

A scanning electron micrograph (SEM) of a composite material, showing a central region with a rough, granular texture and surrounding areas with distinct, wavy, layered structures. The image is in grayscale and serves as the background for the book cover.

# THERMOPLASTIC AROMATIC POLYMER COMPOSITES

F N COGSWELL

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# Thermoplastic Aromatic Polymer Composites

a study of the structure, processing and  
properties of carbon fibre reinforced  
polyetheretherketone and related  
materials

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Frederic Neil Cogswell



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# Foreword

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At a SAMPE Conference in 1980 I lamented the lack of long fibre reinforced thermoplastic composites compared with thermosets. I said 'I believe that reinforced thermoplastics have a brighter future in the long run because the physical properties of the plastic arise from a more stringent chemistry, namely that necessary to produce linear polymerization, and hence should lead to better controlled and more reproducible physical properties'. At that time, Neil Cogswell was working on his magnificent invention which revolutionized the field of thermo-formable composite materials by finding a commercially viable method for introducing long fibres into a high-performance thermoplastic resin.

The basic idea was very simple, as in so many inventions. The unique step was that of applying the force to the fibres in the direction in which they are strong so as to force the fibres into the resin and to coat them while preserving fibre alignment. Because the fibres are forced into the resin by applying the force along the direction in which they can sustain maximum force, they are individually wetted, the void content is kept to a minimum, and in addition the fibres can be uniformly distributed without the formation of islands of resin.

Thermoplastic composite materials of course embrace a wide field. But this book considers in detail only the material made possible by Cogswell's invention, namely carbon fibre reinforced polyetheretherketone at about 60% of volume reinforcement. Because the matrix of the resin is highly controlled, practically void-free, highly crystalline and a thermoformable plastic, many of the inherent properties of reinforced plastics and the methods of forming and manufacturing these can be demonstrated with this system. That is what this book is about and it gives me great pleasure, and indeed pride, to be able to write a foreword to it. The book covers all the difficult as well as the easy parts of composites engineering, dealing well with processing science and manufacturing technology, durability, temperature sensitivity, and environmental resistance. Neil Cogswell also recognizes that the performance of a structural material will outlast the usefulness of the structure. The issue of reclaiming high value materials is a significant one. This book deals, in an interesting way, with how thermoplastic structural materials can be re-cycled.

It is a book pointing the way to the future and I heartily recommend it to all those interested in composite materials.

*Anthony Kelly*  
Vice-Chancellor University of Surrey

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## Preface

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This book is designed to review our understanding of the field of thermoplastic composite materials through a detailed study of one member of that family – carbon fibre reinforced polyetheretherketone.

No prior knowledge of the field is required in order to read these chapters. The opening chapter is intended to lead the newcomer into the field. There follow detailed discussions: of the ingredients of these designed materials, of how they are made into composites, and, of their microstructure. Chapter 5 addresses the way in which such materials can be converted into structures. This is followed by a series of short reviews of the performance of carbon fibre reinforced polyetheretherketone and a discussion of the application of such materials in service. The final chapter considers the directions of research in this field and attempts to project their likely influence on the development of new businesses.

The work concludes with a number of appendices, and author and subject indexes.

*Neil Cogswell*

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My daughter Frederica read the chapters with the eyes of a scientist, but not one familiar with the field. She purged the text of jargon and pointed out where simplification or amplification were necessary.

The word processing was carried out with meticulous care and unfailing good humour by Margaret Tarry with contributions from Fiona Hack and Heather Dobson.

By her encouragement and forbearance during the long hours of writing, my wife Valerie reinforced the respect and esteem that is the basis of my love for her.

*Neil Cogswell*

As Materials Scientists, my colleagues and I have been encouraged, by ICI, to explore what things might be. This book is respectfully dedicated to our associates of the Engineering, Marketing and Management disciplines who actually make them happen.

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# **1 An introduction to thermoplastic composite materials**

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## **1.1 Towards designed materials**

The history of mankind can be written in terms of his use of materials. In the first place such materials were provided by nature; wood and stone are still abundant and can be both aesthetically pleasing and extremely serviceable. A second stage was to fashion those materials for a purpose: for example by hardening wood in a fire, or chipping flints to provide sharp edges. The discovery that nature also provided metals expanded the technological horizon of our ancestors and initiated a search for new and improved materials: it is no accident that, in a great many of our universities today, the disciplines of metallurgy and materials science are strongly coupled. However, in the last fifty years, following the chemical discoveries of nylon and polyethylene, the emphasis for new materials research has progressively moved towards non-metallic materials and especially the family of polymeric materials known as plastics. Simple plastics have limitations as structural materials, and it is with structural materials that man builds his world. In order to overcome these limitations recourse has been made to the expedient of reinforcing those resins with fibres to provide a family of composite materials, which, since the development of carbon fibres, have been able to compete with metals as structural materials. In this family technologists bring together the skills of diverse scientific disciplines to provide materials whose properties can be tailored to a specific need. Such structural composite materials are the heralds of the Age of Designed Materials.

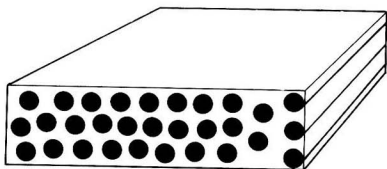
Fibre reinforced polymeric composite materials have three elements: the reinforcing fibre, the matrix resin and the interface between them. Consider a piece of composite material the size of a little finger with a volume of 10 millilitres. Such a piece of composite, based on 60% by volume of carbon fibres of diameter 7 micrometers, contains 160 kilometres of fibre, 4 millilitres of resin and 3½ square metres of interface – the distance from London to Birmingham, the volume of a thimble, and the area of a large dining table respectively. The reinforcing fibres are stiff, often with a modulus higher than that of steel, but because they are also slender – 7 microns is just visible to the naked eye – they feel silky to touch. It is only when they are stuck together with resin that their rigidity becomes apparent. It is the reinforcing fibre which largely determines the stiffness and strength of the composite. For optimum effect they are highly collimated so as to provide a high

volume packing: hexagonal close packing would, in theory, allow 91% by volume of fibres to be achieved, but, in practice, most commercial structural composite materials utilize 60–65% by volume of fibres.

High collimation of the fibres provides the maximum possible reinforcing effect along the axis of the fibre. Transverse to that direction there is little effective reinforcement. This anisotropy of properties provides added freedom to the designer, who can now arrange the reinforcement in his materials according to the load paths in the structure that he is building. The matrix resin transfers stress between the fibres and stabilizes those fibres when the structure is subjected to compression loadings. It must provide this service when under attack by hostile environments. The resin is also the medium which determines the processes by which the composite material is shaped into a structure and, during that process, it protects the reinforcing fibres from damage by attrition. The stiffness and strength of the resin is usually low in comparison to that of the fibres – a factor of 100 between reinforcement and resin modulus is common – but the resin plays a vital role both in determining the serviceability and the processability of the material.

The third element in a composite material is the interface between the resin and the reinforcement. The physical constraints provided by a high loading of fine diameter fibres is often sufficient to affect the properties of the resin in the neighbourhood of the fibre. In addition the fibres themselves may have chemically activated surfaces or be coated to promote adhesion of the resin. Thus, instead of a simple interface between materials, it may be more correct to consider an interphase. In a system containing 60% by volume of reinforcing fibres 7  $\mu\text{m}$  in diameter the mean thickness of resin coating on each fibre is 1  $\mu\text{m}$  and any 'interphase' may extend through the whole of the matrix. The integrity of the interface plays a critical role in optimizing the service performance of the composite material, especially in respect of the resistance to hostile environments and in determining the toughness of a composite. The reinforcement, matrix and interface act together to achieve optimized serviceability.

There are several texts<sup>1–10</sup> that describe the science of fibre reinforced composite materials – their history, application and potential – as viewed from different perspectives. Particular emphasis is naturally placed upon their mechanical performance, which depends upon their laminar construction. The basic building block of composite structures is a simple lamina of collimated fibres typically  $\frac{1}{8}$  mm thick (Figure 1.1).



**Figure 1.1** Basic building block: a lamina of collimated fibres

Along the fibre direction the theoretical stiffness of the composite lamina is given by:

$$\text{AXIAL STIFFNESS} = v_F E_F + v_M E_M$$

where  $v_F$  is the volume fraction of the reinforcing fibre

$v_M$  is the volume fraction of the matrix resin

$E_F$  is the modulus of the reinforcing fibre

$E_M$  is the modulus of the matrix resin

Usually the modulus of the fibre is much greater than that of the resin, and a good approximation to the axial stiffness of the composite can be made by ignoring the resin component. Transverse to the fibre direction there is much less reinforcement. In this direction the fibres themselves may be significantly less stiff than along their axis, and since their cross-section has a very low aspect ratio, they will have little reinforcing effect but simply act as a filler. As a first approximation the transverse stiffness can be taken as:

$$\text{TRANSVERSE STIFFNESS} = E_M / v_M$$

In general, composite materials are not used as simple axial laminates, because structures have to accept a variety of loading patterns. To accommodate such loads, simple shell structures are usually laminated with the individual plies or laminae oriented in different directions (a description of such laminates is given in Appendix 1). A quasi-isotropic laminate is one in which the composite layers have been arranged so that, in the plane of the moulding, the properties are the same in any direction. High stiffness and strength are only part of the equation in the design of structures. Compared to metals, composite materials have a relatively low density: the single outstanding property of carbon fibre reinforced plastics is their stiffness per unit weight (Table 1.1).

**Table 1.1 Comparative weights of panels with same bending stiffness**

| <i>Material</i>          | <i>Modulus<br/>GN/m<sup>2</sup></i> | <i>Relative<br/>thickness</i> | <i>Specific<br/>gravity</i> | <i>Relative<br/>weight</i> |
|--------------------------|-------------------------------------|-------------------------------|-----------------------------|----------------------------|
| Metal                    |                                     |                               |                             |                            |
| Steel                    | 210                                 | 1                             | 7.8                         | 7.8                        |
| Aluminium                | 73                                  | 1.4                           | 2.7                         | 3.8                        |
| Aircraft grade composite |                                     |                               |                             |                            |
| Quasi-isotropic          | 40                                  | 1.7                           | 1.6                         | 2.7                        |
| Uniaxial                 | 120                                 | 1.2                           | 1.6                         | 1.9                        |
| Space grade composite    |                                     |                               |                             |                            |
| Uniaxial                 | 300                                 | 0.9                           | 1.6                         | 1.4                        |

The low density of composite materials increases the thickness of a panel. This further increases the stiffness, allowing composites to achieve 30% weight-saving in comparison to aluminium structures of the same flexural stiffness. There are still

the through thickness properties of the laminate to be considered. In general, structures are not designed to carry loads in this direction but adventitious loads may occur, and the design of composite structures should also take account of those through thickness properties. This is one of the areas where we shall see that thermoplastic composites have demonstrated exceptional advantage.

A further major structural advantage of composite materials is that they have proved themselves to be exceptionally resistant to fatigue in comparison with metals. In addition, because it is possible to design the material at the point of manufacture, it is possible to tailor in certain features, such as dielectric properties, to achieve highly specific effects: one of the earliest and most successful uses of glass fibre reinforced plastics has been in the provision of radomes in aircraft<sup>11</sup>. A further service advantage is resistance to corrosion, where polymeric materials have an excellent record.

As well as their advantages in service, the introduction of polymeric composite materials can significantly reduce the total part count in building a structure. This leads to economies of manufacture. There is one area where composite materials have yet to attain their full potential. At this time the field of structural design is, in practice, largely based on a metals history, i.e. design practice is to assume isotropic materials. At the present time many of the structures that are built from composite materials are based upon modified 'metal' designs, but there are notable exceptions where the principle of anisotropy is a cornerstone. The theory of anisotropic design is established<sup>12</sup> but it has only become so during the last twenty years. It will be of great significance to the future of designed materials to see how those who have been schooled in anisotropic design apply those principles in practice.

As well as the bulk properties of materials, there is a growing opportunity to tailor the surface of a material. At this time such tailoring in composite materials tends to be at the interface between fibre and resin or a surface modification to functionalize two surfaces in order to facilitate joining them together. Ultimately that principle of surface modification will also be expressed as a way of adding service function to the exterior of a structure.

Our present generation of reinforced plastics is only making relatively limited use of the composite concept. Fibres can carry messages as well as loads; the incorporation of piezo-electric elements in a structure can make it responsive; the notion of combining 1 kg of computer for every 10 kg of structure would provide memory and adaptive learning ability; the principle of 'smart' materials is, of necessity, a composite concept. The present generation of composite materials offers significant advantages to the designer of today; the designer of tomorrow has the opportunity to tailor those materials to the needs of the function he seeks to achieve.

From this introduction it is necessary to refine the objectives of this work. It is my belief that, provided the broad picture is retained in view, the study in depth of a narrow part of the field of the science of materials can lead to the proposition of general principles whose validity can subsequently be tested. Thus I seek to provide that study in depth within a narrow field. This study provides a self-consistent body

of data from which the relation between different functions of the material can be established. The organization of this work, which necessarily encompasses a wide range of scientific disciplines, should then provide a picture against which other systems may be compared and contrasted. Lastly, it is desirable that the subject matter of the detailed study should be both timely and of lasting value. These considerations lead to the selection of thermoplastic structural composites and, in particular, their paradigm – carbon fibre reinforced polyetheretherketone – as the theme.

## 1.2 Why thermoplastic structural composites?

In 1990 thermoplastic composites represented about 3% of the total market for polymer matrix structural composites. The greater part of organic matrix composites presently in service are based on crosslinkable thermosetting resins. Of these, epoxy resins are the most prolific representatives. When carbon fibres were first introduced, there were several attempts<sup>13–17</sup> to develop composite materials based on thermoplastic polymers such as the polysulphone family. By creating low viscosity polymer solutions, the reinforcing fibres could be impregnated with such resins<sup>18</sup>. However, it proved extremely difficult to eliminate residual solvents from such materials<sup>19,20</sup>, and their retention caused problems, including blistering of the moulding and a reduction in properties, particularly at high temperature. Further, the use of solution technology betrayed a sensitivity of those amorphous polymers to attack by chemical reagents. Since composites were of particular interest to the aerospace industry, where hydraulic fluids, aviation fuels and the use of paint strippers are widely encountered, soluble materials were placed at a severe disadvantage. Not all thermoplastic composites were made by solution processing: it was possible to interleave layers of reinforcing fibres and resin films and then, in a protracted moulding operation, wet out the fibres in a high-pressure moulding process<sup>21–3</sup>. Such film stacked composites gained a small niche in the market place but, for the most part, the field of structural composite materials was ceded to crosslinkable thermosetting resins. Because of the convenience with which epoxy resin systems could be hand layed up into structures, thermosetting composite materials became established as excellent prototyping materials and were gradually translated into full scale production.

By 1980, three problems had become evident with epoxy composite materials: their brittleness, their sensitivity to water, and the slow manufacturing technology. Although it was possible to improve either the toughness or the water resistance of epoxy composite materials, a common experience was that an improvement in one property usually led to a falling off in the other. The introduction of preimpregnated carbon fibre reinforced polyetheretherketone, a high temperature semi-crystalline polymer, in continuous tape form<sup>24</sup> simultaneously offered a solution to the problems of toughness and environmental resistance, with the added bonus of potentially developing high rate processing: thermoplastic materials were translated into a major platform for research and product development. These material forms are now becoming qualified products. They extend the range of

applications established for their thermosetting cousins in particular into that segment of industrial activity that requires high rate automated fabrication.

Thermoplastic matrix materials derive their properties from their long chain entangled molecules. The entanglement of the chains provides the matrix with strength and effectively acts as a temporary crosslink. Because the chains are not fixed by their chemical structure, they have the ability to slip past one another when subjected to intense local stress; thus, whereas a crosslinked polymer has no alternative but to be strong or to break in a brittle fashion, a linear chain polymer has the ability to dissipate energy locally by chain slippage. This ability confers the property of toughness on the composite. Some linear chain polymers also have the ability to pack tightly together in a semi-crystalline network. This network also provides an effective physical crosslink in the system, enhancing strength. The crystalline structure further provides resistance to attack by hostile reagents. When a linear chain, thermoplastic, polymer is melted the chains may move freely with respect to one another, so that the composite can be formed into shape. In contrast to their thermosetting cousins, with long chain thermoplastic materials this shaping process is a purely physical one, depending on heat transfer, geometry and the forces applied. The absence of chemistry, the necessary companion of thermosetting processing, means that thermoplastic polymers can be fabricated into structures rapidly and with a high level of quality assurance: all the chemistry has been carried out by those people whose business is chemistry, leaving the fabricator free to concentrate wholly upon his art of making shapes.

The potential for rapid processing with thermoplastic structural composites is of particular significance. With high performance thermosetting resins the cure cycle is usually several hours long; with thermoplastics the absence of chemistry means that structures can be formed in minutes, or even seconds. The protracted nature of thermoset processing is not necessarily a constraint in industries, such as aerospace, where the required rate of production may be less than one a day and each individual structural component must be optimally tailored to shape. In such circumstances the advantages of low capital expenditure on tooling may justify the use of slow, labour intensive, fabrication processes. Such a vision, however, unnecessarily limits the horizon of structural composite materials. For the first twenty years of their life it was widely believed that carbon fibre reinforced plastics would make the transition from specialist aerospace materials to general industrial products: considerable investment in carbon fibre capacity testifies to that belief, but, except in the area of high performance sporting goods and short fibre moulding compounds, the penetration has been disappointingly small. The difficulty in achieving that translation has been the requirement for appropriate mass production technology for high performance structural composites. Thermoplastic structural composites offer the potential for mass production, which may provide the key to the metamorphosis of high performance composite materials into high quality mass production materials for the general industrial designer.

The thermoplastic family of materials is particularly broad in respect of the service it can offer. There are a wide range of resins: elastomeric materials such as polyurethanes, general purpose resins such as polypropylene, engineering plastics