to an increase in the effective carbon yield (Granda *et al.*, 1998). It also reduces pore closure, thereby improving densification efficiency. It has also been shown that closed porosity may be transformed into open porosity via graphitization (Savage, 1993b).

4 Matrix precursors

The matrix of a C–C composite acts as a binder by maintaining the alignment and position of the fibers, and protects them from damage. It also distributes stresses, transferring the external load to single reinforcing filaments. The structural characteristics of the matrix and their interaction with the fibers contribute significantly to the properties of the composite. These characteristics depend on the chemical composition and physical properties of the precursor, as well as on the processing conditions. As the preparation of C–C composites involves heat treatment in an inert atmosphere to transform the matrix precursor into carbon form, the chemical and rheological behavior of the matrix precursor on pyrolysis is of considerable importance for selecting the optimum processing conditions. Generally speaking, a good matrix precursor should have a high carbon yield while at the same time retaining its fluidity and ability to wet the fibers. Moreover, low volumetric contraction is necessary in order to avoid fiber damage and matrix shrinkage cracks. It is not easy to find a product which fulfills all of the requirements at the same time. As an example, a high carbon yield is usually associated with high organic precursor viscosity, which may impede infiltration and wetting. On the other hand, a high carbon yield may be accompanied by an adequate viscosity but also by considerable matrix bloating on carbonization. Two main types of matrix precursors are currently used in the preparation of C–C composites by liquid impregnation: one is based on resins and polymers and the other is based on pitches.

4.1 Resin precursors

In this group, phenolic and epoxy resins are the most commonly used and both are thermoset and need curing prior to carbonization (Fig. 7.4a). Apart from the above mentioned matrix requirements, it is necessary that the resin cures rapidly at low temperature (without the evolution of volatiles). The carbon yield in commercially available resins usually ranges from 50 to 70 wt%, depending on the type of resin and the processing conditions (Murdie *et al.*, 1992). These yields cannot be increased by the application of pressure during carbonization. New resin precursors (Fig. 7.4b) have been developed with carbon yields of up to 85 wt% (800 °C) (Savage, 1993c), but the price of these products is extremely high and in some

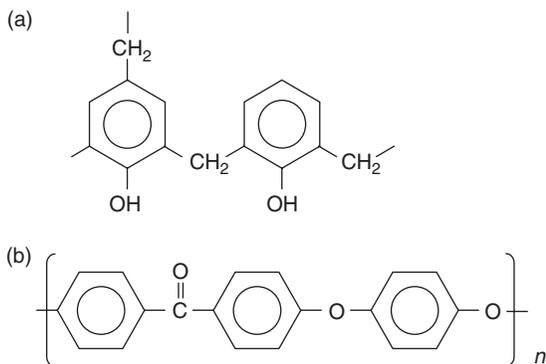


Figure 7.4 Chemical structure of (a) thermosetting phenolic resin precursor; and (b) PEEK thermoplastic resin precursor.

cases the preparation procedures for bulk resin production are difficult to scale up. Furthermore, the resins tend to form closed porosity on carbonization, preventing further densification.

The processing of resin composites includes initial partial curing for polymerization to take place and thereby increase the carbon yield. This is followed by hot-pressing (150–300 °C) or curing in an autoclave to produce a rigid solid via three-dimensional cross-linking. Then pyrolysis and a series of infiltration/carbonization cycles are carried out. The processing conditions used in the preparation of the composite depend on the time/viscosity properties of the resin. In general, the carbonization of composites to temperatures of about 800–1,000 °C is carried out slowly in order to prevent the rapid evolution of gases (H₂O, CH₄, CO, H₂). The carbonization step may take many hours or even days to be completed. During carbonization, the resin is converted into a glassy, isotropic carbon (shrinkage stresses in the vicinity of the fibers may cause graphitization at temperatures >2,500 °C). The shrinkage of the resin during curing and carbonization produces slit-shaped pores which need to be filled by a liquid matrix precursor for subsequent carbonization if the density and mechanical properties of the composite are to be improved. The fine micropore network developed during the carbonization of the resin cannot be easily reinfiltreated even when the pores are open (Rand, 1993).

The density of resin-based carbons is relatively low. So, when using resin, the number of densification cycles is higher than with other precursors. As an example, six cycles were required to achieve a density of 1.65 g cm⁻³ in order to process multidirectional cylinders with phenolic resin (Mullen and Roy, 1972). Unfortunately, none of the resins available at the moment, even the more recent ones with high carbon yields, can fulfill all the requirements of an optimum carbon matrix precursor.

4.2 Pitch precursors

4.2.1 Pitch composition

Pitches offer good possibilities as carbon matrix precursors, mainly because of the wide range of pitch products with different characteristics that are available, their relatively low

price, easy manipulation, and the possibility of achieving high carbon yields. Pitches come primarily from coal and petroleum. Both petroleum-derived and coal-derived pitches (so called coal-tar pitches) are residues from the distillation or heat treatment of petroleum fractions and coal-tar, respectively, and contain a large range of aromatic molecular types and sizes (Zander, 1997). These pitches differ from one another in their chemical composition (aromaticity, aromatic condensation degree, molecular size, functionality, etc.), physical properties and consequently, in their pyrolysis behavior (Pérez *et al.*, 2000). This is because of differences in their origin. Figure 7.5 shows two average molecular structures for coal-tar and petroleum pitch proposed by Kershaw and Black (1993). Coal-tar pitches are more aromatic, with a higher degree of ring condensation than petroleum pitches and they contain carbonaceous particles ($<1\ \mu\text{m}$) called primary Quinoline Insolubles (QI). These particles are generated during the coke oven operation and are entrained by gases to form part of the tar. Consequently they remain in the pitch which is obtained by tar distillation. Two types of commercial coal-tar pitches are produced mainly for the aluminum and steel industry: binder pitches and impregnating pitches. These pitches differ in their specifications (softening point, carbon yield, QI content, toluene insoluble content, etc.) depending mainly on the preparation process used (vacuum distillation, thermal treatment, etc.). However, the composition of the tar will also have some influence.

In general, pitches are extremely complex in composition. They are composed of several hundreds and even thousands of aromatic compounds which are present in different concentrations and differ in molecular size and topology. These compounds cover a very wide

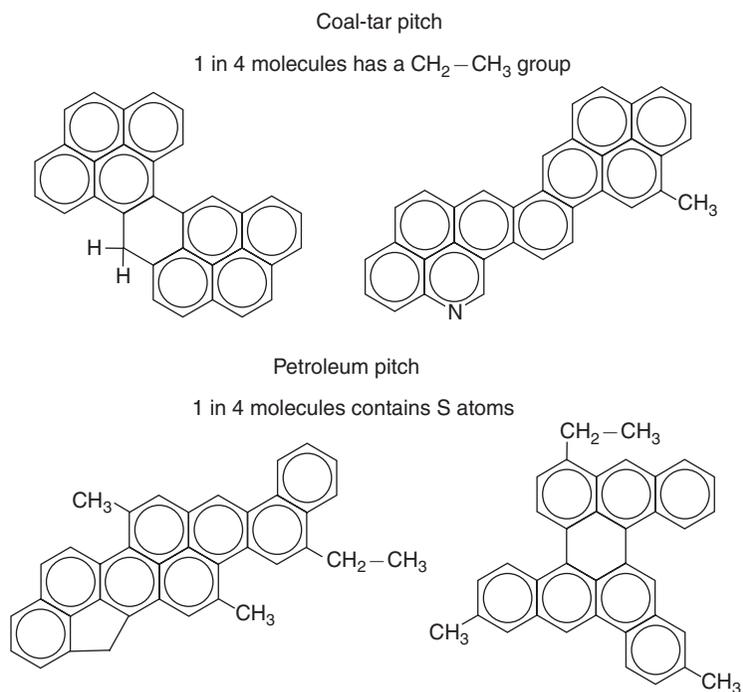


Figure 7.5 Average molecular structures for coal-tar and petroleum pitch (Kershaw and Black, 1993).

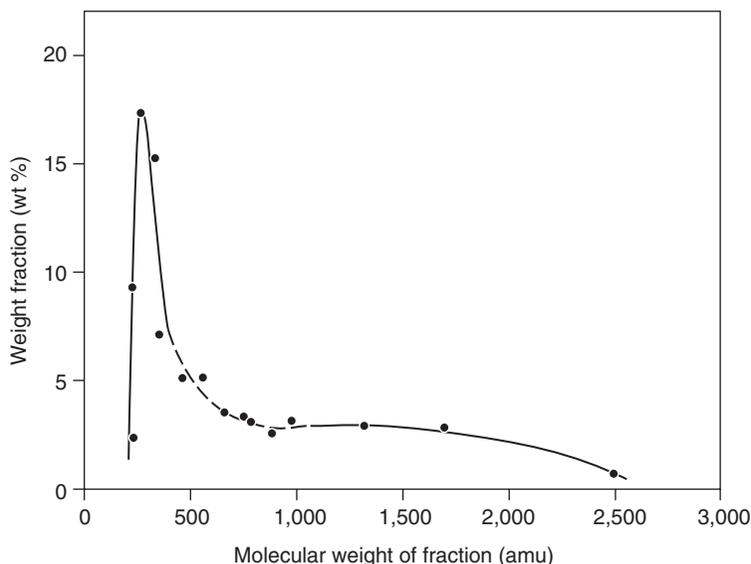


Figure 7.6 Molecular weight distribution of the pyridine-soluble part of coal-tar pitch (Boenigk *et al.*, 1990).

range of molecular weight from ~200 to >3,000 amu (Zander, 1997). As an example, Fig. 7.6 shows the molecular weight distribution determined by preparative size exclusion chromatography (SEC) of the pyridine-soluble fraction (95 vol%) of a coal-tar pitch (Boenigk *et al.*, 1990). From results obtained by preparative SEC and other techniques, these authors conclude that a typical coal-tar pitch consists of ~40 wt% of compounds with a molecular mass of ≤ 330 amu, ~50 wt% of compounds with a molecular mass ~330–1,500 amu, while 10 wt% of the remaining pitch consists of high-molecular weight material (between ~1,500 and > 3,500 amu).

Coal-tar pitches are mainly composed of polycyclic aromatic hydrocarbons (PAH) and to a lesser extent of polycyclic aromatic compounds containing alkylsubstituents and/or heteroatoms (O, S, and N). These compounds can be compiled into categories by fractionation by means of extrography (Granda *et al.*, 1990). This technique is able to distinguish between pitches differing in origin (coal-tar or petroleum), their uses (binding or impregnating) and also the preparation process (thermal treatment, vacuum distillation, etc.). Thus impregnating and binder pitches mainly differ in the distribution of PAH and the amount of basic polycyclic aromatic compounds (Bermejo *et al.*, 1994). A typical impregnating pitch has a higher content in both PAH of lower molecular weight and basic nitrogen compounds.

There is also what is considered to be a third generation of pitches. Some of these are commercially available (Mitsubishi Gas Chemical and Mitsubishi Oil) and others are still under development. This third group includes the mesophase pitches (from organic precursors and from the pyrolysis of commercial pitches) and isotropic pitches of high carbon yield (from the direct treatment of tar, commercial pitches, and other tar distillation fractions such as anthracene oil). These will be discussed in Section 5 of this chapter.

4.2.2 From pitch to carbon matrix

The processing of pitch-based composites involves a carbonization step (650–1,000 °C) which transforms the pitch into a graphitizable carbon, through a liquid crystal stage called mesophase. The conditions used are strongly dependent on the chemical composition and the rheological behavior of the pitch.

All pitches, petroleum- and coal-based have in common the fact that their constituents are polycyclic aromatic compounds. But, their differences in molecular structure lead to different behaviors during carbonization (Pérez *et al.*, 2000), thereby influencing the properties of the resultant composite.

In the initial stages of carbonization, the lightest compounds are released and the remaining polycyclic aromatic compounds polymerize and condense. The generation of gases, as a consequence of polymerization reactions, and the dimensional shrinkage that accompanies pitch carbonization, leads to the development of open and closed porosity in the composites. The improvement of the density and mechanical properties of the composites requires the elimination or reduction of this porosity by subsequent liquid impregnation (or CVI) followed by carbonization (Section 3 of this chapter).

A knowledge of the temperatures at which all the physico-chemical changes involved in pitch carbonization occur is of great importance for the selection of an adequate precursor and optimum conditions for the preparation of a pitch-based C–C composite. The main factors that must be borne in mind are the temperature of volatiles removal on pitch pyrolysis (Bermejo *et al.*, 1994), viscosity/temperature history (Rand *et al.*, 1989), and temperature interval between mesophase development and solidification, all of which can be monitored by thermogravimetric analysis, rheometry, and hot-stage microscopy, respectively. The information obtained is useful even if the experimental conditions used in the preparation of a C–C composite are rather different. For example, a reduction in the porosity (as determined by optical microscopy) of undensified unidirectional C–C composites, prepared by a wet-winding procedure, from 12 to 4 vol%, was achieved by the adjustment of the operational parameters (heating rate, molding temperature, duration of molding) to the characteristics of the binder pitch that was used as matrix precursor (Casal *et al.*, 1998).

Carbon yields of commercial coal-tar pitches are about 50 wt% under atmospheric conditions, but these can be substantially increased to 80 wt% by reducing the carbonization heating rate or by using pressure. Carbonization under high pressure (100 MPa) results in yields of 90 wt%. The use of a pressure of up to 207 MPa reduces the temperature associated with thermal degradation and improves the carbon yield by reducing the loss of volatiles. McAllister and Lachman (1983) have shown that high pressure impregnation/carbonization of multidirectional fiber preforms with pitch increases the yield and density of the final composite. After six cycles of pitch impregnation/carbonization under pressure, a composite of about 1.9 g cm⁻³ was obtained.

4.2.3 The optical texture of the matrix

The morphology, size, and orientation of the microcrystalline structures which constitute the optical texture of the carbon matrix can differ greatly depending on the composition of the pitch. As shown in Fig. 7.7, they can vary from a very small size (<10 μm), mosaic-like structures, to large size (>60 μm) domains (Marsh and Latham, 1986). Pitches which contain compounds with a higher capacity of hydrogen transfer, i.e. hydroaromatics and naphthenics, tend to produce better ordered structures of a larger size. The same tendency

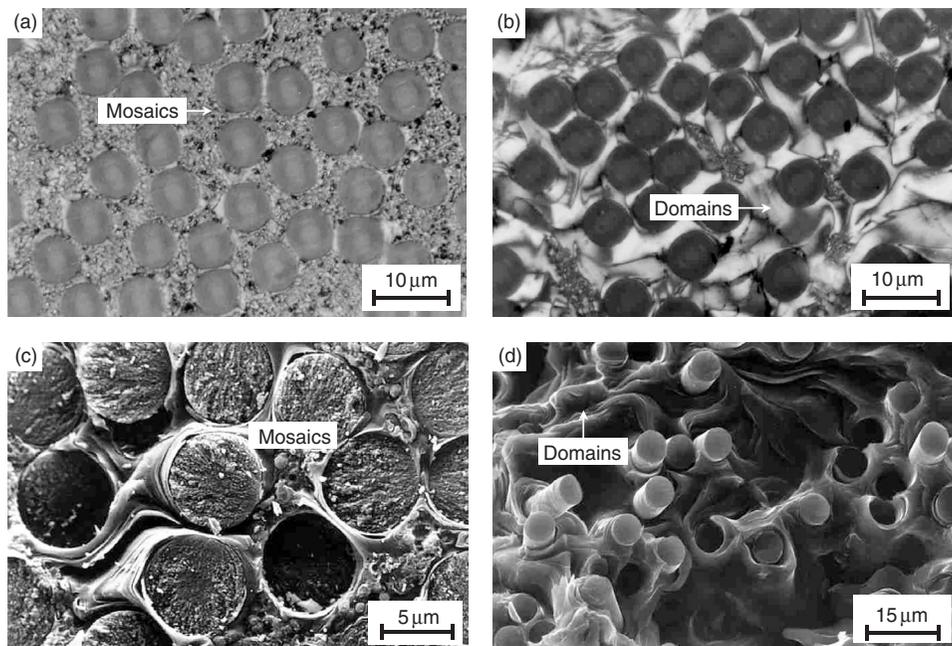


Figure 7.7 Pitch-based unidirectional C–C composites exhibiting different (a)–(b) optical textures; and (c)–(d) SEM fracture surfaces. (See Color Plate V.)

was observed for those containing basic-nitrogen compounds. However, the presence of oxygen functional groups (phenolic, carbonyl, etc.) has a negative effect on the optical texture (Menéndez *et al.*, 1997), generating small size textures and even destroying pitch graphitizability when occurring in high concentrations. Primary QI, present in coal-tar pitches, also yield optical textures of a small size (Fig. 7.7). These differences are related to the thermal reactivity of the compounds and the viscosity of the pyrolysis system which addresses the development of mesophase and finally the carbon microstructure. Moreover, for a given pitch the optical texture of the resultant carbon can be modified by variations in the carbonization conditions (heating rate, use of pressure).

When dealing with C–C composites, the presence and characteristics of the fiber through fiber–matrix interfacial effects also yield preferential orientations of the matrix with respect to the fiber (Appleyard *et al.*, 1995) as shown in Fig. 7.7.

The wide range of optical textures which can be generated is of special relevance to the properties of the C–C composites. Large-size optical textures are currently associated in coke with high electrical conductivity, while small sizes are associated with improved mechanical strength. However, recent studies have shown that domain-like structures (from petroleum pitches) can also give high strength carbon materials (Pérez *et al.*, 2000). This suggests that other factors related to packing or interlaminar bonding/interactions also play a role. But it is not only the microstructure of the matrix, but also the strength of the fiber–matrix bonding that is critical in the behavior of the C–C composite under mechanical loading, and this can be influenced by the optical texture of the matrix. Matrices with a dominant mosaic texture exhibited stronger bonding with AS4k fibers than those with domains. Whereas the former resulted in a pure brittle failure mode (Fig. 7.7c), the latter

was pseudoplastic (Fig. 7.7d). It has also been observed that matrices with domain textures, which mainly develop in pitch containing aliphatic hydrogen, have a higher propensity to form intramatrix and interface cracks (Figueiras *et al.*, 1995).

The presence of primary QI particles in coal-tar pitches restricts the development of mesophase during pyrolysis, producing matrices with a smaller size of optical texture, a lower amount of cracks and stronger fiber–matrix bonding (Figueiras *et al.*, 1998). Figure 7.8 illustrates how the QI affects the mechanical properties and failure mechanism of the material. For an undensified composite prepared from a pitch with 11 wt% of QI (Fig. 7.8a) the flexural strength is higher than for a composite prepared from a free QI pitch (Fig. 7.8b). The increase in the strength of the composites containing QI is accompanied by a change in the mode of failure. Composite from QI free pitch shows a classical multiple fracture mode

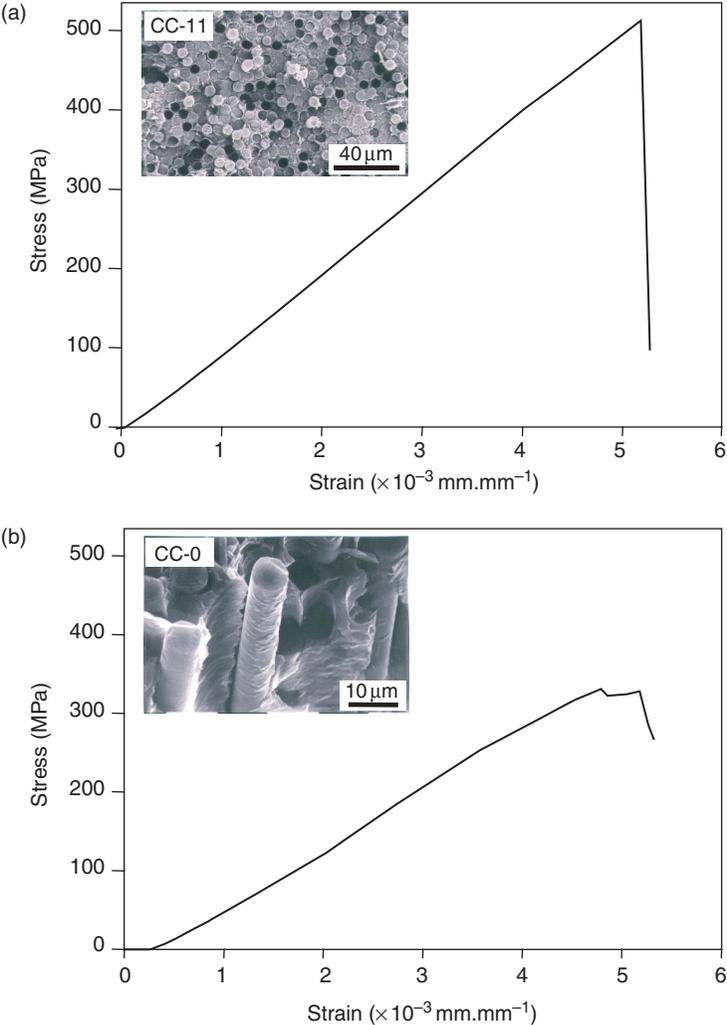


Figure 7.8 Stress–strain curves and fracture surfaces for (a) composite from a pitch with 11 wt% of QI and (b) composite from a QI free pitch.

of failure (pseudoplastic behavior) leading to the relative movement of the two phases as the load is transferred to the fibers. However, composite from pitch with 11 wt% of QI (Fig. 7.8a) failed in a catastrophic way (brittle behavior). In this case, the stronger fiber–matrix bonding increases the transfer of the load to the fiber, which in turn increases the overall strength of the composite, causing the composite to fail in a catastrophic-like tensile fracture (Fig. 7.8a).

As an improvement in the strength of the material is accompanied by an increase in its brittleness, possible ways to overcome this problem could be the use of matrix precursors prepared from two individual components in order to obtain a blend which gives on pyrolysis a carbon with a combined optical texture, yielding both strength and capability of fracture propagation. The mechanical properties of the composite could also be improved by using the appropriate fiber, depending on the type of carbon matrix.

5 New developments in C–C composites

Alternatives to the use of pressure and extended impregnation/carbonization cycles for preparing high density composites are the new developments in high carbon yield pitch-based matrix precursors or the application of oxidative stabilization treatments at the prepreg stage.

Some pitches can be pre-treated to induce the polymerization of the components of the pitch in order to obtain high density C–C composites (in the range of 1.6–1.8 g cm⁻³), without the need for applying further impregnation/carbonization cycles or reducing the number of those currently applied. Densities may be even higher than the above mentioned values when using blends of thermally treated pitch powder and phenolic resin as matrix precursor of unidirectional C–C composites (Tsushima *et al.*, 1993). In this way, the use of pressure, which substantially increases the price of the composite, can be avoided. However, an increase in carbon yield is the result of an increased content in high molecular weight compounds, which may lead to greater viscosity. The new pitches can be expected to have a high beta resin (toluene insolubles/quinoline solubles) content. This entails large molecules that do not distil on carbonization, thereby giving rise to high carbon yields but a low enough viscosity for the penetration and wetting of the carbon substrate. The use of thermal treatment to remove volatiles and promote dehydrogenative polymerization reactions, either individually or combined with coking accelerators, such as sulfur (Fernández *et al.*, 1998; Oh and Park, 1999) or AlCl₃ (Mochida *et al.*, 1985) has been tested mainly at laboratory scale. However, in recent years considerable attention has been given to air-blowing, because of its effectiveness and for economic reasons. The oxygen in the air acts as a polymerization promoter, increasing the molecular size of light compounds through dehydrogenative polymerization reactions (Barr and Lewis, 1978; Zeng *et al.*, 1993; Fernández *et al.*, 1995), thus preventing their distillation and removal during the carbonization stage. The result is an increase in viscosity and a more disordered orientation of the lamellar aromatic molecules, limiting the growth and coalescence of mesophase, but still giving graphitizable or partially graphitizable carbon. With air-blown impregnating pitches (250 °C, 18 h) and AS4k carbon fibers, unidirectional composites of bulk densities up to 1.59–1.60 g cm⁻³ were achieved without any further densification. Composites showed high flexural strength, but fiber–matrix bonding was too strong, leading to a brittle failure. A possible way to overcome this problem could be the use of untreated fibers which yield weaker fiber–matrix bonding.

Other recent developments, designed to reduce costs by avoiding the pre-treatment step, include the direct oxidative stabilization of impregnated carbon preforms or pitch-based

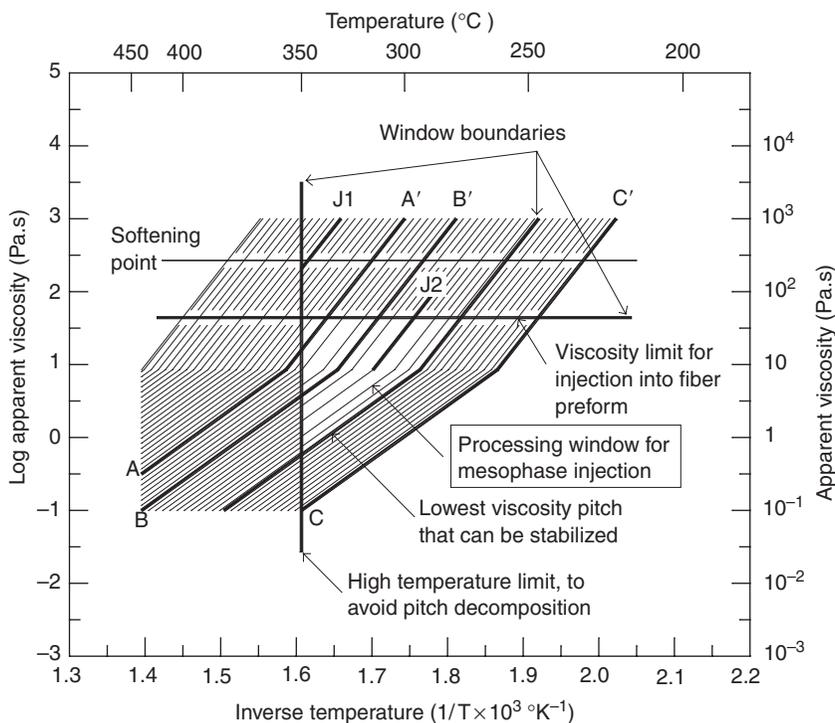


Figure 7.9 Processing window for mesophase injection (White *et al.*, 1994).

tow-pregs (Casal *et al.*, 1999), in order to obtain composites with a total absence of pores (after carbonization at 1,200 °C) and a graphitic matrix excepting the edges of the laminate.

A remarkable achievement in recent years has been the development of synthetic mesophase pitches from aromatic compounds (Mochida *et al.*, 1988; Mochida *et al.*, 2000). Mesophase pitches were initially prepared by thermal treatment of isotropic pitch (Singer *et al.*, 1987). These pitches have no light compounds which makes it possible to obtain high carbon yields and shorter processing times on carbonization. Moreover, they also have a low enough viscosity for infiltration purposes. In relation with this, White *et al.* (1994) developed a processing window for the injection of mesophase pitch into fiber preforms (Fig. 7.9). This processing window, expressed in terms of apparent viscosity and temperature, illustrates three competitive requirements: (i) the pitch must be sufficiently fluid to flow without any excessive distortion of the preform; (ii) possess the required thermal stability for completing the injection process; and (iii) be sufficiently viscous to retain the shrinkage-crack porosity essential for stabilization in depth by oxidation. If these requirements are fulfilled, a preliminary evaluation of the flow properties of a candidate pitch for a specific preform can be achieved.

The oxidative stabilization mentioned above is related to the problem of matrix bloating on carbonization when using mesophase pitches. The oxidative stabilization of preforms and woven fabrics impregnated with mesophase pitch, prior to the carbonization process, has been shown (White and Sheaffer, 1989; Christ and Hüttinger, 1993) to be an efficient way of preventing bloating, while preserving the matrix microstructure. However, further research is needed to make it more efficient and economical.

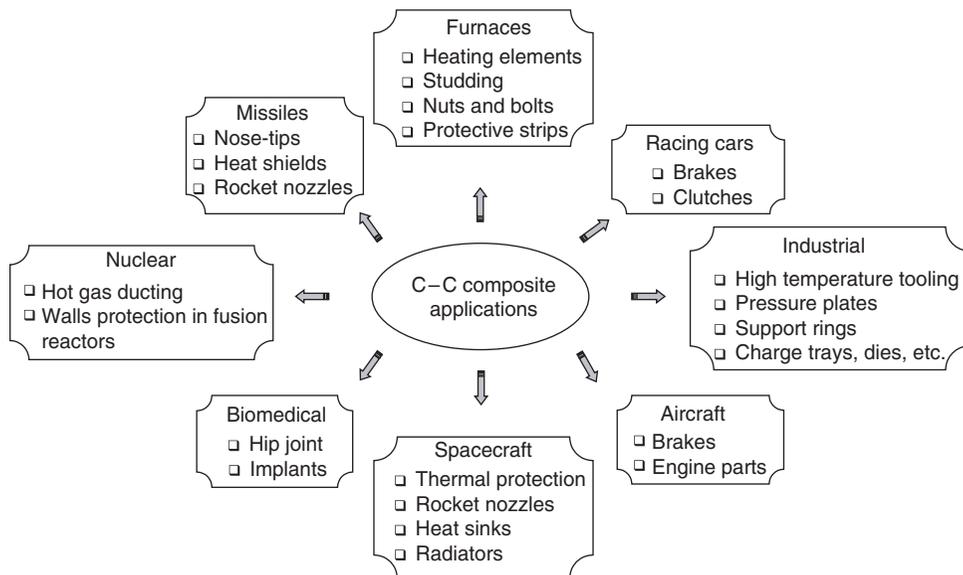


Figure 7.10 Main applications of C–C composites.

6 Summary and conclusions

C–C composites have a great potential for a wide range of applications (Fig. 7.10), not only for high-technology but also for industrial uses (Savage, 1993d; Walker, 1993). However, to exploit the full potential of the excellent properties of these materials requires the overcoming of drawbacks such as price, brittleness, and oxidation resistance. This would be possible only with the combined multidisciplinary effort of expertise from different fields, such as chemists, physicians, engineers, etc.

Further research into new aspects concerning the technology involved in the preparation of C–C composites by liquid impregnation is needed before they can be industrially applicable, in addition to a deeper understanding of the mechanisms involved in the formation of the matrix microstructure and its interaction with the fiber.

However, the development of new matrix precursors of high carbon yield with optimum viscosity, and the use of blends which individually yield different microstructures offers a promising future for these materials.

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