THE EXPERIENCE OF THERMOPLASTIC STRUCTURAL COMPOSITES DURING PROCESSING

F N COGSWELL
ICI Wilton Materials Research Centre
ICI Advanced Materials
PO Box 90
Wilton
Middlesbrough
Cleveland
TS6 8JE
England

SUMMARY

The factors which must be considered during processing of thermoplastics structural composites include : chemical change, thermophysical experience, deformation, crystallisation, and the generation of internal stress. These factors are considered with special reference to carbon fibre reinforced polyetheretherketone composites. Despite the very high processing temperatures PEEK composites are strongly resistant to chemical change. The high temperatures means that the thermophysical effects are large, but can be readily predicted. The inextensibility of the fibres, combined with the high viscosity of the matrix, limits the deformation processes available to shape the material : those same factors assure that, within the range of allowable deformations, the fibre collimation and matrix distribution of the prepreg are preserved in the final product. The microstructure of the composite includes the semi-crystalline nature of the matrix phase. There is a broad processing window for optimum crystallisation and the penalty for working outside that window is small. Because of the high processing temperatures, coupled with the absence of stress relief mechanisms such as microcracking and debonding, high levels of internal stress are built up during processing. The inherent toughness of the matrix ensures that this is not deleterious to the service performance of the material. These different elements of the response of the material combine to form the processing science which underpins all forms of manufacturing technology

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1 INTRODUCTION

The objectives of studying processing science are threefold: to be able to predict how a material will behave in a known manufacturing operation; to learn how to tailor a material product form so that it processes better; and to devise novel conversion processes to achieve designed end products. There are two approaches to these goals. Analysts (1-4) start by trying to isolate relevant elements of the process and to measure the response of the materials: they then seek to synthesise a process model. Modellers (5-9) prefer to define the process dynamics; by using that model in conjunction with experiments they then deduce the apparent characteristics of the material. Ideally these two approaches should meet on common ground. At this time the conclusions can differ significantly and there is a considerable amount of work to be done in order to rationalise these different views and arrive at a consensus.

The analytical approach, taken in this paper, must separately address three areas of materials science: chemical change, thermophysical properties, and deformation characterisation. It is also necessary to consider the interaction of the processing history with the microstructure of the formed component. As a vehicle for this study, this paper reviews the experience of carbon fibre reinforced polyetherketone (CF/PEEK) during processing operations.

2 CHEMICAL CHANGE

In thermoplastic processing there are three common factors which may lead to chemical change: heat, oxygen and water (10).

Thermoplastic structural composites are processed at high temperature, and thermal stability sets an upper limit to the processing window of materials like PEEK. Groves (11) and Scobbo (12) have demonstrated that there is no significant change in the melt viscosity of CF/PEEK for one hour under normal processing conditions. Besides melt viscosity another property which is sensitive to any changes in chemical structure is crystallisation behaviour. Sichina and Gill (13) have shown that the crystallisation behaviour of the optimized CF/PEEK prepreg does not change with normal melt history, and Ma (14) has shown that there are no significant changes in crystallisation behaviour even after repeated processing. Direct measurements of the molecular weight of polymer extracted from such a composite (1) indicates that after two hours at 400°C there is a slight (10%) increase in molecular weight. Two hours is a longer time than would be anticipated for processing with fully impregnated thermoplastic composite materials and we may safely conclude that, for preimpregnated carbon fibre/PEEK, processing within the manufacturers recommended temperature range, 360 to 400°C, leads to no deleterious effect.

Carpenter (15) shows no significant weight loss in carbon fibre/PEEK preimpregnated tape products until 550°C. Thus processing is possible at higher temperatures provided that the time scale is reduced and oxygen is excluded.

The effects of heat are aggravated by the presence of oxygen. With PEEK resin, oxygen tends to produce crosslinking and so an increase in viscosity and a reduction in ease of crystallising. Oxygen, from the air, first attacks any exposed surface of the material. The issue of oxidation is of particular importance in those product forms, such as commingled fibres or powder impregnated materials, which have a large surface to volume ratio. Where this is the case, inert atmosphere or vacuum processing is strongly recommended. This issue is less critical in the case of the boardy preimpregnated product forms where there is only approximately one twentieth of the surface area exposed, but, even so, Cattanach (16) strongly recommends vacuum wherever possible.

Many commercial engineering polymers are formed by condensation reactions. Such polymers can be prone to degradation when melted if they contain any water. In such polymers water content must be closely controlled. Other polymers will absorb significant quantities of water which will normally volatilise during processing. Prepregs made by solution impregnation may contain residual solvents which will volatilise during processing. Such volatilisation processes can result in a scarred surface on the moulding or blisters in the structure. Polyetheretherketone resin is strongly resistant to water pick up. It has an equilibrium water content of about 0.25% achievable after prolonged exposure to boiling water. Although such saturation has no detectable effects on the properties of carbon fibre/PEEK composites, it can give rise to cosmetic defects during processing. If water is present then drying is recommended.

The commercial grades of melt preimpregnated CF/PEEK have excellent chemical stability. This allows a broad processing window to be established in which the physical properties of the composite structure resulting from the processing operation can be accurately defined.

3 THERMOPHYSICAL PROPERTIES

In any thermoplastic polymer heat exchange, and the thermodynamic properties associated such temperature changes, play an important role in defining process economics. Often it is the time taken to solidify a formed component which will be the dominant factor in determining the rate at which components can be made. For structural composite materials such as carbon fibre/PEEK the processing temperatures are high and so the associated thermophysical effects are large, but only as large as would be expected. Working values of the heat transfer characteristics of carbon fibre/PEEK composite materials based on 61% by volume of high strength carbon fibres, as they relate to processing, are noted in Table 1.

TABLE 1 : WORKING VALUES OF HEAT CONTENT AND HEAT TRANSFER OF PEEK/AS4 (1)

Heat content at 400°C relative to 20°C	540 kJ/kg
Specific heat at 400°C	1.7 kJ/kg °C
Coefficient of thermal diffusion (20°C to 400°C):	
across the fibre direction	0.3×10^{-6} m^2/s
along the fibre direction	2.9×10^{-6} m^2/s

It is important to note the anisotropy of thermal conductivity associated with the anisotropic nature of the reinforcing fibres. Usually heat transfer across the fibre direction - through the thickness of the moulding - is the dominant property of interest but axial heat transfer can also be important especially in continuous processes such as filament winding, tape laying, roll forming and pultrusion.

As well as the heat transfer characteristics within the composite material it is also desirable to consider the surface heat transfer coefficient with any contacting medium, (10). As a "black body" carbon fibre composites are especially suitable for radiative heat transfer, where Scobbo (17) deduces a heat transfer coefficient of about $30W/m^2{}^\circ C$

From this basis of understanding excellent thermal modelling capability has been demonstrated (18-25). During normal processing (18,21) the crystalline structure will be similar throughout the whole thickness of the moulding so that it can be inspected non-destructively using surface X-ray reflectance techniques (26).

In any heat exchange process there will be dimensional change. In carbon fibre composites, axial expansion is constrained by the low thermal expansion coefficient of the fibre. Across the fibre direction the thermal expansion is more closely related to that of the resin. These properties have been characterised by Barnes (27). Table 2 shows typical working values for carbon fibre/PEEK composites based on 61% by volume of high strength carbon fibre.

TABLE 2 : LINEAR THERMAL EXPANSION OF CARBON FIBRE/PEEK COMPOSITES

	Solid State 23 to 143°C per °C	Rubbery Region 143 to 343°C per °C
<u>Uniaxial Moulding</u>		
Along fibres (0°)	0.4×10^{-6}	(0)
Transverse (90°)	30×10^{-6}	(80×10^{-6})
<u>Quasi isotropic Moulding</u>		
In plane (-45°,90°,45°,0)	2.9×10^{-6}	(7×10^{-6})
Through thickness	58×10^{-6}	(130×10^{-6})

(estimated values in parenthesis)

The low thermal expansion of the moulding is beneficial in giving accurate dimensional control, but note that the difference between in plane and through thickness properties can also cause distortion of shaped mouldings, as discussed in section 5. It is desirable to match the thermal expansion of the tool to that of the material (28), however, when transferring hot composite into a cold metal tool, the thermal excursion of the tooling is small by comparison to that of the composite being moulded. When the requirement is for precision structures it is necessary to take detailed account of the thermal expansion of both the composite and the mould.

The density of carbon fibre/PEEK composite based on 61% by volume carbon fibres decreases from 1,600 kg/m^3 at 20°C, to 1,583 kg/m^3 at the glass transition temperature, and 1,530 kg/m^3 in the melt. There is a small change in density at the cystalline melting point during heat up of the moulding. The temperature at which this occurs during cooling depends upon the temperature of crystallisation and so on the cooling rate: this effect is discussed in section 4.

During normal processing the crystallisation temperature will be about 250°C. The total density change during a processing cycle is about 4%: virtually all this change is in the thickness of the moulding. Much of this volume change occurs in the melt or during crystallisation where the matrix is able to flow: the majority of the remainder of the shrinkage occurs in the rubbery region above the glass transition temperature where relaxation can occur to relieve the build up of stress.

3 RHEOLOGY

In continuous fibre reinforced plastics, deformation is constrained by the high loading of continuous collimated fibres. The inextensibility of these fibres effectively means that tensile deformations along the fibre axis are forbidden. To understand how to mould double curvature structures from inextensible material is a non-trivial exercise and requires an appreciation of those deformations processes which are allowable. These are summarised in Figure 1. They include: resin percolation through and along the fibre bed; transverse fibre flow; shearing of individual fibres past one another along the fibre direction; and lamina slip of plies past one another.

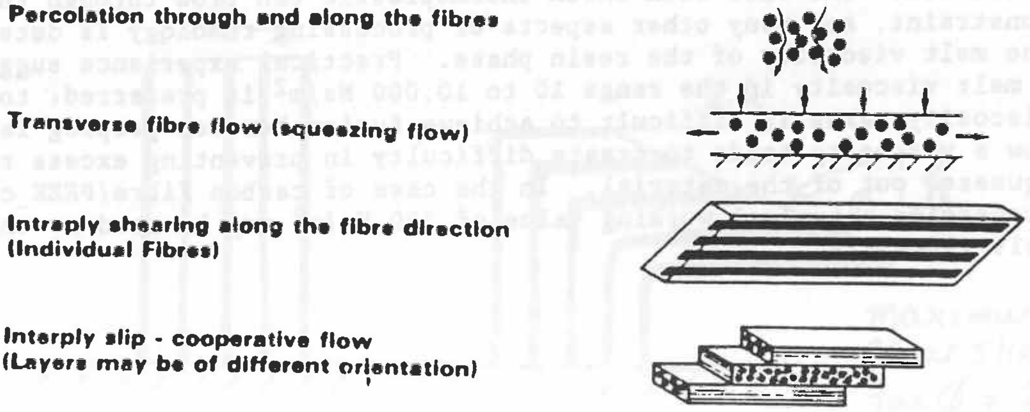

Figure 1 : Flow Mechanisms in Preimpregnated Products

In addition to these flow mechanisms, in continuous collimated products it is possible to incorporate additional stretching by replacing the continuous collimated fibres by discontinuous aligned fibres (29) or crimped or twisted fibres (30).

Percolation of resin through the reinforcing fibres is a healing flow. It allows local redistribution of resin and, in particular, the formation of a resin rich interlayer which permits bonding of different ply layers. The bed of reinforcing fibres is anisotropic: there can be resin percolation both along and across the fibres. The description of such percolation can be made in terms of the D'Arcy Permeability Coefficient (31).

There are several studies of resin permeability in fibre beds (1,2,32-35). Analytical studies (1, 32) indicate that the permeability along the fibre direction is significantly greater than that through the thickness. The permeability is higher with large diameter fibres: larger fibres, larger holes, easier flow. The permeability decreases by approximately one order of magnitude as fibre volume fraction increases from 50% to 65% by volume. Wheeler (32) notes that transverse permeability is not significantly affected by local fibre organisation at those high volume fractions. Lam and Kardos (36) have made direct measurements of axial and transverse permeability of carbon fibres using viscous oils. Their results - Table 3 - are in satisfactory agreement with the analytical predictions (1).

TABLE 3 : PERMEABILITY OF CARBON FIBRES BY VISCOUS RESINS
(CARBON FIBRE DIAMETER 7μm).

D'Arcy Permeability Coefficient (m^2)

Volume Fraction %	Analytical Solution (1) Axial	Analytical Solution (1) Transverse	Experimental Results (36) Axial	Experimental Results (36) Transverse
60	2.3×10^{-13}	0.5×10^{-13}	1.9×10^{-13}	0.5×10^{-13}

The permeability coefficient is determined by the geometric constraint of the fibre bed. The ease with which thermoplastic can flow through that constraint, and many other aspects of processing rheology is determined by the melt viscosity of the resin phase. Practical experience suggests that a melt viscosity in the range 10 to 10,000 Ns/m^2 is preferred: too high a viscosity makes it difficult to achieve fusion between prepreg layers; too low a viscosity tends to create difficulty in preventing excess resin being squeezed out of the material. In the case of carbon fibre/PEEK composites processing a typical working value of 300 Ns/m^2 may be used as the polymer melt viscosity.

At rest, the polymer molecule occupies an entangled random coil configuration. During flow this configuration is disturbed. The recovery from such disturbance is characterised by the natural time of the melt (10): this is defined as the ratio of melt viscosity to melt elastic modulus. For PEEK melts the elastic modulus is about 3000 N/m^2 (37) so that, for a melt viscosity of 300 Ns/m^2, the relaxation time is about 0.1 seconds. If the duration of deformation is longer than this time scale then the flow will be essentially viscous, if shorter the material will have a strong memory of its former state. Similar mechanisms determine the interdiffusion of polymer chains across a boundary and, as a first approximation, full adhesion across such a boundary will be expected in about five relaxation times. This suggests a time scale for self diffusion of two melt fronts in contact as about half a second. Like resin percolation, which enables resin surfaces to come into contact, the self diffusion process is a major healing flow which helps to determine the quality of the laminate.

The fibrous network also has deformation characteristics. Ideally the rod like reinforcements all lie parallel: in practice they are slightly twisted and intermingled so that individual fibres are slightly bent. This bending of the fibres makes the fibre bed elastic and, in the absence of resin, it would fluff up slightly. Once the fibres are impregnated with resin this tendency to spring apart is suppressed but, as Gutowski (2) indicates, the elasticity of the fibre network cannot be ignored, especially when considering consolidation processes. The work of Barnes (38) suggests that for fully impregnated CF/PEEK composites, of 61% by volume fibre, a pressure constraint of 0.25 atmospheres is sufficient to overcome this elasticity of the fibre network and prevent void formation in the material.

When considering the rheology of a composite material as applied to processing science the first question that must be asked is "Is the rheology measured under laboratory conditions the same as pertains in processing?" (10). The two factors to be considered are the scales of the deformation history in respect of strain amplitude and process time. In respect of strain amplitude, most composite processes involve strains of less than two units of shear. Thus, if we consider the simple bending of a beam through a right angle, Figure 2,

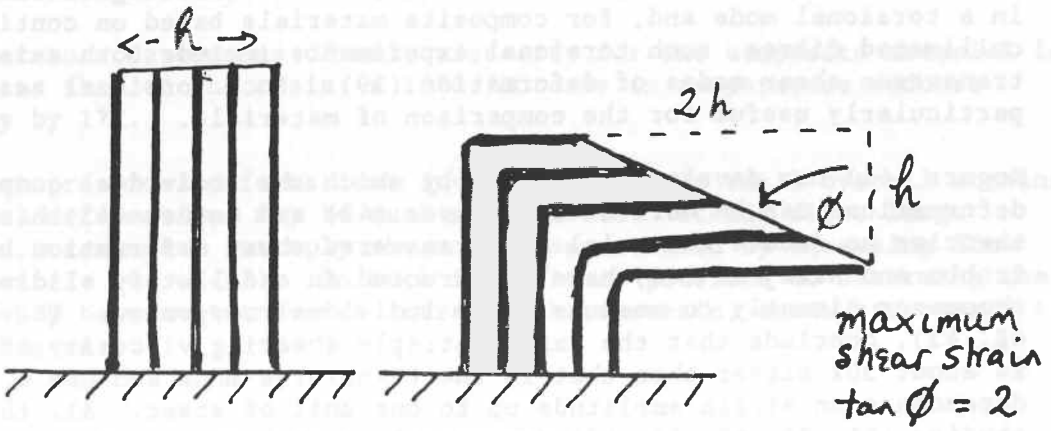

Figure 2 : Bending of an inextensible beam

the magnitude of the shear strain can be readily shown to be two units of shear. A right angle is a not uncommon deformation requirement, but most shaping process will involve smaller deformations. There will, of course, be certain occasions where a small part of the material is subjected to much larger deformations but, in terms of composite processing 10 units of shear would be a large deformation indeed. In respect of time scales we are concerned with processes which may take less than one second in respect of rapid stamping to up to one hour in the case of autoclave processing. These scale of deformation and time are both convenient and conventional to measure rheological response in the laboratory.

The questions remain: what rheological responses, and how should they be measured? In a system wherein extension is forbidden by the inextensible fibres, deformation must rely on shear processes. Two modes of intraply shearing, wherein individual fibres move relative to one another, can be distinguished: axial and transverse intraply shear - Figure 3.

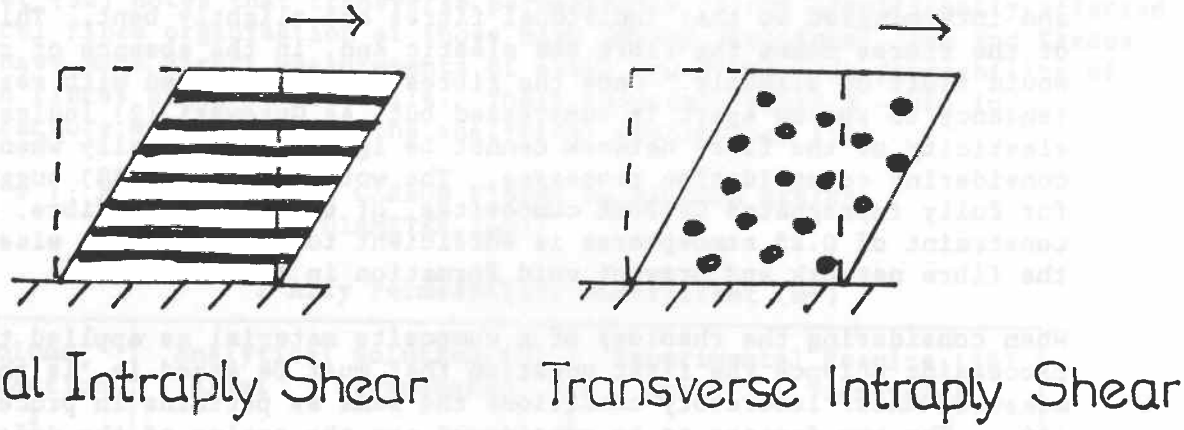

Figure 3 : Intraply shearing modes

At small amplitude of deformation these can be conveniently studied in oscillatory flow (11, 39, 40). Conventional oscillatory rheometers operate in a torsional mode and, for composite materials based on continuous collimated fibres, such torsional experiments include both axial and transverse shear modes of deformation (39). Such torsional testing is particularly useful for the comparison of materials.

Rogers (41) has developed a method by which the individual components of such deformations can be derived and Groves (42) and Cathey (43) have applied such theories to deduce the axial and transverse shear deformation behaviour. Scobbo and Nakajima (40) have constructed an oscillatory sliding plate rheometer directly to measure those individual responses. Those studies (40, 42, 43), conclude that the axial intraply shearing viscosity at low amplitude is about 30% higher than that in the transverse mode and has a similar dependence on strain amplitude up to one unit of shear. All the experimental studies (11, 39, 40, 42, 43) demonstrate a markedly non linear response with indications of a yield stress of about 10^3 N/m^2. The interpretation of dynamic viscoelastic response in oscillatory shear depends upon the model used. My preference (10) is to use the Maxwell model instead of the more commonly used Voigt elements. Using this interpretation and translating to equivalent steady flow response, the oscillatory flow results can be substantially simplified (39) and presented in a form that is directly relevant to processing calculations.

Figure 4 : shows typical data for axial and transverse intraply shear for CF/PEEK composite, based on 61% by volume carbon fibre, for small stains.

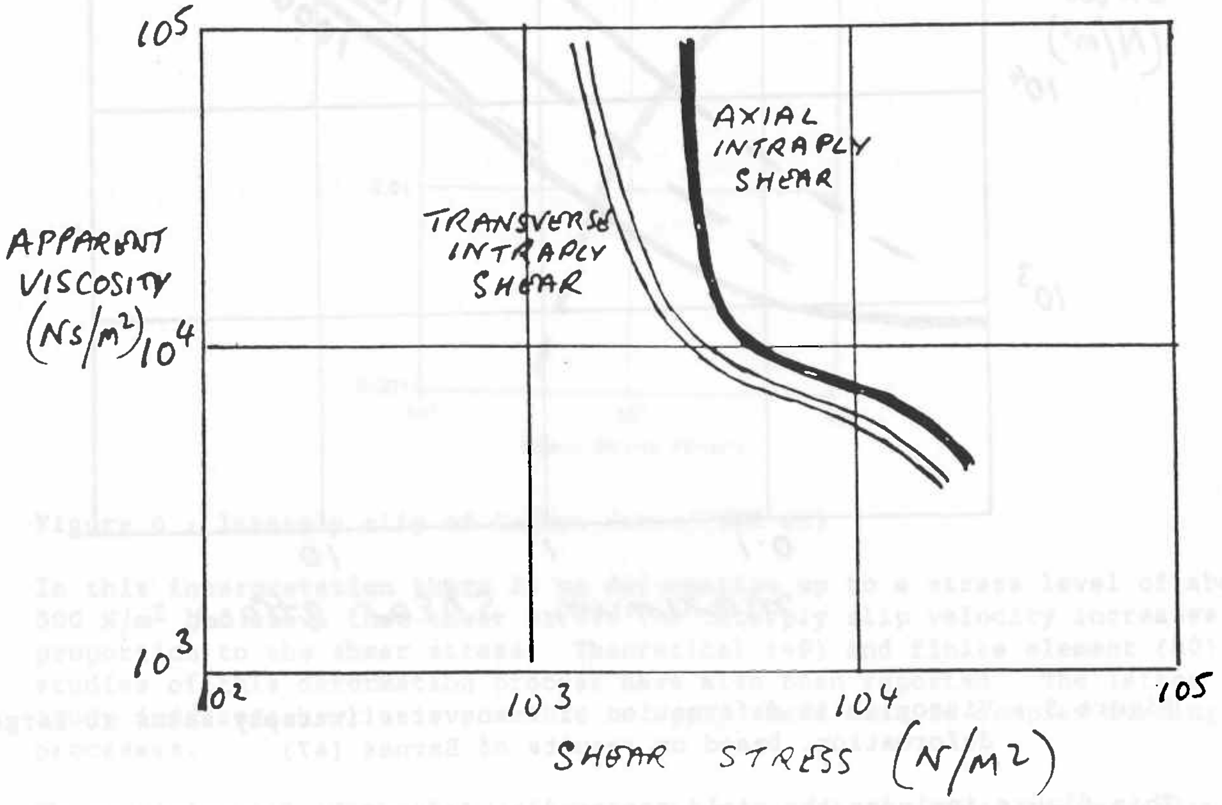

Figure 4 : Comparison of axial and transverse shearing modes of CF/PEEK composite at 380°C (42)

The temperature dependence of melt viscosity for the composite material is the same as that of the resin: a 10°C increase in temperature reduces viscosity by 17%.

While most practical deformations involve relatively small overall strains some local deformations may be much more severe. Steady flow, large amplitude, transverse intraply shear has been studied by squeezing flow techniques (1, 38, 44-47). In such flows it is possible to determine the relationship between transverse intraply shear strain, shear stress and time scale - Figure 5.

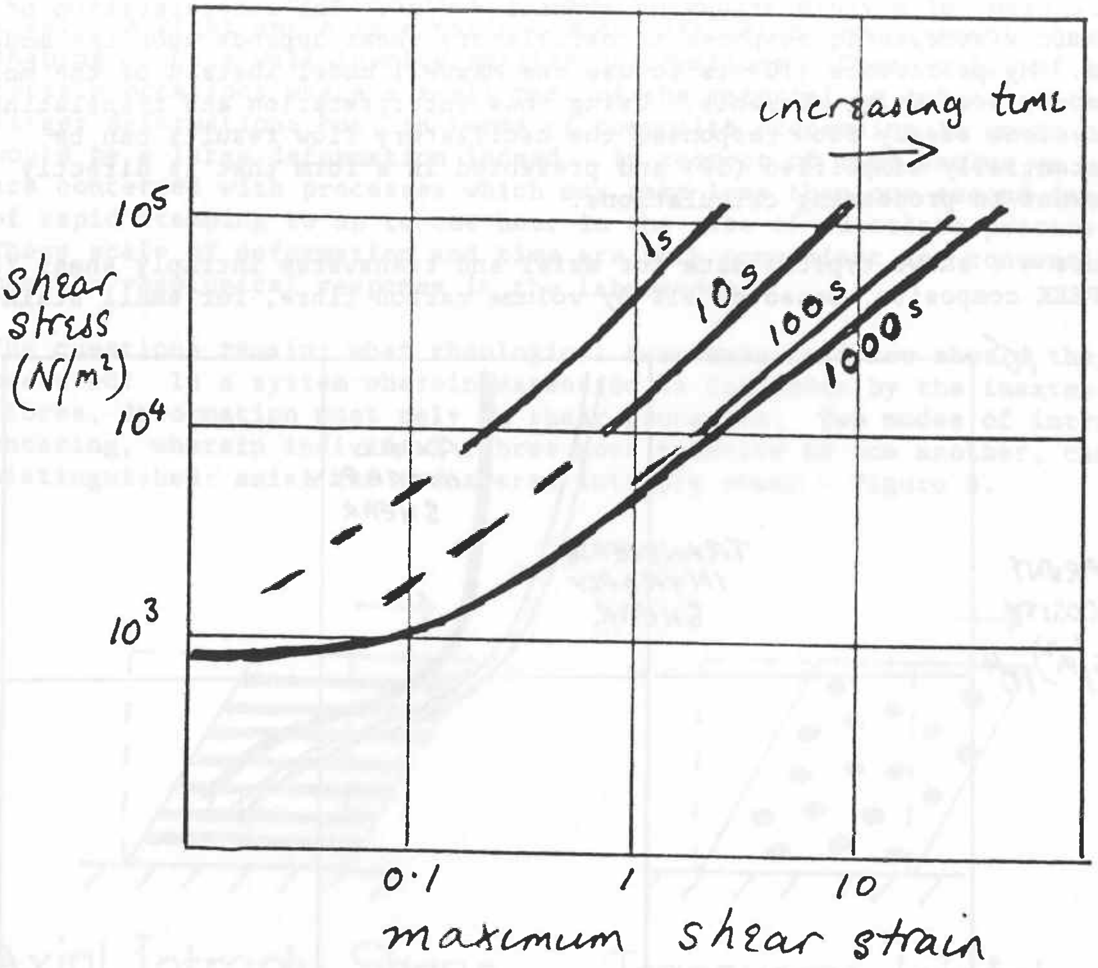

Figure 5 : Viscoplastic deformation of transverse intraply shear at large deformation, based on results of Barnes (47)

This figure includes the yield stress data determined from oscillatory rheometry studies (39) which are found to be in satisfactory agreement with the trends from the large amplitude, steady flow, squeezing studies.

As well as shear within the ply it is possible for individual plies to move past one another. This deformation is limited to the resin rich layer in between plies that is of the same thickness as the fibre diameter, about 7μm. It is conveniently observed between plies of different orientation. Experimental studies (1, 16, 45) suggest that this flow is a true viscous deformation in the resin rich surface layer. Such deformations in practice are often of the order 10mm. When the thickness of that resin rich interply region is considered, this implies that the shear strain amplitudes in the resin can be of the order 1000 units of shear. For practical purposes a convenient interpretation is to consider the flow as an interply slip - Figure 6.

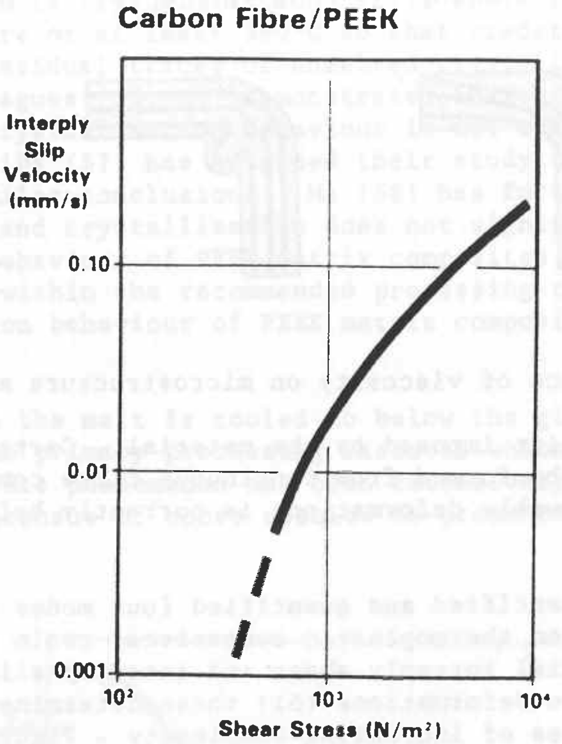

Figure 6 : Interply slip of Carbon Fibre/PEEK (1)

In this interpretation there is no deformation up to a stress level of about 500 N/m^2 but above that shear stress the interply slip velocity increases in proportion to the shear stress. Theoretical (49) and finite element (50) studies of this deformation process have also been reported. The latter study indicates how it is possible to apply these data to complex forming processes.

The optimization of rheology of composite materials requires optimization of the viscosity of the resin and optimization of the distribution of the fibres in the material. The consideration of resin viscosity must also take account of the time scales of the process. If the process time scale is long and the resin viscosity is low then shaping flows may cause resin to be squeezed out or there may be excessive transverse flow. By contrast too high a viscosity and too short a time scale means that the reinforcing fibres are unable to adjust to the flow and may become buckled or distorted, particularly on the inside of curved surfaces. Correct tailoring of matrix viscosity and control of resin fibre distribution allows interply slip to occur and the microstructure to be preserved - Figure 7.

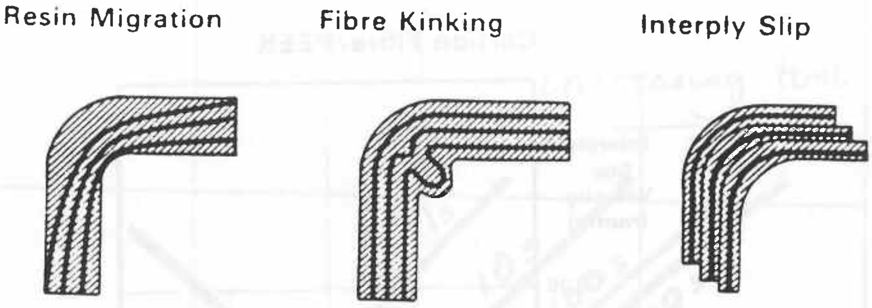

Figure 7 : Influence of viscosity on microstructure after flow

Besides the constraint imposed by the material. Certain geometries of deformation cannot be formed from continuous fibre composites. The theory of the concept of allowable deformations is currently being developed by Rogers (51).

This section has identified and quantified four modes of deformation which can occur with molten thermoplastic composites: resin percolation, transverse intra ply shear, axial intraply shear and interply slip. Together with the concept of allowable deformations (51) these determine a hierarchy of deformation processes of increasing complexity - Figure 8.

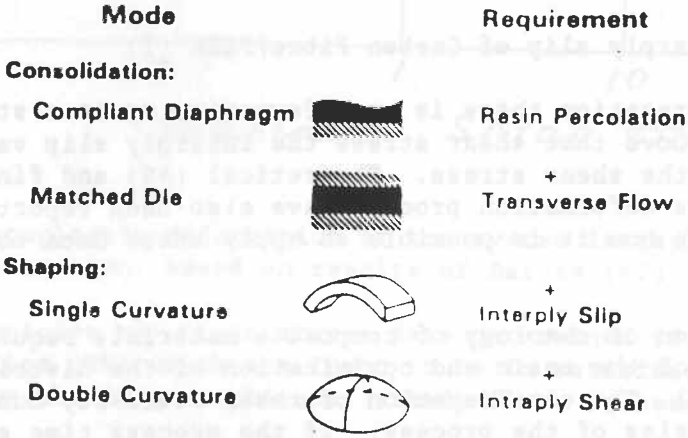

Figure 8 : A hierarchy of deformation processes

4 CRYSTALLISATION AND CRYSTALLINITY

In semi crystalline polymers such as PEEK the levels of crstyallinity, and so the service performance of the material, depends upon the history of the material during processing (52). The recognition that there is an optimum processing window has stimulated a wealth of studies of what happens if the material is processed outside that window. These studies have been reviewed by Corrigan (53) who concludes that only minor changes in performance can be attributed to such deviations.

The matrix in PEEK based composites crystallises slightly more slowly than neat resin under the same conditions (1). This slowing down can be interpreted as due to the physical constraint of the fibres on the matrix.

The crystallisation of polyetheretherketone depends first on the state of the melt from which it is crystallisated. It is preferred that this melt should be at a temperature of at least 360°C so that predetermined nucleii associated with residual traces of unmelted crystallites are eliminated (54). Sichina and colleagues (55, 56) demonstrated that, in the optimized version of CF/PEEK, the crystallisation behaviour is not affected by time at temperature. Saliba (57) has extended their study to hold times of two hours at 400°C with similar conclusions. Ma (58) has further demonstrated that repeated melting and crystallisation does not significantly alter the crystallisation behaviour of PEEK matrix composites. Provided the melt has been established within the recommended processing range of 360°C to 400°C the crystallisation behaviour of PEEK matrix composites can be accurately defined.

The rate at which the melt is cooled to below the glass transition temperature is the primary processing variable which controls the level of crystallinity. This phenomenon has been extensively studied experimentally (59-62) and a concensus of those results is presented in Figure 9.

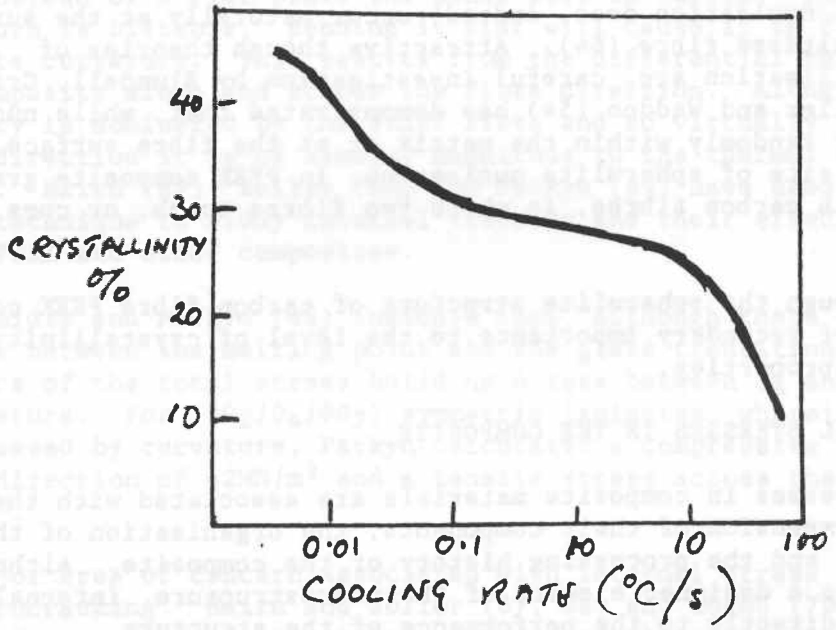

Figure 9 : Crystallinity in matrix of CF/PEEK as a function of cooling rate based on the review by Corrigan (11).

The dependence of crystallinity on cooling rate naturally causes concern about crystallinity gradients within a moulding. That anxiety has been dispelled by Willmouth (18) who showed that, during normal processing, although the centre of a moulding naturally solidifies after the surfaces, the cooling rate experienced through the critical temperature region of crystallisation is virtually independent of position in the moulding. Only in extreme cases, when cooling thick mouldings into cold tools, was it possible to achieve amorphous surfaces and crystalline central regions. In such cases a short annealing cycle at 220°C crystallises the surface layer.

The most distinctive feature of the crystalline texture of polyetheretherketone is the spherulitic structure. Spherulites are families of crystallites radiating from a single nucleation point. Dramatic early pictures (52) illustrated an influence of fibres on the nucleation of spherulitic structure when a single fibre was embedded in the resin. Theories of transcrystallisation were evolved wherein the matrix resin crystallised onto the fibre surface turning that interface into a continuum. So important was this considered to be that there were expressions of the desirability of destroying all the nuclei in the matrix phase so that the crystallisation was preferentially seeded at the fibre surface (63). That argument leads to a preference for long times at high melt temperature. Preferential nucleation does, indeed, occur naturally at the surfaces of highly graphitised fibre (64). Attractive though theories of transcrystallisation are, careful investigation by Blundell, Crick, Fife, Peacock, Keller and Waddon (54) has demonstrated that, while nucleation can occur either randomly within the matrix or at the fibre surface, the predominant site of spherulite nucleation, in PEEK composite grades based on high strength carbon fibres, is where two fibres touch, or come very close together.

Dramatic though the spherulite structure of carbon fibre PEEK composite is, it is only of secondary importance to the level of crystallinity in determining properties.

5 INTERNAL STRESSES IN THE COMPOSITE

Internal stresses in composite materials are associated with the difference in thermal expansion of their components, the organisation of those ingredients, and the processing history of the composite. Although not introduced as a designed element of the microstructure, internal stress contributes directly to the performance of the structure.

In a simple uniaxial carbon fibre composite the thermal expansion of the fibres is nearly zero while that of the resin phase is large and positive. As the composite is cooled from its processing temperature the resin tries to shrink, but that shrinkage is resisted by the stiff inextensible fibres. This places the resin in tension and the fibres in compression.

In addition to the constraint imposed by the fibres on the resin the whole of the composite is placed under constraint by the solidification taking place as a result of cooling. Cooling takes place from the outside inwards. The surface layers of a moulding are thus solidified first. They will be placed in compression by the subsequent shrinkage of the internal core and will themselves represent a tensile constraint on that part of the moulding. Manson (66) used an elegant method of demonstrating this effect by the use of release plies between each layer of his moulding. He was then able to study the deformation in each layer independently. For carbon fibre reinforced polyetheretherketone he showed an approximately parabollic stress profile with a maximum compressive stress of about $40MN/m^2$ on the surface and a maximum tensile stress in the interior of the moulding of about $18MN/m^2$. Chapman (67) has provided a detailed theoretical account of this mechanism. This stress applies to the composite as a whole and not just the components.

Uniaxial mouldings are rarely used in practice; angle plied laminates are more common. All those ingredients to internal stress noted above will also apply to angle plied laminates but there is extra constraint imposed by the lay up. This constraint is most clearly demonstrated by taking a two ply 0/90 laminate, moulding it and cooling it in a flat press and then inspecting it. Instead of a flat plate the panel will be curved. Further that curvature is bistable. Bending it flat will cause it to flip over to the opposite curvature. This results from the differential thermal expansion of the composite along and across the fibre direction. Along the fibres this property is dominated by the stiff fibre and so virtually zero, across the fibre direction it is of similar magnitude to the thermal expansion of the matrix. Nairn (67), Zoller (68) and Parkyn (69) have used this bimetallic strip technique to study internal stresses and their effects in carbon fibre/PEEK and other composites.

Jeronimidis and Parkyn (69) indicate that, although there are large volume changes between the melting point and the glass transition temperature, three quarters of the total stress build up occurs between Tg and ambient temperature. For $(90_2/0_4/90_2)$ symmetric laminates, wherein the stress cannot be released by curvature, Parkyn calculates a compressive stress along the fibre direction of $42MN/m^2$ and a tensile stress across the fibre direction of $42MN/m^2$.

One major area of concern associated with internal stress is the possibility of microcracking. Nairn and Zoller (67, 68) and Coxon (70) have studied this effect for a range of composites. The internal stress levels in CF/PEEK are higher than those with the other thermoplastic and thermosetting resins studied by Nairn but CF/PEEK is reported to be much less susceptible to microcracking. Nairn and Zoller attribute this to the toughness of PEEK resin; but Coxon suggests that the uniformity of fibre/resin distribution is also a significant factor. The resistance of thermoplastic composites to microcracking depends both on the ingredients and how they are integrated.

All the previous arguments been directed to flat laminates. Most practical mouldings are shaped and we must also consider thermal stresses and deformations associated with the difference in the low thermal expansion in the plane of the moulding (fibre dominated) and the high value through its thickness (resin dominated). Spencer (71) shows that, as a moulding cools and becomes thinner, the radius of curvature tightens, Figure 10.

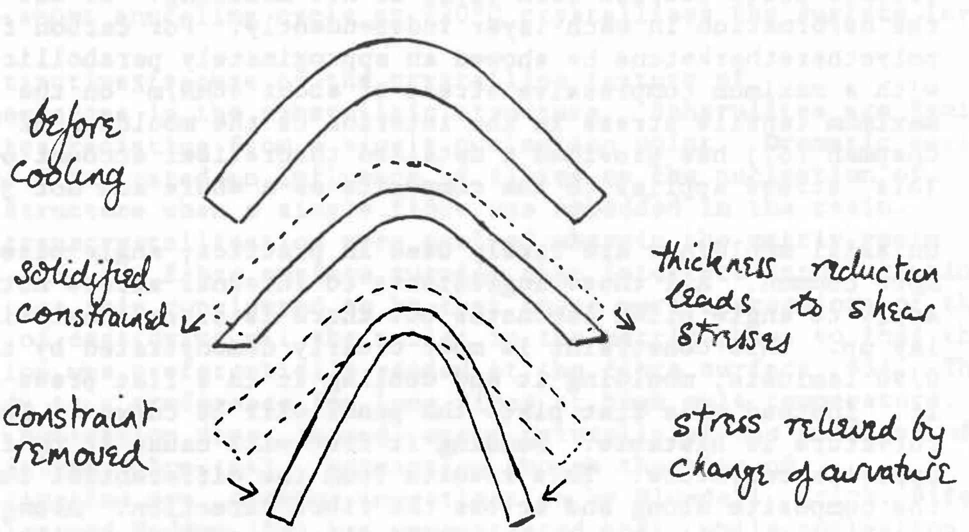

Figure 10 : Influence of differences in thermal expansion through the thickness and in the plane of the moulding (exaggerated sketches)

This phenomenon is sometimes called "spring forward" or "tow in " on moulding. Typically a 90° bend will spring forward as a result of this thermally induced stress by about 2°. Zahlan (72) has extended the rigorous analysis for single curvature structures by the use of finite element modelling to achieve capacity for predicting such distortions in double curvature structures.

There are four factors which contribute to internal stress in a composite structure: the difference in thermal expansion of the matrix and reinforcement; temperature gradients through the thickness of the laminate; the lay up geometry; and the shape of the moulding. These factors are not unique to carbon fibre/PEEK or indeed to thermoplastic composites in general but, because of the high processing temperatures involved, the thermal stresses and strains are higher in such composites than are found in most other systems.

6 THE ANALYSIS OF PROCESSING OPERATIONS

Having established the basic physical properties of the material, which are relevant to processing operations it is now appropriate to consider how to model those technologies. An excellent modelling framework has already been established (5-9). By empirical studies of the various forming processes with constant reference to the basic physical properties of the material, which are independent of the technology, it should be possible to refine those models to achieve sound predictive capacity. In respect of heat transfer (18-24) such divination is already possible. For shaping flows, and even for consolidation, we still have work to do before a full consensus is achieved, but the auguries must be considered fair. The plastics industry has already established predictive capability for highly complex processes like injection moulding, and, although different, the processes of composite manufacture should be amenable to a similar analytical approach.

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