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FUTURE REQUIREMENTS IN THE CHARACTERIZATION OF CONTINUOUS FIBER-REINFORCED POLYMERIC COMPOSITES

(IUPAC Technical Report)

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Future requirements in the characterization of continuous fiber-reinforced polymeric composites

(IUPAC Technical Report)

Abstract: Characterization of continuous fiber-reinforced composites is examined in terms of processing, properties, and structure. Five processing and five property topics are then examined in terms of reviewing some of the historic background in these areas with the aim of identifying current issues and requirements for the future. The topics covered in the processing section are: polymeric matrix, impregnation, interfacial effects, residual stresses, and pre-preg tack. In the mechanical properties section the topics are: choice of standard, recycling and reusability, durability, environmental strength, and toughness. The paper provides a ten-point plan for future requirements.

1. PREAMBLE AND AIMS

There has been enormous activity in the field of continuous fiber-reinforced polymeric composites research, particularly in the period between 1980 and the present. There has also been a decline in this activity in the last few years. Nevertheless, there is likely to be future expansion for these materials in a range of areas, most of which will be motivated by a specific property per unit weight. Consequently, characterization of composites is likely to remain a key issue.

Much of the historic activity on characterization has been associated with processing, properties, and structure. In addition, there remains plenty yet to explore. A number of the scientists associated with the historic activities are active on one of the International Union of Pure and Applied Chemistry work groups (IUPAC Working Party IV.2.1). Therefore, this group has considered what activities might be required in the future in order to better characterize continuous fiber-reinforced composites and, in addition, to contemplate some current and future issues.

The presentation of their views on future requirements will be in two broad areas, namely processing and properties. Each topic will be tackled with some limited background followed by discussion of where new work could be focused. The following topics and contributing authors are involved:

Processing:	Polymeric matrix	C. B. Bucknall
	Impregnation	R. S. Bailey
	Interfacial effects	B. Pukansky
	Residual stresses	A. Galeski
	Pre-preg tack	D. R. Moore
Properties:	Mechanical properties:	
	Choice of standard	L. Glas and W. Alstadt
	Recycling and reusability	B. Gunesin
	Durability	A. Cervenka
	Environmental strength	D. R. Moore
	Toughness	J. G. Williams

2. FUTURE REQUIREMENTS ASSOCIATED WITH PROCESSING ASPECTS

2.1 Requirements for characterization of the polymeric matrix of composites

The polymeric matrix plays a very important part in determining the performance of composites. All polymeric materials lose stiffness as temperature is increased; matrix resins also absorb water (another cause of reduced stiffness), shrink during cure, and are prone to brittle fracture. Furthermore, the final stage in the manufacture of composites is a curing reaction carried out by a component manufacturer on a resin system prepared many days (or even weeks) in advance. During this reaction, the thermal history of the resin varies from point to point across and through the thickness of the component. The need to generate optimum interactions between resin and fibers is an added complication. For all these reasons, considerable care is necessary to ensure consistency in the final product. With the increasing use of composites in Class 1 structures for civil aircraft, the importance of improved methods of characterization is obvious.

Considerable progress has already been made in characterizing the behavior of resin systems during the cure cycle. Reproducibility in the performance of a composite cannot be guaranteed simply by controlling temperature and pressure during cure, because variations can occur in the extent of chemical reaction taking place before the curing cycle begins. Small batch-to-batch changes in the curing process itself are another potential source of variability. These problems, combined with a demand for proper quality assurance procedures, have led to an increasing industrial interest in cure-monitoring techniques.

In recent years, this interest has centered on the development of dielectric monitoring techniques. Flat, inter-digitated capacitor sensors are inserted between plies, and connected via a suitable signal generator/detector to a computer. Measurements of dielectric permittivity and loss are then recorded over a range of frequencies as the cure proceeds. Armed with this information and a record of local temperature at the location of the sensor, it is thus possible to follow the cure reaction in real time. Dipolar groups attached to resin and hardener become more mobile as the laminate is heated to the processing temperature, then decline on both mobility and concentration as the reaction proceeds. Ionic impurities show similar variations in mobility. The dielectric data provide a record of these changes, and can determine, for example, whether the reaction has proceeded to completion, or whether pressure was applied at the correct stage in the cure cycle. Records of this type could obviously be used to certify that aircraft components have been manufactured in accordance with prescribed standards.

This technology offers a number of challenges for the future. The first is to develop prototype dielectric monitoring systems to the stage at which they can be used in a factory environment, for monitoring and controlling the production of composites parts. A second is to examine the potential of alternative cure-monitoring techniques, which at present have not been developed to the same level, but might eventually prove equally or more effective. Infrared and Raman spectroscopy are two such techniques, which rely on embedded optical fibers to transmit the input and output signals to the appropriate point in the laminate. The third major challenge is to increase the rate of data capture, so that monitoring techniques can be applied to rapidly curing resin systems. Economic considerations are already forcing manufacturers to examine faster methods of production, and that trend will undoubtedly continue. Looking further ahead, there is a requirement for less-invasive monitoring techniques, which do not involve the presence of potential defects in the form of embedded capacitors or large-diameter (0.1 mm) optical fibers.

Cure conditions affect the resin matrix in two important ways: they influence its morphology, and they determine the degree of cross-linking in each of the polymeric phases present. Questions of morphology and multi-phase structure arise because the matrix resins used in modern advanced composites are complex mixtures, typically prepared from two or more species of thermosetting resin (e.g., a blend of several different epoxy resin "monomer" molecules), a cocktail of hardeners, and at least one ductile thermoplastic. The function of the thermoplastic component is to provide a combination of toughness with stiffness at elevated temperatures, which means that the thermoplastic should have a T_g in the

region of 200 °C or higher. It must be soluble in the initial resin-hardener mixture, but undergo phase separation during the early stages of cure. Some reactivity with the resin or hardener molecules is also desirable, to render the thermoplastic insoluble at the end of the curing process. In practice, this usually means providing reactive terminal groups, but the required functionality can also be introduced at other points on the thermoplastic molecule. Preferred thermoplastic toughening agents for advanced resin matrices are polyimides (PI) and polysulfones (PS).

Characterizing morphology is relatively straightforward when the resin mixture is cured without fiber reinforcement, the best method being to prepare ultra-thin sections using an ultramicrotome, and examine them in a transmission electron microscope (TEM). Where necessary, staining can be used to improve contrast. Alternatively, thin cast or microtomed sections can be examined under the optical microscope, which has adequate resolution for the purpose. One advantage of optical microscopy is that it can be used, with the aid of a hot stage, to observe phase separation from the liquid resin mixture while it is taking place. The concentrations of thermoplastic required to provide good toughness are typically >20 % by volume, at which level the plastic forms a continuous phase during cure. The resulting morphology may be described literally as an interpenetrating network, because both thermosetting resin and functionalized thermoplastics become cross-linked during cure. These are important reactions, which ensure that the matrix is resistant to attack by organic solvents such as paint removers. Adequate methods for characterizing the degree of cross-linking in this type of blend have yet to be developed. Samples of neat resins or laminates can of course be subjected to preliminary screening by immersing them in a range of solvents and measuring the degree of swelling (or, in some cases, disintegration), but there is a need for more sophisticated approaches to the problem.

Characterization of resin morphology becomes significantly more difficult when the resin is reinforced with fibers. Microtoming is not a viable option, and studies of morphology have therefore relied heavily on scanning electron microscopy (SEM) of fracture surfaces. This method is not ideal, because it reveals only the morphological features that interact with growing cracks, but it can nevertheless be informative, especially when SEM observations are compared with TEM data from the corresponding neat resin. It is important to recognize that fibers can effect the morphology of a complex resin matrix. For example, a resin-rich phase can segregate preferentially at the surface of the fibers. This effect has been observed in epoxy/thermoplastic blends by Lowe [1] and by Partridge and Turmel [2]. In the first case, observations were made using SEM to study fracture surfaces from a carbon-fiber laminate; in the second, an optical microscope fitted with a hot stage was used to follow phase separation near a single glass fiber embedded in a curing resin matrix. It is obviously undesirable to form a brittle, resin-rich layer around each fiber in this way, and improved methods for characterizing matrix-morphology in fiber-reinforced systems would be beneficial. At present, only relatively coarse phase segregation can be detected near fiber surfaces, and it is therefore possible that the phenomenon is relatively widespread, but has gone undetected because in many laminates the resin-rich regions are not thick enough to be seen easily using available methods.

New resin formulations and more rapid processing techniques will raise further challenges in the future. The pace of development of new resins declined sharply in the early 1990s essentially because aircraft manufacturers had by then obtained certification for several existing combination of fibers and polymeric matrix materials, and needed good reasons for investing money in qualifying new ones, at a cost of about \$10 million per material. Considerations of this kind place the emphasis firmly on proper characterization of existing formulations. On the other hand, there is continuing strong pressure to develop more economical processing technology based on rapid production methods, notably resin transfer molding (RTM) and pultrusion. As existing tough resin formulations, containing 20–30 % of dissolved thermoplastic, are too viscous for use in the RTM process, new approaches to the problem are needed, backed by new quality assurance and morphological characterization procedures.

2.2 Issues relating to the impregnation of fibers during the production of fiber composites

2.2.1 Introduction

In considering the production quality of continuous fiber composites, the bringing together of the key constituents plays an obviously important role. It is rarely possible to produce perfectly polymer-impregnated fibers in commercial processes. However, the critical limits need to be set with regard to what is an acceptable defect level for each application. In the aerospace industry, the components are rigorously tested by nondestructive methods to ensure component quality. Often, the optimization of the actual production process and the raw materials used are overlooked in relation to the ease of wetting and flow into fiber bundles. In this document, the range of continuous fiber-reinforced thermosets and thermoplastics are dealt with separately since they generally employ different impregnation regimes.

2.2.2 Thermoplastic composites

Thermoplastic composites technology is relatively new compared to that employed in the vastly higher-volume thermoset industry, and is generally based on adoptions of thermoplastic melt-processing equipment. The common types of process employed can be distilled into the following four classes:

- i) melt extrusion to a simple coating dye
- ii) melt extrusion to a pultrusion device
- iii) powder infiltration to a pultrusion device
- iv) in situ polymerization.

These processes are used commercially and produce thermoplastic composites in the following product forms:

- continuous fiber unidirectional lamina
- continuous fiber pultruded shapes, components, and profiles
- discontinuous fiber feed stock for extrusion, injection molding
- infiltrated pre-form shapes.

In a thermoplastic composite production process, the polymer and fiber are brought together in order to wet-out the fibers and hence with adequate coupling agent chemistry produce as uniform and strong interfacial bond as possible before shaping is possible. Unlike thermoset resins, which have low shear viscosities in the pre-cure state, the most prevalent route to manufacturing thermoplastic polymer composites is by melt processing and impregnation. Thermoplastics have high melt viscosity, and attaining a high degree of impregnation is often very challenging. Plasticizers and lubricants can be employed to lower apparent viscosities in composites manufacture, but these may need to be removed from the finished product. In order to make a product that is commercially viable, manufacturers must consider the balance between productivity and quality, that is, the level of impregnation is a function of production speed.

The aim in the production of strong fiber composite materials seeks to approach the theoretical strengths for ideal materials. It follows, therefore, that the fiber form is supplied in a packaged bundle, with fibers wound up on reels with a surface coating that both protects and prepares the fibers for their end use application. In order to protect the strong but often brittle fibers (C, B, glass for instance), they are coated and bundled, making their subsequent separation a problem in an impregnation processes. If it were viable, it would make better sense to produce fibers and impregnate them on-line in one process. This would allow excellent separate of the fibers, without the need to devise a protective film former on the fiber surfaces.

The underlying feature of composites production is the reproducibility of the fiber supply. In all high-fiber volume operations, fibers (in whatever form) must be unwound and conveyed into the impregnation part of the process. This infers that the fiber arrives intact at the contact point with the

molten polymer, and with adequate mechanical properties to fulfill the needs of the process, and the ultimate composite being produced. In defining areas of future study for impregnation science, the key area of understanding is the permeability of the fiber roving. The roving permeability is not only related to the surface area of fiber in a commercial roving or strand, but also to the physical ability of the fiber bundle to be spread. This is related to the twist and entanglement of the fibers in relation to its neighbors, the fiber bundle itself, and any effects associated with the positional variability within the reel. As a fiber roving is unwound, traditionally sized fiber (surface coatings containing film formers, coupling agents, and lubricants) tends to converge at the edges of the reels during the drying processes. This introduces an inherent variability in the spreading ability of the fiber, which causes a characteristic periodic quality minimum for the composite.

Additionally, the permeability of the fiber bundle is affected by the chemical reactivity in relation to the polymer or resin that is brought into contact. This may also be a function of temperature, pressure, humidity, or other salient features of the impregnation process under scrutiny.

If a fiber can be produced that can be handled and has sufficient permeability for impregnation to be viable, the requirements of the polymer need to be considered. Clearly, the polymer can be monomeric, powder, or in molten form. The relationship between the fiber geometry and permeability needs to be well understood in order for manufacturers to have knowledge of the polymer, monomer, or resin shear viscosity function that would be most suitable, or powder characteristics. In many impregnation processes, knowledge of the elongational flow component would also be beneficial.

To date, relatively simple models have been proposed for composite production processes involving impregnation, and these make many assumptions for simplification. These models assume that the fibers are of infinite strength, the permeability is governed solely by physical considerations, and the fibers are constant along the length of fiber bundles. Polymers are assumed to be Newtonian in their rheological behavior, and the processes take place isothermally. In view of the immaturity of this area of science, and proprietary nature of fiber and composites manufacture, it is clear that most processes owe their success to an empirical approach. Equally, the fibers produced are offered in a form that suits the process economics, and processes are best adapted accordingly. In order to develop impregnation techniques further, unflawed parallel fibers, with uniform reactive interfacial coupling agent, would further aid quality and productivity. Additional refinement of the process models would allow tailoring of polymer rheology to allow for enhanced composites processing and the level of impregnation attainable at economic rates.

2.2.3 Thermosetting polymers

The impregnation of fibers with thermosetting compounds is carried out by sandwiching a layer of fibers between two layers of a thermosetting film or solution. The manufacturing process is usually continuous and subject to high degrees of material wastage. Line tension, resin transfer rate, and voidage all need to be carefully controlled by the operator, making the process labor intensive. Greater understanding of the effect of process variables and thermoset compound chemistry and the final compound properties would lead to a more automatic (and thus less labor intensive) process which would obviously be more desirable from a cost viewpoint.

The processing issues that require study include the effect of solvent shrinkage and volatilization on resin “wet out” together with a detailed study of the interaction of time/temperature and viscosity on relevant industrial processes. Because of the wide range of resins available, an equally diverse range of industrial manufacturing processes exist—the one factor common to all processes, however, being the desire to keep resin heating times to a minimum.

A final area of study would include the design of thermoset resins that are more robust in terms of their shelf life and “transportability” at ambient temperatures.

2.3 Interfacial effects in continuous fiber-reinforced polymeric materials

2.3.1 Introduction

Interfacial interactions are crucial for the application of fiber-reinforced composites. Nevertheless, monographs on composites treat this question only marginally by mentioning the methods of treatment without the very important details of chemistry and physics involved [3–5]. A widely accepted handbook on composite design does not even mention interfacial adhesion, it assumes that adhesion is perfect [6]. Interfaces and surface treatment are involved in all aspects of composite design and use as it is illustrated in Fig. 1. Although exhaustive discussion of all aspects of interfacial interactions is impossible because of limited space, the most important points needing further study will be discussed in the following sections.

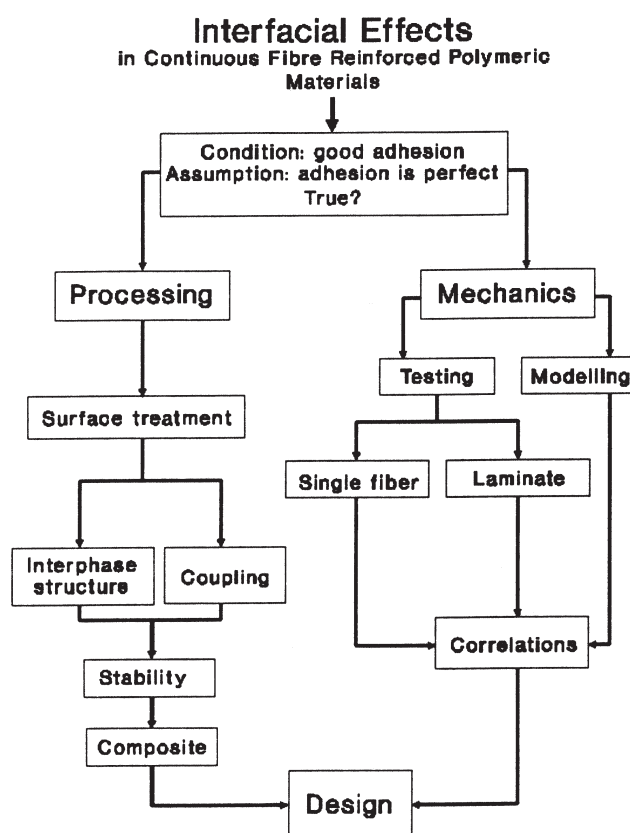


Fig. 1 Role of interfaces in composites.

The basic condition of the application of fiber-reinforced composites is perfect adhesion between the components. This is necessary to transfer load from the matrix to the fiber. Without adhesion the principle of fiber-reinforced systems would not work, the strong fiber carries the load, while the matrix distributes it and transfers from one fiber to the other. Too strong an interface leads to a rigid composite, while in the case of weak adhesion the above-mentioned principle does not work, thus optimum adhesion is required. However, a clear distinction must be made here between interface and interphase. In composites, interphase forms spontaneously even in the absence of surface treatment, but treatment is always used in continuous fiber-reinforced composites, which invariably leads to the formation of an

interphase of very complex structure [7]. The thickness and properties of this interphase have a crucial impact on composite properties

As a consequence, adhesion must be perfect but the properties of the interphase must be optimized in order to achieve advantageous or desired properties of the composite. The correlations among the chemistry/processing conditions/ composition/structure/ properties of the interphase have not been fully understood yet, they need further extensive study.

2.3.2 Processing

Surface treatment is usually applied during the preparation of the fibers. In order to achieve high productivity, the fibers must be processed at a high rate. This requires special sizing, which prevents fiber breakage and facilitates processing. As a consequence, surface coating of all fibers usually contains a number of additives of which the coupling agent comprises only a small part. Only a limited number of studies have been carried out on the analysis of the composition of the sizing and its effect on composite properties [8,9]. Nevertheless, surface coating of the fiber determines the structure and properties of the interphase, as well as the quality of coupling.

Coupling is believed to be of the utmost importance for perfect adhesion. Organofunctional silanes are used the most often. The chemistry and physics of coupling in glass fiber-reinforced thermosets is sufficiently known [10,11], but there is much to be done in the case of carbon, aramide, and polyethylene (PE) fiber-reinforced composites. Efficient coupling is usually not that simple, the lack of reactive groups on the polymer prevents direct coupling of the components. Often the modification of the matrix is required or a modified polymer is introduced into the composite. Sufficient coupling is often achieved by chemical coupling and interdiffusion [e.g., polypropylene (PP)/glass]. It must be emphasized here that chemical coupling is system specific, the coupling agent and the treatment technique must be selected according to the characteristics of both components, i.e., fiber and matrix.

An often-neglected issue is the amount of coupling agent used. The treatment is usually done by the producer of the fiber according to a proprietary technique, which is not disclosed to the customer. The treatment (sizing, coupling agent, composition) might be optimized for a certain fiber/matrix combination, but it does not necessarily work in other systems. It has been shown many times that structure and properties of the interphase change with the amount of coupling agent used [11], thus optimization is necessary in order to achieve maximum efficiency.

2.3.3 Interphase structure

The structure of the interphase is usually very complicated. In the case of the most often used silane treatment, chemical coupling occurs on the surface of the fiber. This is followed by a polysiloxane layer, and finally physical interdiffusion of the matrix and the polysiloxane layer occurs [7,11]. The structure and composition of the layers can cover a very wide range. They depend on the chemical composition of the components (fiber, matrix, coupling agent), but the interplay is strongly influenced also by the composition of the sizing. It often happens that the first layer of matrix has a lower degree of curing that leads to a weaker interlayer. Application of an elastomeric interlayer was also suggested to decrease stress concentration around the fibers [12]. Although this might be advantageous to the properties, the technique is rarely (or never) used in industrial practice. Correlations between the structure and properties of the interphase and the properties of the composites are not known yet, much more research must be done in this field. Experience indicates that a thin rigid interphase leads to a low fracture resistance, while a thick soft interphase results in better fracture resistance, but a lower composite stiffness. However, quantitative correlations to transfer these observations into practice are still lacking.

Concerning the stability, coupling reactions of organofunctional silanes are usually reversible. As a consequence, excessive water cleaves the Si–O–Si bonds and a good adhesion ceases to exist. Hydrothermal stability is an important property of composites and environmental testing is an essential part of their characterization. However, the chemistry involved is not studied in detail. More attention must be paid to this question in the future. The knowledge of the kinetics of bond formation and break-

age, and the determination of the correlations between chemistry and composite properties may lead to better treatment technology and improved composites.

It must be clear from the previous that coupling, adhesion, structure, and properties of the interphase have a pronounced effect on the mechanical properties of the composites. The importance of adhesion is shown also by the numerous attempts to characterize it. Due to its importance, however, more attention should be paid to the role of the interphase in future studies.

Finally, the modeling is mostly done by finite element analysis, which is a powerful tool for the determination of stresses and displacements in the vicinity of the fibers. Although interfacial adhesion appears more and more frequently in these models—sometimes even an interphase is included—more work must be done in this field. The properties of the interphase are not constant, they are changing from the interface of the fiber toward the matrix. Very few models exist which take such an interphase into account [13]. Moreover, the results of finite element calculations depend very much on the mesh and boundary conditions used. The results of the calculations are not always verified by experiments. Approximate analytical solutions and experimental verification of the models would give more credit to modeling. Similarly, calculation carried out on single fiber composites or on simple laminates should be related to the properties of real composites.

2.3.4 Testing

The measurement of interfacial adhesion—or its effect—is an important part of the development of composites. Testing is done on various levels; single-fiber composites, laminates, and full composites. All are studied by different techniques. Adhesion, however, features in a different extent at two different levels: that of a single fiber and that of a laminate.

Single-fiber testing is usually directed toward the determination of interfacial shear stress, which is regarded as the most important quantity characterizing interaction. The various tests used for the determination of this quantity (single fiber pull out, push in, fragmentation, microbond) usually do not give the same result. One of the major reasons of the discrepancy is the different stress distribution in these tests and especially the different stress concentrations at fiber ends [14,15].

An even larger problem is that much less attention is paid to transverse adhesive strength. In real composites, failure is often initiated in the cross-ply laminates, debonding takes place if the adhesion is weak or matrix failure (yielding, cracking) in the case of strong adhesion. These questions have been addressed only lately [16], much more effort must be devoted to this field. Correlation between the results of various single fiber tests and composite properties must be also established.

In laminates, another factor plays also an important role. Distribution of fibers in a single ply may determine its strength. Preparation of laminates with a well-defined structure is difficult. In multi-ply composites, interlaminar shear stress is one of the most important characteristics to be determined, but this quantity is not related to interfacial interactions or to the characteristics of the interphase. Due to the large number of factors influencing laminate properties and owing to their complicated interrelations, it is rather difficult to draw conclusions about the effect of interfacial adhesion on laminate properties. More efforts must be concentrated also on the relationships of single fiber and laminate tests.

2.3.5 Correlations and design

Most of the work done in the various areas of composite mechanics (modeling, testing) concentrates on a very limited area. General correlations relating the results of modeling and various tests are badly needed in order to facilitate composite design.

As mentioned earlier, perfect adhesion is very often assumed in composite design. The complicated relationships of the factors discussed in previous sections are completely ignored. This approach is partly justified due to complicated structure/property correlations of the composites and insufficient knowledge and adequate tools currently available. Nevertheless, with increasing knowledge, the new information will be also incorporated into design and the techniques will be definitely upgraded.

2.3.6 Conclusions

Interfacial effects definitely play an important, perhaps crucial role, in the determination of the properties of continuous fiber-reinforced composites. Although some of the aspects are addressed in detail (testing, modeling), a number of questions need much more attention (interface chemistry, interphase) and sometimes new aspects must be included even in the areas actively studied. Besides the detailed investigation of particular questions of interfacial interactions, general correlations of the various factors must be established and included into the schemes of composite design.

2.4 Origin and influence of residual stresses

Residual stresses are an important factor influencing the strength of polymeric composites. The causes of residual stresses are usually differences in thermomechanical properties of constituents. They are often observed when composite materials are formed at temperatures higher than the use temperature. For example, residual stresses arise during curing of epoxy resins embedding another reinforcing material or during solidification of thermoplastic-containing continuous fibers. Residual stresses were the subject of extensive investigation in the past as they determine the overall strength and durability of polymeric composites. There are two main reasons for the residual stresses: thermal stresses due to differences in expansion coefficients, and stresses due to shrinkage during curing or solidification of the matrix or the inclusion. According to theoretical consideration, isolated short fiber reinforcement produces the stress field around inclusion in which principal tensor components: radial and tangential decrease as the reciprocal of third power of distance from the center of inclusion. This implies that the residual stresses (independently of their origin) around short fibers, spheres, or at long fibers ends are extending for short distances only, not exceeding 2–3 diameters of the inclusion. The measured residual stresses (by photoelastic method) in cured epoxy around glass beads or at fiber ends approach -70 MPa at the interface. On the other hand, the thermal stresses originating from thermal expansion coefficient mismatch can be described by eq. 1 [17]:

$$\sigma_0 = \{(\gamma_m - \gamma_p)\Delta T[-4(1 + \nu_p)G_m]\} / (2(1 - 2\nu_p)(G_m / G_p) + 3(1 + \nu_p)) \quad (1)$$

where G_m and G_p are the shear moduli of the matrix and the inclusion, respectively, γ_m and γ_p are the volume thermal expansion coefficients for the matrix and the inclusion, ν_p is the Poisson ratio for the inclusion, and ΔT is the temperature change. Simple calculation shows that the thermal expansion coefficient mismatch leads to nearly one order of magnitude lower residual stresses than those arising from curing or solidification shrinkage. Residual stresses were extensively studied in various systems and varying composite parameters. It is concluded that the microstresses at the matrix-inclusion interface do not depend on the dimension of inclusion, but depend on the type of the inclusion, its adhesion to the matrix, and the thermal history.

In the case of long continuous fibers, the Nairn–Wagner approach [18,19] allows us to calculate the distribution of stresses along and around long fiber. In Fig. 2, the theoretical distribution of radial and tangential stress components are plotted as a function of distance from the fiber axis. Also, the stress component along the fiber axis is plotted. In calculation, it was assumed that the continuous glass fiber is $20 \mu\text{m}$ thick and that the stresses arise from the mismatch caused by epoxy curing. It is seen that the stresses are not very high but in contrast to short fibers or fibers ends they extend over large distances from the fiber axis. These important aspects of the composite science are discussed in relation to the two generic types of matrices.

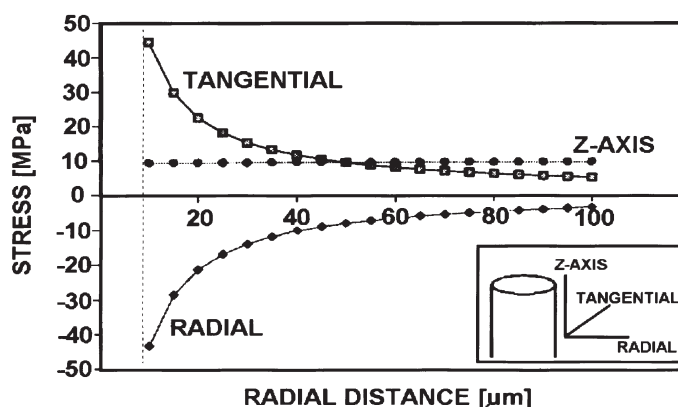


Fig. 2 Distribution of radial and tangential stresses around and along 20 μm thick glass fiber embedded in Araldite epoxy cured at 135 $^{\circ}\text{C}$ and post-cured at 190 $^{\circ}\text{C}$ calculated according to the Nairn–Wagner [18,19] approach. The data are plotted as a function of distance from the fiber axis. The stress arises from the mismatch caused by epoxy curing.

2.4.1 Thermosets

Usually, the curing of the resin is associated with shrinkage of the matrix which is the main source of residual stresses. These residual stresses are much higher than the stresses arising from thermal contraction difference between the thermal contraction of fibers and the matrix. The fibers are usually compressed along their length. As a result of this component of the residual stresses, a periodic crimping of the reinforcing fibers occurs. This effect is undesirable.

The other components of residual stresses generated by shrinkage of the resin are deviatoric stresses acting in the matrix around fibers: the radial stress is in most cases compressive, while the tangential component is tensile. Both of these stress components are advantageous in the sense that they act to maintain a closer contact between matrix and fibers. However, both stress components should be kept at a low level in order not to overload the matrix.

In long fiber composites, the stress fields around each single fiber overlap with others. The resulting complicated stress field can hardly be evaluated on a theoretical basis. There is a need for experimental investigation of these residual stresses. The overlap of stress fields and their strong interference result from long-range residual stresses for the case of continuous fibers. Figure 3 illustrates an example of complicated stress field, wherein the photoelastic image of an assembly of long graphite fibers embedded in Araldite epoxy matrix is presented. The brighter areas represent stressed regions of the matrix. It is seen that strongly stressed regions between fibers are present. Figure 3 illustrates also another important phenomenon of extremely high stresses near fiber ends. These regions are most vulnerable to damage and fracture.

Hydrothermal aging decreases the residual stresses by partial relaxation and decrease of glass transition temperature. However, the relaxation of stresses is temporary, and the stresses recover nearly to their initial level when the water is desorbed from the composite.

Curing of thermosets is often nonuniform owing to insufficient temperature control, poor mixing of components, influence of mold walls, etc. Additional long-range residual stresses arise due to such conditions, but they do not originate from the presence of continuous-reinforcing fibers.

From the above remarks, it follows that there should be action taken against excessive stresses between fibers and the matrix, prestressing the fibers during curing, choice of low shrinking matrices, choice of fibers with high thermal expansion coefficients, and care about continuity and good dispersion of embedded fibers. A suitable method for studying residual stresses is photoelasticity using micropolarimeters.

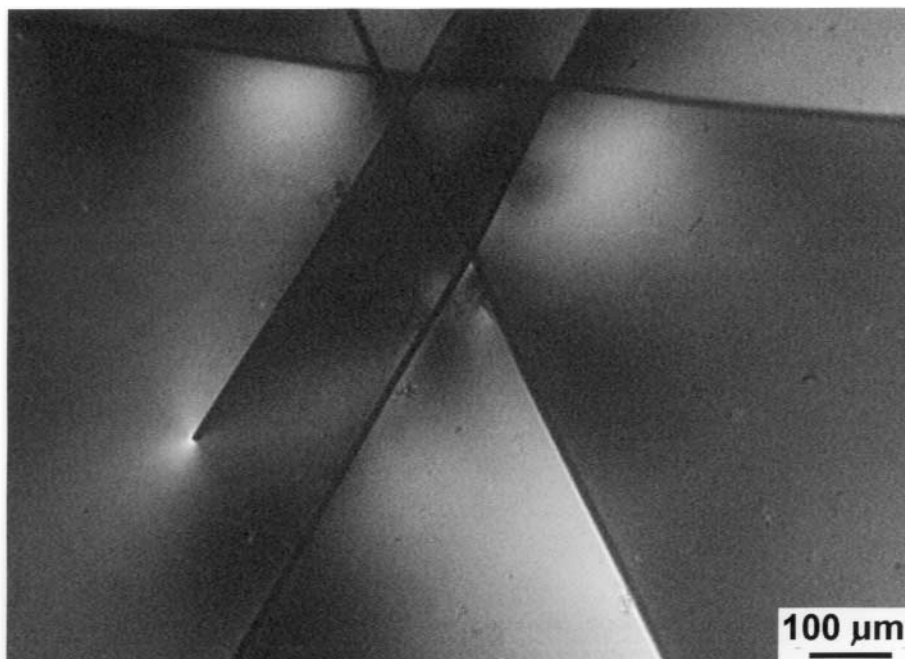


Fig. 3 An example of a complicated stress field illustrated by a photoelastic image of an assembly of long graphite fibers embedded in Araldite epoxy matrix. Brighter areas are regions of increased residual stresses. Note the strong brightening near fiber ends.

2.4.2 Thermoplastics

Semicrystalline thermoplastics are particularly relevant in studies of residual stress. The transcrystallinity at the interface is a visible sign of good physical contact between the matrix and fibers. The density of surface nucleation and the extent of the transcrystalline layer could be a measure of nucleating activity of the fiber toward a particular matrix. The occurrence of transcrystallinity depends on the type of fibers and the temperature. In contrast to transcrystallinity in quiescent crystallization, the application of stress at the interface between a fiber and polymer melt results in the crystallization on row-nuclei around the fiber. This effect is caused by strain-induced nucleation via some self-nucleation mechanism and is independent of the type of fiber and less dependent on the temperature of crystallization [20,21].

Axial stresses arise also during cooling of two materials with large differences in thermal expansion coefficients. As such, the stress-induced nucleation in reinforced thermoplastics depends also on the cooling rate, fiber length, position along the fiber, and viscoelastic properties of the thermoplastics melt.

Molecular orientation of the matrix at interfaces (obtained by shear originating from pulling or differences in thermal expansion coefficients) enhances the adhesion. Characterization of this effect will be required either by measuring the orientation at interfaces or by its effect on transcrystallinity. The remarks concerning shrinkage (in this case due to volume change during crystallization) and deviatoric stresses are valid also for reinforced thermoplastics. Pockets of molten polymer are formed between transcrystalline layers during their growth. The stresses, which may lead to cavitation, are generated in these pockets due to volume change in the course of further crystallization [22,23]. Uni- or bi-directional fiber-reinforced composites are especially vulnerable to producing excessive negative pressure and cavitation due to localized accumulation of volume deficiency. The negative effects of stresses should be considered when designing the composite.

2.5 Measurement of pre-preg tack

Pre-preg is the precursor of the continuous fiber-reinforced composites industry and the building block for many complex geometric shapes. In constructing these structures, it is necessary to assemble the pre-preg into the required shape prior to consolidation. In order to achieve this, it is helpful if there is a certain stickiness between one pre-preg layer and its neighbor. This property is known as tack, and a minimum level of pre-preg tack is vital for forming preconsolidated shapes. However, because structures cannot be constructed without occasional error then too much tack associated with a pre-preg is equally a problem. Therefore, some rectification of misaligned fibers or shape errors needs to be accommodated. So, pre-preg tack should not be too “low” or too “high”!

In order to improve on such vagueness, it is clearly necessary to have some objective means of measuring tack. Historically, this has relied on a subjective “feel” of the ease in either sticking or separating pre-preg by hand. Perhaps the major advance in converting such art to science has been conducted by Seferis and coworkers [e.g., 24]. Their principle approach has involved pressing layers of pre-preg together by instrumented compression (under load control) and then separating the stack by tension (in displacement control). Their approach involves measurement of a stress vs. strain curve during this cycle, and the results are interpreted in terms of aspects of the energy of separation and a modulus during separation, which is then used as an index of tack. Seferis has further developed the analysis in other publications [25].

One apparent weakness of this approach is the lack of similarity in their configuration of separation with that which happens in practice. For example, if you were to separate by hand a stack of compressed pre-pregs, it is unlikely that you would approach the problem by the application of a normal force. A peeling approach is perhaps more likely. Therefore, an alternative approach to the measurement of tack utilizes the use of a peel test. Seferis’s work provided a number of important insights into both measurement and understanding of pre-preg tack. Not least of his findings led to the recognition that pre-preg tack is a bulk viscoelastic property, as opposed to a surface property. This has several important ramifications, which lead to the conclusion that fiber anisotropy, composite heterogeneity, and the viscoelastic features of the resin will have important contributions to pre-preg tack. However, it is also apparent that the process of joining two pre-pregs is to press two surfaces together, and the prospect of some active chemistry should not be ruled out.

Measuring tack through the use of a peel test can have some practical benefits. The effective tack of a pre-preg can be related to the ability to peel apart the layers of a pre consolidated structure. If this can be done too easily then the effective tack is too low, whereas if the peeling is too difficult then the effective tack is too high. The ability to peel apart two layers of pre-preg can be measured via peel strength, i.e., the force per unit width of peel (P/B). Therefore, the measurement of peel strength can be used to articulate tack. Recent work by Kinloch et al. [26] has demonstrated that the interfacial work of fracture can be determined from a peel strength measurement together with the tensile stress-strain properties of the peel arm. This has been applied to some carbon fiber laminates by Moore et al. [27] where a convenient apparatus for the measurement of peel strength at a range of peel angles between 30 °C and 180 °C is described. These approaches have been adopted in this work for both the measurement of peel strength (at various peel angles) as well as converting the measured peel strength to the adhesive fracture toughness (G_A). This adhesive fracture toughness is considered to be related to tack rather than the measured peel strength, which is complicated by elastic and plastic deformations in the peel arm and at the peel front.

The adhesive fracture toughness is determined by subtracting the energy term associated with plastic deformation (G_{db}) from that associated with elastic deformation (G_A^{eb}):

$$G_A = G_A^{eb} - G_{db} \quad (2)$$

where the term G_A^{eb} is obtained by determination of the peel toughness (G_A^{infE}) at various peel angles and from the tensile stress-strain measurements [as described in ref. 26]. In summary, this term is given by:

$$G_A^{eb} = (1 + \varepsilon - \cos \theta) - h \int_0^{\varepsilon} \sigma \, d\varepsilon \quad (3)$$

where σ and ε are stress and strain, respectively, and h is the thickness of the peel arm. The second term in eq. 2 is obtained by computer calculation and enables the dissipated or plastic energy term to be accounted [26].

In summary, therefore, the measurement of peel strength (P/B) at a particular peel angle θ together with the tensile stress-strain characteristic (σ v ε) for the material in the peel arm, will enable the adhesive fracture toughness (G_A) to be determined.

The approaches of Seferis and Moore in the determination of tack could usefully be integrated with the practical experience of pre-preg manufacturers in order to establish a credible and objective means of assessing pre-preg tack and also of determining pre-preg outlife.

3. FUTURE REQUIREMENTS ASSOCIATED WITH PROPERTY ASPECTS

3.1 Mechanical properties: Selection of standardized test methods

Over the past 30 years, composite materials have continuously been improved and fine-tuned so as to meet increased toughness, strength, durability, and environmental requirements. Testimony to these improvements can be found in the data published in the open literature [28–32]. However, the extent of improvement is not always clear from the published data. It is a considerable drawback that a wide variety of test methods have been used and that data are not easily comparable. This diversity in test methods has had a negative effect on the knowledge concerning the relations between the composite properties and the neat resin properties. For structural applications it is now common practice to design the structural element with computer-aided engineering (CAE) software [33]. These computer codes require mechanical property data to calculate the stiffness and the maximum loading conditions of the structural component. Confusion on the quality of the input data is bound to lead to confusion in the quality of the output of these numerical simulation codes. In this important area of application, the diversity in test methods also leads to poor relations between composite properties and full-scale component behavior. To overcome these negative effects, and to increase the value of the mechanical property data for their users, it is necessary to reduce the number of test methods [34,35].

Hence, there is an increasing amount of literature discussing and reviewing extensively the differences in test methods that describe the same properties [36,37]. As a direct consequence of this “test method jungle”, a large amount of effort has been devoted to determine the precision of these test methods in terms of their repeatability and reproducibility, to the establishment of relations between the various test methods, and to further fine-tuning toward the improved test method.

Is this continuous improvement of test methods the preferred way to obtain a better characterization of composite behavior, or are there alternatives to be considered? This question cannot be answered without considering the purpose of measuring these data, which is twofold: to represent the full-scale component behavior of composite materials under actual service conditions and to assist the determination of the contributions of the individual constituents (matrix, interfaces, reinforcements) and their interactions to the composite properties.

For the full-scale component behavior, data are needed on two levels of the design process. The first level is the preliminary design stage where mechanical property data are required for the screening of materials. To screen materials it is important to have an overview of the responses of a simplified structural element, made from the composite material, to a representative—with respect to the applica-

tion—number of loading conditions. Such a response must include the maximum sustainable loading and a first estimate of failure limits. As the loading conditions can vary with application, this would require development of a large number of test methods if this overview is to be obtained through experimentation only. In view of the experiences with the diversity of test methods this cannot be the recommended way to obtain these data. For simple structures (hemispherical objects, bars, box-type specimens, etc.) it must be possible to obtain sufficiently good responses by modeling only. The selection of test methods for this preliminary design stage must be done on basis of their ability to produce data that can be used in the modeling. CAMPUS and ISO have taken up the role to provide a first set of screening data for short fiber-reinforced thermoplastics [38]. Recent initiatives have started to link CAMPUS with CAE programs. For sheet molding compound (SMC), glass mat thermoplastic (GMT) and bulk molding compound (BMC) composites, FUNDUS is an example of a screening data provider [39]. FUNDUS was created by the cooperation of a number of SMC, BMC, and GMT producers with the support of the German “Arbeitsgemeinschaft Verstärkte Kunststoffe”. The aim of FUNDUS—in analogy with CAMPUS—is to provide a material database for plastics reinforced with continuous fibers and a definition of sensible and comparable material properties. It may be argued whether the test methods selected are the best ones in terms of precision and property definition. But in both cases (CAMPUS and FUNDUS) there seems to be a significant misfit between the data that composite producers offer and the data that the CAE programs require.

There appears, therefore, to be a need to rethink the selection of test methods in terms of their ability to provide data that can be used in modeling [40]. In the first design stage, standardized methods clearly are important, but are standardized methods equally important at the second level of design—the detailed design stage? The answer depends completely on the complexity of the design. For simple structures, translation of standardized properties into performance indices or engineering maps already gives considerable added value compared to the case where the data are used in isolation.

For more complex structures there are two options. The first option is to rely on CAE software and to generate the mechanical property data required by the constitutive equations used in these software packages. It is a matter of agreeing first on the constitutive equations that best represent the mechanical behavior (eventually coupled with environmental effects including the time) and then deciding on the methods used. Literature shows that there is still a large difference between the properties required by the CAE software and the properties now measured by standard characterization tests [34]. Future efforts should, therefore, be directed toward selection and development of test methods in close collaboration with the researchers working on the constitutive equations and software developers.

The second option is to start from design codes. This seems far away from standard test methods, but it is at present the only route to follow when premature failure during service must be avoided. CAE software delivers the best results when stiffness is the main criterion, and this occurs notably in the applications where a relative high risk of failure is accepted (e.g., combat fighter). Although the software used can include failure criteria, the modeling itself is not the prime source of its unreliable prediction under service conditions. For any polymeric composite, its properties depend on the local microstructure. For any large-size product made from polymeric composite, the microstructure will vary throughout the product and knowledge on the variation of the microstructure will be limited. Behavior of a full-scale component, therefore, has to be based on the assumption of an “average, homogeneous microstructure”. As failure will occur due to excessive variations in local microstructure, mostly induced in the manufacturing stage, it is impossible to take this into account in the modeling.

Design codes deal, among other issues, with stiffness and the failure of structures on a pragmatic and empirical basis. What are the consequences for standardized testing? Design codes limit the number of test methods and focus attention on those properties that are critical for the structures. In this respect, there is not much difference as to the requirements for standardized test methods in the preliminary design stage. Further developments along the lines of ISO 10350 and FUNDUS should, therefore, be encouraged. This positive point is counterbalanced by the practical observation that design codes usually include requirements that have to be checked in dedicated tests. These dedicated tests add

to the number of test methods and require specifically designed test specimens that have an intermediate shape between the bar-type laboratory specimen and the full-scale component [36,41].

The overall choice of the type of test methods is, therefore, a matter of "expected reliability" of the end product. At present, design codes seem to be the only way to secure a high reliability. Future changes in the direction of more use of CAE software can only come through improvement in end product manufacturing techniques so that microstructural morphology variations can be controlled. The test methods selection will have to follow this trend.

Up to this point, the focus of this contribution has been on the characterization of mechanical properties for end use applications. There remains another domain, namely characterization of composites aiming at increasing scientific knowledge, that has to be discussed. The main elements in the choice of a test method for characterization concern the manufacturing of the test specimen, the homogeneity of the test specimen with respect to the local microstructure, the strain/stress state definition of the test specimen, the uniformity of stress/strain over the specimen, and the interactions between the individual constituents of the composite—fiber/matrix and fiber/fiber interactions.

With the present state of sample manufacturing, the conditions (homogeneous microstructure, uniform stress/strain state, only fiber matrix interactions) are only approached for test specimens containing one single fiber, or multiple fibers carefully spaced over the sample. Optimum conditions may appear as a rather subjective term [42]. These are only optimum conditions because the micromechanical models cannot deal with more complex structures. In the case of multiple fibers—not carefully spaced—an idealized average microstructure must be assumed. This way of working prevents the establishment of good-quality relations between the composites, the fibers, and the matrix. Specimen design, with the objective to simplify the problem, will only work for a limited number of materials and loading cases. In view of the large variety of types of composites (long fiber, short fiber, GMT, unidirectional reinforced, etc.) specimen design is not an appropriate solution.

The progress in the characterization field will not come by a further development of new test methods or refining of existing test methods. Progress will have to come through a better analysis of experimental results by combining powerful microscopy tools—to describe the microstructure—and micromechanical modeling that is able to take into account not only fiber/fiber interactions as well. It is only through a better description of the events happening at the microstructural level that their influence on the macroscopic level can be understood.

3.2 Recyclability of continuous fiber-reinforced composites

This area of composites has not been fully investigated; we can say that it will probably see more attention in the next decade. The presented survey focuses on all types of composite matrices (thermoplastics, rubbers, and blends) with and without reinforcing fibers.

Generally, in the composite recycling, worldwide activity is quite low when compared with the other thermoplastics, such as polystyrene (PS), polyolefins (PE and PP), polyvinyl chloride (PVC), nylons, poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT), polycarbonate (PC), etc. Some auto manufacturers have their own in-house recycle methods which are not clearly discussed in the open literature.

The worldwide consumption of all the composites in 1995 has reached 3.4 million metric tons. Before 1994, the composites were really on a rough ride. The difficult periods for composites caused shut-down of processor plants and even some of the composite resin producers. The area of composites that will continue to grow will be in the reinforced thermoplastics sector. The major users are auto manufacturers, the aviation industry, construction, and the marine sector. Since the lifetime of a composite part is quite long, averaging 10–20 years, recyclability issues will see more attention in the next century.

Recycling of continuous fiber-reinforced composites can be illustrated by few examples: An appreciable attention has been paid to composites reinforced with glass fibers. In this area, Huels, maker

of SMC and woven thermoplastic pre-pregs, claims to include 15 % of regrind in their glass fiber-modified nylon sheet. Mauves, producer of Mayflex flexible automotive exterior body panels, claims that they utilized 25 % of regrind in some of their formulations.

The regrinding of a large glass fiber mated panel is a costly step. In order to mix with the new batch, the final particles of the regrind have to be below 1 cm radius. When the continuous fiber-reinforced composite is chopped, final regrind will have a discontinuous fiber with an uneven length. To utilize this regrind in other applications, such as mixing with other thermoplastics, will be more practical than trying to recycle into its original application.

Tertiary recycling has been applied to glass-reinforced nylons, PET and PBT. Solvolysis techniques worked, yet they are extremely costly and not 100 % effective. During the solvolysis, the proper solvent extractions have been done for all three of these thermoplastics. The polymer has been recovered only up to 75–80 %, the remaining polymer was not separable from the glass fiber [43]. The AT&T group claims to use regrind of 20 % glass-filled PBT sheet in Protector Housing. The regrind itself had poor properties, yet when blended with 50 % of virgin PBT the properties were acceptable [44].

We have not come across any literature on the recyclable continuous carbon-filled reinforced polyetheretherketone (PEEK). This could be due to the low volume application and long-term durability of this composite.

The current state of the art seems to be typified as follows.

- Recyclability of continuous fiber-reinforced composites presently is extremely rare. This might change when more volume picks up by the year 2000.
- Discontinuous fiber-reinforced plastics are already being recycled more than the continuous types.
- Grinding and followed by mixing techniques will be the most likely to find applications.
- Tertiary recycling, like solvolysis, will be very costly and not practical.
- Reshaping by thermoforming or proper cutting techniques of used composites might become a good solution to find secondary applications. These lower-cost techniques could find new uses for old reinforced thermoplastics.
- Reusability for the same application via proper repairing could also become another solution for a composite on its last lap.

3.3 Practical methods for predicting durability of polymeric composites

3.3.1 Introduction

To address a complicated issue in a practical manner is important to industries either producing composite constituents or involved in operations of composite structures. The adjective practical is important for four reasons.

- i) Whereas a constituent producer will be continuously bringing new candidates to the market, a composite user will be always concerned about the structure performance spanning over tens of years. There is, thus, a need to develop methodology yielding relevant information within a shorter time: weeks or months.
- ii) During its service life, any composite structure will be subjected to changing multiaxial mechanical stresses under temperature and exposure to an environment. A practical experimental approach must cope with this complexity or, alternatively, identify the most crucial combination of the factors involved.
- iii) The complexity of external factors, cumulatively called the aging process, will perturb the original composite. Resulting damage will have to be quantified, and involved mechanisms assessed by means of an extensive theoretical support. The models must address these mechanisms on the platform of their reversibility, linearity, and others. Quite a wide spectrum of models have been developed both for the polymers and their composites, the rest will still have to be formulated.

Again, the modeling should be on a practical level—simple, but adequate, and aiming at general features rather than the behavior of a particular composite material/structure.

- iv) The three involvements above should determine the state of an aged/damaged material so that the remaining life of a composite structure can be quantified. Availability of nondestructive testing procedures that would allow to assess/verify this state would grossly contribute to this practicality.

The concept of durability is closely associated with time. As the steps to be taken toward composite acceptance are felt to be timely, exposures themselves will span over a time period and laborious experimentation will be time consuming. The time to start this initiative is now. There is a need to discontinue the ritual dance performed by constituent producers, formulators, and composite users and to stop the endless and unproductive discussion revolving around underwriting composite performance, defining the material consumption, and who is responsible for the design data.

Using even the most rational approach, experimental and theoretical programs will be still extensive from the material, labor, and money point of view. It might be possible that even resources of the richest companies will not be adequate to achieve the goal as defined by the title. Collaboration of parties with an invested interest in the topic is thus foreseen to be the most significant factor contributing to this practicability concept. Undoubtedly, a body such as IUPAC, successful in establishing a strong working partnership between industries and academic centers of excellence, might and should here play a major role. If, however, any collaborative effort is to be fruitful, a plan needs to be conceived so that the overall effort is concerted, action harmonized, and available resources maximized. We envisage that the following scheme might become a nucleus of this plan:

- inventarization of the procedures used to analyze hygrothermal aging of epoxy-based composites
- extension of these procedures to other composite/environment combinations
- adoption of meaningful experimental techniques
- formulation of missing models and analytical methods

These broad groups of activities should encompass issues that are further developed in the following four sections:

3.3.2 *Hygrothermal aging of epoxy-based composites*

For epoxy composites reinforced with continuous glass fiber, understanding of the aging process of a given lamina appears to be adequate for predicting composite response under combined effects of water and temperature. The approach is based on the following premises backed up by successful simulations of several sets of experimental data. These premises are:

- Matrix properties are governed by a difference between the glass transition temperature of the polymer and envisaged service temperature. The glass transition temperature is controlled by the structural features of the network (nature of polymer chains between cross-links, stoichiometry, functionality of the hardener, cross-linking density as a result of the curing process) and the level of moisture responsible for plasticization of the polymer.
- Diffusion process (often Fickian) controls ingress of the water into the lamina. The actual process type must be established experimentally. Temperature-dependent diffusion coefficient predetermines the rate of degradation in the matrix stiffness and strength. The equilibrium water concentration depends on the chemical build-up of the network.
- Reinforcing fibers are inert, and matrix/fiber interface is assumed to be absent.
- Micromechanical modeling is valid. Thus, stiffness characteristics of the lamina can be generated for any stage of the aging process from the properties/concentrations of an aged matrix and invariant reinforcement.
- The expansion coefficients, i.e., that associated with swelling (α) and thermal effects (β), can be also obtained micromechanically.

- As there is no way to arrive theoretically at the lamina strength characteristics, these have to be mapped using temperature and water concentration as independent variables. Experimental data are smoothed by power laws with the exponent approaching zero for the fiber-dominated properties and attaining a positive value for the strength characteristics dominated by the matrix.
- Classical lamination theory using a failure criterion is adequate for describing inter-ply interaction through the laminate thickness. The nonmechanical forces and moments are accounted for by using the extended “state equation” for composites.
- Finally, a simple composite structure such as a laminate plate or a GRP pipe is modeled by using appropriate construction elements (ply angle, number of plies) of the stacking sequence in accord with the manufacturing process used.

3.3.3 Extension to other composite/environment combinations

Steps toward a more general concept follow from the limitations of the model in hand in conjunction with the views expressed in the introduction should involve a further four areas:

3.3.3.1 From epoxy to any polymer matrix including thermoplastics

The problems relevant to this heading are:

- conformation that the temperature dependencies of properties of a matrix can be related to those of all possible laminates
- identification of a reference temperature that enables these relations
- effects of crystallinity on the temperature dependence of the properties of semicrystalline polymers
- applicability of transposition principles such as the time/temperature concept well established for polymers, also to composite polymeric laminates
- simplification of aging effects by ignoring a positive contribution of the “physical” aging
- generation of the data bank for all investigated matrices in the format as available for epoxy composites

3.3.3.2 From glass to any reinforcement type

The following challenges are likely to be tackled:

- accounting for possible reduction in properties of organic fibers such as Kevlar and Twaron and any other liquid crystalline polymer
- stability of the interfacial region fiber/matrix either to be demonstrated or consequences of any deterioration to be enumerated (see Section 2.3)

3.3.3.3 From water to any environment

A wealth of experience and knowledge generated for polymers and their dilute solutions might be utilized in this effort, namely:

- Flory–Huggins’ interaction parameter ζ as the yardstick for chemical inertness of a given polymer matrix to chemical species constituting a given environment
- a danger of a multicomponent environment where synergism among nonsolvents might lead to a strong polymer/environment interaction,
- effect of the service pressure on a level of chemical species/polymer interaction
- relationship between the service stress and attributes of the aging process: mechano-sorptive behavior

3.3.3.4 From a composite material to a composite structure of any shape or size

Here, attention should be paid to:

- capitalization on Finite Element analysis packages using properties reduced by the aging process as the input

- support of the frequently used strength analysis by the strain energy density concept
- realization that composite aging in the practice might lead to unbalanced laminates

3.3.4 Adoption of meaningful experimental procedures

If the aging of a polymeric lamina can be accepted as the key issue in coping with the aging aspects of composites, possible approaches appear to be assessment of residual properties, stress rupture testing and studies of the damage accumulation. Phenomenological and micromechanical “field case” studies of observation made on performance of structural elements during their service would be helpful. Possible composite structures that might be considered are wind-mill blades, car leaf-springs, and pipes. Laboratory investigations should concentrate on the unidirectional construction, tested in a simple deformation mode (tension) revealing matrix-dominated properties (transverse direction). Data generated could be accelerated by working with slender specimens exposed, and also tested, at a higher temperature. Attempts to accelerate the aging process should ascertain that the damage initiation and its accumulation follow the same path as under service conditions. This might be the most difficult issue to be resolved! Characterization of polymeric composites for their fracture toughness (see Section 3.5) will form an integral part of the aging investigations. Composite anisotropy leading to a multiaxial stress field will require different deformation modes to be assessed including that under the “mixed mode” loading for laminates of different construction.

3.3.5 Formulation of missing models and analytical methods

A substantial progress will have to involve the following issues:

- generalization of the stress/strain behavior of matrices and composites by accommodating nonlinear effects due to viscoelasticity
- generic relationships between structural aspects of thermoset networks and characteristics such as the equilibrium uptake and the diffusion coefficient
- relationships between thermodynamically behavior of a low-molecular-weight solute/polymer matrix and mechanical response of a reinforced composite
- quantification of the damage, such as matrix cracking, interfacial failure, and fiber bucking/failure
- coupling of this damage concept with nonlinear behavior of composites
- damage due to nonmechanical loading
- blend morphology of toughened epoxies during aging
- accommodation of complications arising from the dynamic loading (i.e., features associated with the fatigue response) frequency, loading pattern, stress ratio R .

3.4 Environmental strength

3.4.1 Introduction

Continuous fiber-reinforced composites are consolidating their potential as load-bearing structures in aerospace applications. Toughness is also important, and this can be strongly influenced by the formulation of the resin. In particular, thermoplastic toughening of the epoxy has been shown to be especially effective [45].

The use of composite materials in a cost-effective manner necessitates that their engineering design properties are well articulated. Therefore, performance in the context of a stress concentration, variations in temperature, the complex combinations of stress fields relative to fiber alignments, and so on have to be given consideration. Perhaps one of the areas that receives less attention is the influence of fluid environments on the engineering properties. This is an important future area in its own right, since there are a number of fluids that are used in and around aerospace structures.

The polymer industry has seen many cases involving the interaction of plastics and environments [e.g., 46–49] and this experience provides a useful guide. One of two issues has to be addressed in con-

templating the interaction between a plastic and an environment (which can be considered as anything from air to a hostile liquid chemical). First, does the interaction lead to a primary or chemical attack or, second, is there a secondary or physicochemical attack [46]? It is important to understand the consequence of these alternatives. For a primary attack, immersion of the plastic in the environment will lead to chemical interaction between the environment and the main polymer chain which will become radically changed or broken (i.e., primary chain scission). For a secondary attack, the environment will alter (reduce) the interaction between the main polymer chains. Such secondary attack requires both an environment and a stress field to trigger the effect, i.e., environmental stress cracking (ESC). It is of interest to observe the absence of a third alternative, i.e., no change at all! All polymeric systems experience aging phenomena, free volume changes, or secondary crystallization [50] even in an air environment such that if no primary attack occurs from immersion in the environment then there must be a secondary attack. The secondary attack should then be classified in terms of degree of hostility of the environment (i.e., on a scale from mild to hostile).

The purpose of this section is to describe some steps that are required in establishing the nature of the environmental interaction. This will be examined with a mind to whether the attack is primary or secondary.

3.4.2 Investigation of primary environmental attack

3.4.2.1 Tactical approach

Primary attack by a fluid on these materials will lead to chemical interaction between the fluid and the main polymer chain. Naturally, a direct method of seeking such interaction would involve immersion of the materials in the fluid and a subsequent chemical analysis via various spectroscopic methods. This will not of necessity provide the required evidence, and, therefore, an additional approach is to explore any changes in the properties that are related to engineering design, namely stiffness, toughness, and strength. The issue relating to possible primary environmental attack and the consequential influence on properties associated with engineering design require an investigation of how such properties may be influenced by immersion in the fluid. Therefore, our approach will involve the preparation of three types of specimen for testing:

- i) Dried thoroughly in air prior to testing.
- ii) Immersion of dried specimens (as above) in the fluid prior to testing. The procedure of immersing specimens for 6 days at 23 °C prior to testing is commonly used.
- iii) Redrying of dried and immersed specimens prior to testing. That is, specimens are subjected to procedure (i) followed by procedure (ii) followed by procedure (i) again.

3.4.2.2 Influence of immersion in the fluid on the stiffness of neat resin

A simple and direct way to investigate primary attack by the fluid on the resin is to observe the change in modulus as a function of immersion time. The accuracy of such a study can be considerably enhanced by using a single specimen (eliminating inter-specimen variability). A flexural creep apparatus described by Dunn et al. [51] enables a beam specimen of the neat resin (span 100 mm × width 10 mm × depth 3.2 mm) to be subjected to three-point bending for 100 s to a maximum deformation in the skin of a strain of less than 0.1 % (i.e., sufficient for a specimen to fully recover from the deformation). Adopting the procedure described by Dunn, it is then possible to obtain a 100 s modulus to better than 1 % accuracy. The use of flexure as a means of deformation has the effect of ensuring that the immersed specimen, with absorption of the fluid highest near a surface, can expose the region of highest absorption to the maximum deformation. In this way, it was possible to measure modulus of the neat resin dry, after various times immersed in the fluid and after redrying. Results that indicate no change in modulus suggest that no primary environmental attack is occurring between the fluid and the neat resin system.

3.4.2.3 Influence of immersion in the fluid on fracture toughness of the composite

Unidirectional laminates can be used to prepare single-edge notched-beam (SENB) specimens for conducting linear elastic fracture mechanics measurements at 23 °C and at 10 mm/min according to the test protocol of the European Structural Integrity Society (ESIS) Technical Committee 4 on Polymers and Composites [52]. The notch was machined in such a way as to initiate crack growth between the fibers (intralaminar fracture), and the fracture mechanics parameters then relate to initiation values. Tests can be conducted on the composite for the three conditions described in Section 3.4.2, namely, dry, immersed in the fluid, and redried.

If the fracture results indicate that immersion in the fluid has no influence on the toughness properties, then no primary attack by the fluid on the composite is occurring.

3.4.3 Investigation of secondary environmental attack

When it is clear that primary environmental attack is not occurring, then secondary environmental matters are inevitable. The question of degree then has to be qualified, and clearly this will depend on two issues—the environment and the nature of the chemical or physical interactions between the main polymeric chains. The latter is seldom easy to describe, but the nature of the environment and its potential as an environmental stress cracking agent can be described [e.g., 47]. This can be prescribed in one of two ways:

- First, in terms of the size of the molecule where a relatively small molar volume will suggest a hostile environment. For example, methyl ethyl ketone (MEK) has a molar volume of 90 where a range between 50 and 400 can be anticipated [54] for chemical environments (i.e., MEK is a relatively small molecule).
- Second, in terms of the hydrogen bonding parameter, where a modest value will suggest a hostile environmental agent. For example, MEK has a hydrogen bonding parameter of 5.1 MPa^{1/2} where a range of 4 to 20 MPa^{1/2} can be anticipated [54] for most chemical environments (i.e., MEK has a relatively modest hydrogen bonding parameter and on this count can also be expected to be a hostile environmental agent).

Therefore, without consideration to the plastic or composite that may be used with MEK in our example, it is clear that we can expect MEK to behave relatively aggressively in terms of its secondary environmental interactions, that is, as an environmental stress cracking agent.

Secondary interactions require a combination of stress and the environment for full investigation. This is because the ability of the composite or resin to absorb the environment in the absence of a stress field is likely to be small. The presence of the stress field accelerates the absorption of the environment, although this can be anticipated to be a process of selective absorption [46], particularly in the vicinity of flaws in the solid material. In this context, it might be difficult to identify a flaw in a strictly physical sense, but the adoption of Griffiths' concept of a flaw can readily accommodate these arguments. Therefore, experimental investigation of secondary environmental interaction should involve the combination of the fluid and an applied stress.

One experimental approach has involved the measurement of the creep function in both air and the fluid environment in order to study the influence of the fluid as an environmental stress cracking (ESC) agent. If the creep function (strain vs. time under load for a constant applied stress) can be described in both air and the fluid environments, then any difference between the functions relates to the influence of the fluid as an ESC agent. It is anticipated that the rate of creep strain with time will become higher for the test conducted in the fluid and that the position in time when these two rates differ will be the onset of crazing of the composite or resin in the fluid. If the ESC effect is catastrophic, then the composite or resin may even crack during creep in the fluid without the onset of crazing.

The tensile creep apparatus described by Turner [55] can be used to measure the creep function in air at 23 °C. This apparatus is modified to house the specimen in a rectangular vessel sufficient to surround about 70 % of the parallel-sided creep specimen in the fluid environment in order to conduct

the creep test in fluid. We believe that the Rubber and Plastics Research Association (RAPRA) [54] first used this technique for conducting such experiments. In order to make a comparison between the two creep functions, it is necessary to use two separate test specimens. Therefore, the possibility of inter-specimen variability can arise. It is known that the creep curves will be the same in the two environments prior to the onset of crazing or cracking provided that the compliances of the two specimens are identical. They can be adjusted to be identical, provided any short-term differences in compliance are small, by adoption of the method described by Barrie et al. [56].

Turner's tensile creep apparatus is also capable of measuring the recovery strains after removal of the applied stresses. Therefore, secondary environmental interactions can also be investigated in terms of the ability of a specimen to recover after craze initiation.

Therefore, a tactical approach is developed around both creep and recovery experiments in both air and the fluid environments.

3.4.4 Concluding comments

It has been shown that a strategic issue relates to whether primary chemical attack or secondary environmental interaction occurs. For primary attack by the environment, then conditioning experiments will define the problem. Therefore, a combination of stiffness, strength, and toughness measurements for dry and immersed samples provides an indication of both whether primary chemical attack is occurring. For secondary interactions, it is necessary to combine stress with the environment, and tensile creep experiments provide a useful vehicle for investigation.

As a future requirement for composite materials characterization, it is suggested that this test philosophy be adopted.

3.5 Toughness and international standards

3.5.1 Introduction

Failure of composite laminates is a major concern in design, and there has been much discussion to establish a proper philosophy for a rational design procedure. There are many possible failure modes in such systems, so one option is to track all these possibilities. This is rather difficult and would depend on a level of understanding we do not yet have. With this in mind, the route adopted is that of traditional fracture mechanics in pursuing the worst case. For laminates, this is delamination between the plies, and many failure situations do involve such fractures. They often arise from impacts and result in a loss of stiffness and vulnerability to environmental attack.

Such failures often involve shear cracking, of which more will be said later, but the lowest toughness failures are opening or Mode I cracks. Thus, the critical characterizing parameter for determining the toughness of a laminate is taken as G_{Ic} , and this is the first fracture toughness parameter for which an international standard has been developed.

3.5.2 Mode I standard

The method embodied in this standard [57] is to measure the G_{Ic} vs. crack growth relationship, or "R" curve, for a unidirectional laminate using a double cantilever beam (DCB) specimen. The laminates are usually thin plates, so it is convenient to use such slender beam-type specimens. There is also an advantage in that the calculations of G_{Ic} can be effected using either beam theory or compliance measurements, which provide useful cross-checks on consistency. It is usual to fabricate special sheets for the tests and to mold in an edge defect at the sheet mid-thickness from which the delamination is propagated. There is some uncertainty inherent in this procedure since molded-in defects are often not sharp and give high-initiation toughness values. There is also scope for debate on what constitutes initiation and how it can be detected. Thus, the standard allows for several schemes including visual detection, the onset of nonlinearity in the loading curve, a change in compliance (5 %), and maximum load. In addition, the initiation process is repeated after first determining these values from the initial defect and

then unloading and reloading to determine them from the newly grown defect. Subsequent growth, which is usually stable for the DCB, is then used to find the “R” curve.

This curve, with its associated initiation values, is the characterizing parameter for the laminate toughness. The method is robust and reliable, as has been demonstrated via numerous round-robin testing exercises. The “R” curves show good repeatability between groups using samples of the same laminate, but there is some variability in the somewhat more subjective initiation values. Overall, the method is satisfactory.

Some issues remain, however, to be resolved. The notion that the unidirectional laminate gives minimum values is not proven, and testing is going on using the method on cross-ply systems [58]. These often show instabilities with crack jumping (stick-slip). There is also an enhanced, though unstable, “R” curve. Indeed, the whole notion of a rising “R” curve in composites raises many issues. The increased toughness associated with such increases is traditionally associated with plastic deformation, whereas in laminates the deformations are wholly elastic. The prevalent view is that the increases come from fibers bridging the delamination and are more extensive, though less stable, in cross-ply laminates. In utilizing the data in characterizing toughness, should one include such effects, or stick to the minimum value philosophy? In metals, the plasticity embodied in the “R” curve is exploited in design, but some in composites feel that bridging is not so reliable and should be ignored. Thus, there is an emphasis on the lower, but more ephemeral, initiation values.

The standard does not purport to resolve these issues. It provides a scheme for determining the values and leaves deciding on their usage to another forum. Such issues are likely to be important in the future exploitation of composites.

3.5.3 Mode II failures

A further factor that casts some doubt on the utility of the Mode I data is that lateral impacts often induce failures in the shear or sliding Mode II. There is, thus, a call for characterizing laminates via their Mode II fracture toughness performance, and to this end there has been considerable effort expended on developing a G_{IIc} standard test. For the G_{Ic} test, there was general agreement on the approach in Europe [59], the United States [60], and Japan [61], in that all three groups used the DCB specimen. This has not been so for Mode II. In the United States, the emphasis has been on the end-notch flexure (ENF) test [62], while in Europe the end-loaded split (ELS) [63] has been favored. The former is a type of three-point bend test and, as such, is easy to perform. It is unstable, however, and therefore more difficult to calibrate and, of course, does not measure the “R” curve. The ELS test is stable for some of the crack growth, but is mechanically more difficult because of clamping. Both present problems in compliance calibration because the zero crack length compliance is large and the changes with crack length are much less than in the DCB. There is, thus, an inherent inaccuracy in the calibration which plagues repeatability.

A fundamental difference between Modes I and II, is that in the latter there is no opening of the crack and only relative sliding of the faces. This makes crack growth difficult to observe and also leads to the possibility of frictional forces on the crack faces, particularly when the surfaces are rough. These forces can affect both the compliance calibration and the measured toughness. As with fiber bridging, which is less prevalent but not absent, in Mode II, there is a fundamental question of whether frictional energy dissipation should be included in toughness or whether it is too ephemeral.

At the time of writing these issues are unresolved. Round-robin testing has revealed significant variability in calibration procedures and large differences in final toughness values. The role of friction is unclear, but G_{IIc} is always greater than G_{Ic} , which is reassuring if one adopts the minimum value philosophy. There are some new test methods on offer, including the four-point bending test (4ENF) [64] and a stabilized ENF test [65] which shows some promise, but much remains to be done.

3.5.4 Mixed Mode I/II testing

A complete characterization involves determining toughness over a whole range of G_{II}/G_I ratios, both at initiation and during propagation. There is some activity [66] in determining such data using the

mixed mode bending (MMB) test, which is an elaboration of the ENF test. Most of the Mode II problems are present in this procedure, and there is a worrying tendency to have G values much greater than G_{Ic} when a small percentage of Mode II is present. The results are also subject to a large degree of scatter, and the procedure must be regarded as developmental at this stage.

3.5.5 Conclusions

A robust and well-tried procedure for measuring the Mode I delamination toughness for uniaxial laminates is now available. It is easy to calibrate and gives a range of fracture initiation values depending on the criteria used as well as a crack propagation resistance curve. For Mode II and combinations of Modes I and II, the situation is much less satisfactory. The geometries used are more problematic to calibrate, and the results apparently influenced by friction. These issues remain to be clarified.

4. CONCLUDING COMMENTS

In contemplating future requirements in the characterization of composites, a number of issues have been identified as possibly key features for the future:

- New resin formulations and more rapid processing techniques will raise further challenges in the future, notably resin transfer molding (RTM) and pultrusion.
- The impregnation process would benefit from a reduction in heating times and better fiber-handling science.
- It is recognized that interfacial adhesion between fiber and resin is poorly understood, but will likely account for many crucial properties.
- Residual stresses need to be kept to a minimal level particularly in thermosetting composites. For thermoplastic composites, control of the nature of crystallization at the fiber–matrix boundary will be important.
- The available approaches for measuring pre-preg tack need to be calibrated against practical experience.
- There are too many test methods for obtaining property data, and, moreover, these methods can produce poorly understood results. It is only through a better description of the events happening at the microstructural level that their influence on the macroscopic level can be understood.
- Recycling of general composites is developing, whereas recycling of continuous-fiber composites has yet to start.
- Long-term durability requires practical pragmatism.
- Environmental properties should be resolved initially between whether primary chemical attack or secondary environmental interaction occurs. For primary attack by the environment, then conditioning experiments will define the problem. For secondary interactions, it is necessary to combine stress with the environment, and tensile creep experiments provide a useful vehicle for investigation.
- A robust and well-tried procedure for measuring the Mode I delamination toughness for uniaxial laminates is now available. For Mode II and combinations of Modes I and II, the situation is much less satisfactory.

5. LIST OF ABBREVIATIONS

BMC	bulk molding compound
CAE	computer-aided engineering
DCB	double cantilever beam
ELS	end-loaded split
ENF	end-notched flexure
4ENF	four-point bending test

ESC	environmental stress cracking
ESIS	European Structural Integrity Society
GMT	glass mat thermoplastics
GRP	glass-reinforced plastic
ISO	International Organization for Standardization
IUPAC	International Union of Pure and Applied Chemistry
MEK	methyl ethyl ketone
MMB	mixed mode bending
PBT	poly(butylene terephthalate)
PC	polycarbonate
PE	polyethylene
PEEK	polyetheretherketone
PET	poly(ethylene terephthalate)
PI	polyimide
PP	polypropylene
PS	polystyrene
PS	polysulfone
PVC	poly(vinyl chloride)
RAPRA	Rubber and Plastics Research Association
R curve	plot of fracture toughness vs. crack length
RTM	resin transfer molding
TEM	transmission electron microscopy
T_g	glass-rubber transition temperature
SEM	scanning electron microscopy
SENB	single-edge notched beam
SMC	sheet molding compound

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